

PHOTOCATALYTIC OXIDATION OF HUMIC ACID IN HETEROGENEOUS
AQUEOUS SYSTEMS: A COMPARATIVE INVESTIGATION BETWEEN
MONTMORILLONITE AND KAOLINITE

by

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Dedicated to my family...

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ABSTRACT

Humic acids representing the major fraction of the naturally occurring humic substances are composed of highly functionalized carbon rich polydisperse organic fractions. Clay minerals which are responsible for the transport of inorganic and organic contaminants constitute the main component of the suspended inorganic material in natural waters. The understanding of interactions between humic substances and clay minerals is an important task for the achievement of an effective water treatment performance. The aim of this research was to investigate the influence of montmorillonite and kaolinite as representative clay minerals on the TiO_2 photocatalytic degradation of humic acid as the model compound of natural organic matter. The interactions prevailing between humic acid, montmorillonite, kaolinite and TiO_2 surface were assessed prior to the application of photocatalysis in order to evaluate the adsorptive and photolytic behavior of humic acids. Adsorption of humic acid onto sole TiO_2 and TiO_2 in the presence of clay minerals either montmorillonite or kaolinite were assessed by batch adsorption experiments.

The changes attained in humic acid were described by UV-vis spectroscopic parameters i.e. color forming moieties (Color_{436}) and UV absorbing centers (UV_{365} , UV_{280} and UV_{254}), and dissolved organic carbon (DOC) contents. Photocatalytic oxidation of humic acid in the presence of clay particles i.e. montmorillonite or kaolinite was also followed by using specific UV-vis parameters (SUVA_{365} , SUVA_{280} , SUVA_{254} and SCoA) calculated by respective absorbance measurements (E) through conversion to mass of carbon. Fractional UV-vis parameters (E_{254}/E_{365} ; E_{254}/E_{436} ; E_{280}/E_{365} ; E_{280}/E_{436} , and E_{365}/E_{436}) that signify the removal of color forming groups in relation to the removal of UV absorbing centers revealing further information on the different oxidation pathways through photocatalysis. No noteworthy variation could be detected for fractional UV-vis parameters under photocatalytic conditions for sole humic acid as well as for humic acid in the presence of either montmorillonite or kaolinite. However, a significant correlative interaction was attained between the specific UV-vis and fractional UV-vis parameter (E_{254}/E_{436}) ($r^2 > 0.80$). Therefore, it could be concluded that E_{365}/E_{436} parameter could be effectively used as a discriminative indicator parameter for the type of clay minerals.

Application of the pseudo first order kinetic model revealed both enhancement and retardation effect with respect to the applied montmorillonite and kaolinite doses. Upon non-selective oxidation, a slight rate enhancement could be indicated for Color_{436} , UV_{365} , UV_{280} and UV_{254} of HA in the presence of either montmorillonite or kaolinite. However, the presence of clay particles did not significantly change the DOC degradation rate of HA. The effect of ionic strength (Ca^{2+} loading from 5×10^{-4} M to 5×10^{-3} M) was also assessed for the photocatalytic degradation of sole HA and HA in the presence of either montmorillonite or kaolinite. The overall effect of montmorillonite and kaolinite on the photocatalytic degradation of humic acid was also evaluated in terms of molecular size distribution profiles (0.45 μm filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction) described by the specified and DOC normalized specific UV-vis parameters. Besides the effective removal of higher molecular size fractions (100 kDa and 30 kDa fractions), transformation to lower molecular size fractions ($< 3\text{kDa}$) was more pronounced for sole humic acid rather than humic acid in the presence of clay minerals. Scanning electron microscopic (SEM) images accompanying with energy dispersive X-ray analysis were also examined for the elucidation of the surface morphologies of the binary and ternary systems composed of humic acid, TiO_2 and montmorillonite or kaolinite both prior to and following photocatalysis. Excitation emission matrix (EEM) fluorescence spectral features were also evaluated for the elucidation of the photocatalytic degradation of sole humic acid and humic acid in the presence of clay minerals either as montmorillonite or kaolinite. The role of Ca^{2+} ions was also visualized through EEM under the specified conditions. EEM features reflected the irradiation time dependent transformation of the humic like fluorophores to fulvic like fluorophores in accordance with the photocatalytic removal of humic acid. Adsorption of humic acid onto sole TiO_2 and TiO_2 in the presence of either montmorillonite or kaolinite with Ca^{2+} were evaluated by the application of batch adsorption experiments.

Adsorption properties of humic acid onto sole TiO_2 and TiO_2 in the presence of clay minerals either as montmorillonite or kaolinite were evaluated in terms of the specified UV-vis parameters as well as DOC. Adsorption isotherms were evaluated in terms of the adsorption isotherm types (Types S, L, and C). Adsorption data of the indicated humic parameters were further modeled by Freundlich and Langmuir adsorption isotherm model.

It could be concluded that, the presence of clay particles i.e. montmorillonite and kaolinite would not significantly alter the photocatalytic degradation efficiency of humic acid. This result signifies that photocatalysis could be an alternative treatment option for the successful removal of natural organic matter in water treatment systems. As shown by the results attained through the application of the UV-vis and fluorescence spectroscopic techniques, the chemical composition of the resultant organic matter would be the indicative parameter for the assessment of the drinking water quality. Since chlorination and/or ozonation is widely applied as the final disinfection step, from public health point of view, it is highly recommended that further research should be directed to the evaluation of the possible side effects related to the formation of the disinfection by-products.

ÖZET

Hümik maddelerin temel alt gruplarından birini temsil eden hümik asitler yüksek karbon içerikli polydisperse organik maddelerdir. Kil mineralleri doğal sulardaki inorganik ve organik maddelerin taşınmasından sorumlu olan temel maddeleri oluşturmaktadır. Kil mineralleri ve hümik asitler arasındaki etkileşimin anlaşılabilmesi, su arıtma sistemlerinin performansının artırılmasının sağlanması bakımından önemlidir. Bu çalışmanın amacı kil minarelerini temsil etmesi amacıyla kullanılan montmorillonite ve kaolinitin, doğal organik maddeleri temsilen kullanılan model bileşiklerden hümik asitlerin TiO_2 fotokatalitik yöntemle giderimi üzerindeki etkisinin araştırılmasıdır. Fotokatalizin uygulanmasından önce, hümik asitin adsorpsiyon ve fotolitik davranışlarının açıklanabilmesi için, hümik asit, montmorillonit, kaolinit ve TiO_2 arasında oluşan etkileşimler incelenmiştir. Batch adsorpsiyon denemeleri ile hümik asitin, sadece TiO_2 ve montmorillonit / kaolinit varlığında TiO_2 'nin adsorpsiyonu incelenmiştir.

Hümik asitte oluşan değişimler UV-görünür bölge sepektroskopik parametreleri; renk oluşturan gruplar (Renk_{436}) ve UV absorplayan merkezler (UV_{365} , UV_{280} ve UV_{254}) ve çözünmüş organik karbon (ÇOK) giderimi ile tanımlanmıştır. Hümik asitin monmorillonit ve kaolinit varlığında gerçekleşen fotokatalitik degradasyonu, UV-vis görünür bölge parametrelerinin karbon değerlerine oranı olan spesifik UV-görünür bölge parametreleri (SUVA_{365} , SUVA_{280} , SUVA_{254} ve SRenkA) ile de takip edilmiştir. Renk oluşturan grupların giderimi ile UV absorplayan grupların giderimi arasındaki ilişkilerin göstergesi olan oransal UV-görünür bölge parametreleri (E_{254}/E_{365} ; E_{254}/E_{436} ; E_{280}/E_{365} ; E_{280}/E_{436} , ve E_{365}/E_{436}), fotokataliz ile gerçekleşen farklı oksidasyon yolları hakkında bilgilerin ortaya çıkmasını sağlamaktadır. Fotokatalitik degradasyon sırasında, sadece hümik asitin bulunduğu durumda görüldüğü gibi montmorillonit ve kaolinit varlığındaki humik asit için elde edilen bu orantılı UV-görünür bölge parametreleri arasında çok önemli değişiklikler görülmemiştir. Ancak spesifik UV-görünür bölge parametreleri ve oransal UV-görünür bölge parametreleri arasında (E_{254}/E_{436}) ($r^2 > 0.80$) çok yüksek korelasyon olduğu görülmektedir. Bu nedenle, E_{254}/E_{436} parametresinin kil çeşitleri için ayırıcı bir indikatör parametre olarak uygun bir şekilde kullanabilir olduğu sunucuna varılabilir.

Montmorillonit ve kaolinit varlığının arttırıcı ve inhibe edici özelliği psödo birinci derece kinetik modeli uygulaması ile gösterilmiştir. Seçici olmayan oksidasyon ile humik asitin Renk_{436} , UV_{365} , UV_{280} ve UV_{254} giderim oranlarının montmorillonit ve kaolinit varlığında az miktarda arttığı belirlenmiştir. Ancak kil minerallerinin varlığının humik asitin ÇOK giderim oranı üzerinde bir etkisi olmadığı gözlenmiştir. Ayrıca iyonik kuvvetin (Ca^{2+} iyon miktarı, 5×10^{-4} M to 5×10^{-3} M) sadece humik asitin ve montmorillonit ve kaolinit varlığındaki humik asitin fotokatalitik degradasyon ile giderimine olan etkileri incelenmiştir.

Montmorillonit ve kaolinit varlığının humik asitin fotokatalitik degradasyonu üzerine genel etkisi moleküler boyut dağılımları (0.45 μm filtrelenmiş fraksiyonu, 100 kDa fraksiyonu, 30 kDa fraksiyonu and 3 kDa fraksiyonu) ile de incelenmiş ve spesifik UV-görünür bölge ve ÇOK değerlerine göre belirtilmiştir. Yalnız humik asitin bulunduğu sistem için yüksek molekül boyutlu fraksiyonların (100 kDa fraksiyonu ve 30 kDa fraksiyonu) verimli bir şekilde giderimi ve bunların düşük moleküler boyutlu fraksiyona (< 3 kDa) dönüşümü kil minerallerinin varlığındaki humik asit için daha yüksektir. Humik asitlerin fotokataliz öncesinde ve sonrasında TiO_2 , montmorillonit ve kaolinit varlığındaki ikili ve üçlü sistemler için yüzey yapılarının anlaşılması amacıyla taramalı elektron mikroskobu görüntüleri enerji dağılımlı X-ray analizi ile birlikte elde edilmiştir. Montmorillonit ve kaolinit varlığında humik asitin fotokatalitik degradasyonu ile giderimi eksitasyon emisyon matris (EEM) floresan spektrum analizleri ile de incelenmiştir. Belirlenmiş olan koşullar için EEM floresan spektrum değişimlerinde Ca^{2+} iyonlarının rolü incelenmiştir. EEM flüoresan spektrum analizleri ile humik asitin fotokataliz ile humik benzeri floroforlardan fülvik benzeri floroforlara dönüştüğünü görülmektedir.

Humik asitin adsorpsiyonu, sadece TiO_2 , montmorillonit ve kaolinit varlığında TiO_2 ve bu sistemlerin Ca^{2+} iyonlarının varlığındaki batch adsorpsiyon deneyleri ile incelenmiştir. Humik asitin sadece TiO_2 , montmorillonit ve kaolinit varlığında TiO_2 'nin adsorpsiyon verileri belirlenmiş UV-vis parametreleriyle olduğu gibi çözünmüş organik karbon giderimi ile de belirtilmiştir. Adsorpsiyon izotermi, adsorpsiyon izoterm tiplerine göre değerlendirilmiştir (S, L ve C). Humik asitin belirtilen verileri Freundlich ve Langmuir adsorpsiyon izoterm modelleri ile açıklanmıştır.

Sonuç olarak montmorillonit ve kaolinit varlığının hümik asitin fotokatalitik degradasyon verimi üzerine belirgin bir etkisi olmadığı anlaşılmaktadır. Bu sonuc fotokatalizin su arıtma sistemlerinde doğal organik maddenin giderimi için alternatif bir yöntem olarak kullanılabilir olduğunu göstermektedir. UV-görünür bölge ve floresan spektrum teknikleri ile elde edilen sonuçlara göre, ortaya çıkan organik maddelerin kimyasal içeriği, içme suyu kalitesinin değerlendirilmesinde indikatör bir parametre olarak kullanılabilir. Klorlama ve/veya ozonlama prosesleri son dezenfeksiyon aşamasında geniş kapsamlı olarak uygulandığı için bundan sonraki çalışmalarda dezenfeksiyon yan ürünleri oluşumunun ve bunların olası yan etkilerinin değerlendirilmesi halk sağlığı açısından önemle tavsiye edilmektedir.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iv
ABSTRACT	v
ÖZET	viii
LIST OF FIGURES	xvii
LIST OF TABLES	xxxix
LIST OF ABBREVIATIONS	xxxvii
1. INTRODUCTION	1
2. THEORETICAL BACKGROUND	4
2.1. Natural Organic Matter/ Humic Substances/ Humic and Fulvic Acids	4
2.2. Clays and Clay Minerals	7
2.3. Natural Organic Matter-Clay Complexes in Soil	12
2.4. Natural Organic Matter -Clay complexes in Aquatic Systems	13
2.5. Adsorption of NOM on the clay minerals	13
2.6. Humic Acid/Natural Organic Matter Type	15
2.7. Effect of Solution Matrix: pH and Ionic Strength	19
2.8. Adsorption Isotherm Modeling of Humic Substances with Clay Minerals	21
2.9. Evaluation of the Adsorption Studies of the Clay-Humic System	23
2.10. Advanced Oxidation Processes	25
2.10.1. Photocatalysis	25
2.10.2. Photocatalyst type	28
2.10.3. Kinetics of photocatalytic degradation	29
2.11. Photocatalytic degradation of natural organic matter	31
3. MATERIALS AND METHODS	36

3.1. Materials	36
3.1.1. Humic acid	36
3.1.2. Titanium dioxide powder	36
3.1.3. Clay minerals	36
3.1.4. Other hemicals and reagents	36
3.1.4. Laboratory equipments	37
3.2. Methods	37
3.2.1. Photocatalytic degradation	37
3.2.1.1. Experimental set-up	37
3.2.1.2. Experimental procedure	38
3.2.2. Adsorption	39
3.2.2.1. Experimental procedure	39
3.2.3. Molecular size fractionation with ultrafiltration	39
3.2.4. Analytical methods	41
3.2.4.1. Total organic carbon (TOC) analysis	41
3.2.4.2. UV-vis spectroscopic measurements	41
3.2.4.3. Fluorescences spectroscopic measurements	42
3.2.4.4. Fluoresence excitation emission matrix (EEM)	42
3.2.4.5. Scanning electron microscopy (SEM) analysis	42
4. RESULTS AND DISCUSSION	
4.1. Photocatalytic Degradation of Humic Acid in the Presence of Clay Minerals	43
4.1.1. Baseline experiments; humic acid, montmorillonite or kaolinite and TiO ₂ interactions	47
4.1.2. Preliminary experiments performed both under dark conditions in the presence of TiO ₂ and in the absence of photocatalyst	53

4.1.2.1. Preliminary experiments performed under dark conditions in the presence of TiO_2	53
4.1.2.2. Preliminary experiments performed under irradiation in the absence of TiO_2	65
4.1.3. Comparative evaluation of the baseline experiments and preliminary experiments	76
4.1.4. Photocatalytic degradation of sole humic acid	79
4.1.4.1. UV-vis spectroscopic evaluation of raw humic acid during photocatalytic degradation	79
4.1.4.2. Fluorescence spectroscopic evaluation of raw humic acid during photocatalytic degradation	81
4.1.5. Photocatalytic degradation of humic acid in the presence of montmorillonite	84
4.1.5.1. UV-vis spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.05 mg mL^{-1} montmorillonite	84
4.1.5.2. Fluorescence spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.05 mg mL^{-1} montmorillonite	86
4.1.5.3. UV-vis spectroscopic evaluation humic acid during photocatalytic degradation in the presence of 0.10 mg mL^{-1} montmorillonite	89
4.1.5.4. Fluorescence spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.10 mg mL^{-1} montmorillonite	90
4.1.5.5. UV-vis spectroscopic evaluation humic acid during photocatalytic degradation in the presence of 0.20 mg mL^{-1} montmorillonite	93

4.1.3.6. Fluorescence spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.20 mg mL ⁻¹ montmorillonite	94
4.1.6. Photocatalytic degradation of humic acid in the presence of kaolinite	97
4.1.6.1. UV-vis Spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.05 mg mL ⁻¹ kaolinite	97
4.1.6.2. Fluorescence spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.05 mg mL ⁻¹ kaolinite	98
4.1.6.3. UV-vis spectroscopic evaluation humic acid during photocatalytic degradation in the presence of 0.10 mg mL ⁻¹ kaolinite	102
4.1.6.4. Fluorescence spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.10 mg mL ⁻¹ kaolinite	103
4.1.6.5. UV-vis spectroscopic evaluation humic acid during photocatalytic degradation in the presence of 0.20 mg mL ⁻¹ kaolinite	106
4.1.7. Effect of Ca ²⁺ on the photocatalytic degradation of humic acid and clay system	110
4.1.8. Evaluation of humic acid photocatalytic oxidation by UV-vis absorption spectra	114
4.1.8.1. Evaluation of humic acid photocatalytic oxidation by specific UV-vis absorbance parameters	115
4.1.8.2. Evaluation of humic acid degradation by fractional UV-vis parameters	117
4.1.9. Kinetic evaluation of the photocatalytic degradation of humic acid in the presence clay minerals	123

4.1.9.1. Kinetic modeling of photocatalytic degradation of raw humic acid	124
4.1.9.2. Kinetic modeling of photocatalytic degradation of raw humic acid in the presence of montmorillonite	126
4.1.9.3. Kinetic modeling of photocatalytic degradation of raw humic acid in the presence of kaolinite	130
4.1.9.4. Comparative evaluation of kinetic modeling of the photocatalytic oxidation of humic acid in the presence of clay minerals	133
4.1.10. SEM analysis prior to and following photocatalysis	140
4.1.11. Molecular size fractionation of humic acid in the presence of clay minerals prior to and after photocatalysis	142
4.1.11.1. Molecular size fractionation of humic acid prior to photocatalysis	142
4.1.11.2. Molecular size distribution of humic acid followed by photocatalytic degradation	147
4.1.11.3. Molecular size distribution of humic acid followed by photocatalytic degradation in the presence of montmorillonite	152
4.1.11.4. Molecular size distribution of humic acid followed by photocatalytic degradation in the presence of kaolinite	156
4.1.11.5. Comparative Evaluation	160
4.1.12. Excitation–emission matrix (EEM) fluorescence spectra to monitoring the photocatalytic degradation of humic acid in the presence of clay particles	165
4.1.12.1. Removal efficiencies of unoxidized and photocatalytically oxidized humic acid in the presence of clay minerals	166
4.1.12.2. EEM matrices of humic acid under post photocatalytic oxidation conditions	170

4.1.12.3. Role of Ca^{2+} ions on the EEM fluorescence spectral features of photocatalytically oxidized HA in the presence of either montmorillonite or kaolinite	173
4.1.11.4. Quantification approach	177
4.2. Adsorption of Humic Acid onto TiO_2 in the Presence of Clay Minerals	180
4.2.1. Humic acid adsorption onto sole TiO_2	180
4.2.2. Humic acid adsorption onto montmorillonite	184
4.2.3. Humic acid adsorption onto kaolinite	189
4.2.4. Humic acid adsorption onto TiO_2 in the presence of montmorillonite	193
4.2.5. Humic acid adsorption onto TiO_2 in the presence of kaolinite	198
4.2.6. Humic Acid Adsorption onto TiO_2 in the presence of Ca^{2+}	202
4.2.7. Humic Acid Adsorption onto montmorillonite in the presence of Ca^{2+}	207
4.2.8. Humic acid adsorption onto kaolinite in the presence of Ca^{2+}	211
4.2.9. Humic acid adsorption onto TiO_2 in the presence of montmorillonite and Ca^{2+}	215
4.2.10. Humic acid adsorption onto TiO_2 in the presence kaolinite and Ca^{2+}	220
4.2.11. Evaluation of adsorption properties of humic acid onto TiO_2 and TiO_2 in the presence of clay minerals	225
5. CONCLUSIONS	231
REFERENCES	235
APPENDIX A: ADSORPTION ISOTHERM OF HUMIC ACID ADSORPTION ONTO TiO_2 IN THE PRESENCE OF CLAY MINERALS FOR UV_{280} AND UV_{365} PARAMETERS	251

LIST OF FIGURES

Figure 2.1.	Partial pseudo-structure of humic acid	6
Figure 2.2.	Approximate sizes of chemical and biological components of natural waters	7
Figure 2.3.	Silicate clay minerals	9
Figure 2.4.	The 1:1 structure of kaolinite	10
Figure 2.5.	The structural and chemical characteristics of the expandable 2:1 trioctahedral phyllosilicates hectorite, saponite, sauconite, and trioctahedral vermiculite	10
Figure 2.6.	Interlayer reactions of 1:1 and 2:1 clay minerals	11
Figure 2.7.	The pH-dependent ion and ligand exchange reactions at the edges of the clay mineral layers, shown for 2:1 clay minerals	11
Figure 2.8.	Interaction of a humic model molecule and a clay particle,	15
Figure 2.9.	Simplified TiO ₂ photocatalytic mechanism	26
Figure 3.1.	Schematic diagram of stirred cell system	40
Figure 3.2.	The parts of Amicon 8050 stirred ultrafiltration cells	40
Figure 4.1.	Schematic presentation of photocatalytic degradation of humic acid	45
Figure 4.2.	Reaction occurring between clay minerals and humic acid in aqueous medium	46
Figure 4.3.	Tail-train and loop model of humic acid	46

Figure 4.4.	Electrostatic attractions between charged surfaces and humic sub-fractions	47
Figure 4.5.	UV-vis spectra of humic acids recorded for the baseline experiments performed for all of the specified systems	48
Figure 4.6.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the baseline experiments performed for all of the specified systems composed of montmorillonite	49
Figure 4.7.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the baseline experiments performed for all of the specified systems composed of kaolinite	50
Figure 4.8.	UV-vis spectra of humic acid recorded for the preliminary experiments performed under dark conditions in presence of TiO_2	54
Figure 4.9.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under dark conditions in presence of TiO_2	55
Figure 4.10.	UV-vis spectra of humic acid recorded for preliminary experiments performed under dark conditions in the presence of montmorillonite and TiO_2	58
Figure 4.11.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under dark conditions in presence of montmorillonite and TiO_2	59
Figure 4.12.	UV-vis spectra of humic acid recorded for preliminary experiments performed under dark conditions in presence of kaolinite and TiO_2	62

Figure 4.13.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under dark conditions in presence of kaolinite and TiO ₂	63
Figure 4.14.	UV-vis spectra of humic acid recorded for the preliminary experiments performed under irradiation and in the absence of TiO ₂	66
Figure 4.15.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under irradiation and in the absence of TiO ₂	67
Figure 4.16.	UV-vis spectra of humic acid recorded for the preliminary experiments performed under irradiation in the presence of montmorillonite and in the absence of TiO ₂	70
Figure 4.17.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under irradiation in the presence of montmorillonite and in the absence of TiO ₂	71
Figure 4.18.	UV-vis spectra of humic acid recorded for the preliminary experiments performed under irradiation in the presence of kaolinite and in the absence of TiO ₂	73
Figure 4.19.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under irradiation in the presence of kaolinite and in the absence of TiO ₂	74
Figure 4.20.	UV-vis spectra of humic acid recorded for the photocatalytic degradation	80
Figure 4.21.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the photocatalytic degradation	81

Figure 4.22.	UV-vis spectra of humic acid recorded for the photocatalytic degradation in the presence of 0.05 mg mL^{-1} montmorillonite	85
Figure 4.23.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.05 mg mL^{-1} montmorillonite recorded for the photocatalytic degradation	87
Figure 4.24.	UV-vis spectra of humic acid recorded for the photocatalytic degradation in the presence of 0.10 mg mL^{-1} montmorillonite	90
Figure 4.25.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.10 mg mL^{-1} montmorillonite recorded for the photocatalytic degradation	91
Figure 4.26.	UV-vis spectra of humic acid during photocatalytic degradation in the presence of 0.20 mg mL^{-1} montmorillonite	94
Figure 4.27.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.20 mg mL^{-1} montmorillonite during photocatalytic degradation	94
Figure 4.28.	UV-vis spectra of humic acid during photocatalytic degradation in the presence of 0.05 mg mL^{-1} kaolinite	98
Figure 4.29.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.05 mg mL^{-1} kaolinite during photocatalytic degradation	99
Figure 4.30.	UV-vis spectra of humic acid during photocatalytic degradation in the presence of 0.10 mg mL^{-1} kaolinite	102
Figure 4.31.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.10 mg mL^{-1} kaolinite during photocatalytic degradation	103

Figure 4.32.	UV-vis spectra of humic acid during photocatalytic degradation in the presence of 0.20 mg mL ⁻¹ kaolinite	106
Figure 4.33.	Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.20 mg mL ⁻¹ kaolinite during photocatalytic degradation	107
Figure 4.34.	Effect of pCa (pCa: 2.5-3.5) on the photocatalytic removal efficiency of humic acid both in the presence and absence of clay minerals with respect to time	113
Figure 4.35.	UV-vis absorption profiles of (A) humic acid in the presence of montmorillonite (B) humic acid and montmorillonite, 0.10 mg mL ⁻¹ , (C) humic acid and kaolinite, 0.10 mg mL ⁻¹	114
Figure 4.36.	Removal of specific UV-vis parameters of humic acid by baseline (A) and preliminary interactions (B) both in the presence and absence of clay minerals i.e. montmorillonite/kaolinite	116
Figure 4.37.	Removal of fractional UV-vis parameters of humic acid by baseline (A) and preliminary (B) interactions both in the presence and absence of clay minerals i.e. montmorillonite/kaolinite	118
Figure 4.38.	A-C. Change of fractional UV-vis parameters of humic acid with respect to irradiation time (x axis: irradiation time 0-90 min) both in the presence and absence of clay minerals i.e. montmorillonite/kaolinite	119
Figure 4.39.	A: Specific SCoA and SUVA ₃₆₅ variation with respect to E ₃₆₅ /E ₄₃₆ ratio of humic acid and B: Specific SCoA and SUVA ₂₅₄ variation with respect to E ₂₅₄ /E ₄₃₆ ratio of humic acid in the presence of montmorillonite or kaolinite upon photocatalysis irrespective of clay dose and irradiation conditions	121

Figure 4.40.	Photocatalytic degradation of humic acid illustrated by normalized specified UV-vis spectroscopic parameters correlated with DOC removal	124
Figure 4.41.	Photocatalytic degradation of humic acid in the presence of 0.05 mg mL ⁻¹ montmorillonite illustrated by normalized specified UV-vis spectroscopic parameters correlated with DOC removal	126
Figure 4.42.	Photocatalytic degradation of humic acid in the presence of 0.10 mg mL ⁻¹ montmorillonite illustrated by normalized specified UV-vis spectroscopic parameters correlated with DOC removal	127
Figure 4.43.	Photocatalytic degradation of humic acid in the presence of 0.20 mg mL ⁻¹ montmorillonite illustrated by normalized specified UV-vis spectroscopic parameters correlated with DOC removal	127
Figure 4.44.	Photocatalytic degradation of humic acid in the presence of 0.05 mg mL ⁻¹ kaolinite illustrated by normalized specified UV-vis spectroscopic parameters correlated with DOC removal	130
Figure 4.45.	Photocatalytic degradation of humic acid in the presence of 0.10 mg mL ⁻¹ kaolinite illustrated by normalized specified UV-vis spectroscopic parameters correlated with DOC removal	131
Figure 4.46.	Photocatalytic degradation of humic acid in the presence of 0.20 mg mL ⁻¹ kaolinite illustrated by normalized specified UV-vis spectroscopic parameters correlated with DOC removal	131
Figure 4.47.	Pseudo first order kinetic model parameters of photocatalytic degradation of humic acid in the presence of montmorillonite and kaolinite	135
Figure 4.48.	Comparative presentation of pseudo first order rates	139

- Figure 4.49. A-F SEM images of sole TiO_2 (A), TiO_2 and humic acid (B), TiO_2 and montmorillonite (C), TiO_2 and kaolinite (D), TiO_2 , montmorillonite and humic acid (E), TiO_2 , kaolinite and humic acid 140
- Figure 4.50. A-C SEM images of photocatalytically treated humic acid (A), photocatalytically treated HA in the presence of montmorillonite (B) and photocatalytically treated HA in the presence of kaolinite (C) 141
- Figure 4.51. UV-vis spectra of raw, 0.45 μm filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction of humic acid 143
- Figure 4.52. Emission scan (A) and synchronous scan (B) fluorescence spectra of raw, 0.45 μm filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction of humic acid 145
- Figure 4.53. UV-vis spectra of raw, 0.45 μm filtered fraction, treated 0.45 μm filtered fraction, 100 kDa,t fraction, 30 kDa,t fraction and 3 kDa,t fraction of humic acid 148
- Figure 4.54. Emission scan (A) and synchronous scan (B) fluorescence spectra of raw 0.45 μm filtered fraction, photocatalytically treated humic acid 0.45 μm filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid 149
- Figure 4.55. UV-vis spectra of raw, 0.45 μm filtered fraction, treated 0.45 μm filtered fraction, 100 kDa,t fraction, 30 kDa,t fraction and 3 kDa,t fraction of humic acid in the presence of 0.2 mg mL^{-1} montmorillonite 152
- Figure 4.56. Emission scan (A) and synchronous scan (B) fluorescence spectra of raw, 0.45 μm filtered fraction, photocatalytically treated humic acid 0.45 μm filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid in the presence of 0.2 mg mL^{-1} montmorillonite 153

- Figure 4.57. UV-vis spectra of raw, 0.45 μ m filtered fraction, treated 0.45 μ m filtered fraction, 100 kDa,t fraction, 30 kDa,t fraction and 3 kDa,t fraction of humic acid in the presence of 0.2 mg mL⁻¹ kaolinite 157
- Figure 4.58. Emission scan (A) and synchronous scan (B) fluorescence spectra of raw, 0.45 μ m filtered fraction, photocatalytically treated humic acid 0.45 μ m filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid in the presence of 0.2 mg mL⁻¹ kaolinite 158
- Figure 4.59. Molecular size distribution pattern of humic acid both in the presence and absence of montmorillonite and kaolinite under oxidative and non-oxidative conditions 164
- Figure 4.60. EEM fluorescence spectra of humic acid (A), humic acid in the presence of TiO₂ (B), humic acid in the presence of montmorillonite (C), humic acid in the presence of kaolinite(D), humic acid in the presence of TiO₂ and montmorillonite(E), humic acid in the presence of TiO₂ and kaolinite(F) 169
- Figure 4.61. Irradiation time dependent EEM fluorescence spectra of humic acid 170
- Figure 4.62. Irradiation time dependent EEM fluorescence spectra of humic acid in the presence of montmorillonite 171
- Figure 4.63. Irradiation time dependent EEM fluorescence spectra of humic acid in the presence of kaolinite 173
- Figure 4.64. Ca²⁺ effect on EEM fluorescence spectra of humic acid in the presence of either montmorillonite or kaolinite 175
- Figure 4.65. Correlations between FI and specified and specific humic parameters recorded under non-oxidative (dark) and oxidative (photocatalytic) conditions 178

Figure 4.66.	Color ₄₃₆ adsorption isotherm of humic acid adsorption onto TiO ₂	181
Figure 4.67.	UV ₂₅₄ adsorption isotherm of humic acid adsorption onto TiO ₂	181
Figure 4.68.	DOC adsorption isotherm of humic acid adsorption onto TiO ₂	182
Figure 4.69.	Emission scan fluorescence spectra of humic acid: Humic acid adsorption onto TiO ₂	183
Figure 4.70.	Synchronous scan fluorescence spectra of humic acid: Humic acid adsorption onto TiO ₂	184
Figure 4.71.	Color ₄₃₆ adsorption isotherm of humic acid adsorption onto montmorillonite	185
Figure 4.72.	UV ₂₅₄ adsorption isotherm of humic acid adsorption onto montmorillonite	185
Figure 4.73.	DOC adsorption isotherm of humic acid adsorption onto montmorillonite	186
Figure 4.74.	Emission scan fluorescence spectra of humic acid; Humic acid adsorption onto montmorillonite	188
Figure 4.75.	Synchronous scan fluorescence spectra of humic acid; Humic acid adsorption onto montmorillonite	188
Figure 4.76.	Color ₄₃₆ adsorption isotherm of humic acid adsorption onto kaolinite	190
Figure 4.77.	UV ₂₅₄ adsorption isotherm of humic acid adsorption onto kaolinite	190
Figure 4.78.	DOC adsorption isotherm of humic acid adsorption onto kaolinite	191
Figure 4.79.	Emission scan fluorescence spectra of humic acid; Humic acid adsorption onto kaolinite	192

Figure 4.80.	Synchronous scan fluorescence spectra of humic acid; Humic acid adsorption onto kaolinite	192
Figure 4.81.	Color ₄₃₆ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of montmorillonite	194
Figure 4.82.	UV ₂₅₄ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of montmorillonite	194
Figure 4.83.	DOC adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of montmorillonite	195
Figure 4.84.	Emission scan fluorescence spectra of humic acid: Humic acid adsorption onto TiO ₂ in the presence of montmorillonite	196
Figure 4.85.	Synchronous scan fluorescence spectra of humic acid; Humic acid adsorption onto TiO ₂ in the presence of montmorillonite	197
Figure 4.86.	Color ₄₃₆ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of kaolinite	199
Figure 4.87.	UV ₂₅₄ adsorption isotherm of humic acid onto adsorption TiO ₂ in the presence of kaolinite	199
Figure 4.88.	DOC adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of kaolinite	200
Figure 4.89.	Emission scan fluorescence spectra of humic acid: Humic acid adsorption onto TiO ₂ in the presence of kaolinite	201
Figure 4.90.	Synchronous scan fluorescence spectra of humic acid: Humic acid adsorption onto TiO ₂ in the presence of kaolinite	202

Figure 4.91.	Color ₄₃₆ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of Ca ²⁺	203
Figure 4.92.	UV ₂₅₄ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of Ca ²⁺	204
Figure 4.93.	DOC adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of Ca ²⁺	204
Figure 4.94.	Emission scan fluorescence spectra of humic acid adsorption onto TiO ₂ in the presence of Ca ²⁺	206
Figure 4.95.	Synchronous scan fluorescence spectra of humic acid adsorption onto TiO ₂ in the presence of Ca ²⁺	206
Figure 4.96.	Color ₄₃₆ adsorption isotherm of humic acid adsorption onto montmorillonite in the presence of Ca ²⁺	207
Figure 4.97.	UV ₂₅₄ adsorption isotherm of humic acid adsorption onto montmorillonite in the presence of Ca ²⁺	208
Figure 4.98.	DOC adsorption isotherm of humic acid adsorption onto montmorillonite in the presence of Ca ²⁺	208
Figure 4.99.	Emission scan fluorescence spectra of humic acid adsorption onto montmorillonite in the presence of Ca ²⁺	209
Figure 4.100.	Synchronous scan fluorescence spectra of humic acid adsorption onto montmorillonite in the presence of Ca ²⁺	210
Figure 4.101.	Color ₄₃₆ adsorption isotherm of humic acid adsorption onto kaolinite in the presence of Ca ²⁺	212

Figure 4.102. UV ₂₅₄ adsorption isotherm of humic acid adsorption onto kaolinite in the presence of Ca ²⁺	212
Figure 4.103. DOC adsorption isotherm of humic acid adsorption onto kaolinite in the presence of Ca ²⁺	213
Figure 4.104. Emission scan fluorescence spectra of humic acid adsorption onto kaolinite in the presence of Ca ²⁺	214
Figure 4.105. Synchronous scan fluorescence spectra of humic acid adsorption onto kaolinite in the presence of Ca ²⁺	215
Figure 4.106. Color ₄₃₆ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of montmorillonite and Ca ²⁺	216
Figure 4.107. UV ₂₅₄ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of montmorillonite and Ca ²⁺	217
Figure 4.108. DOC adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of montmorillonite and Ca ²⁺	217
Figure 4.109. Emission scan fluorescence spectra of humic acid adsorption onto TiO ₂ in the presence of montmorillonite and Ca ²⁺	219
Figure 4.110. Synchronous scan fluorescence spectra of humic acid adsorption onto TiO ₂ in the presence of montmorillonite and Ca ²⁺	220
Figure 4.111. Color ₄₃₆ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of kaolinite and Ca ²⁺	221
Figure 4.112. UV ₂₅₄ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of kaolinite and Ca ²⁺	221

Figure 4.113. DOC adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of kaolinite and Ca ²⁺	222
Figure 4.114. Emission scan fluorescence spectra of humic acid adsorption onto TiO ₂ in the presence of kaolinite and Ca ²⁺	223
Figure 4.115. Synchronous scan fluorescence spectra of humic acid adsorption onto TiO ₂ in the presence of kaolinite and Ca ²⁺	224
Figure A.1. UV ₂₈₀ adsorption isotherm of humic acid adsorption onto TiO ₂	252
Figure A.2. UV ₃₆₅ adsorption isotherm of humic acid adsorption onto TiO ₂	252
Figure A.3. UV ₂₈₀ adsorption isotherm of humic acid adsorption onto montmorillonite	253
Figure A.4. UV ₃₆₅ adsorption isotherm of humic acid adsorption onto montmorillonite	253
Figure A.5. UV ₂₈₀ adsorption isotherm of humic acid adsorption onto kaolinite	254
Figure A.6. UV ₃₆₅ adsorption isotherm of humic acid adsorption onto kaolinite	254
Figure A.7. UV ₂₈₀ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of montmorillonite	255
Figure A.8. UV ₃₆₅ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of montmorillonite	255
Figure A.9. UV ₂₈₀ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of kaolinite	256

Figure A.10. UV ₃₆₅ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of kaolinite	256
Figure A.11. UV ₂₆₅ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of Ca ²⁺	257
Figure A.12. UV ₃₆₅ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of Ca ²⁺	257
Figure A.13. UV ₂₈₀ adsorption isotherm of humic acid adsorption onto montmorillonite in the presence of Ca ²⁺	258
Figure A.14. UV ₃₆₅ adsorption isotherm of humic acid adsorption onto montmorillonite in the presence of Ca ²⁺	258
Figure A.15. UV ₂₈₀ adsorption isotherm of humic acid adsorption onto kaolinite in the presence of Ca ²⁺	259
Figure A.16. UV ₃₆₅ adsorption isotherm of humic acid adsorption onto kaolinite in the presence of Ca ²⁺	259
Figure A.17. UV ₂₈₀ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of montmorillonite and Ca ²⁺	260
Figure A.18. UV ₃₆₅ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of montmorillonite and Ca ²⁺	260
Figure A.19. UV ₂₈₀ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of kaolinite and Ca ²⁺	261
Figure A.20. UV ₃₆₅ adsorption isotherm of humic acid adsorption onto TiO ₂ in the presence of kaolinite and Ca ²⁺	261

LIST OF TABLES

Table 2.1.	Silicate clay mineral groups	9
Table 2.2.	Batch adsorption studies: humic-clay systems	16
Table 2.3.	Specifications of clays used in elucidation of the clay-humic system interaction	17
Table 2.4.	Adsorption models and respective parameters of clay-humic system	24
Table 3.1.	Physical and chemical properties of montmorillonite, kaolinite and TiO ₂	37
Table 4.1.	Specified and specific UV-vis and fluorescence parameters and DOC of humic acid attained for baseline experiments	52
Table 4.2.	Specified and specific UV-vis and fluorescence parameters of humic acid for preliminary experiments performed under dark conditions in presence of TiO ₂	56
Table 4.3.	Specific and specified UV-vis and fluorescence parameters of humic acid during preliminary experiments performed under dark conditions in the presence of montmorillonite and TiO ₂	60
Table 4.4.	Specified and specific UV-vis and fluorescence parameters of humic acid during preliminary experiments performed under dark conditions in presence of kaolinite and TiO ₂	64
Table 4.5.	Specified and specific UV-vis and fluorescence parameters of humic acid during preliminary experiments performed under irradiation and in the absence of TiO ₂	69

Table 4.6.	Specified and specific UV-vis and fluorescence parameters of humic acid during preliminary experiments performed under irradiation in the presence of montmorillonite and in the absence of TiO_2	72
Table 4.7.	Specified and specific UV-vis and fluorescence parameters of humic acid during preliminary experiments performed under irradiation in the presence of kaolinite and in the absence of TiO_2	75
Table 4.8.	Removal of humic acid by baseline and preliminary interactions in the presence and in the absence of montmorillonite and kaolinite	78
Table 4.9.	Specific and specified UV-vis and fluorescence parameters of humic acid recorded during photocatalytic degradation	83
Table 4.10	Specific and specified UV-vis and fluorescence parameters of humic acid in the presence of 0.05 mg mL^{-1} montmorillonite recorded during photocatalytic degradation	89
Table 4.11.	Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of 0.10 mg mL^{-1} montmorillonite recorded during photocatalytic degradation	92
Table 4.12.	Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of 0.20 mg mL^{-1} montmorillonite recorded during photocatalytic degradation	96
Table 4.13.	Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of 0.05 mg mL^{-1} kaolinite recorded during photocatalytic degradation	101
Table 4.14.	Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of 0.10 mg mL^{-1} kaolinite recorded during photocatalytic degradation	105

Table 4.15.	Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of 0.20 mg mL ⁻¹ kaolinite recorded during photocatalytic degradation	109
Table 4.16.	Photocatalytic first order kinetic decay model rate constant ($k \times 10^{-3}$, min ⁻¹) of the specific UV-vis parameters of HA both in the presence and absence of either montmorillonite or kaolinite	117
Table 4.17.	Pseudo first order kinetic model parameters for the photocatalytic degradation of humic acid	125
Table 4.18.	Pseudo first order kinetic model parameters for the photocatalytic degradation of humic acid in the presence of montmorillonite	128
Table 4.19.	Pseudo first order kinetic model parameters for the photocatalytic degradation of humic acid in the presence of 0.05-0.2 mg mL ⁻¹ kaolinite	132
Table 4.20.	Specified and specific UV-vis and fluorescence parameters of raw, 0.45µm filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction of humic acid	146
Table 4.21.	Specified and specific UV-vis and fluorescence parameters of 0.45µm filtered fraction, photocatalytically treated humic acid 0.45µm filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid	151
Table 4.22.	Specified UV-vis and fluorescence parameters of 0.45µm filtered fraction, photocatalytically treated humic acid 0.45µm filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid in the presence of 0.20 mg mL ⁻¹ montmorillonite	155

Table 4.23.	Specified UV-vis and fluorescence parameters of 0.45 μ m filtered fraction, photocatalytically treated humic acid 0.45 μ m filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid in the presence of 0.20 mg mL ⁻¹ kaolinite	159
Table 4.24.	Descriptive UV-vis spectroscopic parameters and DOC for unoxidized and photocatalytically oxidized humic acid in the presence of clay minerals	167
Table 4.25.	Regional speciation of the EEM fluorescence spectral features of the humic acid treated under non-oxidative as well as oxidative conditions	176
Table 4.26.	Freundlich isotherm model coefficients of humic acid adsorption onto TiO ₂	183
Table 4.27.	Freundlich isotherm model coefficients of humic acid adsorption onto montmorillonite	187
Table 4.28.	Freundlich isotherm model coefficients of humic acid adsorption onto kaolinite	191
Table 4.29.	Freundlich isotherm model coefficients of humic acid adsorption onto TiO ₂ in the presence of montmorillonite	196
Table 4.30.	Freundlich isotherm model coefficients of humic acid onto TiO ₂ in the presence of kaolinite	200
Table 4.31.	Freundlich isotherm model coefficients of humic acid adsorption onto TiO ₂ in the presence of Ca ²⁺	205
Table 4.32.	Freundlich isotherm model coefficients of humic adsorption onto montmorillonite in the presence of Ca ²⁺	209

Table 4.33.	Freundlich isotherm model coefficients of humic acid adsorption onto kaolinite in the presence of Ca^{2+}	213
Table 4.34.	Freundlich isotherm model coefficients of humic acid adsorption onto TiO_2 in the presence of montmorillonite and Ca^{2+}	218
Table 4.35.	Freundlich isotherm model coefficients of humic acid adsorption onto TiO_2 in the presence of kaolinite and Ca^{2+}	223
Table 4.36.	Langmuir isotherm model parameters of DOC adsorption onto TiO_2 , montmorillonite and kaolinite	228

LIST OF ABBREVIATIONS

Symbol	Explanation	Unit Used
$\Delta\lambda$	Bandwidth	
HA	Humic acid	
AOP	Advanced oxidation processes	
BLF	Black Light Fluorescent Lamp	
C	Related UV-vis parameter or TOC content of HS	(m^{-1}) (mg L^{-1})
Color ₄₃₆	Absorbance at 436 nm	
Da	Dalton	
DBP	Disinfection byproduct	
DOC	Dissolved organic carbon	
DOM	Dissolved organic matter	
E	Absorbance value	
EEM	Excitation emission matrix	
F.I.	Fluorescence index	
FA	Fulvic acid	
FTIR	Fourier transformation infrared	
HA	Humic acid	
HPLC	High pressure liquid chromatography	
HS	Humic substances	
IHSS FA	International humic substance society fulvic acid	
IHSS HA	International humic substance society humic acid	
IHSS SHA	International humic substance society soil humic acid	
k	Pseudo first order reaction rate constant	(min^{-1})
K_{LH}	Adsorption coefficient	(m)
k_{LH}	Reaction rate constant	($\text{m}^{-1} \text{min}^{-1}$)
Kt	Kaolinite	
L-H	Langmuir Hinshelwood	
Mt	Montmorillonite	

NHA	Nordic humic acid	
NMR	Nuclear magnetic resonance spectroscopy	
NOM	Natural organic matter	
QS	Quinone sulfate	
R	Pseudo first order rate	
RHA	Roth humic acid	
R _{LH}	Rate of the reaction	
ROS	Refractory organic substances	
SCOA	Specific color absorbance at 436 nm	
SOM	Soil organic matter	
SUVA	Specific UV absorbance	
SUVA ₂₅₄	Specific UV absorbance at 254 nm	
SUVA ₂₈₀	Specific UV absorbance at 280 nm	
SUVA ₃₆₅	Specific UV absorbance at 365 nm	
t	Irradiation time	(min)
t _{1/2}	Half life	(min)
THM	Trihalomethane	
THMFP	Trihalomethane formation potential	
UV ₂₅₀	Absorbance at 250 nm	
UV ₂₅₄	Absorbance at 254 nm	
UV ₂₈₀	Absorbance at 280 nm	
UV ₃₆₅	Absorbance at 365 nm	

1. INTRODUCTION

Water quality and treatment issues related to the removal of natural organic matter have gained a lot of focus in many countries over the last years. The requirement for the improvement of drinking water standards, and the related technological advances for the removal of natural organic matter, brings about the need for the understanding of the basic chemical and physical properties of natural organic matter (NOM). The selection and optimization of water treatment processes with respect to cost efficient removal of NOM are subjects of growing concern. Organic matter is derived from natural terrestrial and aquatic sources or anthropogenic origins. Humic substances represent the major fraction of naturally occurring organic substances comprised of highly functionalized carbon rich polydisperse polyelectrolytes. Based on their solubility in water and as a function of pH, humic substances are generally classified into humic acids (HA), fulvic acids (FA) and humin. HA are comprised of high-molecular-weight organic substances that are soluble in alkaline media and insoluble in acidic media, whereas FA comprise moderate molecular weight organic substances of nonspecific composition that are soluble at all pH values.

Humic acids, have an important role in binding and fate of inorganic and organic compounds in natural environment (vanLoon and Duffy, 2000). Humic acids express amphiphilic character due to the presence of both hydrophobic domains as well as hydrophilic parts. The presence of organic matter displays yellow to brownish color that is mainly related to an aesthetic problem thereby considered as a secondary water quality parameter. Another topic that makes humic acids weighty to examine is their interaction with halogenated oxidizing agents during drinking water treatment and these interactions result with the formation of halogenated carcinogenic disinfection by- products, like chloroform. When these chemical compounds are introduced to the public drinking water directly the outcome of this would be undesired health consequences (Hayes, 1998). Therefore, the removal of natural organic matter namely humic acids from a water supply is essential, in order to prevent direct health effects and the problems that may occur during water treatment processes.

Besides natural organic matter, clay minerals also constitute a major fraction of the colloidal constituents in soil and aqueous environment. In natural waters, clay minerals expose surfaces open to interactions due to their diverse surface properties. Humic substances could form strong complexes with clay minerals. Formation of clay-humic complexes mainly proceeds through various interactions as anion and ligand exchange to clay edges, cation or water bridges to basal clay surfaces, H-bonding, van der Waals forces, and adsorption in the interlayer spaces. Moreover, electrolyte concentration leading to ionic strength effects, pH condition and the presence of natural organic matter exert substantial effects on the interactions (Sondi and Pravdi, 1996).

Besides the conventional water treatment methods used for the successful removal of the natural organic colloidal matter, application of advanced oxidation processes in particular photocatalysis had received widespread attention (Matilainen and Sillanpää, 2010). The major advantage of photocatalysis could be attributed to the observed performance as a substitute for the energy-intensive conventional treatment methods. Moreover, contrary to these methods, photocatalysis could precede to complete mineralization of the organic components by the formation of innocuous end products *i.e.* CO₂ and H₂O. With reference to the previous studies and with the aim of investigating the photocatalytic degradation of HA as a representative compound of NOM under natural water conditions, the role of clay particles should also be elucidated. Due to turbidity constraints, clay minerals could significantly affect the efficiency of photocatalysis by diminishing the absorbed light intensity. The presented study covers the effect of a 1:1 type clay mineral, *i.e.* kaolinite (Kt) in comparison to the photocatalytic degradation of HA performed in the presence of a 2:1 type clay mineral *i.e.* montmorillonite (Mt) (Sen Kavurmaci and Bekbolet, 2013a). Therefore, the main purpose of this research was to elucidate the interactive behavior of humic and diverse clay minerals towards non-selective TiO₂ photocatalytic oxidative treatment. Considering the ionic strength effect on the clay-humic-oxide system, the role of calcium ions should also be investigated. Moreover, referring to the polydisperse properties of HA, elucidation of molecular size fractionation both prior to and following photocatalysis would be helpful in understanding of the non-selective oxidative degradation of humic acid.

In the present work, as a complementary step to the elucidation of the photocatalytic degradation of humic acid under natural water conditions, the possible effects of the clay minerals are investigated. Regarding the previous publications of Bekbolet and colleagues published since 1996, it is very well documented that the photocatalytic degradation of humic acid as a model compound of natural organic matter has been successfully achieved under various conditions resembling natural waters. However, the role of clay minerals has not been studied so far. Therefore, the outcome of this work will certainly fulfill this gap and the results will bring significant contribution to this research area.

2. THEORETICAL BACKGROUND

2.1. Natural Organic Matter/ Humic Substances/ Humic and Fulvic Acids

Natural organic matter (NOM) is ubiquitous in terrestrial and aquatic ecosystems, and it plays a crucial role in the evolution of soils, the transport of pollutants, and the global carbon cycle. NOM is a complex mixture of molecules and is thus heterogeneous in structure and composition. As NOM passes through an ecosystem, it is acted upon by a variety of processes, such as microbial degradation, adsorption to mineral surfaces, and photochemical reactions that can change its properties and reactivity. The evolution of NOM in space and time thus is an important research area in biology, geochemistry, ecology, soil science, and water resources. Due to its complex structural and chemical heterogeneity, new innovative approaches are needed to help better understand the evolution of NOM properties and reactivity as it passes through an ecosystem.

The content of natural organic material occurring in terrestrial environments as well as in aquatic systems is defined as withering material from plants and animals as well as their degradation products. Total organic carbon (TOC) is the most comprehensive measurement to quantify the presence of organic matter in aquatic systems and often used as synonymous to (NOM). The simplest characterization of NOM can be based on the subdivision of TOC into operationally defined fractions such as DOC and POC. DOC represents the organic carbon smaller than 0.45 μm in diameter whereas POC signifies the fraction of TOC that is retained on a 0.45 μm porosity membrane.

Humic substances mainly humic acids (HA) constitute the major fraction of natural organic matter (NOM) in water supplies. They are known to be a complex class of biogenic polyelectrolytes with varying molecular weight distribution and comprise a wide range of functional groups, which can react with metal ions (Stevenson, 1994). Over the years many subfractions of humic substances have been isolated. Because of the complex nature of the humic substances, they have traditionally been classified according to the operational procedures needed to separate them. Oden's classification has been used since 1919.

Humic Acid: The fraction of humic substances that is not soluble in water under acidic conditions ($\text{pH} < 2.0$) but is soluble at higher pH values.

Fulvic Acid: The fraction of humic substances that is soluble in water under all pH conditions.

Humin: The fraction of humic substances that is not soluble in water at any pH value (Suffet and McCarthy, 1989).

The term humic substance refers to the organic material in the environment those results from the decomposition of plant and animal residues. Humic substances are ubiquitous, being found in all soils, sediments and waters (Suffet and MacCarty 1989). Aquatic humic substances are the degradation products of polymers of natural origin involving depolymerization and oxidation reactions that are catalyzed by enzymes. They lead to yellow to brown color in water. In natural waters, 50-70% of dissolved organic carbon (DOC) consists of humic substances.

Humic substances are mixed with, or chemically or physically associated with other classes of materials. In natural waters, humic acids are mixed with amino acids, sugars, various aliphatic and aromatic acids and other organic compounds. In soil and sediments, they are frequently bound to the mineral components. The molecular weight of humic substances is ranging from 500 to 5000 Da. Typical average molecular weights of aquatic fulvic acids are 800-1000 Da, and those of aquatic humic acids are 2000-3000 Da. In contrast, the molecular weights of soil humic acids are several hundred kDa. The basic structure of humic substances consists of aromatic rings of the di-or trihydroxy-phenol type bridges by $-\text{O}-$, $-\text{CH}_2-$, $-\text{NH}-$, $-\text{N}=\text{}$, $-\text{S}-$, and other groups and contains both free OH groups and the double linkage of quinones (Stevenson, 1994).

Some investigators proposed structural formula for humic and fulvic acids, but to this day none have proven satisfactory. A model used to demonstrate the general structure and function of humic acids is presented in Figure 2.1. Humic substances generally exhibit similar elemental and functional group composition in spite of the origin and environmental conditions of their formation. However, humic substances formed under different climatic regimes and natural soils contain different ranges of aromaticity and

functional group contents. The aromatic component of soil humic substances has been reported to range from 35 to 92% (Hatcher et al., 1981).

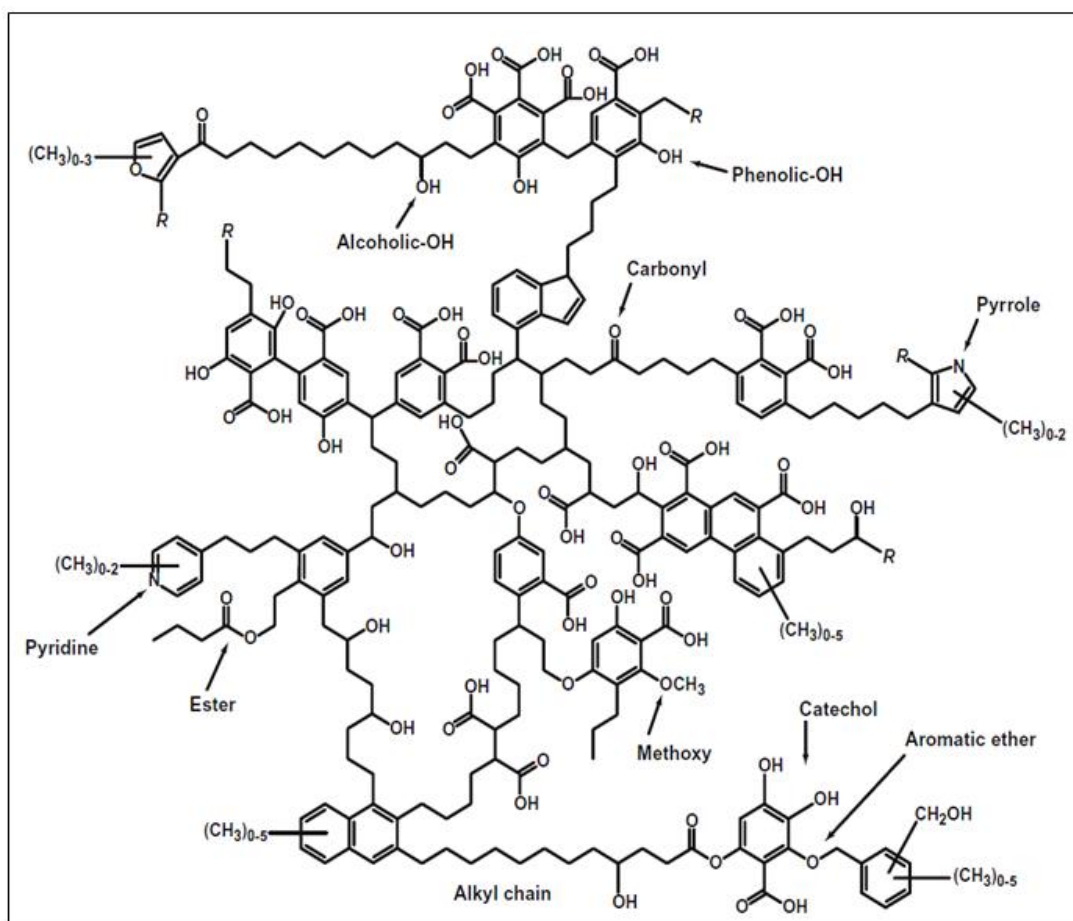


Figure 2.1. Partial pseudo-structure of humic acid (Schulten and Schnitzer, 1997).

Humic substances comprise one of the major components of natural organic matter in waters in close vicinity of the inorganic matrix as well as microbiological constituents (Kördel et al., 1997) (Figure 2.2). Humics express diverse actions primarily related to the formation of potentially harmful disinfection byproducts (DBP)'s. gains high importance. Humic substances in natural waters have been shown to be especially reactive with a variety of oxidants and disinfectants that are used for the purification of drinking water, particularly chlorine. These substances react with chlorine species (OCl/HOCl) to produce trihalomethanes (THMs), haloacetic acids (HAAs) and other halogenated DBPs (Singer, 1999). Therefore, the removal of DBP precursors through numerous treatment techniques from public health point of view (Uyguner and bekbolet 2007a and 2008).

2.2. Clays and Clay Minerals

Clay is general terms for inorganic material that has a particle size $<2\ \mu\text{m}$ in size, whereas clay mineral term refers to a specific mineral, which mainly occurs in the clay-sized fraction of the soil (Moore and Reynolds, 1989). Clays constitute a major part of the colloidal consortium present in natural waters (Figure 2.2) expressing close size similarities to the microbiological component. Clay mineral term signifies a class of hydrated phyllosilicates making up the fine-grained fraction of rocks, sediments, and soils. The secondary clay minerals (phyllosilicates) in soils play a profound role in affecting numerous soil chemical reactions and processes. They tend to have large surface areas, often-high cation exchange capacities, high adsorption capacities and some have swelling properties.

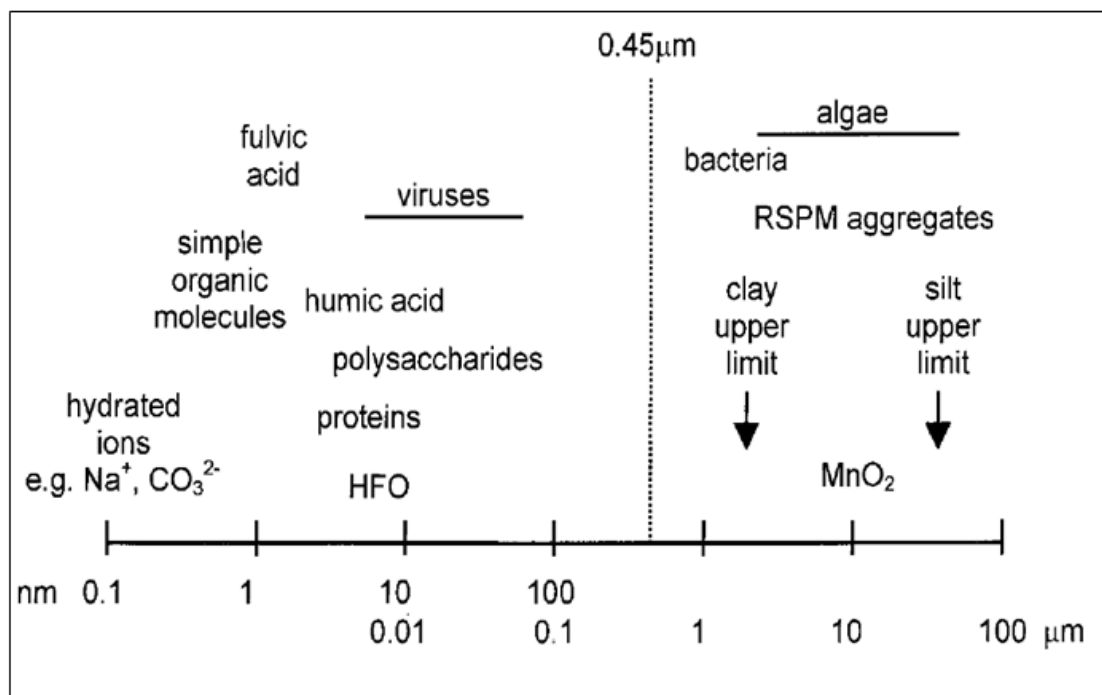


Figure 2.2. Approximate sizes of chemical and biological components of natural waters, (Stumm and Morgan, 1996). HFO, hydrous ferric oxide (primary particles); RSPM, riverine suspended particulate matter at moderate flow; the MnO_2 particle size refers to lake water precipitates. The $0.45\ \mu\text{m}$ line indicates the size of filter conventionally used to distinguish dissolved from 'particulate' components.

Clay minerals consist of Si-O tetrahedrons, in which one silicon atom (Si^{4+}) is centered between four oxygen atoms, and Al-O octahedrons, in which one aluminum atom (Al^{3+}) is centered between six oxygen atoms ($-\text{O}^{2-}$) (OH minerals may also be included depending on mineral type). The cations of Si^{4+} and octahedral structures form sheets by sharing oxygen atoms. The simple Si-O octahedral structures form sheets by sharing oxygen atoms. The substitution of an aluminum atom for silicon in the tetrahedron or the substitution of divalent cations (e.g. Fe^{2+} and Mg^{2+}) for aluminum in the octahedral sheet is a common occurrence. The amount of substitution in the tetrahedral and octahedral sheets and the ratio of octahedral to tetrahedral sheets are the primary differentiating characteristics between the many clay minerals. These sheet arrangements give rise to various mineral surface identities such as magnitude (specific surface), functional groups, and interactions with solution species. Substitution of a given coordinating cation by a cation with lower valence in a mineral gives rise to permanent negative charge or cation exchange capacity, CEC. Location of this substitution (e.g. tetrahedral sheet or octahedral sheet) gives rise to clay minerals with unique physicochemical properties.

Different clay minerals are made up of various combinations of tetrahedral and octahedral sheets composed of various oxides. For example, kaolinite is made up of one tetrahedral sheet plus one octahedral sheet (1:1 layer), while smectite and illite are made up of two tetrahedral sheets and one octahedral sheet (2:1 layer). The space between layers (for example, two tetrahedral sheets plus one octahedral sheet) is known as the interlayer space. The interlayer space may contain positive ions known as cations (for example, potassium- K^+). Different clay minerals contain different cations in the interlayer space. The interlayer spacing of kaolin does not contain cations, because the layers are held together by hydrogen bonding. The basal spacing of a clay mineral is the distance from the top of one layer to the top of the next layer. The basal spacing varies among clay minerals. The major silicate clay mineral groups as representatives of 1:1, 2:1 and 2:1:1 clay minerals are presented in Table 2.1. Selected descriptive properties were layer type, specific surface area (m^2g^{-1}), cation exchange capacity (CEC, mol kg^{-1}) and type of chemical formula. Kaolinite belongs to phyllosilicates, 1:1 Phyllosilicates (Kaolinite-serpentine) and kaolinite subgroup. Montmorillonite belongs to phyllosilicates, 2:1 phyllosilicates, smectites and dioctahedral smectites. The silicate clay minerals are shown in Figure 2.3 (Rieder et al., 1998).

Table 2.1. Silicate clay mineral groups, (Sposito1989).

Group	Layer Type	Specific Surface area m^2g^{-1}	CEC cmolkg^{-1}	Type of Chemical Formula
Kaolinite	1:1	10-20	3-15	$[\text{Si}_4]\text{Al}_4\text{O}_{10}(\text{OH})_8 \cdot n\text{H}_2\text{O}$ ($n= 0$ or 4)
Illite	2:1	40-180	20-40	$\text{M}_x[\text{Si}_{6.8}\text{Al}_{1.2}]\text{Al}_3\text{Fe}_{0.025}\text{Mg}_{0.75}\text{O}_{20}(\text{OH})_4$
Vermiculite	2:1	600-800	110-160	$\text{M}_x[\text{Si}_7\text{Al}]\text{AlFe}_{0.05}\text{Mg}_{0.5}\text{O}_{20}(\text{OH})_4$
Montmorillonite	2:1	600-800	60-100	$\text{M}_x(\text{Al}, \text{Fe}^{2+}, \text{Mg})_4\text{Si}_8\text{O}_{20}(\text{OH})_4$
Chlorite	2:1:1	70-150	10-30	$(\text{Al}(\text{OH})_{2.55})_4[\text{Si}_{6.8}\text{Al}_{0.2}]\text{Al}_{3.4}\text{Mg}_{0.6}20\text{OH})_4$

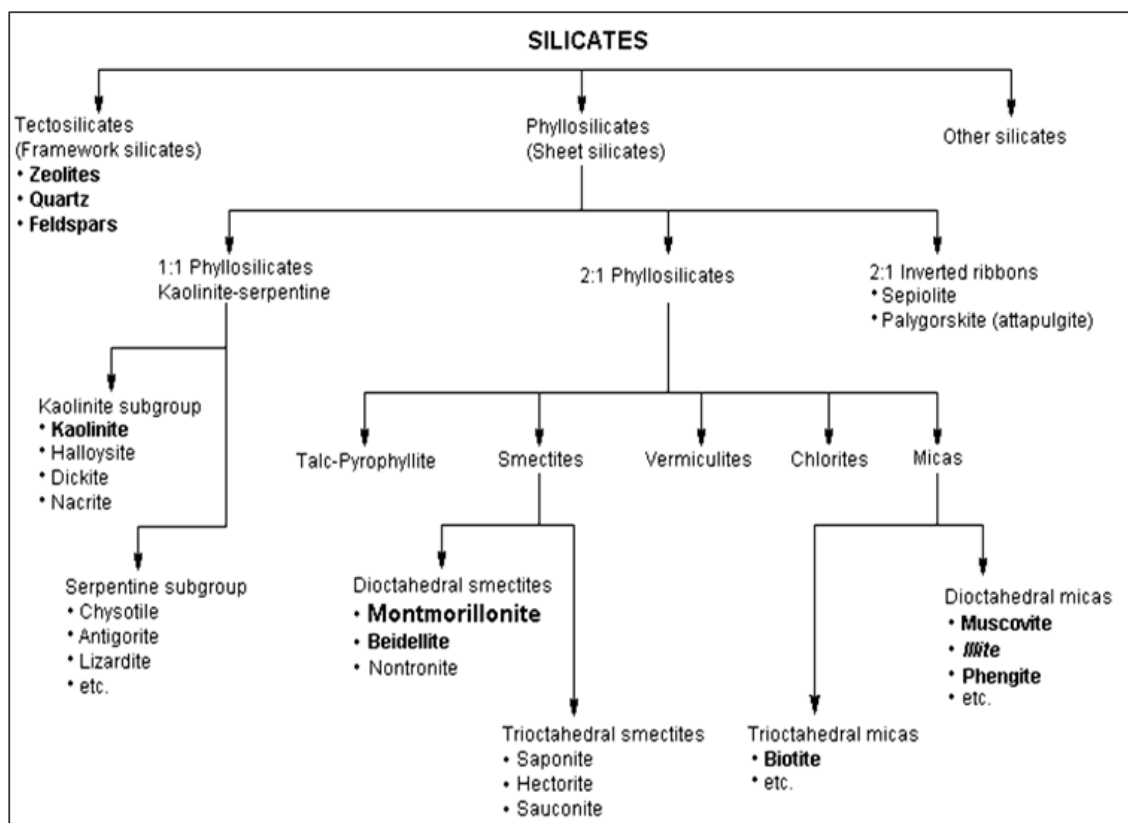


Figure 2.3. Silicate clay minerals, (Rieder et al., 1998).

Schematic presentation of kaolinite is given in Figure 2.4, displaying 1:1 layers of alumina and silica layers composed of one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina.

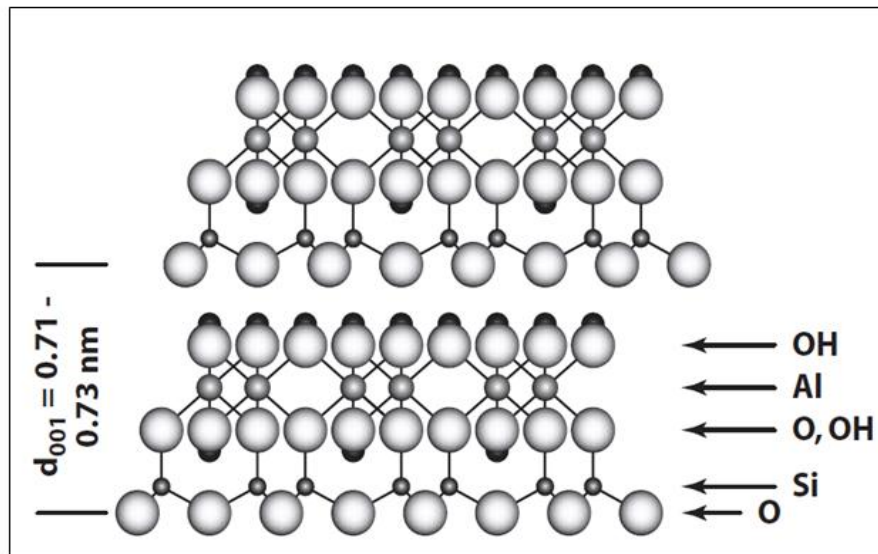


Figure 2.4. The 1:1 structure of kaolinite, (Essington, 2004).

Schematic presentation of montmorillonite is given in Figure 2.5 displaying tetrahedra sheets containing Si⁴⁺ ions. Aluminium is the normal ion in the central sheet, but about one-eighth of the octahedra contain Mg²⁺ as a substituting ion for Al³⁺.

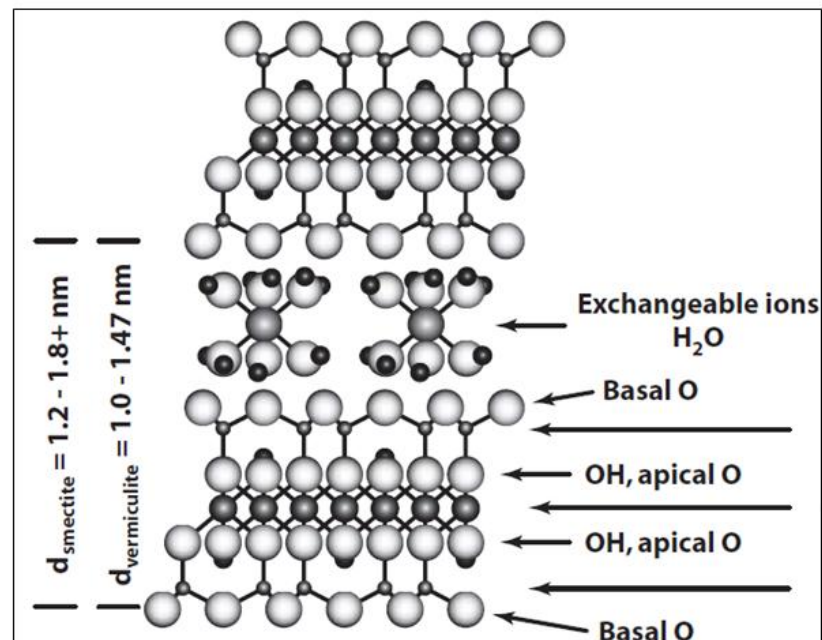


Figure 2.5. The structural and chemical characteristics of the expandable 2:1 trioctahedral phyllosilicates hectorite, saponite, sauconite, and trioctahedral vermiculite, (Essington, 2004).

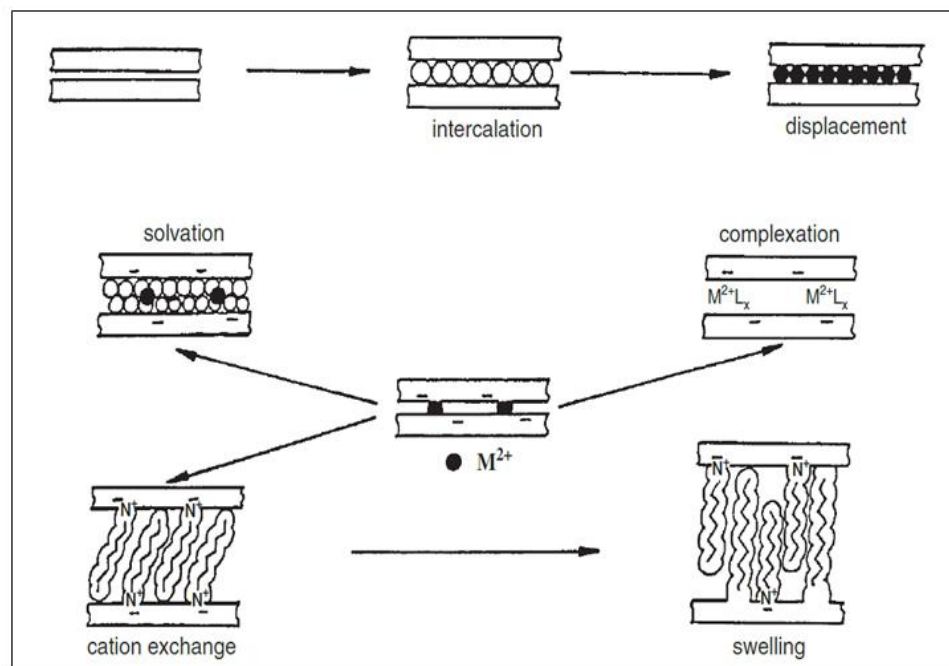


Figure 2.6. Interlayer reactions of 1:1 and 2:1 clay minerals, (Jasmund and Lagaly, 1993).

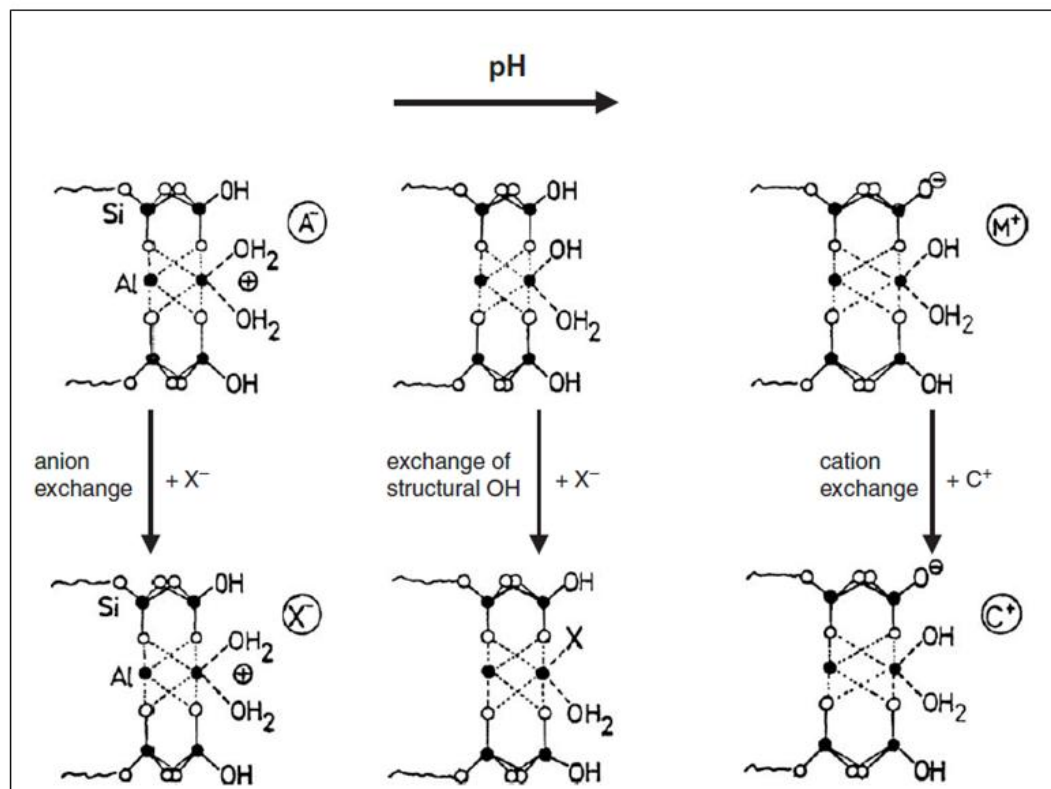


Figure 2.7. The pH-dependent ion and ligand exchange reactions at the edges of the clay mineral layers, shown for 2:1 clay minerals, (Lagaly, 1993).

Interlayer reactions occurring in aqueous medium lead to swelling of 1:1 type and 2:1 clay minerals moreover clay minerals could host organic molecules as well as display cation exchange properties (Figure 2.6). Swelling properties could form the basis of the modified oxide surfaces *i.e.* pillared clay photocatalysts (Damardji et al., 2009, Vimonses et al., 2010). On the other hand, with reference to the acid-base properties originating from the edges of 2:1 clay minerals, pH dependent ion and ligand exchange reactions could lead to various important reactions (Figure 2.7).

2.3. Natural Organic Matter-Clay Complexes in Soil

Humic substances are the major organic components of soils. They interact with clay minerals to form organo-mineral complexes and composites. They account for 70% of soil organic matter (NOM) (Kodama, 1994), and the soil aggregation, mechanical properties, exchange capacity and other physical and chemical properties are largely affected by the features of humic substances (Huang and Schnitzer, 1986). Soil organic matter complexes can occur with clay minerals that are coated with metal oxides such as Al and Fe oxides. Clays tend to stabilize SOM, and a correlation is often observed between the clay content and SOM. Some organic substances bridge soil particles together, resulting in stable aggregates. In some soils, particularly those high in humic substances, all of the clay may be coated with HS. It has been estimated that from 5% to 98% of all C in soils occurs as clay-SOM complexes (Stevenson, 1994). In the complex of NOM and clay minerals, humic acids do not form intercalation complexes, probably because of their large molecular weight; however, fulvic acid can penetrate in the interlayers of clay minerals.

The types of interactions involved in SOM-clay complexes include physical adsorption or interactions via van der Waals forces, electrostatic interactions (cation and anion exchange processes), cation and anion bridges whereby the polyvalent metal forms a bridge between the organic molecule and the inorganic surface to which it is bound (clay mineral-metal-HS), often referred to as coordination complexes, chemical adsorption, and H-bonding. Two or more of these mechanisms may occur simultaneously, depending on the type of organic material, the nature of the exchangeable sites in on the clay surface, the surface acidity, and the moisture content of the system (Huang and Schnitzer, 1986).

2.4. Natural Organic Matter -Clay Complexes in Aquatic Systems

Natural waters such as rivers, estuaries and the sea are complex systems of electrolytes, dissolved and particulate organic matter, and inorganic particulates, comprised of clays, quartz, carbonates, and a variety of metal oxides (most frequently Al, Fe and Mn). Clay minerals are the main component of suspended solid material in natural waters, responsible for the transport of inorganic and organic contaminants. One of the most important characteristic of clay mineral particles is colloidal stability in the aquatic environment. Clays surpass carbonates and many metal oxides in their chemical persistence, colloid stability and adsorption capacities. Geochemical processes that govern the land/sea interaction occur in rivers and effectively regulate the adsorption and deposition phenomena in estuaries in the transition between soft river water and seawater (O'Melia, 1989). Research into the physical and colloid chemistry designed to reveal single processes are difficult, or nearly impossible. As a way out of these problems, model minerals and simple electrolyte solutions were used in carefully designed experiments. Clays have been studied extensively from various aspects and for various purposes. The overwhelming diversity of clays, their chemical composition, structural properties, ionic exchange capacities and the related surface charge phenomena are responsible for their role in the transport of micro constituents of the aquatic phase (Stumm, 1992). Significant numbers of studies have been applied in the literature about humic substances and clay minerals interactions, the results of which are evaluated and discussed with respect to the relevant operational parameters (Ohassi and Nakazawa, 1996; Liu and Gonzalez, 1999; Meier et al., 1999; Elfariasi and Pefferkorn, 2000; Specht et al., 2000; Tombácz and Szekeres, 2004; Ghabbour et al., 2004; Abate and Masini, 2005; Feng et al., 2005; Wang and Xing, 2005; Salman et al., 2007; Balcke et al., 2002; Majzik and Tombácz, 2007a; Majzik and Tombácz, 2007b; Doulia et al., 2009).

2.5. Adsorption of NOM on the Clay Minerals

The understanding of interactions between humic substances and charged solid surfaces is important for modeling the geochemical fate and biological availability of nutrients and pollutants in aquatic environments (Stevenson, 1994). It is also important from the technological point of view due to the problems caused in water treatment plants.

The interaction of humic substances with clay mineral surfaces depends on a variety of mechanisms. These interactions may occur through processes like ion exchange, adsorption-desorption, precipitation--dissolution and diffusion. Adsorption describes the process of enrichment (positive adsorption) or depletion (negative adsorption) of one or more chemical species in an interface region. Absorption involves the transfer of a molecule from the bulk state of one phase to the bulk state of another. In the solution a mixture of molecules and/or ionic species interacts with a mixture of different sorbents. Adsorption processes are fundamental for the interactions, which take place between the organic and inorganic colloids in water.

Adsorption is directly related with surface area of the adsorbent, pore size distribution, as well as the characteristic of the adsorbed molecules. Diffusion coefficients, in particular, decrease as molecular size increases, and thus longer times are required to remove the large-molecular-weight humic substances than are needed for the low-molecular-weight phenols, for example. Adsorbent particle size is also important because it determines the time required for transport within the pore to available adsorption sites (Letterman et al., 1999). Interaction of humic substances with clay mineral surfaces depend upon the intrinsic nature and properties of the organic species, the properties of the clay mineral with special knowledge of the kind of exchangeable cation at the clay surface, the water content of the system.

Other factors affect the adsorption like pH and temperature. Generally, adsorption is increased at pH ranges where the species has not any charge. Many organics form negative ions at high pH, positive ions at low pH, and neutral species in intermediate pH ranges. Moreover, pH affects the charge on the surface, altering its ability to adsorb materials. Likely many organic pollutants in water, humic substances are highly adsorbed by decreasing pH because of neutralization of negative charges at the carbon surface with increasing hydrogen concentration. When temperature is increased, the adsorption extent decreases because adsorption reactions are exothermic. These adsorptive integrations could be visualized in Figure 2.8. The functional groups (mainly carboxylic and phenolic type groups) and hydrogen bonding express the organic matter or electrostatic attractions could mainly describe the attractive forces.

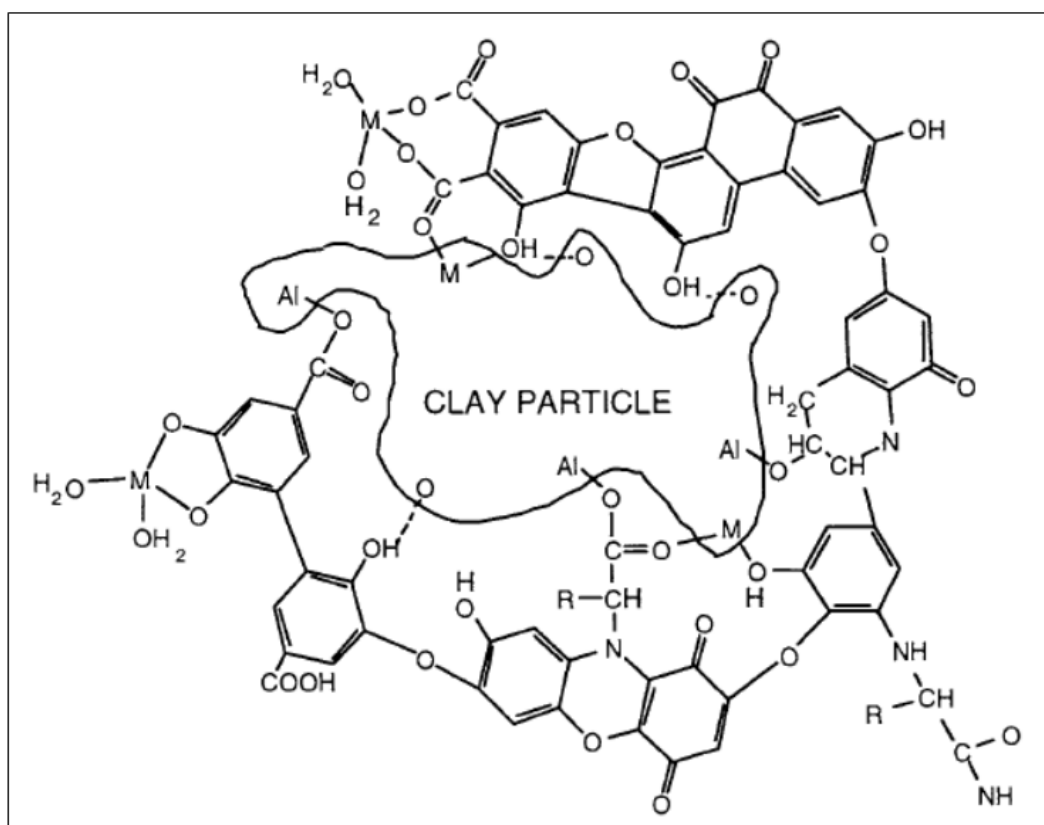


Figure 2.8. Interaction of a humic model molecule and a clay particle, (Koskinen and Harper 1990).

2.6. Humic Acid/Natural Organic Matter Type

The relative contribution of the various mechanisms to forming clay-humic complexes is different for different clay minerals and humic substances. Application of adsorption process to natural organic matter with clay minerals could be achieved either by taking natural water samples from the sources or by using model compounds resembling natural organic matter (mainly humic acids originating both from terrestrial and aquatic sources). Moreover, some commercial humic and fulvic acids also found a wide application area. The results of the literature survey on the adsorption studies revealed the type of natural organic matter and clay minerals as presented in the following Table 2.2. Importance is directed to the type of NOM, model NOM compounds and clay minerals in connection with the experimental details such as reactor type, equilibrium time, pH and the measured humic parameters.

Table 2.2. Batch adsorption studies: humic-clay systems.

Humic acid type Natural/commercial	Parameter	References
HA, Telnite	XRD, TEM UV 254 nm	Ohassi and Nakazawa, 1996
HA, Aldrich	Atomic absorption Vis 400 nm	Liu and Gonzalez, 1999
River water sample DOC: 37.0 mg L ⁻¹ Swamp water sample DOC: 41.5 mg L ⁻¹	XAD-8 chromatography UV 400 nm DOC HPSEC	Meier et al., 1999
Peat HA	Turbidity UV 280 nm	Elfarisi and Pefferkorn, 2000
Water sample DOC : 16.4 mg L ⁻¹ - 23.7 mg L ⁻¹	SEC, UV 254 nm, DOC, Fluorescence	Specht et al., 2000
Soil, peat, lignite, and a brown water lake.	UV 240 nm, DOC, Elemental analysis, SEC C ¹³ NMR spectra	Balcke et al., 2002
HA, Aldrich	TOC	Naceur et al., 2003
Plants, peats, and soils HA	UV 280 nm FTIR spectra C ¹³ NMR spectra	Ghabbour et al., 2004
Brown coal HA	450 nm	Tombácz and Szekeres et al., 2004
Soil HA , HA, Aldrich	Vis 400 nm	Abate and Masini, 2005
Peat HA	C ¹³ NMR, spectroscopy, DOC	Feng et al., 2005
HA, Amherst	C ¹³ NMR spectra GC E4/E6 (Abs 465nm/665nm)	Wang and Xing, 2005
Soil HA	Vis 400 nm	Salman et al., 2007
Peat HA	Vis 450 nm SUVA ₂₅₄ E3/E4 (Abs 300nm/400nm)and E4/E6 (Abs 465nm/665nm)	Majzik and Tombácz, 2007a; Majzik and Tombácz, 2007b
Fluka Humic acid	Vis 400 nm	Doulia et al., 2009

In most of the research, peat humic acid have been used as the model of humic substances (Elfarisi and Pefferkorn, 2000; Balcke et al., 2002; Ghabbour et al., 2004; Feng et al., 2005; Majzik and Tombácz, 2007a; Majzik and Tombácz, 2007b). In several studies, humic acid salts supplied from Aldrich have been investigated as the model of humic substances (Liu and Gonzalez, 1999; Naceur et al., 2003; Abate and Masini, 2005).

In approximately all of the research, UV spectrum were used to express parameters for detection of humic acid in solution (Ohassi and Nakazawa, 1996; Liu and Gonzalez, 1999; Meier et al., 1999; Specht et al., 2000; Elfarisi and Pefferkorn, 2000; Balcke et al., 2002; Ghabbour at al., 2004; Tombácz et al., 2004; Abate and Masini, 2005; Wang and Xing, 2005; Salman et al., 2007; Majzik and Tombácz, 2007a; Majzik and Tombácz, 2007b; Doulia et al., 2009).

Table 2.3. Specifications of clays used in elucidation of the clay-humic system interaction.

Clay Type	Surface area BET, m^2g^{-1}	Point of Zero Charge pH_{zpc}	CEC meq/100 g	Clay Characterization Method	References
Montmorillonite	-	-	-	X-ray defraction X-ray fluorescence	Ohassi and Nakazawa, 1996
Montmorillonite, Clay Minerals Society	-	2.5	80	-	Liu and Gonzalez, 1999
Kaolinite, (kga-1b) Clay Minerals Society	12.6	5.3	-	Atomic force microscopy	Meier et al., 1999
Kaolinite, French origin	18.5	-	9	Zeta potential	Elfarisi and Pefferkorn, 2000
Kaolinite, Dorfner	-	5	-	X-ray defraction, Zeta potential	Specht et al., 2000
Montmorillonite, Merck	-	-	-	X-ray defraction, Zeta potential	Specht et al., 2000
Kaolin, Caminauer	15	2.2	-	Elemental analyses	Balcke et al., 2002

Table 2.3. Continued.

Montmorillonite, Algerian	-	-	-	Electron micrograph	Naceur et al., 2003
Kaolinite	-	-	-	FTIR spectra	Ghabbour at al., 2004
Kaolin, Zettlitz	-	-	-	Zeta potential	Tombácz et al., 2004
Vermiculite	-	-	-	X-ray diffraction, thermal analysis	Abate and Masini, 2003
Montmorillonite (saz-1), Clay Minerals Society	97.42	-	120	-	Feng et al., 2005 ; Karapanagioti and Sabatini, 2000
Kaolinite (kga-1b) Clay Minerals Society	10.05	-	2.0	-	Feng et al., 2005 ; Karapanagioti and Sabatini, 2000
Kaolinite Fluka	15.9	-	-	Elemental analyses (C, H, N)	Wang and Xing, 2005
Montmorillonite Fluka	329	-	-	Elemental analyses (C, H, N)	Wang and Xing, 2005
Montmorillonite, Clay Minerals Society		2.5	105	Zeta Potential	Tombácz and Szekeres, 2004; Tombácz et al., 2004; Majzik and Tombácz, 2007a; Majzik and Tombácz, 2007b
Bentonite, Jordanian	-	-	-	X-ray fluorescence	Salman et al., 2007
Bentonite	-	-	-	SEM, XRD	Doulia et al., 2009

In half of the research, kaolinite have been used as adsorbent clay minerals of humic substances (Meier et al., 1999; Karapanagioti and Sabatini, 2000; Elfarisi and Pfefferkorn, 2000; Specht et al., 2000; Balcke et al., 2002; Ghabbour at al., 2004; Tombácz et al., 2004; Feng et al., 2005; Wang and Xing, 2005). Other clay minerals used for adsorption of humic substances are montmorillonite (Ohassi and Nakazawa, 1996; Liu and Gonzalez, 1999;

Karapanagioti and Sabatini, 2000 ; Specht et al., 2000; Naceur et al., 2003; Feng et al., 2005; Tombácz and Szekeres, 2004; Tombácz et al., 2004; Wang and Xing, 2005; Majzik and Tombácz, 2007a; Majzik and Tombácz, 2007b), bentonite (Salman et al., 2007; Doulia et al., 2009), vermiculite (Abate and Masini, 2003).

In most of the research, X-ray diffraction (Ohassi and Nakazawa, 1996; Specht et al., 2000; Abate and Masini, 2003) and zeta potential measurement (Elfarisi and Pefferkorn, 2000; Specht et al., 2000; Tombácz and Szekeres 2004; Tombácz et al., 2004; Majzik and Tombacz, 2007a; Majzik and Tombacz, 2007b;) were used for characterization of clay minerals.

Based on the presented information, no significant attention has been paid upon neither to pH_{zpc} nor to CEC.

2.7. Effect of Solution Matrix: pH and Ionic Strength

In addition to the clay minerals and humic substance type, solution matrix should be considered as effective parameters of the interaction of humic clay parameters because rarely clay minerals and humic substances occur alone in soils, sediments and particulate material suspended in aquatic environments. The solution matrix constitutes are the major background parameters effective on the adsorption processes and interaction mechanisms of humic clay systems. aquatic systems are include of humic substances in the presence of various chemical, physical and biological in nature, the adsorption process should be evaluated under simulated conditions. Therefore, several studies have been carried out for the assessment of the analytical factor on the adsorption mechanism and performance (Ohassi and Nakazawa, 1996; Salman et al., 2007; Liu and Gonzalez, 1999; Elfarisi and Pefferkorn, 2000; Specht et al., 2000; Wang and Xing, 2005; Balcke et al., 2002; Doulia et al., 2009; Meier et al., 1999; Majzik and Tombácz, 2007a; Majzik and Tombácz, 2007b; Tombácz et al., 2004; Ghabbour at al., 2004; Abate and Masini, 2005).

A distinction of the predominant interaction mechanism is very difficult because of the physical and chemical heterogeneity of the humic substances, with probable occurrence of several processes simultaneously. A general trend observed is that adsorption of humic

substances onto clay minerals increases with the decrease of pH (Ohassi, 1996; Liu and Gonzalez, 1999; Elfarisi and Pefferkorn, 2000; Doulia et al., 2009;) and increase of ionic strength (Liu and Gonzalez, 1999; Elfarisi and Pefferkorn, 2000).

At low pH, there are three possible mechanisms governing the adsorption of humic acid on montmorillonite. They are cation bridging, water bridging, and H-bond complexation (Ohassi and Nakazawa, 1996; Abate and Masini, 2005). The reason of these characteristics that protonated humic acids form aggregates under low pH conditions with silicate layers of Na-montmorillonite having permanent negative charges. (Ohassi and Nakazawa, 1996). In low pH, the surface of montmorillonite is negatively charged. The results of the zeta-potential measurements show that the negative charge density on montmorillonite will increase with increasing pH. The same trend occurs with the molecules of humic acid. The higher the pH, the greater will be the dissociation of the functional groups $-\text{OCOOH}$ and $-\text{OCOH}$ to $-\text{OCOO}_2^-$ and $-\text{OCO}_2^-$. The net effect will result in an increase in negative charges on humic acid. The electrostatic interaction between the charges will repel the humic acid from the surface of montmorillonite (Liu and Gonzalez, 1999).

At low pH and high ionic strength, humic acid tends to aggregate into spherical particles through van der Waals forces. Bonding between the humic acid segments is mainly by hydrogen bonding, which makes the structure flexible.

Electrostatic bonding can occur via cation or anion exchange or protonation. The cationic property of a weakly basic organic molecule is strongly pH dependent. Thus, this mechanism is dependent on the basic character of the organic molecule, the pH of the system, the properties of the organic cation or chain length, and the type of cation on the clay surface. Sorption of HS on negatively charged clays occurs only when polyvalent metal cations such as Al^{3+} , Fe^{3+} , and Ca^{2+} are present on the clay exchanger since they can neutralize the negative charge on the clay and the charge on the deprotonated organic functional group. Calcium is weakly held as a cation bridge and can be easily displaced, whereas Al^{3+} and Fe^{3+} are usually bound nonelectrostatically and are difficult to remove (Huang and Schnitzer, 1986).

Whereas at higher pH, carboxylic and phenolic groups of humic substances dissociate, increasing their hydrophylic character and the ability for complexation of cations, favoring cation bridging as the predominant adsorption mechanism. The mechanism of water bridging could exist under conditions of low and high pH (Liu and Gonzalez, 1999; Abate and Masini, 2005). At the same time, the adsorption of cations becomes more significant at high pH, so that cation bridging becomes the main mechanism. The mechanism of water bridging could exist under conditions of both low and high pH (Liu and Gonzalez, 1999). Physical adsorption or retention via van der Waals forces is weak and results from changes in the electric charge density of individual atoms. An electrically positive fluctuation in one atom causes an electrically negative fluctuation in a neighboring atom, resulting in a net attractive force. Adsorption due to physical forces occurs with neutral polar and nonpolar molecules, particularly those with high molecular weight (Huang and Schnitzer, 1986).

Clay minerals do not occur alone in soils, sediments in aquatic environments. In these environmental compartments the clay minerals are associated with other particles such as hydrated oxides of Fe (III), Al (III) and Mn (IV), besides to organic compounds such as humic substances, polysaccharides, proteins and aminoacids, which constitute NOM (Vermeer et al., 1998). Humic acid molecules adsorbed onto the surface of clay minerals could increase the adsorption capacity of metallic cations because humic substances have strong complexing sites. Besides, the complexation capacities of humic acids (in terms of mol g^{-1}) are significantly higher than usually reported for the adsorption capacities of clay minerals. On the other hand, the aggregation of clay particles in presence of humic acids could decrease the specific area, leading to a decrease of the adsorption capacity of metallic cations (Abate and Masini, 2005).

2.8. Adsorption Isotherm Modeling of Humic Substances with Clay Minerals

Adsorption isotherms are equilibrium equations that are defined as the functional expression for variation with the concentration of adsorbate in bulk solution, at constant temperature. Generally, the amount of adsorbed material per unit weight of adsorbent increases with increasing solute concentration, but not in direct proportion (Weber, 1972). Adsorption isotherms can be classified into four major classes (S, L, H, C) and five

subgroups (Sposito, 1989; Sparks, 1995). The S (cooperative adsorption) curve signifies an increase in the affinity for the adsorbate after the initial adsorption. This is attributable to strong inter molecular bonds. The L (Langmuir) curve indicates that the adsorption becomes increasingly difficult as the adsorption sites are filled. The H (high affinity) curve is a special case of L curve, the adsorbate in dilute solutions is completely removed, and the initial part of the curve is thus vertical. The C curve represents constant partition of adsorbate between solution and adsorbent to the maximum possible adsorption. Additional information such as the rate of change of site availability with increased adsorption and the energy barrier to be overcome before the surface will adsorb more adsorbate can be obtained by examining the variation in the initial slope and plateau length of the subgroups.

Basic adsorption isotherms commonly used are Langmuir, Freundlich and, BET (Brunauer- Emmet and Teller) equations (Huang, 1980).

Linear Model: Linear model can be used if the accumulation of solute on the adsorbent is directly proportional to the solution phase concentration. The general formula is:

$$C_s = K_d C_e \quad (2.1)$$

Here, K_d represents the distribution coefficient, which can also named as partition coefficient. C_e is the amount of adsorbate remaining in solution at equilibrium whereas; C_s stands for the concentration of adsorbate adsorbed on the adsorbent.

Freundlich Isotherm: The Freundlich isotherm or van Bemmelen isotherm is the most widely used nonlinear adsorption equilibrium model. The Freundlich relation assumes that not all sites on the surface are considered equal, and adsorption becomes more difficult as more and more adsorbate accumulates on the surface. It is assumed that once the surface is covered, the additional adsorbed species can still be accumulated and no maximum adsorption can be predicted. The empirical equation does not imply any particular mechanism of adsorption (vanLoon and Duffy, 2000).

The general formula is:

$$q_A = K_F C_e^{1/n} \quad (2.2)$$

Where: q_A = The amount of solute adsorbed per unit weight of solid adsorbent, C_e = The concentration of the solute remaining in the solution at equilibrium, K_F = The constant which relates to adsorption capacity, $1/n$ = The constant which relates to adsorption intensity.

For determination of these empirically derived coefficients, data are usually fit to the logarithmic form of equation:

$$\log q_A = \log K_F + \frac{1}{n} \log C_e \quad (2.3)$$

Langmuir Isotherm: The Langmuir adsorption model is valid for single-layer adsorption. The Langmuir assumes a surface with specific number of sites each of which is capable of reacting with and binding to a solution molecule. All of the sites are considered to be equivalent and when all are occupied, no further adsorption can occur. Hence, the quantity adsorbed reaches the maximum quantity adsorbable when all sites are occupied. Its equation follows as:

$$q_A = \frac{q_{\max} K_L}{1 + K_L C_e} \quad (2.4)$$

where, $q_{\max}$ expressed maximum surface coverage indicating “monolayer” coverage or site saturation, and K_L was Langmuir constant. Through the plot of $1/q_A$ versus $1/C_e$;

The linearized form of the Langmuir equation:

$$\frac{1}{q_A} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L C_e} \quad (2.5)$$

q_A and K_L could be deduced from intercept ($1/q_{\max}$) and slope ($1/K_L q_{\max}$) respectively.

2.9. Evaluation of the Adsorption Studies of the Clay-humic System:

Several adsorption models describing the mechanism of adsorption of humic acid on to clay minerals, parameters and adsorption reactor types have been illustrated in Table 2.4.

Table 2.4. Adsorption models and respective parameters of clay-humic system.

Humic acid type	Clay type	Investigated Parameters	Adsorption Modeling	References
Soil, peat, lignite and brown water lake.	Kaolin, Caminauer	UV 240 nm, DOC	Langmuir, Freundlich models	Balcke et al., 2002
Soil, HA, Aldrich	Vermiculite	Vis 400 nm	Langmuir model	Abate and Masini, 2003
Plants, HA, peats, HA, Soil, HA	Kaolinite	UV 280 nm	Langmuir model	Ghabbour et al., 2004
Brown coal HA	Na-montmorillonite, Kaolin, Zettlitz	Vis 450 nm	Langmuir model	Tombácz, et al., 2004
Peat, HA	Montmorillonite (saz-1), Clay Mineral Society	DOC	Freundlich and Langmuir models	Feng et al., 2005
HA, Amherst	Kaolinite, Fluka, Montmorillonite, Fluka	E4/E6	Freundlich models	Wang and Xing, 2005
Peat, HA	Na-montmorillonite, Clay Mineral Society	Vis 450 nm, SUVA ₂₅₄ , E3/E4 and E4/E6	Langmuir models, H Type isotherm	Majzik and Tombácz, 2007a
Soil HA	Bentonite, Jordanian	Vis 400 nm	Langmuir models,	Salman et al., 2007
HA, Fluka	Bentonite	Vis 400 nm	Langmuir, Freundlich, Temkin models	Doulia et al., 2009

In most of the research Langmuir adsorption model were used (Balcke et al., 2002; Abate and Masini, 2003; Ghabbour et al., 2004; Tombácz, et al., 2004; Feng et al., 2005; Majzik and Tombácz, 2007a; Salman et al., 2007; Doulia et al., 2009). In some of the research Freundlich adsorption model were used (Balcke et al., 2002; Feng et al., 2005; Wang and Xing, 2005; Doulia et al., 2009). Approximately, in all of the research, remaining humic acid concentration in solution were determined UV spectroscopy at 240 nm (Balcke et al., 2002), 254nm (Ohassi and Nakazawa, 1996; Specht et al., 2000), 280nm

(Elfarisi and Pefferkorn, 2000; Ghabbour et al., 2004) 400 nm (Liu and Gonzalez, 1999; Meier et al., 1999; Abate and Masini, 2003; Doulia et al., 2009; Salman et al., 2007;), 450 nm wavelengths (Majzik and Tombacz, 2007a, Tombacz et al., 2004)

2.10. Advanced Oxidation Processes

Advanced Oxidation Processes (AOPs), which involve the *in-situ* generation of highly potent chemical oxidants, such as the hydroxyl radical ($\text{HO}^\bullet$) ($E_v = 2.80 \text{ V}$), have emerged as an important class of technologies for accelerating the oxidation and hence removal of a wide range of organic contaminants in polluted water and air (Bolton et al., 1994). AOPs are approaches that are particularly appropriate for effluents containing refractory, toxic and/or non-biodegradable materials. There are a variety of advanced oxidation processes including: (1) homogeneous ultraviolet irradiation-either direct irradiation of the contaminant or photolytic oxidation mediated by hydrogen peroxide ($\text{UV}/\text{H}_2\text{O}_2$), and/or ozone ($\text{UV}/\text{H}_2\text{O}_2/\text{O}_3$ or UV/O_3), (2) Fenton and photo-Fenton processes, (3) heterogeneous photocatalysis using semiconductor catalysts (e.g. UV/TiO_2), (4) ultrasonic irradiation (sonolysis), (5) supercritical water oxidation, (6) electrochemical water oxidation, (7) X-ray or gamma-ray radiolysis, (8) electron-beam irradiation. The effectiveness of an AOP is mainly related to the efficiency of these oxidants with organic contaminants. Although these technologies involve different methods of activation, as well as oxidant generation, most of them are electric-energy-driven and share the common denominator of hydroxyl radical chemistry for contaminant removal (Malilainen and Silanpää, 2010). The brief explanation of photocatalysis that will be used throughout this study is given below.

2.10.1. Photocatalysis

Photocatalytic oxidation, has been applied in water, and wastewater treatment studies (Turchi and Ollis, 1989 and 1990; Matthews, 1992; Carp et al., 2004). Photocatalysis relies on oxidative degradation reactions, where organic radicals are generated upon photolysis of the organic substrate or by reactions with generated hydroxyl radicals. These radicals are subsequently trapped by dissolved molecular oxygen and lead via peroxy radicals and

peroxides to an enhancement of the overall degradation process and finally to complete mineralization (Legrini et al., 1993).

ZnO, TiO₂, and CdS are the examples of semiconductors used as photocatalysis. Because of its stability, non-toxicity, and low energy band-gap, TiO₂ is accepted to be one of the most suitable semiconducting materials for photocatalysis. The presence of natural organic matter, mainly humic substances in surface waters, constitutes the main route for the absorbance of solar energy in aquatic systems through which a series of photophysical and photochemical processes occur. Recently, the destruction of humic acids has become an important task and TiO₂ catalyzed photodegradation of humic acids has been subject to many projects utilizing artificial light sources as well as solar light (Bekbølet et al., 2002).

In photocatalysis, a suspension of a particulate metal oxide or other insoluble inorganic semiconductor powder is irradiated with natural or artificial UV light. This excitation promotes an electron from a bonding or non-bonding level in the solid to a highly delocalized level, creating a localized oxidizing site (a hole) and a mobile reducing site (an electron). The holes react with the electron donors in the electrolyte to produce powerful oxidizing agents such as HO• (radicals) (Bahnemann et al., 1994).

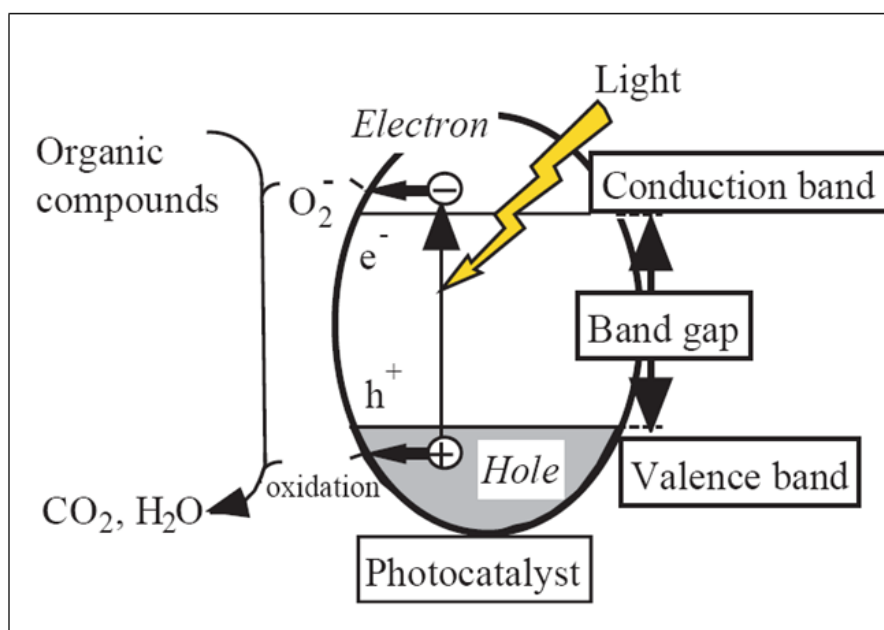


Figure 2.9. Simplified TiO₂ photocatalytic mechanism.

Many semiconducting oxides as catalysts have been tested, although TiO₂ in the anatase form performed the most interesting and efficient features, such as high stability, good performance, ready availability, low toxicity and low cost (Rajeshwar, 1995). The optical absorption of TiO₂ in the near UV region is the major advantage of the photocatalytic method over UV-C driven AOPs (O₃/UV, H₂O₂/UV) that require light of shorter wavelengths ($\lambda < 300$ nm) and hence can not make use of a part of solar irradiation. A simplified TiO₂, photocatalytic mechanism is summarized in Figure 2.9.

Continuous band-gap irradiation (E_{bg} is 3.2 eV (390 nm) in anatase and 3.05 eV (420 nm) in rutile) of an aqueous semiconductor dispersion excites an electron from the valence band (VB) to the conduction band (CB), creating an electron-hole pair. TiO₂ is only active in the ultraviolet region, which is < 10 percentage of the overall solar intensity. The formation of redox pair could be followed either by respective reactions or by a recombination reaction resulting in the dissipation of the reactive species (Equations 2.6-2.7).

Formation of redox pair through light absorption ($E_{hv} > E_{bg}$):



E_{bg} is 3.2 eV ($\lambda = 390$ nm) in anatase and 3.05 eV ($\lambda = 420$ nm) in rutile.

Direct recombination reaction leading to the inactivation of the electron hole pair:

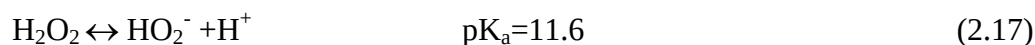


Photogenerated holes (h^+_{VB}) may directly oxidize the organic substrate, S anchored to the oxide surface. The principal hole traps are adsorbed H₂O molecules and OH⁻ forming HO[•] radicals. The HO[•]_(s) radicals adsorbed on the semiconductor surface are the prominent reactive species due to their high oxidant power (+2.80 V) and possible competing reaction leads to the formation of hydrogen peroxide.





On the other hand, in the presence of electron scavengers (i.e. O_2) reduction reactions may take place leading to the following sequence of the reactions:



The heterogeneous photocatalytic process takes place through a complex sequence of reactions. The relevant reactions at the TiO_2 surface causing the degradation of the organic compounds could be outlined by equations (2.8- 2.18).

Hydroxyl radicals are created from water when the titanium dioxide layer absorbs UV light. The energy causes electrons to move to the conduction band of the TiO_2 . The positive holes remaining in the valance band can accept electrons from molecules. A $\bullet OOH$ radical is formed from the reduction of the dissolved oxygen in the aqueous solution combining with a hydroxyl radical.

2.10.2. Photocatalyst type

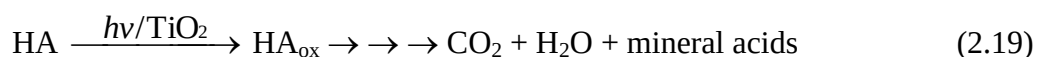
A semiconductor comprises a manifold of electron energy levels filled with electrons called the valence band, VB and at a higher energy, a manifold of largely vacant electron energy levels called the conduction band, CB. Although there are many semiconducting materials in this world (e.g., ZnO , SnO_2 , WO_3 , CdS , and ZnS), TiO_2 has been by far the most popular photocatalyst due to its superior features such as high stability, good performance, availability, low toxicity and low cost (Rajeshwar, 1995).

TiO₂ exists in three crystalline forms namely, anatase, rutile and brookite. Both crystal structures, anatase and rutile, are commonly used as photocatalyst, with anatase showing a greater photocatalytic activity. It has been proposed that this increased photoreactivity is due to anatase's slightly higher Fermi level, lower capacity to adsorb oxygen and higher degree of hydroxylation. A mixture of anatase (70-75%) and rutile (30-25%) is also proven to be more active than pure anatase. The discrepancy could be explained by the intervening effect of various coexisting factors, such as specific surface area, pore size distribution, and crystal size. The behaviour of Degussa P-25 commercial TiO₂ photocatalyst, consisting of an amorphous state together with a mixture of anatase and rutile in an approximate proportion of 70/30 is for many reactions more active than both the pure crystalline phases. The enhanced activity arises from the increased efficiency of the electron-hole separation due to the multiphase nature of the particles. Another commercial TiO₂ photocatalyst, Sachtleben Hombikat UV-100, consisting only of anatase, has a high photoreactivity due to fast interfacial electron-transfer rate. Efforts have also been made to improve the photocatalytic activity of TiO₂ through platinization examples, which have also been presented by Carp and co-workers (2004).

Heterogeneous photocatalysis using TiO₂ has been considered as effective technology for treating refractory organic compound in water and in air. The photocatalytic efficiency of TiO₂ is greatly influenced by crystal structure, particle size, surface area, and porosity, as determined by different methods.

2.10.3. Kinetics of photocatalytic degradation

Chemical kinetics describes the study of both the mechanism and rate of a chemical reaction. The organic compounds (e.g. humic acid, HA) present in the illuminated titania slurry undergo many chain and consecutive reactions. In an ideal case, all intermediate compounds are completely mineralized to carbon dioxide and water (Equation 2.19). the presence of N, S or x (halogen atoms) would lead to the formation of mineral acids.



Several kinetic models describing the mechanism of the photocatalytic oxidation reaction have been proposed starting with a simple pseudo first order reaction kinetic model leading to the application of the adsorption based Langmuir-Hinshelwood (L-H) law (Turchi and Ollis, 1989; Turchi and Ollis, 1990).

The pseudo first order reaction kinetics is expressed as follows;

$$\text{Rate} = R = -dC/dt = k C \quad (2.20)$$

Where the terms represent the following meanings; R: pseudo first order rate ($\text{m}^{-1}\text{min}^{-1}$ in terms of UV-vis parameters or $\text{mg L}^{-1}\text{min}^{-1}$ for TOC removal), C: specified UV-vis parameters of humic substances (m^{-1}) or TOC content of the samples (mg L^{-1}), t: irradiation time (min), k: pseudo first order reaction rate constant, (min^{-1}).

Considering that photocatalysis occurs at the surface, the concentration of substrate adsorbed to the surface directly affects the overall rate of adsorption. A Langmuir-Hinshelwood model is widely used to describe the kinetics of semiconductor photocatalysis (Turchi and Ollis, 1989). Langmuir-Hinshelwood rate expression considers the dependencies of the photocatalytic reaction rates on the concentration of the substrates. It also covers the key role of adsorption constant, K_{LH} on kinetics assuming that adsorption desorption kinetics is faster than the photochemical reaction.

$$R_{\text{LH}} = dC/dt = k_{\text{LH}} K_{\text{LH}} C / (1 + K_{\text{LH}} C) \quad (2.21)$$

In the equation (2.21), the terms represent the following; R_{LH} : Rate of the reaction ($\text{m}^{-1} \text{min}^{-1}$ or $\text{mg L}^{-1}\text{min}^{-1}$), k_{LH} : reaction rate constant ($\text{m}^{-1}\text{min}^{-1}$ or $\text{mg L}^{-1}\text{min}^{-1}$), K_{LH} : adsorption coefficient of the reactant onto TiO_2 under irradiation conditions (m) and C: initial value of the specified UV-vis parameters of humic substances (m^{-1}) or DOC content of the samples (mg L^{-1}). When the chemical concentration C_0 is a millimolar solution (C_0 small) the equation can be simplified to an apparent first-order equation:

$$\ln\left(\frac{C_0}{C}\right) = kKt = k_{\text{app}}t \quad \text{or} \quad C_t = C_0 e^{-k_{\text{app}}t} \quad (2.22)$$

A plot of $\ln C_0/C$ versus time represents a straight line, the slope of which upon linear regression equals the apparent first-order rate constant k_{app} . Generally, first-order kinetics is appropriate for the entire concentration range up to few ppm and several studies were reasonably well fitted by this kinetic model (Bekbolet et al., 1998; Bekbolet et al., 2002, Uyguner and Bekbolet, 2005a).

2.11. Photocatalytic Degradation of Natural Organic Matter

Application of photocatalysis to the destructive removal of NOM is a recent research topic that started only a decade ago (Bekbolet, 1996; Bekbolet and Ozkosemen, 1996; Bekbolet and Balcioglu, 1996). In literature, to investigate the photocatalytic degradation of natural organic matter in relation to the treatment of drinking water supplies model humic and fulvic acids of different origins were used (i.e. humic substances extracted from aquatic sources, commercially available humic or fulvic acid samples, standard and reference aquatic fulvic and humic acids from IHSS).

Eggins and co-workers (1997) investigated semiconductor photocatalysis for the degradation of aquatic humic substances. They have shown that, the absorbance at 254/400 nm of a humic acid test solution was reduced by 50% after 12 min irradiation. However, only 50 per cent mineralization to carbon dioxide and water occurs after 1 hour. In the absence of oxygen, light or TiO_2 no significant degradation occurred. Recently, Wiszniowski and co-workers (2002) investigated the photocatalytic decomposition of humic acids on TiO_2 , and reported that adsorption plays a prominent role in photocatalytic degradation of humic acids. It was presented that 88% TOC removal was achieved with optimum TiO_2 loading of 1.0 gL^{-1} after 6 hour of irradiation.

Bekbolet and Balcioglu (1996) examined the influence of hydrogen peroxide and bicarbonate ion on the photocatalytic degradation of humic acid in aqueous TiO_2 dispersions. The degradation rate constants were found to increase in the presence of hydrogen peroxide, also they explained that bicarbonate ions slowed down the degradation rate by scavenging the hydroxide radicals.

Özkaraova (1996) investigated the influence of nitrate and chloride ions on the

photocatalytic degradation of humic acid in aqueous medium. It has shown that, nitrate ions and chlorine ions caused 40 per cent and 45 per cent adsorption respectively, following the adsorption photocatalytic, degradation took place, and the degradation rate decreased. Later, Bekbolet and co-workers (1998) investigated the influence of common inorganic ions, namely, chloride, nitrate, sulfate, and phosphate ions on the photocatalytic removal of color from humic acid solutions. The presence of chloride, nitrate, and sulfate ions are showed different trends when the rate is expressed as pseudo first-order reaction kinetics. The presence of phosphate ion strongly inhibited the color removal rate.

Boyacıoğlu (1997) studied the influence of pH dependent on phosphate species on the photocatalytic degradation of 10 mg L^{-1} humic acid in aqueous media. Boyacıoğlu reported that, at low pH values, irradiation with $0.25 \text{ mg mL}^{-1} \text{ TiO}_2$ for 1 hour resulted in 95 per cent Color_{436} and 62 per cent TOC removal. Karabacakoğlu (1998) investigated the influence of hardness cations such as calcium and magnesium on the photocatalytic degradation of humic acid. It was reported that, Color_{436} and UV_{254} removal rates increased in the presence of 50 mg mL^{-1} calcium and 5 mg mL^{-1} magnesium hardness. The increase in the removal rate was due to the changes in the humic acid structure due to the presence of divalent cations.

Later, DBPs formation potentials of the natural water samples upon treatment by various oxidative and physico-chemical methods investigated were also using water samples of different origins (Buyukcekmece and Omerli, Istanbul, Turkey, and Alento, Salento, Italy) were treated by coagulation, ozonation, and coagulation followed by ozonation and photocatalysis (Bekbolet et al., 2005).

Disinfection by-products (DBPs) formation potential of raw and treated water samples were compared in relation to removal efficiencies by the respective treatment methods. The major DBPs, namely trihalomethanes (THMs) and haloacetic acids (HAAs), and other DBPs were identified and quantified. Besides major THMs and HAAs, the presence of bromoform in high amounts was also detected due to the high levels of bromide ions in raw Buyukcekmece and Omerli water samples. Depending on the natural organic matter (NOM) removal efficiencies of each treatment process, the distribution of individual THMs and HAAs was found to be NOM-site specific. Other DBPs were also

detected and chloral hydrate was found in significant amounts. The responsible precursor sites could only be reduced by photocatalytic treatment of NOM.

Recently, Li and co-workers (2002) studied the photocatalytic oxidation of humic acid in TiO_2 suspensions at neutral pH in presence of calcium and magnesium ions. They have reported that the degradation of humic acid significantly enhanced by adding calcium and magnesium ions. The increase of cation strength in aqueous solution could provide a favorable condition for adsorption of humic acid on the TiO_2 surface, therefore enhances the photooxidation rate. Interaction of hypochloride ion and humic acid were investigated through photocatalytic and photocatalytic pathways (Gonenc and Bekbolet, 2001).

Bekbölet and co-workers (2002) investigated the photocatalytic efficiencies of TiO_2 powders on the decolorization of humic acids. Decolorization rate of humic acid (Roth) by photocatalytic oxidation in terms of pseudo first-order kinetics in the presence of Degussa P-25 TiO_2 was found to be more efficient than in the presence of Hombikat UV100 TiO_2 specimen. The results of the adsorption experiments for Degussa P-25 indicated higher adsorption capacity for humic acid at pH 6.7.

Photocatalysis was also applied in combination with ozonation for the oxidative removal of humic acid (Kerc et al., 2003; Kerc et al., 2004a and 2004b).

The changes in the UV-vis properties of humic substances during photocatalytic degradation were also determined at discrete absorption wavelengths (Bekbolet, 1996; Bekbolet et al., 1998; Uyguner and Bekbolet, 2005a; Uyguner and Bekbolet 2005b). On the other hand, the indicated parameters should be experimentally significant enough to be determined to follow the oxidative destruction of the humic acids especially when complete mineralization is expected. Therefore, the absorbance measurements in the visible region ($\lambda > 400\text{nm}$) may not serve as a sensitive parameter for humic acid quantification. It should also be cautiously interpreted that the detection of very low levels of DOC should also constitute an experimental barrier. Considering the related constraints, an approach to the incorporation of fluorescence properties besides absorbance ratios as an indicative parameter was proposed by Bekbolet and co-worker (Uyguner and Bekbolet, 2005b; Uyguner and Bekbolet, 2005c).

In a study by Uyguner and Bekbolet, (2005c) the effect of Degussa P-25 TiO_2 loading on the photodegradation of model humic substances; IHSS HA, IHSS FA, IHSS SHA, RHA and AHA were investigated. Increasing the TiO_2 loading was reported to increase the photocatalytic degradation rate of all of the studied humic substances. For IHSS fulvic acid increasing TiO_2 loading from 0.25 mg mL^{-1} to 1.0 mg mL^{-1} had the effect of increasing UV_{254} removal rate by approximately three fold (Uyguner and Bekbolet, 2005c).

Pseudo first order rates for the photocatalytic removal of different humic substances that were calculated in terms of UV-vis parameters followed a general trend as, IHSS soil humic acid (IHSS SHA) > Aldrich humic acid (AHA) > IHSS humic acid (IHSS HA) > Roth humic acid (RHA) > IHSS fulvic acid (IHSS FA). Amongst the studied humic substances, IHSS SHA has the highest removal rate constants. However, the rate constants showed differences depending on the UV-vis parameters employed. A comparison between the first order rate constants of Color_{436} and Color_{400} for the photocatalytic degradation of humic substances of different origins indicated that the rate constants differ from each other by 4% to 7% (Uyguner and Bekbolet, 2005c). The evaluation of the Langmuir-Hinshelwood kinetic model revealed that, Roth humic acid displayed the lowest Langmuir-Hinshelwood rate, rate constant and adsorption coefficient. The ordering of the rates followed the same trend with that of pseudo first order (Uyguner and Bekbolet, 2005c).

Uyguner and Bekbolet (2007) examined the impact of aqueous Cr (VI) and Mn (II) species on the photocatalytic oxidation of humic acids as a major component of natural organic matter in aquatic systems. The experiment results were evaluated in terms of Langmuir-Hinshelwood rate with respect to Color_{436} because of the pseudo-first-order rate constant explains the overall removal tendency covering all competitive and consecutive reactions. The presence of these ions affected the adsorptive properties of the photocatalyst and the photocatalytic oxidation rate of humic acids. The impact of manganese ion on the photocatalytic oxidation could be better explained in terms of L-H kinetics where 15% increase was observed with respect to Color_{436} while 54% decrease observed in the presence of chromium.

Selcuk and Bekbolet (2008) investigated the photocatalytic and photoelectrocatalytic treatment methods for removing humic acid under different experimental conditions. Photoelectrocatalytic system was performed for humic acid oxidation in the presence of chloride anion and humic acid to observe the selectivity of photoelectrocatalytic system. To investigate the inhibitory effect of carbonate species, the system was performed in the presence and absence of carbonate species. It was reported that the attraction of humic acid to the surface of TiO_2 was stronger than that of chloride ions and carbonate ions retarded HA degradation at basic condition.

Uyguner and Bekbolet (2010) investigated the removal efficiency of aqueous humic acid solutions by TiO_2 photocatalytic degradation in the presence of Cu (II) species. The photocatalytic oxidation studies of the molecular size fractions of humic acid were also performed. Both in the presence and absence of copper ions the removal rate constants of the size fractions displayed an increasing trend as $R_{\text{aw}} < 0.45\mu\text{m}$ filtered fraction, 100 kDa fraction, 30 kDa fraction. Even though the presence of Cu (II) species significantly altered the isotherm shape irrespective of the spectral parameters, no significant difference was attained for TOC.

Solution matrix effect was studied using simulated surface and ground waters by Uyguner and Bekbolet (2009). The presence of common anions (SO_4^- , Cl^- , and NO_3^-) and cations (Ca^{2+} and Mg^{2+}) altered the photocatalytic degradation efficiencies. The most pronounced effect was observed in the presence of carbonate species leading to an inhibition on the photocatalytic degradation rate of humic acid. Photocatalytic degradation of humic acid was also evaluated through the application of response surface methodology (Parilti et al., 2011)

Furthermore, the outcome of the studies performed since 1996 were compiled and discussed in detail in book chapters and a review paper by Uyguner and co-worker (Uyguner and Bekbolet, 2007a and 2007b; Uyguner and Bekbolet, 2008; Uyguner-Demirel and Bekbolet, 2011).

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Humic acid

Humic acid (HA) was supplied from Aldrich (Aldrich Co. Ltd., USA). Stock humic acid (1000 mg L^{-1}) solution was prepared by dissolving 1.0 g humic acid in 1000 mL distilled deionized water. In this step, the ultrasonic sonication bath is used to provide complete dissolution of humic acid. Stock humic solution was stored in a dark glass container and was protected from light to prevent light induced degradation. 50 mg L^{-1} solutions, which were used during experiments, were prepared from the stock solution by using distilled deionized water. Humic acid samples were filtered from $0.45 \text{ }\mu\text{m}$ Millipore cellulose acetate membrane filters (Millipore Millex-HA).

3.1.2. Titanium dioxide powder

Semiconductor metal oxide, TiO_2 powders was provided from Degussa (P25 grade). TiO_2 P-25 had a BET surface area of $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ and average particle size of 20-30 nm. TiO_2 P-25 powders were mainly anatase in crystal form (70% anatase and 30% rutile). Homogeneous slurry of TiO_2 was obtained by sonicating the solution for 3 minutes.

3.1.3. Clay minerals

Montmorillonite (Mt) and Kaolinite (Kt) clay mineral were provided by Clay Minerals Society Source Clays Repository (Table 3.1).

3.1.4. Other chemicals and reagents.

Mili-Q water (Conductivity= $5.6 \times 10^{-2} \text{ }\mu\text{S cm}^{-1}$ at 25°C) was used for the water supplies of Total Organic Carbon (TOC) analyzer. All of the experiment were conducted by using distilled deionize water (Conductivity= $1.0 \text{ }\mu\text{S cm}^{-1}$ at 25°C). Aqueous Ca^{2+}

solution was prepared in the concentration range varying from 5×10^{-4} M to 5×10^{-3} M by using $\text{Ca}(\text{NO}_3)_2$.

Table 3.1. Physical and chemical properties of montmorillonite, kaolinite and TiO_2 .

	BET Surface area, $\text{m}^2 \text{g}^{-1}$	CEC ^a , $\text{meq}100\text{g}^{-1}$	pH_{zpc} ^b	Chemical composition, %
Montmorillonite, SAz-1	97.42 ± 0.58	120	6.5 ^c	SiO_2 : 60.4, Al_2O_3 : 17.6, TiO_2 : 0.24, Fe_2O_3 : 1.42, FeO : 0.08, MgO : 6.46, MnO : 0.099, CaO : 2.82, K_2O : 0.19, Na_2O : 0.063, F : 0.287, P_2O_5 : 0.020
Kaolinite, KGa-1b	10.05 ± 0.02	2.0	5.3 ^d	SiO_2 : 44.2, Al_2O_3 : 39.7, TiO_2 : 1.39, Fe_2O_3 : 0.13, FeO : 0.08, MgO : 0.03, MnO : 0.002, CaO : n.d., K_2O : 0.05, Na_2O : 0.013, F : 0.013, P_2O_5 : 0.034
Titanium dioxide, TiO_2 , P25	55 ± 15	-	6.25 ^e	TiO_2 : 99.5, SiO_2 : 0.2, Al_2O_3 : 0.3, Fe_2O_3 : 0.01 70% anatase and 30% rutile, primary particle size: 30 nm

^a CEC: Cation exchange capacity; ^b pH_{zpc} : pH of zero proton condition; ^c Tombácz and Szekeres, 2004; ^d Meier et al., 1999; ^e Kormann et al., 1991.

3.1.4. Laboratory equipments

General laboratory applications and measurements were done by using the following instruments: Memmert Water Bath Shaker Model WB/OB 7-45, Hettich EBA 20 Centrifuge, Ultra Sonic Waterbath LC30, IKA-Labortechnik Magnetic Stirrer, Memmert Oven, Scaltec SBA 31 Balance, and several types of glassware.

3.2. Methods

3.2.1. Photocatalytic degradation

3.2.1.1. Experimental set-up. During experiments, the light source was 125 W Black Light Fluorescent Lamp (BLF) which had an output spectrum ranging between 320-440 nm. The

lamp exhibited a maximum emission at 365 nm and no emission below 300 nm and above 500 nm. The intensity of incident light, measured using ferrioxalate actinometry (Hatchard and Parker, 1956) was $4.73 \times 10^{-2} \mu\text{E s}^{-1}$. The lamp was built into a lamp housing which provides a location of 10 cm above the surface of the solution. The experimental set up was prepared as detailed in previous literature (Bekbolet et al., 2002). A cylindrical pyrex reaction vessel with a diameter of 7.5 cm and a height of 3.5 cm was used as the photoreactor. The volume of reaction mixtures was 50 mL. During experiments, continuous stirring was provided by a magnetic stirrer. The photoreactor was enclosed by a mirror casing and the whole system was placed in a box. The inner walls of the box were covered with Al-foil.

3.2.1.2. Experimental procedure. All experiments were conducted under neutral pH conditions (pH= 6.7). The photocatalytic degradation of humic acid solution was performed in the absence and presence of clay minerals. In order to assess the direct interaction of light with humic acid reactions were carried out in the absence of photocatalyst. Dark reactions were also carried out to evaluate the probable initial adsorption of humic acid onto TiO_2 . Also, the preliminary reactions were also performed in the absence of photocatalyst under irradiation. For each set of experiments, 50 mg L^{-1} humic acid solution was prepared by dilution from the Aldrich humic acid stock solution. 50 mL of 50 mg L^{-1} humic acid was added directly to reaction vessel onto weighted 0.5 mg mL^{-1} TiO_2 . In the presence of clay minerals, clay mineral either Mt or Kt was applied in a concentration of 0.05 mg mL^{-1} , 0.10 mg mL^{-1} , and 0.20 mg mL^{-1} .

The prepared slurry was sonicated for three minutes to provide a homogenous mixture. Then, it was placed on a magnetic stirrer to be irradiated for certain reaction periods. After these steps, the mixture was poured into 50 mL volumetric flask and filled with distilled deionized water up to 50 mL limit to compensate the volume loss due to the evaporation of water observed especially at longer irradiation periods ($t_{\text{irr}} > 60 \text{ min}$). Prior to analysis, TiO_2 was removed from the suspension by filtering through $0.45 \mu\text{m}$ membrane filters. Filtered humic acid samples were analyzed by means of UV-vis spectra and fluorescence spectra as well as by the specified UV-vis and fluorescence parameters.

3.2.2. Adsorption

3.2.2.1. Experimental procedure. Adsorption experiments were conducted to determine the effects of molecular size dependent fractions of humic acid solution on TiO_2 and clay mineral surfaces. 100 mL Erlenmeyer flasks were used for experiments. Each flask was filled with 50 mL humic acid solution. Increased amounts of sole TiO_2 were added into each erlenmeyer flask in the range of 0.10 mg mL^{-1} to 1.0 mg mL^{-1} . In the presence of clay mineral (Mt or Kt), clay mineral dose was kept constant as 0.20 mg L^{-1} and varied amount of TiO_2 doses (0.10 - 1.0 mg mL^{-1}) were applied. In the absence of TiO_2 , increased amounts of clay mineral (Mt or Kt) were added into each erlenmeyer flask in the range of 1.0 mg mL^{-1} to 14.0 mg mL^{-1} . One extra flask was filled with only raw humic acid solution to compare with other sets. Each sample was sonicated for evenly distribution of TiO_2 in the slurry. The samples were immersed in the water-bath at room temperature which is equipped with shaking device. The flasks were kept shaking for 24 hours. After this time period, the samples were centrifuged for 10 minutes at $5000 \text{ cycles min}^{-1}$. The supernatant was filtered by the $0.45 \mu\text{m}$ membrane syringe filter.

3.2.3. Molecular size fractionation with ultrafiltration

Humic acid solutions were fractionated sequentially using a 50 mL Amicon Model 8050 ultrafiltration stirred cell system into appropriate molecular sizes; 100 kDa, 30kDa and 3 kDa. Following filtration through $0.45 \mu\text{m}$ membrane filter, humic acid samples were fractionated to 100 kDa followed by 30 kDa and followed by 3 kDa by using Millipore YM series cellulose membranes of the indicated molecular size dimensions (Uyguner and Bekbolet 2005b). The cell was run on a magnetic stirrer. A nitrogen gas tube equipped with a pressure control valve was attached to the stirrer reactor to provide the operating pressure inside the cell as $P = 3.5 \text{ kg cm}^{-2}$ (Figures 3.1-3.2).

Millipore YM series cellulose membrane filters with 25 mm diameter and with nominal molecular weight cutoffs 100 kDa, 30 kDa and 3 kDa were used within stirred cell. At the beginning of each run, the membranes were kept in distilled deionized water for 15 minutes and then the cell was operated on a magnetic stirrer and run with 50 mL distilled deionized water. After use prior to storage, YM membranes were washed with

0.10 M NaOH solution and stored in 10% ethanol/water solution at refrigerator. Fractionated humic acid solutions were stored in dark glass bottles at cold rooms.

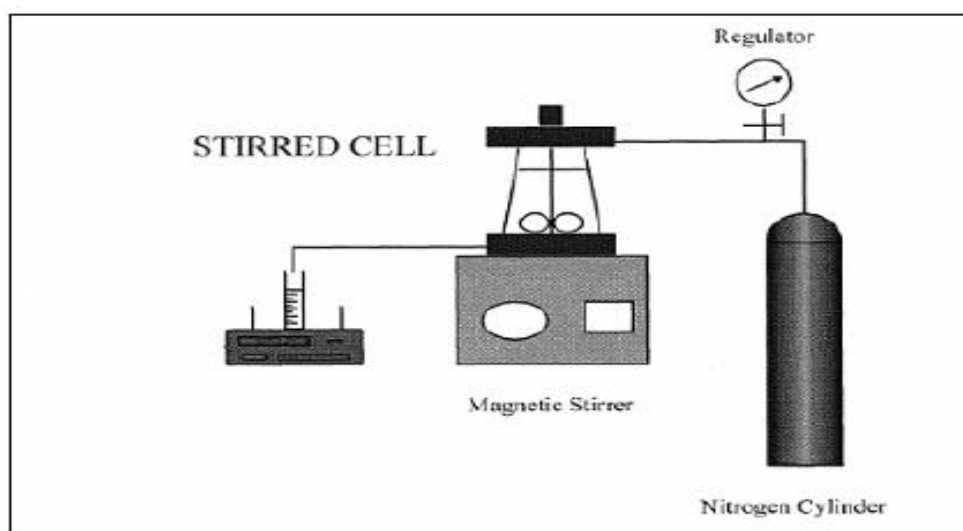


Figure 3.1. Schematic diagram of stirred cell system.

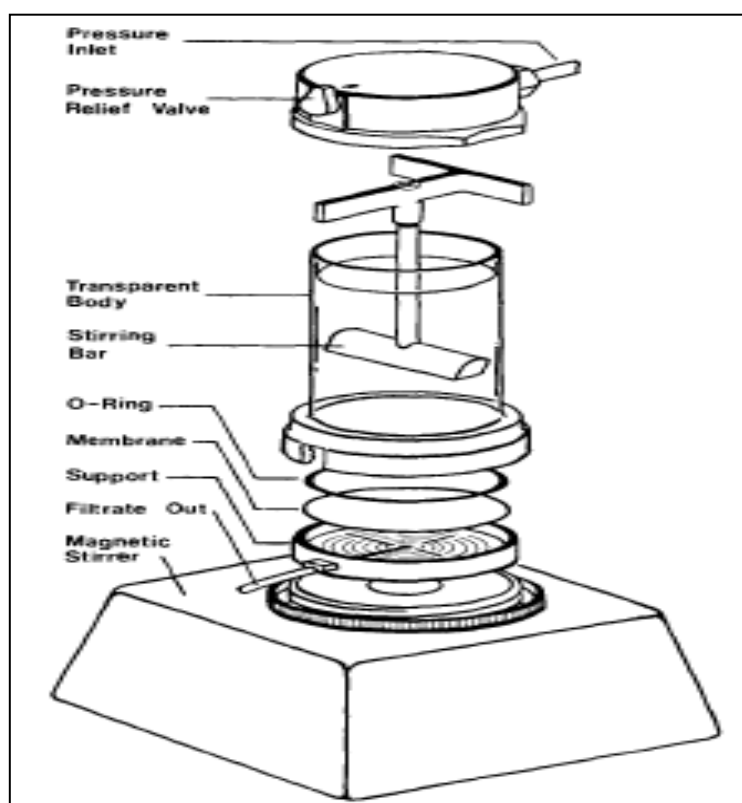


Figure 3.2. The parts of Amicon 8050 stirred ultrafiltration cells.

Molecular size distribution of HA was determined for raw HA acid (50 mg L⁻¹), photocatalytically treated HA acid (50 mg L⁻¹ using 0.5 mg mL⁻¹ TiO₂) followed by an irradiation period of 60 min and photocatalytically treated HA and clay binary systems (50 mg L⁻¹ HA and 0.20 mg mL⁻¹ either Mt or Kt) followed by an irradiation period of 60 min.

3.2.4. Analytical methods

3.2.4.1. Total organic carbon (TOC) analysis. Total organic carbon (TOC, mg L⁻¹) measurements of humic substances were performed on a Shimadzu TOC Vwp Total Organic Carbon Analyzer. TOC is determined as total organic matter in water. Dissolved organic carbon (DOC) is the organic carbon remaining in a sample after filtering the sample typically using 0.45 µm membrane filters.

3.2.4.2. UV-vis spectroscopic measurements. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 35 UV-vis double beam spectrophotometer employing Hellma quartz cuvettes of 1.0 cm optical path length. Humic acid samples were characterized by UV/vis spectra. The UV-vis absorbance values were recorded for specified UV-vis parameters such as Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄. The specified parameters are explained as follows;

Color₄₃₆ : Color forming moieties, absorbance at 436 nm, m⁻¹

UV₃₆₅ : Organic matter content, absorbance at 365 nm, m⁻¹

UV₂₈₀ : Organic matter content, absorbance at 280 nm, m⁻¹

UV₂₅₄ : Organic matter content, absorbance at 254 nm, m⁻¹.

3.2.4.3. Fluorescence spectroscopic measurements. Fluorescence spectra in the emission and synchronous scan modes were recorded on a Perkin Elmer LS 55 Luminescence Spectrometer equipped with a 150W Xenon arc lamp and a red sensitive photomultiplier tube. 1-cm path length quartz cells were used. The method of measuring fluorescence is that the cuvette holder excites the sample over the entire path length and reads the emitted light at right angles. Both the excitation and the emission slits of the instrument were 10 nm. A scan speed of 400 nm min⁻¹ was used with a slit width opening of 10 nm. Opening the slit wider allows more light energy from the xenon light source to excite the molecules

in the sample. The emission fluorescence spectra were scanned over the range of $\lambda_{\text{emis}} = 380\text{-}550$ nm at a constant excitation wavelength of $\lambda_{\text{exc}} = 360$ nm. Synchronous scan fluorescence spectra were recorded in the excitation wavelength range of $\lambda_{\text{exc}} = 200\text{-}600$ nm excitation wavelength range using the bandwidth of $\Delta\lambda = 18$ nm between the excitation and emission monochromators (Senesi, 1990). The specified fluorescence parameters are given as follows:

$\text{FI}_{\text{emis350}}$	maximum fluorescence emission at $\lambda_{\text{max}} = 455$ nm
$\text{FI}_{\text{emis370}}$	maximum fluorescence emission at $\lambda_{\text{max}} = 460$ nm
FI_{syn}	maximum fluorescence emission at $\lambda_{\text{max}} = 475$ nm

3.2.4.4. Fluorescence excitation emission matrix (EEM). To obtain fluorescence Excitation Emission Matrix (EEM), excitation wavelengths were incrementally increased from 200 to 500 nm at 10 nm steps; for each excitation wavelength, the emission at longer wavelengths was detected at 0.5 nm steps. Excitation and emission slit widths were set to 10 nm and photomultiplier tube voltage to 900 V. Three-dimensional contour plots were created by plotting fluorescence intensity as a function of emission (x-axis) and excitation (y-axis) wavelengths. Matlab R2012a was used to processing the EEM data.

3.2.4.5. Scanning electron microscopy (SEM) analysis. Surface morphologies of the humic acid samples were determined by using Scanning Electron Microscopy (SEM) in combination with Energy Dispersive X-ray analysis on an ESEM-FEG/EDX Philips XL-30 instrument operating at 20 kV using sample powders supported on carbon tape. The samples were prepared by using 50 mg L^{-1} HA, 0.50 mg mL^{-1} TiO_2 and 0.20 mg mL^{-1} Mt or Kt both prior to and following photocatalysis ($t_{\text{irr}} = 60$ min). Following each specific preparation step, the samples were dried at 105°C .

4. RESULTS AND DISCUSSION

4.1. Photocatalytic Degradation of Humic Acid in the Presence of Clay Minerals

The major aim of this research was to investigate the influence of clay minerals i.e. montmorillonite and kaolinite representing two different morphological properties on the photocatalytic removal of humic acids that was selected as the model compound of natural organic matter. Photocatalytic degradation kinetics and removal efficiency of humic acids were assessed using UV-vis and fluorescence spectroscopic properties as well as by the total dissolved organic carbon (DOC) contents.

Baseline experiments for the assessment of the interactions between the components of binary and ternary systems were performed. Binary systems were defined as *i.* humic acid and TiO₂ binary system, *ii.* humic acid and montmorillonite binary system, *iii.* humic acid and kaolinite binary system. Ternary systems were defined as composed of *i.* humic acid, montmorillonite and TiO₂ ternary system and *ii.* humic acid, kaolinite and TiO₂ ternary system.

Preliminary experiments prior to the photocatalytic treatment were performed; *i.* preliminary experiments performed under dark conditions in the presence of photocatalyst and *ii.* preliminary experiments performed under irradiation in the absence of TiO₂. These experiments were also performed in the presence of either montmorillonite or kaolinite. Photocatalytic experiments were carried out according to the procedure outlined by Bekbolet and co-workers (Bekbolet et al., 2002). Complementary batch adsorption experiments were also performed (Bekbolet et al., 2002). *i.* humic acid onto TiO₂, *ii.* humic acid onto either montmorillonite or kaolinite, *iii.* Humic acid and monmorillonite/kaolinite binary system onto TiO₂.

The experimental results obtained for all of the above defined systems were evaluated by the sequence of the following descriptive parameters; UV-vis spectral features and related specified UV-vis parameters, described as absorbance measurements at selected wavelengths as 436 nm, 365 nm, 280 nm and 254, i.e. Color₄₃₆, UV₃₆₅, UV₂₈₀

and UV₂₅₄, and fluorescence spectra recorded both in emission and synchronous scan modes with the related specified fluorescence parameters, FI_{emis} and FI_{syn}. Emission fluorescence spectra were recorded both for excitation wavelengths of 350 nm. Comparative evaluation in terms of the specified and specific UV-vis and fluorescence parameters were presented with reference to DOC measurements that were also carried out throughout the experimental study. Since filtration through 0.45 µm membrane filter constitutes a crucial step both in preparation of humic acid solutions and for the successful removal of photocatalyst from the reaction medium, the effect of filtration was also evaluated by demonstrating the comparative results. The following acronyms were used throughout the text to signify; HA_r: raw humic acid (HA: 50 mg L⁻¹ and DOC: 17 mg L⁻¹); HA_{rf}: 0.45 µm filtrated raw humic acid (DOC: 16.48 mg L⁻¹), Mt: montmorillonite, and Kt: kaolinite. Moreover, “t= 0” term expressing the initial adsorptive interactions was used to represent the condition where TiO₂ was introduced to the system and removed immediately. The results obtained for the photocatalytic degradation of humic acid in the presence of either Mt or Kt were discussed separately under appropriate sub-headings.

Humic acid solution was subjected to photocatalytic degradation according to the method explained in the Materials and Methods section. The oxidized humic acid samples were evaluated by UV-vis and fluorescence spectral features as well as by the specified UV-vis and fluorescence parameters. The attained results for humic acid both in the presence and in absence of clay minerals i.e. montmorillonite or kaolinite were presented under appropriate subheadings. For the assessment of the photocatalytic degradation of humic acid employing TiO₂, the photocatalyst loading was kept constant as 0.50 mg mL⁻¹ and Mt or Kt concentrations were chosen as 0.05 mg mL⁻¹, 0.10 mg mL⁻¹ and 0.20 mg mL⁻¹. As a baseline information and for comparative purposes, photocatalytic degradation of sole humic acid (HA, 50 mg L⁻¹) was presented in the following section (Section 2.2.1.).

From a general perspective, with reference to the previous experience of Bekbolet and co-workers, irradiation time dependent changes occurring during photocatalytic degradation of humic acid could be schematically presented (Uyguner-Demirel and Bekbolet, 2011) (Figure 4.1). Interactive reactions prevailing between clay minerals and humic acid in aqueous medium is presented in Figure 4.2 (Majzik and Tombácz, 2007a).

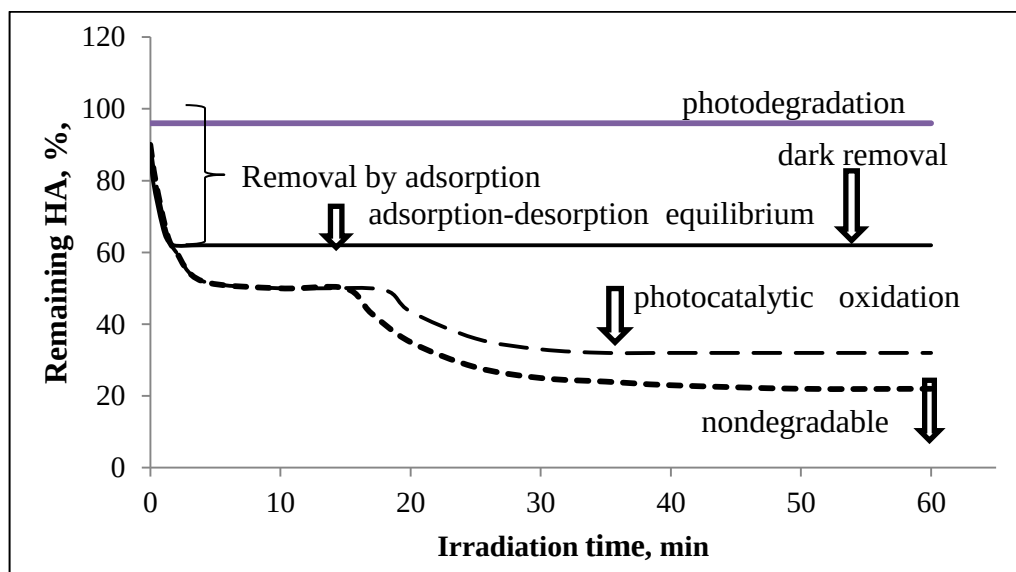


Figure 4.1. Schematic presentation of photocatalytic degradation of humic acid.

Upon introduction of TiO_2 to the aqueous humic acid solution, initial adsorption occurs (up to 40%). During the early stages of irradiation, almost no further removal could be visualized due to the photoadsorption-desorption phase. Upon further irradiation periods, all of the specified humic acid parameters followed a logarithmic decay trend. Moreover, non-degradable humic acid fractions could also be attained, the reason of which could be related to the diversity of the source and origin of the humic matter. In the absence of TiO_2 , only a very slight change due to photodegradation of humic acid could be observed.

In aqueous solution, clay minerals undergo a series of reactions (hydration, ion-exchange, and pH dependent deprotonation-protonation of humic functional groups). In a similar manner, humic acid could also undergo a series of reactions as presented in Figure 4.2. The most significant interaction could be visualized as the role of Ca^{2+} ions representing an ionic strength effect. The resulting effect would be reconfiguration through coiling of humic sub-fractions expressing diverse reactivities towards the oxide surface present in aqueous solution. In the presence of TiO_2 , pH dependent electrostatic attractions take place leading to re-orientation of humic sub-fractions onto the oxide surface expressing a “tail-train and loop” type alignment even displaying an umbrella effect towards irradiation (Figure 4.3).

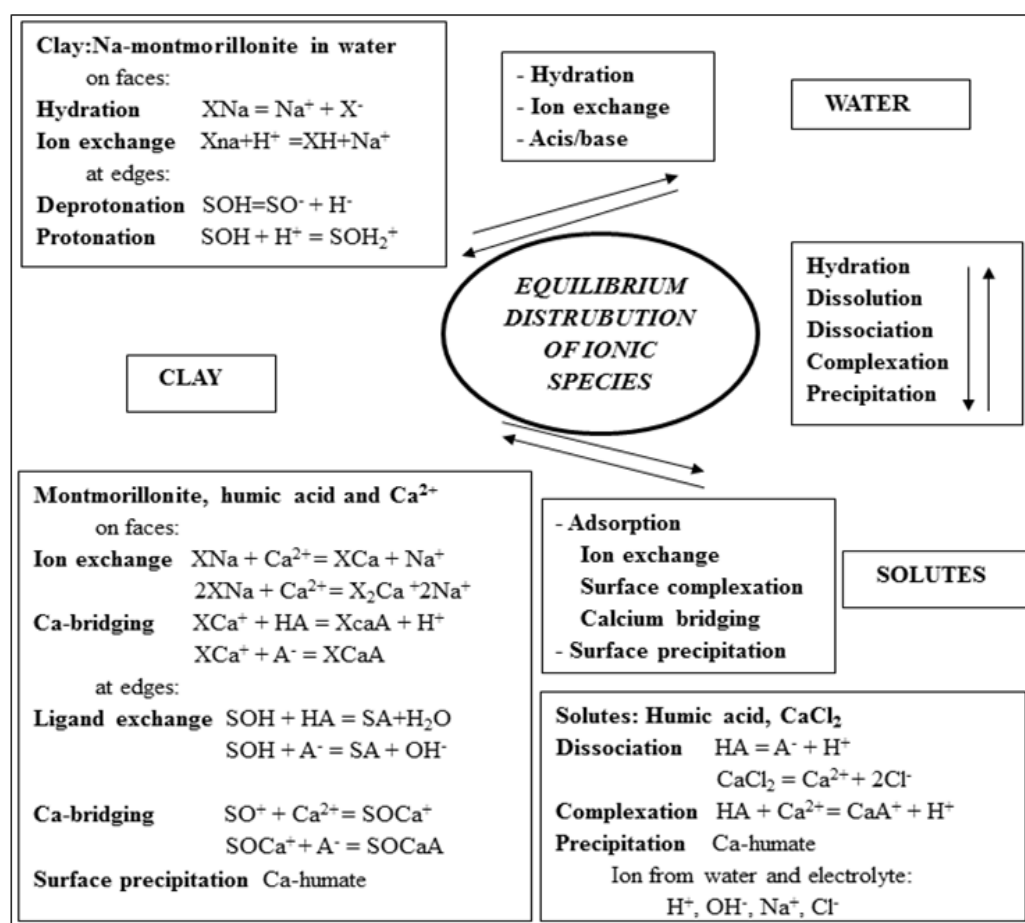


Figure 4.2. Reaction occurring between clay minerals and humic acid in aqueous medium (Majzik and Tombácz, 2007a).

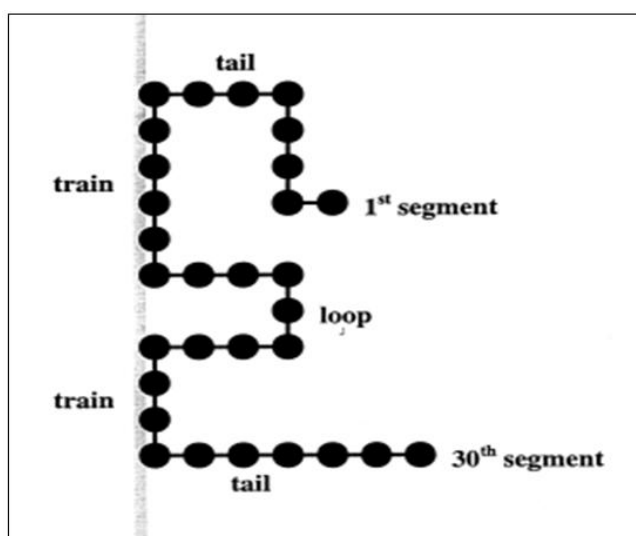


Figure 4.3. Tail-train and loop model of humic acid.

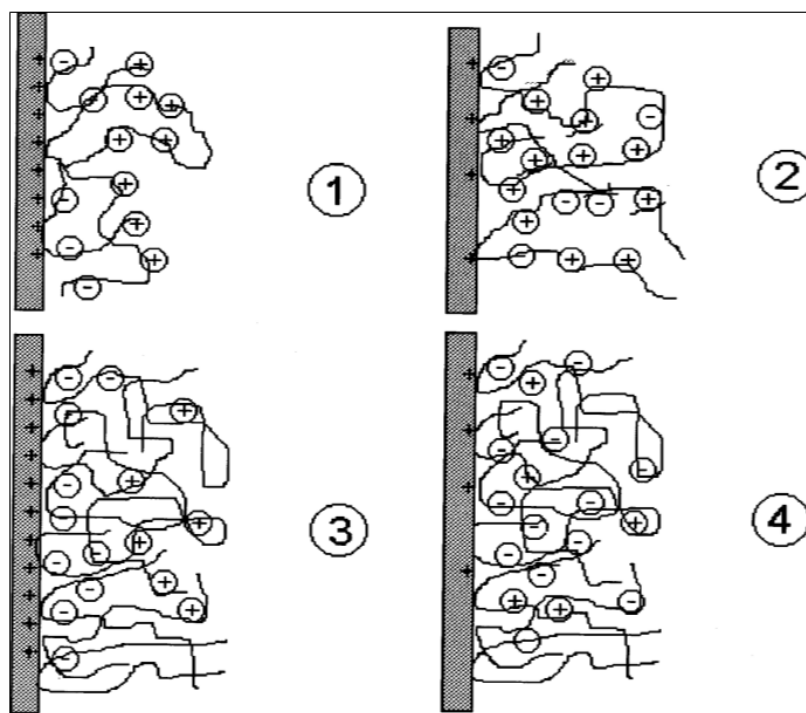


Figure 4.4. Electrostatic attractions between charged surfaces and humic sub-fractions (Elfarissi and Pefferkorn, 2000). 1-4 represent prevailing electrostatic attractions.

The observed structural and conformational diversities of humic acid sub-fractions could be visualized by the simple scheme expressing “tail-train and loop” model (Figure 4.3). In the presence of TiO_2 and clay minerals, humic acid sub-fractions were attracted to the surfaces through electrostatic interactions (Figure 4.4).

4.1.1. Baseline experiments; humic acid, montmorillonite or kaolinite and TiO_2 interactions:

UV-vis spectra of humic acids (HA_r and HA_{rf}), binary systems i.e. “ HA_r and TiO_2 binary system”; “ HA_r and Mt binary system”; “ HA_r and Kt binary system” and ternary systems composed of i.e. “ HA_r , Mt and TiO_2 ternary system” and “ HA_r , Kt and TiO_2 ternary system” were recorded and presented in Figure 4.5 in a comparative style. All of the experiments were performed using 50 mg L^{-1} HA_r in the presence of 0.10 mg mL^{-1} either Mt or Kt and 0.50 mg mL^{-1} TiO_2 . The use of $0.45 \mu\text{m}$ membrane filters is related to the basic definition of DOC representing the dissolved organic contents in aquatic systems (Uyguner –Demirel and Bekbolet, 2011).

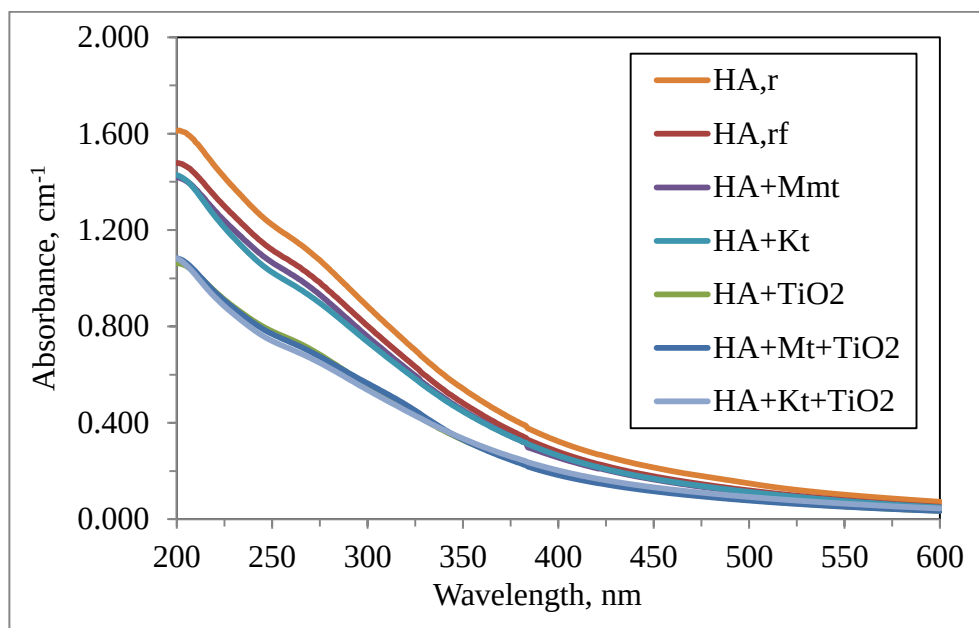


Figure 4.5. UV-vis spectra of humic acids recorded for the baseline experiments performed for all of the specified systems.

Humic acid displayed an exponential decreasing trend in absorbance with respect to increasing wavelength as expected and reported previously (Uyguner and Bekbolet, 2005a). Filtration through 0.45 μm membrane filter slightly removed UV absorbing centers in the 200-350 nm wavelength region. Considerably significant absorbance changes were attained at shorter wavelengths being $\geq 8\%$ (e.g. $\text{UV}_{365} = 12\%$) however no significant absorbance change was recorded in the visible region (350-600 nm). The presence of either Mt or Kt displayed similar decreasing fashion in absorbance spectrum of humic acid recorded in the UV-vis wavelength region. However, addition of Kt to humic acid led to a slight decrease in absorbance spectra between 200 to 350 nm wavelength region followed by an usual trend for longer wavelengths $\lambda \geq 350$ nm. In the presence of TiO_2 , humic acid UV-vis spectra displayed significant decreases in absorbance for the wavelength region of 200-400 nm followed by an overlapping trend in the visible region ($\lambda = 400$ -600 nm). The UV-vis spectra attained for the ternary systems completely overlapped with the UV-vis spectra recorded for the binary system composed of HA,r and TiO_2 . The presence of clay minerals as either Mt or Kt did not significantly alter the basic declining logarithmic shape of the UV-vis spectral profile of humic acid.

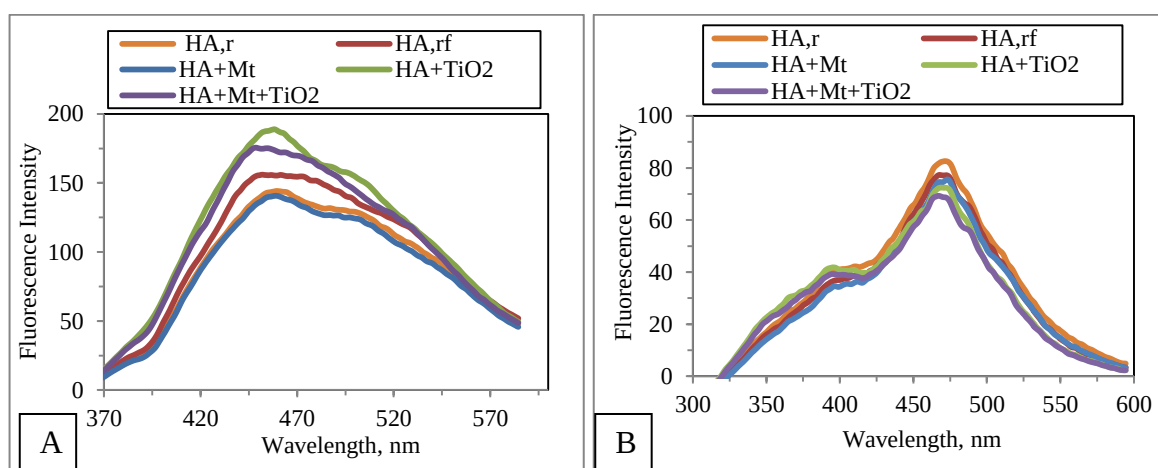


Figure 4.6. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the baseline experiments performed for all of the specified systems composed of montmorillonite.

The emission scan fluorescence spectra of humic acid (HA,r and HA,r,f) displayed a broad peak at about 455 nm wavelength with an increase in fluorescence intensity (FI) for HA,r,f expressing the role of the filtration by the emergence of new fluorophoric groups (Figure 4.6 A). Moreover, a slight increase was also observed for the FI recorded for HA,r and TiO₂ binary system. Adsorptive interaction of HA,r with TiO₂ resulted in the formation of new fluorophores as could be visualized by the emission scan fluorescence spectra. In the presence of Mt (HA,r, Mt and TiO₂ ternary system), a decrease was observed in FI with respect to the HA,r and TiO₂ binary system due to the quenching of fluorophoric groups via ternary oxide surface interactions. On the other hand, no distinct change in fluorescence intensity was observed by the interaction of the montmorillonite and humic acid. The synchronous scan fluorescence spectra of humic acid recorded for the baseline experiments were shown in Figure 4.6 B.

The synchronous scan fluorescence spectra recorded for raw humic acid displayed a sharp peak around emission wavelength of 475 nm and a minor peak at emission wavelength of 390 nm with comparatively lower fluorescence intensity. Filtration of humic acid through 0.45 μm membrane filter led to decreasing of fluorescence intensity. Synchronous scan fluorescence spectra recorded for humic acid and Mt binary system displayed a considerably lower FI profile in the emission wavelength region of 450-600

nm. Although slightly decreasing trend in FI_{syn} was observed for all of the systems, the lowest fluorescence intensity of humic acid was attained in the case of the ternary system composed of humic acid, Mt and TiO_2 .

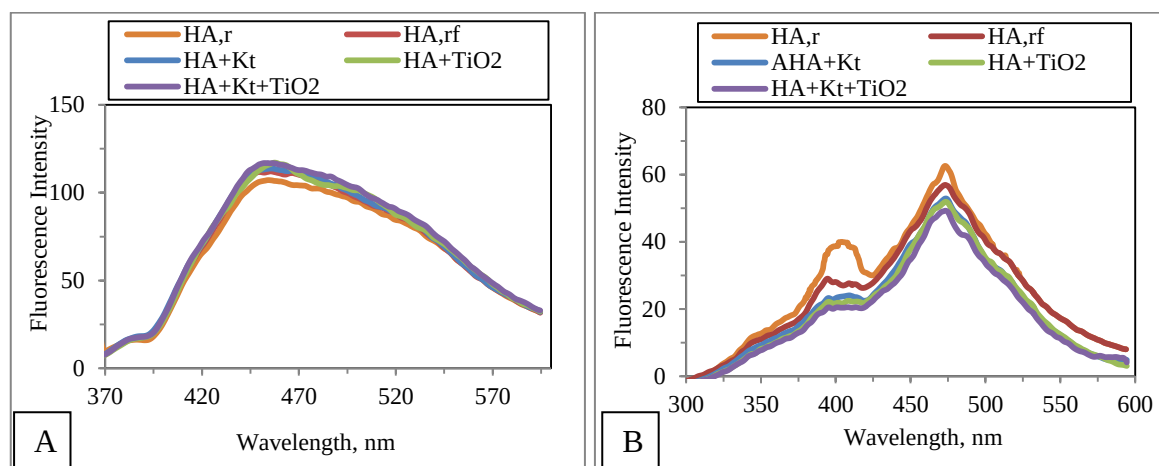


Figure 4.7. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the baseline experiments performed for all of the specified systems composed of kaolinite.

Emission scan fluorescence spectra (A) and synchronous scan fluorescence spectra (B) of humic acid recorded for the baseline experiments performed in presence of Kt were given in Figure 4.7. The emission scan fluorescence spectra of humic acid in the presence of Kt exhibited an expected peak at around emission wavelength of 455 nm (Figure 4.7 A). Fluorescence intensity trend of emission scan fluorescence spectra of humic acid in the binary and ternary systems revealed an increasing trend for the entire wavelength region (300-600 nm). On the other hand, the synchronous scan fluorescence spectral profiles of humic acid for binary and ternary systems displayed a decreasing trend (Figure 4.7 B). The lowest fluorescence intensity of humic acid was recorded for the humic acid, kaolinite and TiO_2 ternary system.

UV-vis and fluorescence spectral features could also be evaluated by the specified parameters for the elucidation of the specific parameters ($Color_{436}$, UV_{365} , UV_{280} and UV_{254}) normalized to the respective DOC contents ($m^{-1}mg^{-1}L$) such as $SCoA_{436}$, $SUVA_{365}$, $SUVA_{280}$ and $SUVA_{254}$ (Table 4.1). Moreover fluorescence parameters ($FI_{emis350}$, $FI_{emis370}$

and FI_{syn}) normalized to respective DOC contents such as $SFI_{emis,455}$, $SFI_{emis,460}$, $SFI_{syn,475}$ were also presented. In a comparative manner, binary and ternary systems were presented with respect to the sole humic acid parameters. In the presence of Mt, $Color_{436}$, UV_{365} , UV_{280} , UV_{254} and DOC parameters of humic acid decreased by 22%, 17%, 14%, 13% and 5%, respectively. The removal percentages of humic acid for $Color_{436}$, UV_{365} , UV_{280} , UV_{254} and DOC parameters in the HA, Mt and TiO_2 ternary system were found to be 45%, 40%, 37%, 37% and 29% respectively, representing the additional role of oxide surface adsorptive interactions.

Moreover, In the presence of Kt, $Color_{436}$, UV_{365} , UV_{280} , UV_{254} and DOC parameters of humic acid decreased by 21%, 18%, 17%, 16% and 6%, respectively. The removal percentages of raw humic acid for $Color_{436}$, UV_{365} , UV_{280} , UV_{254} and DOC parameters in the HA, Kt and TiO_2 ternary system were found to be 38%, 38%, 39.5%, 39.5% and 34% respectively, representing the additional role of titanium dioxide surface adsorptive interactions as expressed for Mt previously. The effect of Mt particles with respect to kaolinite particles could be regarded as more significant in the removal tendency of humic acid as expressed by both UV-vis parameters as well as DOC contents. However in the presence of TiO_2 , $Color_{436}$, UV_{365} , UV_{280} , UV_{254} and DOC parameters of humic acid decreased by 43.5%, 40%, 37%, 36% and 31%, respectively.

Depending on the explanation that specific UV absorbance ($SUVA_{254}$) parameter can be used to describe the composition of humic material in terms of hydrophobicity and hydrophilicity, $SUVA_{254} > 4$ indicates mainly hydrophobic and especially aromatic moieties while a $SUVA_{254} < 4$ represents a hydrophilic organic fraction (Edzwald et al., 1985). Under all of the binary and ternary interactive conditions $SUVA_{254}$ were found to be > 4 indicating the observed predominantly hydrophobic character of humic acid. All specific absorbance values i.e. $SCoA_{436}$, $SUVA_{365}$, $SUVA_{280}$, and $SUVA_{254}$ followed a decreasing trend for HA,r, HA,rf and humic binary and ternary systems. $SCoA_{436}$, $SUVA_{365}$, $SUVA_{280}$, and $SUVA_{254}$ values displayed the highest condition for HA,r whereas the lowest values were attained for humic acid in the presence of Mt and TiO_2 (HA, Mt and TiO_2 ternary system). Moreover, $SUVA_{365}$, $SUVA_{280}$ and $SUVA_{254}$ values followed a decreasing trend independent from the type of the active interactions with respect to sole humic properties.

Table 4.1. Specified and specific UV-vis and fluorescence parameters and DOC of humic acid attained for baseline experiments.

Specified UV-vis and fluorescence parameters and DOC								
Humic acid	UV-vis Spectroscopic parameters, cm^{-1} DOC, mg L^{-1}					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 475 nm
HA,r	0.239	0.465	1.038	1.199	17.00	143.080	124.917	82.196
HA,rf	0.200	0.411	0.947	1.098	16.48	155.556	135.291	76.819
Binary systems								
HA,r and Mt	0.186	0.385	0.898	1.046	16.12	139.344	122.184	75.416
HA,r and Kt	0.181	0.375	0.867	1.005	16.00	113.714	98.965	52.847
HA,r and TiO ₂	0.135	0.280	0.658	0.766	11.80	187.668	152.794	72.001
Ternary systems								
HA,r, Mt and TiO ₂	0.131	0.277	0.653	0.754	12.16	175.111	143.327	67.781
HA,r, Kt and TiO ₂	0.129	0.276	0.638	0.721	11.23	116.718	105.534	49.174
Specific UV-vis and fluorescence parameters, $\text{m}^{-1}\text{mg}^{-1}\text{L}$								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	841.65	734.80	483.51	
HA,rf	1.21	2.49	5.74	6.66	943.91	820.94	466.14	
Binary systems								
HA,r and Mt	1.15	2.39	5.57	6.49	864.42	757.97	467.84	
HA,r and Kt	1.18	2.39	5.42	6.28	710.71	618.53	330.29	
HA and TiO ₂	1.15	2.37	5.58	6.49	1590.41	1294.86	610.18	
Ternary systems								
HA,r, Mt and TiO ₂	1.08	2.28	5.37	6.20	1440.06	1178.68	557.41	
HA,r, Kt and TiO ₂	1.15	2.48	5.68	6.42	1039.34	939.75	437.88	

Specific fluorescence intensity values were also presented in Table 4.1. No significant general trend could be visualized for $SFI_{emis,455}$, $SFI_{emis,460}$ and $SFI_{syn,475}$ parameters that were attained under all conditions. The reason could be attributed to the diversity of the FI trend with respect to a regular decreasing trend of DOC. Moreover, distinctly lower $SFI_{emis,455}$, $SFI_{emis,460}$ and $SFI_{syn,475}$ were calculated for HA,r and Kt binary system with respect to the specific FI parameters of HA,r. Significantly higher $SFI_{em,455}$, $SFI_{em,460}$ and $SFI_{syn,475}$ were determined for HA,r and TiO_2 binary system. Although significantly higher $SFI_{emis,455}$ and $SFI_{em,460}$ were attained for the ternary system, considerably similar $SFI_{syn,475}$ were calculated with respect to the binary system interactions.

4.1.2. Preliminary experiments performed both under dark conditions in the presence of TiO_2 and in the absence of photocatalyst

Photocatalytic degradation of sole humic acid was performed to present a basis for the investigation of the effects of the clays minerals namely montmorillonite and kaolinite on the degradation efficiency. In a typical manner, preliminary experiments were also performed both under dark conditions and in the absence of photocatalyst to display the background interactions prior to photocatalysis. All of the preliminary experiments were performed using 50 mg L^{-1} HA,r in the presence of 0.10 mg mL^{-1} either Mt or Kt and 0.50 mg mL^{-1} TiO_2 .

4.1.2.1. Preliminary experiments performed under dark conditions in the presence of TiO_2 .

In order to observe the plausible adsorptive interactions of humic acid onto oxide surface, both in the presence and absence of clay minerals, preliminary experiments were carried out under dark conditions in the presence of TiO_2 .

Preliminary experiments performed under dark conditions using sole humic acid in the presence of TiO_2 . For the UV-vis spectroscopic evaluation of raw humic acid during preliminary experiments performed under dark conditions with respect to time, UV-vis absorbance values were recorded in the 200-600 nm wavelength regions (Figure 4.8). The UV-vis spectra of humic acids under all reaction periods displayed a monotonously decreasing trend with increasing wavelength in a broad and featureless manner as expected

and presented previously (Uyguner and Bekbolet, 2005a). For comparison purposes filtered humic acid sample ($HA_{r,f}$) was also presented to display the role of filtration effect on the UV-vis spectroscopic properties of humic acid. A considerable decrease was recorded in the UV-vis ($\lambda < 500\text{nm}$) absorbance upon the introduction of the TiO_2 to the humic acid solution representing the role of adsorptive interactions prevailing in between humic acid and titanium oxide surface. As expected, no further significant change was observed with respect to reaction time. The reason could be attributed to the adsorption-desorption equilibria occurring in aqueous solution (Bekbolet et al., 2002). It should also be indicated that TiO_2 surface coverage by humic acid ($t = 0$) could be regarded as sufficient for photocatalysis.

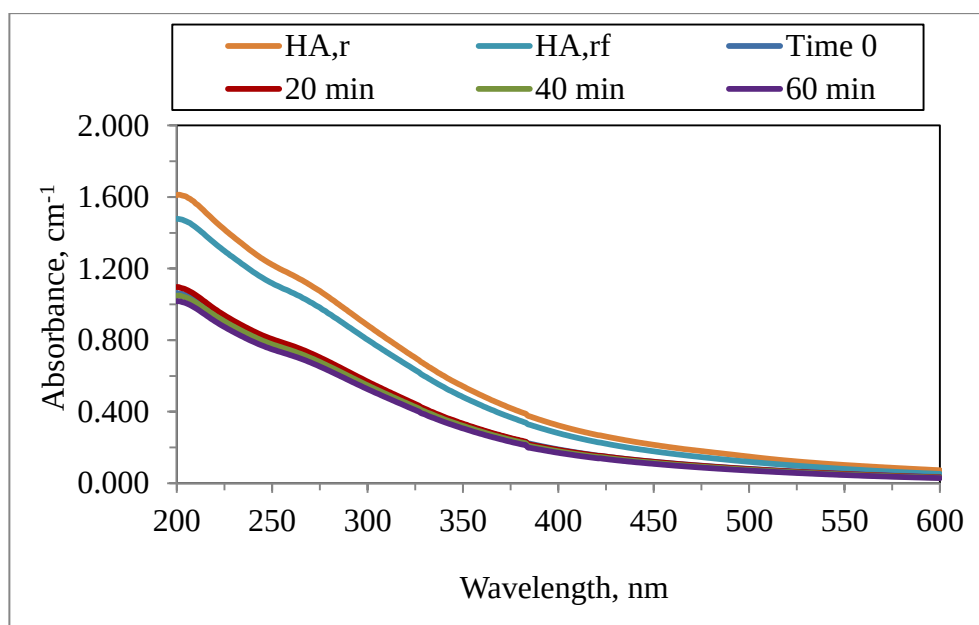


Figure 4.8. UV-vis spectra of humic acid recorded for the preliminary experiments performed under dark conditions in presence of TiO_2 .

For the assessment of the fluorescence spectroscopic evaluation of humic acid during preliminary experiments performed under dark conditions in the presence of TiO_2 , The emission scan (A) and synchronous scan (B) fluorescence spectra was presented in Figure 4.9 A-B. Emission scan and synchronous scan fluorescence spectra emission values were recorded in the 300-600 nm wavelength regions (Figure 4.9).

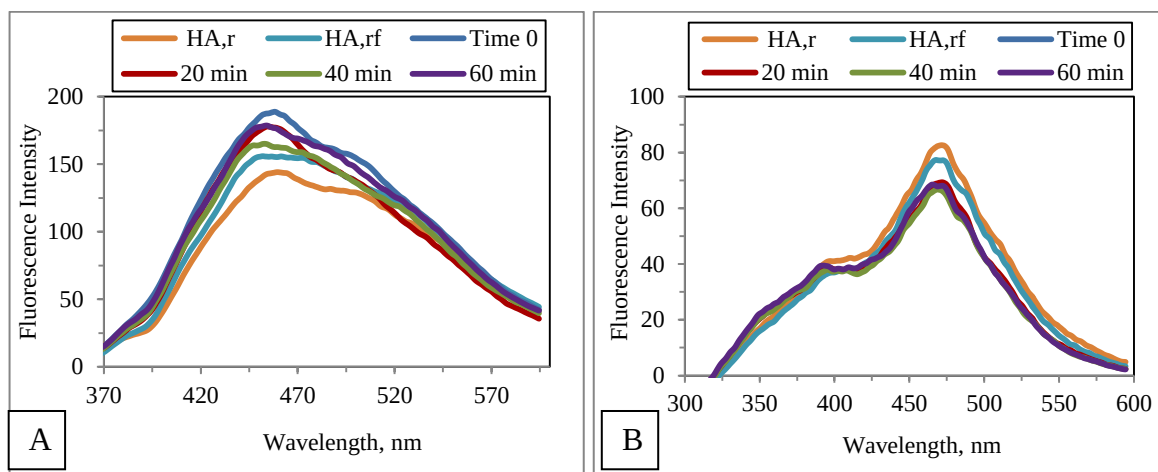


Figure 4.9. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under dark conditions in presence of TiO_2 .

Upon introduction of TiO_2 to the humic acid solution ($t = 0$ condition), a significant increase in $\text{FI}_{\text{emis},350}$ was recorded followed by reaction time independent variations in the fluorescence intensity. The observed discriminative effect could only be visualized at FI maxima recorded at 455 nm wavelength followed by an almost overlapping trend at both wavelength regions of $\lambda_{\text{emis}} > 480$ nm and $\lambda_{\text{emis}} < 420$ nm. The synchronous scan fluorescence spectra recorded for humic acid for the preliminary experiments performed under dark conditions were shown in Figure 4.9. B. The synchronous scan fluorescence spectra for raw humic acid displayed a sharp peak around wavelength of $\lambda_{\text{emis}} = 475$ nm and a moderate peak shoulder at $\lambda_{\text{emis}} = 390$ nm wavelength with a comparatively lower intensity. Following the adsorptive interactions, the synchronous scan fluorescence spectra of humic acid retained similar spectral features under all reaction periods.

Referring to the UV-Vis spectral features observed for humic acid under dark conditions in the presence of TiO_2 (Figure 4.8) it could be indicated that fluorescence spectral features obtained either as emission scan or synchronous scan modes were found to be more discriminative with respect to reaction time periods. During surface interactions, the changes attained in humic structures could well be expressed by fluorescence spectra properties found to be in comparison to UV-vis parameters displaying an additive absorption property.

Table 4.2. Specified and specific UV-vis and fluorescence parameters of humic acid for preliminary experiments performed under dark conditions in presence of TiO_2 .

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm^{-1} DOC, mg L^{-1}					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 475 nm
HA,r	0.239	0.465	1.038	1.199	17.00	143.080	124.917	82.196
HA,rf	0.200	0.411	0.947	1.098	16.48	155.556	135.291	76.819
Irradiation Time, min								
Time 0	0.135	0.280	0.658	0.766	11.80	187.668	152.794	72.001
20	0.135	0.282	0.678	0.791	11.92	177.877	139.770	68.895
40	0.129	0.271	0.652	0.763	12.85	164.341	136.263	65.159
60	0.122	0.259	0.628	0.735	12.02	178.293	142.673	67.475
Specific UV-vis and fluorescence parameters, $\text{m}^{-1}\text{mg}^{-1}\text{L}$								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	841.65	734.80	483.51	
HA,rf	1.21	2.49	5.74	6.66	943.91	820.94	466.14	
Irradiation Time, min								
Time 0	1.15	2.37	5.58	6.49	1590.41	1294.86	610.18	
20	1.13	2.36	5.68	6.64	1492.26	1172.56	577.98	
40	1.00	2.11	5.08	5.94	1278.92	1060.41	507.07	
60	1.01	2.16	5.23	6.12	1483.30	1186.96	561.35	

Moreover, reaction time dependent variations in DOC contents were also determined and presented in Table 4.2. 3% DOC was removed by filtration through $0.45\mu\text{m}$ membrane filter in connection with the removals of 16% for Color₄₃₆, 12% for UV₃₆₅, 9% UV₂₈₀ and 8% for UV₂₅₄. Upon the introduction of TiO_2 , substantial decreases were attained as 43.5% for Color₄₃₆, 39.8% for UV₃₆₅, 37% UV₂₈₀, 36% for UV₂₅₄ and 30.5% for

DOC. The removal due to filtration could be accepted as a background removal extent that would be effective on the successive removal of photocatalyst from the reaction medium. On the other hand, the role of adsorption should be regarded as removal by surface interactions leading to surface coverage that would certainly affect the light absorption capacity of TiO_2 thereby the formation rates of reactive oxygen species.

The resultant effect of the prevailing interactions in between humic moieties and oxide surface could be visualized more significantly in color forming moieties rather than the UV-absorbing aromatic core entities. Considerably similar removals were attained for UV_{254} and DOC representing the importance of the surrogate parameters used for humic quantification (Uyguner-Demirel and Bekbolet, 2011). During the reaction periods, further removals were followed that could be considered as insignificant ($\leq 5\%$). Although inconsistent variations were attained for emission scan fluoroscopic properties of humic acid under the presented conditions of filtration and adsorption, synchronous scan fluorescence intensity trend could be regarded as displaying a decreasing profile with respect to the reaction periods. Under dark conditions, at the end of 60 min of reaction period, 18% removal of fluorophores as expressed by $\text{FI}_{\text{sys } 475}$ parameter was recorded.

Particularly, the above presented UV-vis and fluorescence spectral features could also be evaluated by the specific UV-vis and fluorescence spectroscopic parameters (Table 4.2). More significantly, SUVA_{254} decreased with respect to reaction time and the lowest SUVA_{254} was attained after 40 min of reaction time that could also be accepted as similar to the SUVA_{254} calculated for the humic composition attained at 60 min of reaction period ($\pm 3\%$). Under all of the reaction time periods, SUVA_{254} were found to be > 4 indicating the predominantly hydrophobic aromatic character of humic acid followed by the surface interactions possibly occurring through the outer sphere complexation reactions of humic moieties and oxide surface (Majzik and Tombácz, 2007a). The same decreasing trend was also observed for the other specific parameters as SCoA_{436} , SUVA_{365} , and SUVA_{280} attaining an almost stabilized condition after 40 min of reaction period expressing that the adsorptive surface interactions could be expressed by specific DOC normalized UV-vis parameters with respect to reaction periods. Reaction period of 20 min would be regarded as a period at which adsorption-desorption equilibria would be attained.

Introduction of the TiO_2 particles to the humic acid solution resulted in a substantial increase in the specific fluorescent parameters as expressed by $\text{SFI}_{\text{emis},455}$, $\text{SFI}_{\text{emis},460}$ and $\text{SFI}_{\text{syn},475}$. A decreasing trend with respect to the reaction time periods could also be visualized by $\text{SFI}_{\text{emis},455}$, $\text{SFI}_{\text{emis},460}$ and $\text{SFI}_{\text{syn},475}$ under all conditions up to 40 min. Considerably lower $\text{SFI}_{\text{emis},455}$, $\text{SFI}_{\text{emis},460}$ and $\text{SFI}_{\text{syn},475}$ were calculated for 40 min of reaction time that could be related to the different tendencies observed in the removal trend of fluorophoric groups and DOC. The effect of the extended reaction period (60 min) could be explained by the possible rearrangement of humic moieties on the oxide surface through adsorption-desorption processes. The resultant effect could be visualized by the release of new humic fluorophoric groups that were not used in adsorptive interactions.

Preliminary experiments performed under dark conditions using humic acid and montmorillonite in the presence of TiO_2 . Experiments were carried out using humic acid and montmorillonite in the presence of TiO_2 under dark conditions with respect to time. UV-vis absorbance spectra were recorded in the 200-600 nm wavelength region (Figure 4.10).

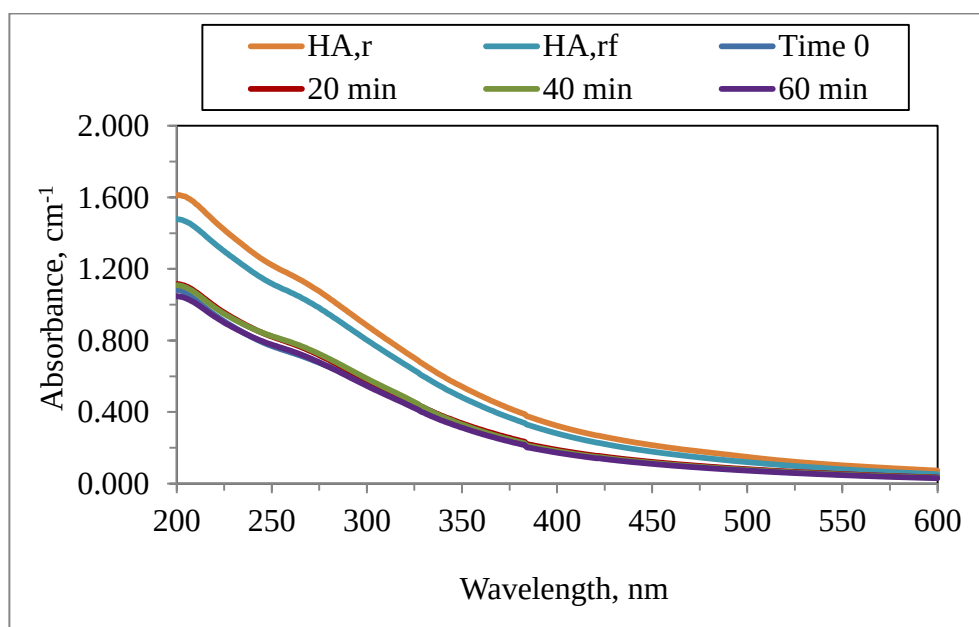


Figure 4.10. UV-vis spectra of humic acid recorded for preliminary experiments performed under dark conditions in the presence of montmorillonite and TiO_2 .

In comparison to the UV-vis spectra recorded for the HA,r and TiO₂ system no significant change was observed with respect to time for the ternary system composed of HA,r, Mt and TiO₂. The presence of Mt did not alter the UV-vis spectral features of HA attained in the presence of TiO₂ (Figure 4.10). UV-vis absorbance profile of humic acid for all irradiation periods were overlapping for the selected wavelength region ($\lambda = 200\text{-}600\text{ nm}$).

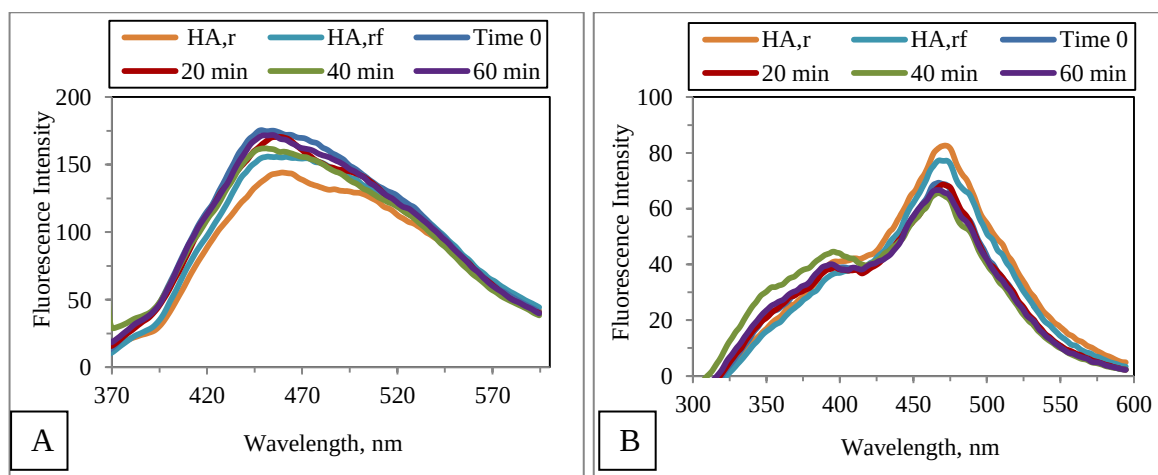


Figure 4.11. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under dark conditions in presence of montmorillonite and TiO₂.

The emission scan (A) and synchronous scan (B) fluorescence spectra recorded for the dark experiments of humic acid in the presence of Mt and TiO₂ and were shown in Figure 4.11. As expected, no significant difference was observed for emission scan FI trend during 60 minutes of time period displaying nearly the same fluorescence intensity values with overlapping trend (Figure 4.11 A). The synchronous scan fluorescence spectra for raw humic acid displayed a sharp peak around emission wavelength of $\lambda_{\text{emis}} = 475\text{ nm}$ as previously indicated (Figure 4.11 B). A moderate peak at 390 nm emission wavelength with a comparatively lower intensity was also detectable under all reaction time periods. Due to the presence of Mt in the reaction medium, minor increases were observed for FI of synchronous scan fluorescence values up to $\lambda_{\text{emis}} = 400\text{ nm}$ wavelength. FI values recorded at longer emission wavelength $\lambda_{\text{emis}} > 450\text{ nm}$ were decreased under all reaction time periods.

Specified and specific UV-vis and fluorescence parameters of raw humic acid during dark experiments performed in the presence of Mt were given in Table 4.3. For comparison purposes, reaction time dependent variations in DOC contents were also determined and presented in Table 4.3.

Table 4.3. Specific and specified UV-vis and fluorescence parameters of humic acid during preliminary experiments performed under dark conditions in the presence of montmorillonite and TiO_2 .

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm^{-1} DOC, mg L^{-1}					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 474 nm
HA,r	0.239	0.465	1.038	1.199	17.00	143.080	124.917	82.196
HA,rf	0.200	0.411	0.947	1.098	16.48	155.556	135.291	76.819
Irradiation Time, min								
Time 0	0.131	0.277	0.653	0.754	12.16	175.111	143.327	67.781
20	0.136	0.285	0.691	0.808	11.87	170.410	140.915	68.056
40	0.130	0.277	0.699	0.811	11.25	161.315	133.094	63.599
60	0.124	0.263	0.653	0.763	12.23	171.852	141.520	65.091
Specific UV-vis and fluorescence parameters, $\text{m}^{-1}\text{mg}^{-1}\text{L}$								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	841.65	734.80	483.51	
HA,rf	1.21	2.49	5.74	6.66	943.91	820.94	466.14	
Irradiation Time, min								
Time 0	1.08	2.28	5.37	6.20	1440.06	1178.68	557.41	
20	1.15	2.40	5.82	6.80	1435.63	1187.15	573.35	
40	1.16	2.46	6.21	7.21	1433.91	1183.05	565.32	
60	1.01	2.15	5.34	6.24	1405.17	1157.15	532.22	

Upon the introduction of TiO_2 to the system composed of humic acid and montmorillonite no significant decrease could be attained with reference to the humic acid and titanium dioxide surface interaction (Table 4.2.) as expressed by 45% for Color_{436} , 40.5% for UV_{365} , 37% UV_{280} , 37% for UV_{254} and 28% for DOC. During the reaction periods, through incremental decreases further removals were observed that could be considered as insignificant as $\leq 3\%$ in 60 minutes. Inconsistent variations were attained for fluoroscopic properties under the presented conditions of both filtration and adsorption.

SUVA_{254} decreased significantly with respect to reaction time and a considerably lower SUVA_{254} was attained after 60 min of reaction time. However highest SUVA_{254} was obtained for reaction time of 40 min the reason of which could be explained by the prevailing adsorption-desorption process. The same trend was also attained for SCoA_{436} , SUVA_{365} , and SUVA_{280} . Under all of the reaction time periods SUVA_{254} were found to be > 4 in the presence of TiO_2 and Mt. In comparison to the humic acid TiO_2 dark interactions, no significant effect could be expressed for the presence of montmorillonite in the reaction medium (Tables 4.2 and 4.3). The overall effect was clearly visualized by the introduction of the multiple oxide surfaces and no further effect could be attained by the applied time dependent reaction conditions. Moreover, the observed discrepancies were more significant in the UV-specific parameters rather than vis-specific parameters i.e. SCoA .

No significant general trend could be visualized for $\text{SFI}_{\text{emis},455}$, $\text{SFI}_{\text{emis},460}$ and $\text{SFI}_{\text{syn},475}$ parameters in the presence of montmorillonite under all reaction periods. The reason could be attributed to the diversity of the FI values with respect to a regular trend of DOC. Moreover, significantly higher $\text{SFI}_{\text{emis},455}$, $\text{SFI}_{\text{emis},460}$ and $\text{SFI}_{\text{syn},475}$ were calculated for reaction period of 20 minutes and distinctly lower $\text{SFI}_{\text{emis},455}$, $\text{SFI}_{\text{emis},460}$ and $\text{SFI}_{\text{syn},475}$ for reaction period of 60 min. The reason could also be attributed to the observed changes in fluorescence parameters with respect to DOC due to the adsorption-desorption phenomenon taking place continuously throughout the reaction period. Based on the differences, under ternary system conditions in the presence of Mt, $\text{SFI}_{\text{syn},475}$ parameter could be regarded as more significant in expressing the time dependent changes in humic moieties.

Preliminary experiments performed under dark conditions using humic acid and kaolinite in the presence of TiO_2 : Preliminary experiments under dark conditions were carried out using humic acid and kaolinite in the presence of TiO_2 . UV-vis absorbance spectra were recorded in the 200-600 nm wavelength region as presented in Figure 4.12. For comparison purposes, UV-vis spectra of raw humic acid (HA,r) and 0.45 μm filtered humic acid (HA,rf) were also given in Figure 4.12.

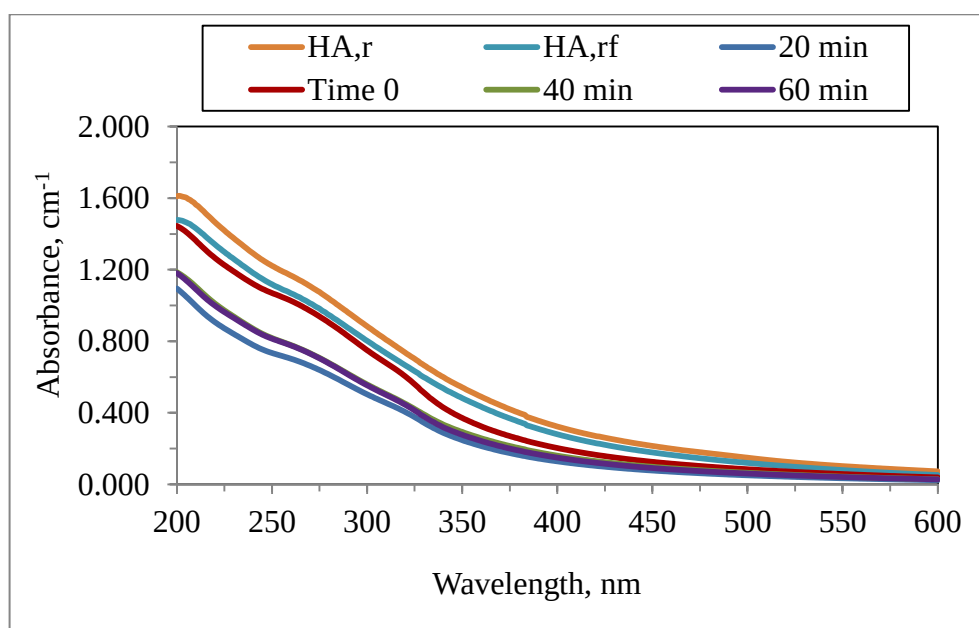


Figure 4.12. UV-vis spectra of humic acid recorded for preliminary experiments performed under dark conditions in presence of kaolinite and TiO_2 .

In a similar manner to the previously studied HA,r, and Mt system in the presence of TiO_2 , no significant change in the UV-vis spectral pattern of humic acid was observed with respect to time for the HA,r and Kt system in the presence of TiO_2 . Although slight differences could be visualized in the UV-region ($\lambda < 325$ nm), UV-vis absorbance profiles of humic acid under all reaction periods displayed an overlapping trend in the wavelength region of $\lambda < 325$ nm. A distinct UV-vis spectral difference could only be observed due to the TiO_2 surface interactions (for $t = 0$ condition), where the role of initial adsorption could be expected as explained previously for the baseline interactions. The presence of Kt significantly changed the initial adsorptive removal of humic acid (Figure 4.5 and Figure 4.12)

The emission scan (A) and synchronous scan (B) fluorescence spectra recorded for dark experiments of humic acid in the presence Kt were shown in Figure 4.13. As expected, no significant difference was observed for emission scan FI trend up to 60 minutes of time period displaying nearly the same fluorescence intensity values with overlapping trend under all reaction periods except that of 20 min reaction time (Figure 4.13 A). Following 20 min of reaction period, although the emission wavelength at which maximum fluorescence was detected remained the same, the fluorescence intensity was found to be slightly higher than the others were. The reason could only be attributed to the unstability of the fluorophoric interactions taking place during adsorptive interactions in the presence of both Kt and TiO_2 . The synchronous scan fluorescence spectra for raw humic acid displayed a sharp peak around emission wavelength of $\lambda_{\text{emis}} = 475$ nm and a moderate peak at 385 nm wavelength with a comparatively lower intensity as explained previously (Figure 2.6.B). In the presence of Kt, inconsistent trend was observed for synchronous scan fluorescence intensities up to emission wavelength of $\lambda_{\text{emis}} = 400$ nm. For longer emission of wavelengths $\lambda_{\text{emis}} > 450$ nm, FI values decreased under all reaction periods. In a similar manner, both the emission scan and the synchronous scan maxima conditions remained the same as observed for sole humic acid and humic acid in the presence of both Mt and TiO_2 (Figure 4.11).

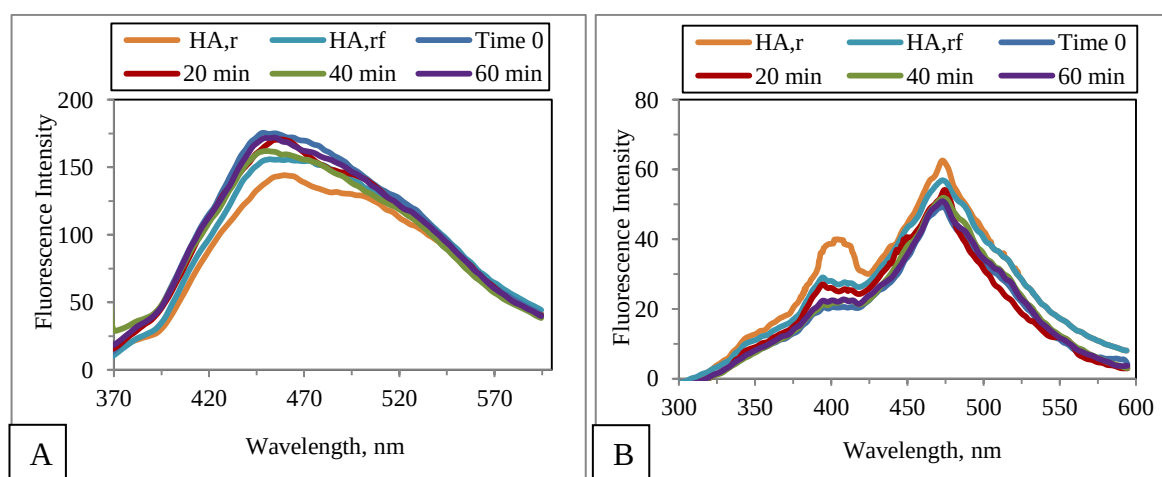


Figure 4.13. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under dark conditions in presence of kaolinite and TiO_2 .

Table 4.4. Specified and specific UV-vis and fluorescence parameters of humic acid during preliminary experiments performed under dark conditions in presence of kaolinite and TiO₂.

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm ⁻¹ DOC, mg L ⁻¹					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 474 nm
HA,r	0.239	0.465	1.038	1.199	17.00	107.091	93.345	62.352
HA,rf	0.200	0.411	0.947	1.098	16.48	112.058	97.334	56.786
Irradiation Time, min								
Time 0	0.129	0.277	0.638	0.721	11.23	116.718	105.534	49.174
20	0.088	0.200	0.614	0.722	11.11	128.748	98.965	54.071
40	0.111	0.242	0.678	0.802	11.22	116.123	96.365	51.893
60	0.104	0.227	0.675	0.799	10.23	113.714	94.839	50.716
Specific UV-vis and fluorescence parameters, m ⁻¹ mg ⁻¹ L								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	629.95	549.09	366.77	
HA,rf	1.21	2.49	5.74	6.46	679.96	590.62	344.58	
Irradiation Time, min								
Time 0	1.32	2.57	7.49	8.73	967.81	875.08	407.74	
20	0.79	1.80	5.52	6.50	1158.85	890.77	486.69	
40	0.99	2.16	6.05	7.15	1034.96	858.87	462.50	
60	1.01	2.22	6.60	7.81	1111.58	927.07	495.76	

Specified and specific UV-vis and fluorescence parameters of raw humic acid during dark experiments in the presence of Kt were given in Table 4.4. Raw humic acid in the presence of both TiO₂ and Kt offered an initial adsorptive removal of 46%, 40%, 39%, and 40% for Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄, respectively. Under prolonged reaction periods i.e. for 60 min, the removal percentages for Color₄₃₆ and UV₂₅₄ were found to be 56% and

33%, respectively. 34% DOC was removed upon introduction of both Kt and TiO₂. Through very small incremental increases, almost 40% of DOC was removed in 60 min of reaction period. It should be indicated that both of the specified UV-vis parameters and DOC followed a similar trend with respect to reaction time periods under dark conditions.

No significant general trend could be visualized for SUVA₂₅₄ parameter in the presence of Kt for all reaction periods. Considerably lower SUVA₂₅₄ was attained after 20 min of reaction time under dark conditions. However highest SUVA₂₅₄ was obtained for reaction time = 0 representing the initial adsorptive removal of humic acid in the presence of Kt. The same trend was also attained for SCoA₄₃₆, SUVA₃₆₅, and SUVA₂₈₀. Under all of the reaction time period SUVA₂₅₄ were found to be > 4 expressing that the aqueous phase humic moieties represented an aromatic character.

A consistent general trend could not be observed for SFI_{emis,455}, SFI_{emis,460} and SFI_{syn,475} parameters in the presence of Kt under all reaction periods. The reason could simply be attributed to the diversity of the FI trend with respect to a regular trend of DOC. The role of physical attraction occurring between the humic fractions, TiO₂ oxide surface, and kaolinite edge/plane oxide surfaces could be expressed by the initial interaction step (t= 0 condition) rather than the time dependent reaction periods.

4.1.2.2. Preliminary experiments performed under irradiation in the absence of TiO₂. In order to observe the effect of irradiation on humic acid, preliminary experiments were carried out under irradiation and in the absence of TiO₂. Similar experiments were also performed in the presence of either Mt or Kt. In a consistent manner, UV-vis spectra were recorded in the 200-600 nm wavelength region for UV-vis spectroscopic evaluation of humic acid during preliminary experiments performed under irradiation and in the absence of TiO₂. Fluorescence spectroscopic evaluation were also assessed through the examination of fluorescence spectra employed in both emission and synchronous scan modes. The main purpose was to elucidate the photolytic interactions of humic acid in the presence of clay particles.

Preliminary experiments performed under irradiation in the presence of humic acid and in the absence of TiO_2 . Preliminary experiments were carried out under irradiation using raw humic acid in the absence of both TiO_2 and clay minerals. UV-vis spectra of raw humic acid under irradiation in the absence of TiO_2 and clay minerals displayed a broad, featureless, and monotonously decreasing trend with increasing wavelength as reported previously (Figure 4.14).

Besides the expected declining trend, no significant change in the UV-vis absorbance spectral pattern was recorded with respect to increasing time under all of the irradiation conditions. Moreover, UV-vis absorbance profiles of humic acid recorded under all irradiation periods displayed an overlapping manner throughout the UV-vis wavelength region (200-600). The reason could be attributed to the insignificant role of photolytic behavior under the irradiation of black light fluorescent lamp (BLF). Irradiation was provided by a 125 W BLF lamp (emission wavelength range of 300-400 nm, maximum intensity at $\lambda = 365$ nm with a photon generation rate of $I_0 = 4.73 \times 10^{-2} \mu\text{Es}^{-1}$).

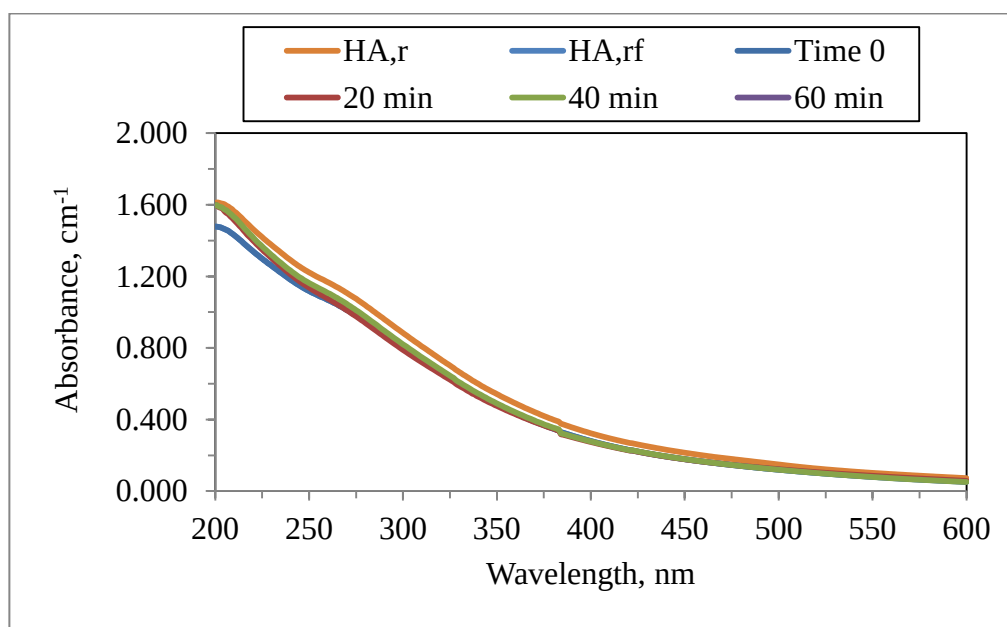


Figure 4.14. UV-vis spectra of humic acid recorded for the preliminary experiments performed under irradiation and in the absence of TiO_2 .

The emission scan (A) and synchronous scan (B) fluorescence spectra recorded for the preliminary experiments of humic acid performed under irradiation in the absence of both TiO_2 and clay minerals were shown in Figure 4.15. With a slight difference as was observed for emission scan FI trend under all irradiation conditions up to 60 minutes of irradiation time period, an overlapping trend could be visualized except that recorded for 20 minutes of irradiation period (Figure 4.15 A). With reference to the synchronous scan fluorescence spectra of raw humic acid displaying a sharp peak around emission wavelength of $\lambda_{\text{emis}} = 475$ nm, by irradiation of humic acid in the absence of both TiO_2 and clay minerals, minor increases were observed for fluorescence index of synchronous scan fluorescence values up to emission wavelength of $\lambda_{\text{emis}} = 400$ nm (Figure 4.15 B). For longer wavelengths $\lambda_{\text{emis}} > 450$ nm, fluorescence index values displayed a decreasing trend under all irradiation time periods. The reason could be explained by the possible structural changes in the fluorophoric groups rather than the light induced photolytic reactions.

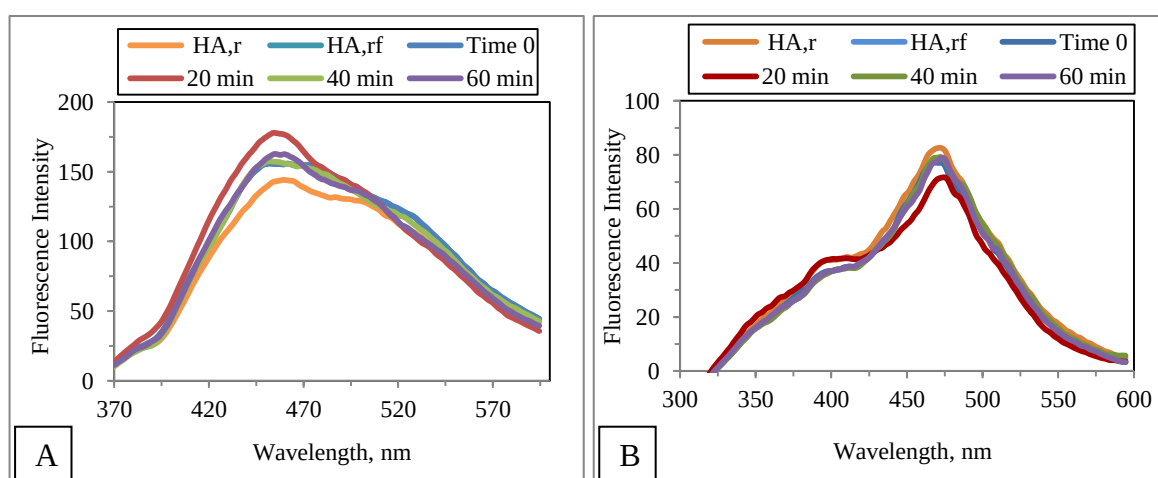


Figure 4.15. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under irradiation and in the absence of TiO_2 .

Specified and specific UV-vis and fluorescence parameters of raw humic acid samples under irradiation in the absence of both TiO_2 and clay minerals were given in Table 4.5. Raw humic acid samples under irradiation in the absence of both TiO_2 and clay minerals presented an initial adsorptive removal of 16%, 12%, 9% and 8.5% for Color_{436} ,

UV₃₆₅, UV₂₈₀ and UV₂₅₄ respectively. Further insignificant removals i.e. < 5% could also be expressed by the specified UV-vis parameters. The resulting depletion effect of irradiation on the DOC content of humic acid was found to be as 5% at the initial stage followed by a slight decrease as 7% in 60 minutes of irradiation time.

Referring to the information presented in Table 4.5, no significant decreasing trend could be attained for SUVA₂₅₄ parameter for raw humic acid samples under irradiation in the absence of both TiO₂ and clay minerals under all irradiation time periods. While, lower SUVA₂₅₄ was attained after initial stage ($t_{irr}= 0$ min), highest SUVA₂₅₄ (7.15 m⁻¹mg⁻¹L) was obtained for 20 minutes reaction time. However, lowest SCoA₄₃₆, SUVA₃₆₅, and SUVA₂₈₀ values were attained for irradiation period of 60 minutes as 1.12, 2.49, and 5.86, respectively. Although those indicated slight variations could be presented, the resultant effect could be accepted as insignificant. Under all of the irradiation periods SUVA₂₅₄ was found to be > 4 for raw humic acid samples in the absence of both TiO₂ and clay minerals.

In a similar manner, no general trend could be observed for SFI_{emis,455}, SFI_{emis,460} and SFI_{syn,475} parameters for raw humic acid samples under irradiation in the absence of both TiO₂ and clay with minerals respect to the irradiation time. The reason could be attributed to the variations attained for both FI and DOC removals. Although, lower SFI_{syn,475} were calculated for the irradiation period of 20 min with respect to the specific FI parameters, significantly higher SFI_{emis,455}, SFI_{emis,460} values were attained for this irradiation period. The highest SFI_{syn,475} value was obtained for irradiation period of 60 minutes for raw humic acid samples under irradiation in the absence of TiO₂ and clay minerals. As explained above all of these variations could be accepted as within experimental error rather than photolytic interactions.

Although slightly alterations were attained for humic acid by photolysis, no significant removal could be deduced either by UV-vis parameters or by fluorescence spectroscopic parameters. Since less than 7% DOC removal was recorded following $t_{irr}= 60$ min, the resultant photocatalytic effect could be regarded as insignificant.

Table 4.5. Specified and specific UV-vis and fluorescence parameters of humic acid during preliminary experiments performed under irradiation and in the absence of TiO_2 .

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm^{-1} DOC, mg L^{-1}					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 474 nm
HA,r	0.239	0.465	1.038	1.199	17.00	143.080	124.917	82.196
HA,rf	0.200	0.411	0.947	1.098	16.48	155.556	135.291	76.819
Irradiation time, min								
20	0.200	0.407	0.940	1.112	15.54	177.877	149.435	71.698
40	0.201	0.417	0.975	1.141	16.11	152.381	126.586	75.486
60	0.193	0.395	0.930	1.084	15.85	162.789	137.490	78.884
Specific UV-vis and fluorescence parameters, $\text{m}^{-1}\text{mg}^{-1}\text{L}$								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	841.65	734.80	483.51	
HA,rf	1.21	2.49	5.74	6.66	943.91	820.94	466.14	
Irradiation time, min								
20	1.29	2.62	6.05	7.15	1144.64	961.61	461.38	
40	1.25	2.59	6.05	7.08	945.88	785.76	468.57	
60	1.21	2.49	5.86	6.84	1027.06	867.44	497.69	

Preliminary experiments performed under irradiation in the presence of humic acid and montmorillonite and in the absence of TiO_2 . Preliminary experiments were carried out using humic acid and Mt under irradiation in the absence of TiO_2 . UV-vis absorbance spectra were recorded with respect to irradiation time in the 200-600 nm wavelength region (Figure 4.16).

In comparison to the UV-vis spectra recorded for humic acid under irradiation in the absence of both TiO_2 and clay minerals no significant change was observed with respect to

irradiation time for the system composed of humic acid with Mt in the absence of TiO_2 (Figure 4.14 and 4.16). UV-vis absorbance profiles of humic acid recorded under all irradiation periods displayed an overlapping trend more significantly in the vis region ($\lambda < 400$ nm). However, slightly variations in absorbance values could be visualized in the UV wavelength region of $200 < \lambda < 400$ nm. The attained UV-vis spectral features indicates the possible use of the specified UV-vis parameters.

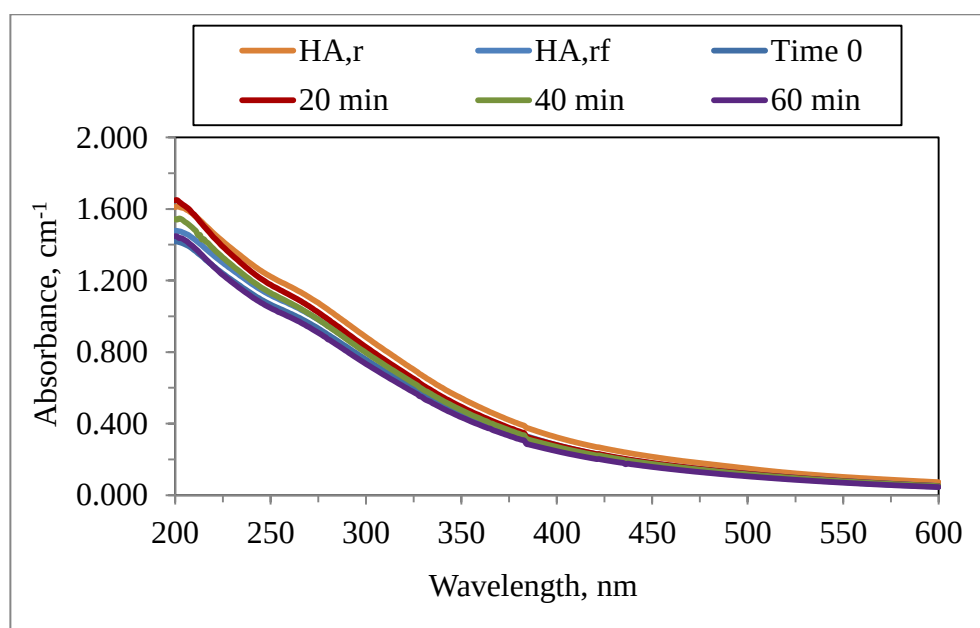


Figure 4.16. UV-vis spectra of humic acid recorded for the preliminary experiments performed under irradiation in the presence of montmorillonite and in the absence of TiO_2 .

The emission scan (A) and synchronous scan (B) fluorescence spectra recorded for the preliminary experiments of humic acid in the presence of Mt and in the absence of TiO_2 under irradiation were shown in Figure 4.17 A-B. Minor diversity was attained for FI trend during 60 minutes of time period exhibiting almost the same fluorescence intensity values with overlapping trend under all irradiation time periods (Figure 4.17 A). The synchronous scan fluorescence spectra for humic acid in the presence of Mt and in the absence of TiO_2 under irradiation displayed a sharp peak around emission wavelength of $\lambda_{\text{emis}} = 475$ nm (Figure 4.17 B). Upon irradiation of humic acid and Mt in the absence of TiO_2 , minor decreases were observed for synchronous scan fluorescence intensity for longer emission $\lambda_{\text{emis}} > 390$ nm wavelength range.

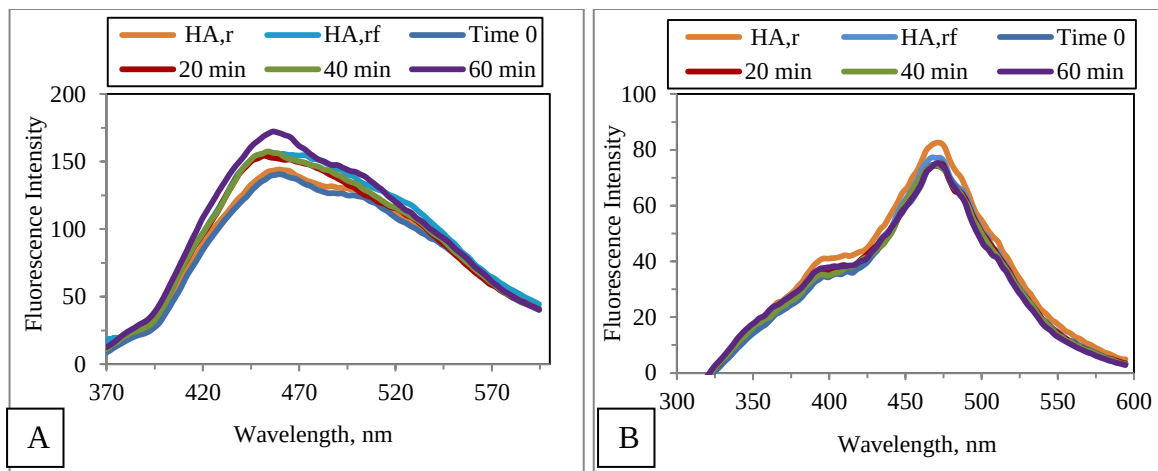


Figure 4.17. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under irradiation in the presence of montmorillonite and in the absence of TiO_2 .

Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of Mt and in the absence of TiO_2 under irradiation were given in Table 4.6. Under irradiation in the presence of Mt and in the absence of TiO_2 humic acid presented in an initial removal of 15%, 9.5%, 5% and 4% for Color_{436} , UV_{365} , UV_{280} and UV_{254} respectively. Further insignificant removals i.e. $< 5\%$ could also be expressed by the specified UV-vis parameters. The resulting depletion effect of irradiation on the DOC content of humic acid in the presence of Mt was found to be as 5% at the initial stage followed by a slight decrease as 7% in 60 minutes of irradiation time.

As indicated in Table 4.6 no general trend was observed for SUVA_{254} parameter of humic acid in the presence of Mt and in the absence of TiO_2 under irradiation for all time periods. While, lower SUVA_{254} was attained for irradiation period of 40 minutes, highest SUVA_{254} was obtained for 20 minutes of irradiation time. Similar to the SUVA_{254} values, lowest SCoA_{436} , SUVA_{365} , and SUVA_{280} values were attained for irradiation period of $t_{\text{irr}} = 20$ min as 1.25, 2.58, 6.07, respectively. The role of montmorillonite on the photolytic attraction of humic acid should be regarded as insignificant. Under all of the irradiation time periods SUVA_{254} were found to be > 4 for humic acid in the presence of Mt and in

the absence of TiO_2 expressing the insignificant effect of irradiation on the aromaticity of humic acids

Table 4.6. Specified and specific UV-vis and fluorescence parameters of humic acid during preliminary experiments performed under irradiation in the presence of montmorillonite and in the absence of TiO_2 .

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm^{-1} DOC, mg L^{-1}					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 474 nm
HA,r	0.239	0.465	1.038	1.199	17.00	143.080	124.917	82.196
HA,rf	0.200	0.411	0.947	1.098	16.48	155.556	135.291	76.819
Irradiation time, min								
20	0.191	0.395	0.894	1.008	15.55	153.123	128.750	74.835
40	0.173	0.372	0.871	1.024	16.12	157.218	128.346	73.389
60	0.200	0.410	0.947	1.098	15.84	171.485	141.012	74.260
Specific UV-vis and fluorescence parameters, $\text{m}^{-1}\text{mg}^{-1}\text{L}$								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	841.65	734.80	483.51	
HA,rf	1.21	2.49	5.74	6.66	943.91	820.94	466.14	
Irradiation time, min								
20	1.25	2.58	6.07	7.13	984.72	827.97	481.26	
40	1.07	2.31	5.40	6.35	975.30	796.19	455.26	
60	1.26	2.59	5.98	6.93	1082.61	890.23	468.81	

Likewise to the SCoA₄₃₆, SUVA₃₆₅, SUVA₂₈₀ and SUVA₂₅₄ parameters, no general mode could be attained for specific fluorescence parameters i.e. SFI_{emis,455}, SFI_{emis,460} and SFI_{syn,475} parameters for humic acid in the presence of montmorillonite and in the absence of TiO_2 with respect to the irradiation time periods. While lower SFI_{syn,475} were calculated

for the initial stage, significantly higher $SFI_{syn,475}$ values were attained for reaction period of 20 minutes. The highest $SFI_{emis,455}$ value as obtained for reaction period of $t_{irr}=60$ min for humic acid in the presence of Mt and in the absence of TiO_2 under irradiation. As previously stated the indicated changes should be regarded as insignificant with respect to the applied photolytic conditions.

Preliminary experiments performed under irradiation in the presence of humic acid and kaolinite and in the absence of TiO_2 . Preliminary experiments were carried out using humic acid in the presence of Kt and in the absence of TiO_2 under irradiation. UV-vis absorbance spectra were recorded in the 200-600 nm wavelength regions under all irradiation periods and presented in a comparative manner in Figure 4.18.

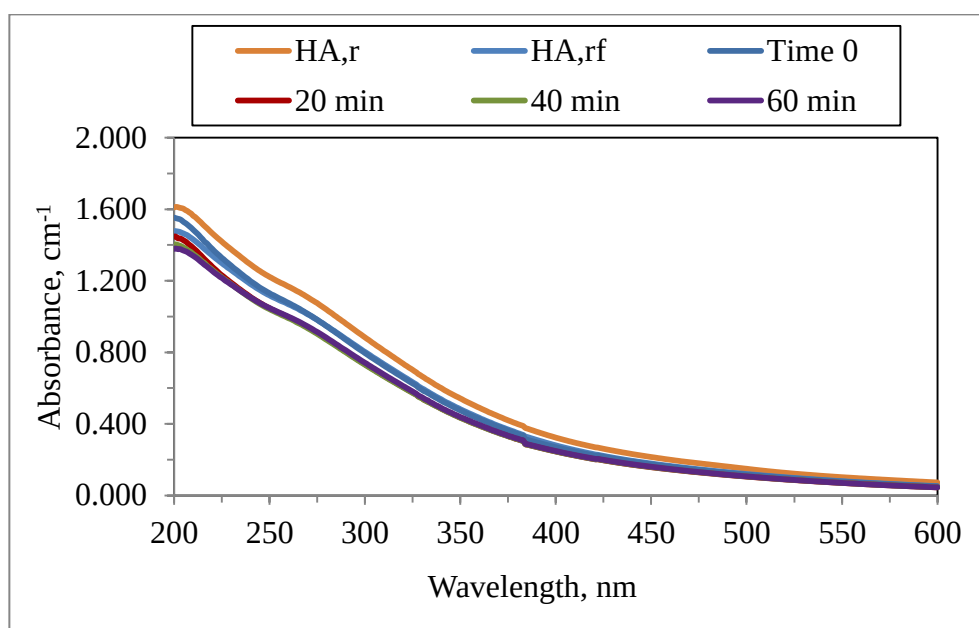


Figure 4.18. UV-vis spectra of humic acid recorded for the preliminary experiments performed under irradiation in the presence of kaolinite and in the absence of TiO_2 .

As expected, UV-vis spectra recorded for humic acid in the presence of Kt and in the absence of TiO_2 under irradiation displayed similar decreasing profile with sole humic acid in the absence of TiO_2 and humic acid in the presence of Mt and absence of TiO_2 under irradiation (Figure 4.14, 4.16, 4.18). UV-vis absorbance profiles of humic acid in the presence of Kt and in the absence of TiO_2 under irradiation for all irradiation periods were

nearly overlapping in the visible region ($\lambda > 400$ nm) whereas slight variations in absorbance values were detectable in the UV region ($\lambda < 400$ nm).

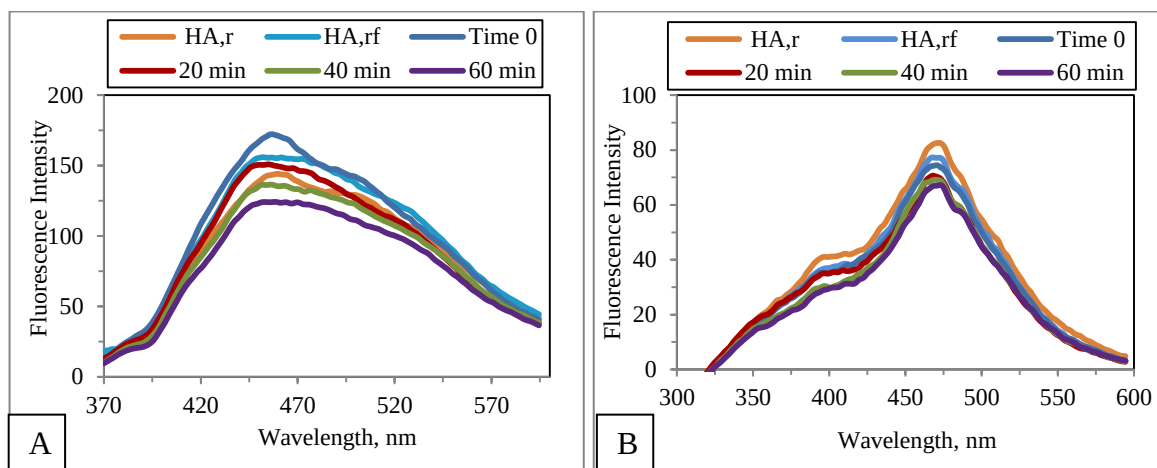


Figure 4.19. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the preliminary experiments performed under irradiation in the presence of kaolinite and in the absence of TiO_2 .

The emission scan (A) and synchronous scan (B) fluorescence spectra recorded for the preliminary experiments of humic acid in the presence of Kt and in the absence of TiO_2 under irradiation were shown in Figure 4.19. The differences attained for the FI trend during the irradiation periods could be considered as insignificant with respect to the effects observed due to the initial adsorptive interactions (Figure 4.19 A). The synchronous scan fluorescence spectra recorded for humic acid in the presence of Kt and in the absence of TiO_2 under irradiation exhibited a sharp peak around emission wavelength of $\lambda_{\text{emis}} = 475$ nm as recorded for sole humic acid (Figure 4.19 B). By irradiation of humic acid with Kt in the absence of TiO_2 , minor decreases were observed for FI of synchronous scan fluorescence for longer emission wavelength region of $\lambda_{\text{emis}} > 370$ nm.

Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of Kt and in the absence of TiO_2 under irradiation were displayed in Table 4.7. Under irradiation in the presence of Kt and in the absence of TiO_2 humic acid presented in an initial removal of 18%, 13%, 9% and 8% for Color_{436} , UV_{365} , UV_{280} and UV_{254} respectively. Further removals i.e. $\leq 8\%$ could also be expressed by the specified UV-vis

parameters. The resulting depletion effect of irradiation on the DOC content of humic acid in the presence of Kt was found to be as 6% at the initial stage followed by a slight decrease as 8.5% in 60 minutes of irradiation time.

Table 4.7. Specified and specific UV-vis and fluorescence parameters of humic acid during preliminary experiments performed under irradiation in the presence of kaolinite and in the absence of TiO_2 .

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm^{-1} DOC, mg L^{-1}					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 474 nm
HA,r	0.239	0.465	1.038	1.199	17.00	143.080	124.917	82.196
HA,rf	0.200	0.411	0.947	1.098	16.48	155.556	135.291	76.819
Irradiation time, min								
20	0.178	0.370	0.873	1.026	15.85	150.892	123.887	68.997
40	0.178	0.369	0.869	1.021	16.15	136.380	114.210	68.457
60	0.181	0.373	0.881	1.028	15.56	124.039	106.224	67.042
Specific UV-vis and fluorescence parameters, $\text{m}^{-1}\text{mg}^{-1}\text{L}$								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	841.65	734.80	483.51	
HA,rf	1.21	2.49	5.74	6.66	943.91	820.94	466.14	
Irradiation time, min								
20	1.12	2.33	5.51	6.47	952.00	781.62	435.31	
40	1.10	2.28	5.38	6.32	844.46	707.18	423.88	
60	1.16	2.40	5.66	6.61	797.17	682.67	430.86	

Similar to the SUVA₂₅₄, SUVA₂₈₀, SUVA₃₆₅ and SCoA₄₃₆ parameters of sole humic acid attained in the absence of TiO_2 under irradiation, no general trend was observed for

these parameters of humic acid in the presence of Kt and in the absence of TiO_2 under irradiation. Slightly lower SUVA_{254} (6.32) was attained for irradiation time period of $t_{\text{irr}} = 40$ minutes with respect to the initial SUVA_{254} of humic acid as expected. Moreover, under all of the irradiation time periods, SUVA_{254} was found to be > 4 for humic acid in the presence of Kt and in the absence of TiO_2 .

Upon irradiation, although $\text{SFI}_{\text{emis},455}$ and $\text{SFI}_{\text{emis},460}$ parameters of humic acid in the presence of Kt and in the absence of TiO_2 were decreasing with increasing irradiation time periods, no general trend was attained for $\text{SFI}_{\text{syn},475}$ parameters for this system with respect to the irradiation time. Considerably lower $\text{SFI}_{\text{syn},475}$ was calculated for $t_{\text{irr}} = 40$ min of irradiation time with respect to the other specific FI parameters. The highest $\text{SFI}_{\text{emis},455}$ was obtained for humic acid in the presence of Kt in the absence of TiO_2 under irradiation.

4.1.3. Comparative evaluation of the baseline experiments and preliminary experiments

Clay minerals constitute the main component of the suspended solid material in natural waters, which are also responsible for the transport of inorganic and organic contaminants (Lagaly, 2006). The understanding of interactions between humic substances and charged solid surfaces i.e. clays is an important task for the achievement of an effective treatment performance. Humic acid molecules adsorbed onto the surface of clay minerals could increase the adsorption capacity of metallic cations since humic substances contain strong complexing sites. Moreover, the complexation capacities of humic acids (in terms of mol g^{-1}) are significantly higher than usually reported for the adsorption capacities of clay minerals. Within the experimental scope of this study, the prevailing interactive systems could be expressed by binary systems i.e. “HA and Mt”; “HA and Kt” and “HA and TiO_2 ” and ternary systems i.e. “HA, Mt and TiO_2 ” and “HA, Kt and TiO_2 ”. Baseline interactions representing the instantaneous interaction of the components of the binary and ternary systems have been evaluated primarily with reference to the UV-vis spectral shape of HA. The presence of either Mt (0.10 mg mL^{-1}) and/or TiO_2 did not alter the basic logarithmic declining features of UV-vis spectra of HA. Therefore, the effective removal of UV-vis parameters due to dark baseline interactions could be displayed through the evaluation of the UV-vis spectra as well as by DOC and derived specific UV-vis

parameters. Upon introduction of sole Mt to the HA solution, Color₄₃₆, UV₃₆₅, and UV₂₅₄ parameters decreased by 22%, 17%, and 13% respectively. Upon introduction of sole Kt to the HA solution, Color₄₃₆, UV₃₆₅, and UV₂₅₄ parameters decreased by 21%, 18%, and 16% respectively. In the presence of sole TiO₂, 43.5% Color₄₃₆, 40% UV₃₆₅, and 36% UV₂₅₄ removals were attained for HA representing the predominant role of the oxide surface. The adsorption of HA onto oxide surfaces could proceed through specific as well as electrostatic attractions (Vermeer et al., 1998; Bekbolet et al., 2002). The removal efficiencies of HA parameters in the ternary system composed of “HA, Mt and TiO₂” were 45%, 40% , and 37% for Color₄₃₆, UV₃₆₅, and UV₂₅₄ respectively. The removal efficiencies of HA parameters in the ternary system composed of “HA, Kt and TiO₂” were 46%, 41%, and 39% for Color₄₃₆, UV₃₆₅, and UV₂₅₄ respectively. Moreover, only 5% in the presence of sole Mt, 31% upon introduction of sole TiO₂ and in the case of the “HA, Mt and TiO₂” ternary system 29% DOC removals were achieved. DOC removals were calculated as 6% in the presence of sole Kt, 31% upon introduction of sole TiO₂ and 34% in the presence of “HA, Kt and TiO₂” ternary system. Dominating over the role of either Mt or Kt surface interactions, the presence of TiO₂ significantly affected the dark adsorptive baseline interactions leading to a significant degree of oxide surface coverage by humic sub-fractions.

Furthermore, specific UV-vis parameters displayed considerably slight variations expressing persistence of the aromatic character. These interactions were further assessed by time dependent preliminary experiments *i.* in the presence of photocatalyst and absence of irradiation and *ii.* in the presence of irradiation and absence of photocatalyst,. In accordance with the previous findings, UV-vis spectral features of HA retained the expected decreasing profiles under all of the reaction conditions (Uyguner and Bekbolet, 2005a and 2005b). Preliminary experiments were also carried out in the presence of either Mt or Kt under the specified experimental conditions. For HA and Mt binary system, the effect of the TiO₂ surface adsorptive interactions achieved under dark conditions for a reaction period of 60 min (36.5-48%) were more pronounced than the effect observed for photolytic interactions (8.5-16%) in the absence of TiO₂ as expressed by the specified UV-vis parameters (Table 4.8). The adsorptive removal of Color₄₃₆ was found to be higher than that of UV₃₆₅ and UV₂₅₄ both in the presence and absence of Mt representing the main role of color forming moieties of HA in adsorptive interactions onto TiO₂. The presence of Kt

also displayed a similar trend. Comparatively lower DOC removals were attained by adsorption of sole HA onto TiO_2 as 29.5% , by “HA and Mt” binary system onto TiO_2 as 28% and by “HA and Kt” binary system onto TiO_2 as 39% with reference to the removals of the UV-vis parameters. As already stated, a slight enhancement could be observed in the DOC removals due to the presence of Kt by adsorption.

Table 4.8. Removal of humic acid by baseline and preliminary interactions in the presence and in the absence of montmorillonite and kaolinite.

	UV-vis parameters, m ⁻¹			DOC, mg L ⁻¹	Specific parameters, m ⁻¹ mg ⁻¹ L		
	Color ₄₃₆	UV ₃₆₅	UV ₂₅₄		SCoA	SUVA ₃₆₅	SUVA ₂₅₄
HA, initial	23.9	46.5	119.9	17.00	1.41	2.73	7.05
Baseline interactions, Removal%							
HA and Mt	22	17	13	5	1.15	2.39	6.49
HA and Kt	21	18	16	6	1.18	2.39	6.28
HA and TiO ₂	43.5	40	36	31	1.15	2.37	6.49
HA, Mt and TiO ₂	45	40	37	29	1.08	2.28	6.20
HA, Kt and TiO ₂	46	41	39	34	1.32	2.57	6.46
Removal,%*							
Adsorptive interactions in the presence of TiO ₂ and absence of irradiation							
HA	49	44.5	39	29.5	1.01	2.16	6.12
HA and Mt	48	43.5	36.5	28	1.01	2.15	6.24
HA and Kt	56	51	33	39	1.01	2.22	6.60
Photolytic interactions in the presence of irradiation and absence of TiO ₂							
HA	17.5	14	9.5	7	1.21	2.49	6.84
HA and Mt	16	12	8.5	7	1.26	2.59	6.93
HA and Kt	25	20	14	8	1.16	2.40	6.61

*Removal efficiency expressed for 60 min of reaction period, HA: 50 mg L^{-1} , TiO_2 loading: 0.50 mg mL^{-1} , montmorillonite or kaolinite dose: 0.10 mg mL^{-1}

Photolytic removal of HA revealed higher efficiency for Color_{436} than UV_{365} and UV_{254} . The presence of Mt slightly altered the photolytic reactivity of HA predominantly the color forming moieties (Color_{436}) possibly due to the increased turbidity of the colloidal medium. UV-vis specified parameters displayed minor variations ($\leq 15\%$) due to the presence of Mt that the attained comparatively lower removal efficiency could be accepted as insignificant. The presence of Mt did not change the removal efficiency of DOC under irradiation revealing a non-specific role of light interaction of “HA and Mt” binary system. Moreover, photolytic removal of DOC attained in 60 minutes of irradiation period (7%) could be considered as comparably insignificant with respect to the removal efficiency attained by adsorption onto TiO_2 under dark conditions ($\sim 30\%$). Comparatively similar results were also obtained in the presence of Kt. Moreover, the presence of clay minerals did not significantly alter the removal of the specified UV-vis parameters through photolytic interactions. The pre-adsorption condition of HA onto TiO_2 surface both in the presence and absence of either Mt or Kt constituted the major step due to the oxide surface oriented nature of photocatalysis. No discrimination could be deduced between the effective oxide surfaces, particle-particle interactions and surface-particle interactions. Specific UV-vis parameters displayed an almost consistent trend under all of the specified experiments expressing both baseline and preliminary conditions. More specifically, $\text{SUVA}_{254} > 4$ representing that the aromatic character of humic acid was not altered during adsorptive interactions as well as under photolytic conditions.

4.1.4. Photocatalytic degradation of sole humic acid

Photocatalytic degradation of sole humic acid was investigated to present a basis for the degradation studies performed in the presence of either Mt or Kt.

4.1.4.1. UV-vis spectroscopic evaluation of raw humic acid during photocatalytic degradation. The UV-vis spectrum of humic acid (HA_r) showed a gradually declining trend with respect to the increasing wavelength in the 200-600 nm region as seen in Figure 4.20. Due to the nature of the reaction conditions that the photocatalyst should be removed following the selected reaction period, filtration through 0.45 μm membrane filter constitutes the crucial step in the assessment of the remaining humic concentration. Although the effect of the filtration was discussed previously in the baseline interactions

Section 4.1.1, presentation of the UV-vis and fluorescence spectra of the HAr,f sample would also bring a clear picture of the assessment of the spectral changes obtained under irradiation conditions. On the other hand, upon introduction of the TiO_2 to the humic acid solution, an instantaneous adsorptive interaction would take place that could be visualized by UV-vis spectra recorded for $t = 0$ condition. Although a significant removal trend could be deduced from the UV-vis spectra recorded at $t = 0$ condition, the humic moieties could undergo oxidative degradation through a subsequent adsorption-desorption phase revealing the significance of the filtration step. Therefore, removal of humic acid by an instantaneous attraction to the oxide surface should be regarded as a fulfillment of the pre-adsorption prerequisite of photocatalysis prior to the initiation of the light exposure.

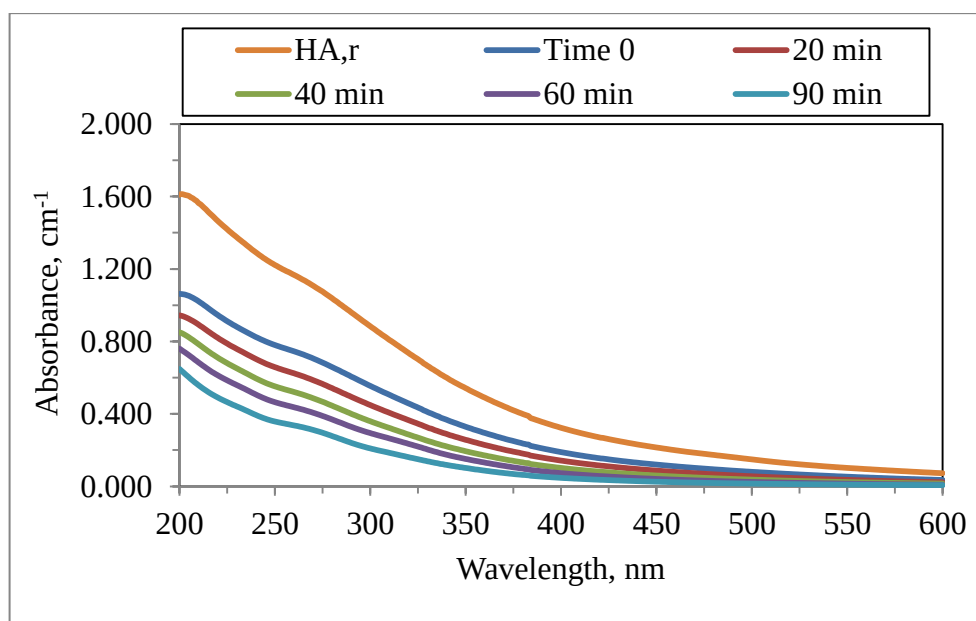


Figure 4.20. UV-vis spectra of humic acid recorded for the photocatalytic degradation.

Initial adsorptive removal of raw humic acid could also be visualized by examining the recorded UV-vis spectra of raw humic acid under dark conditions as presented previously in Figure 4.20. Uyguner and Bekbolet reported (2005) that the UV-vis spectra of humic acids are broad, featureless and monotonously decrease with increasing wavelength during the course of photocatalytic degradation (Uyguner and Bekbolet, 2005a). Irradiation time dependent changes were also followed by spectroscopic properties during humic acid photocatalytic treatment starting with $t = 0$ min which was the initial titanium dioxide introduction to humic acid solution prior to irradiation. Moreover, for

irradiation periods of $t_{irr} = 20$ min to $t_{irr} = 40$ min, the UV-vis spectra followed the same trend with lower absorbance values than $t = 0$ min expressing the oxidative removal of humic acid followed by adsorption. After irradiation time of $t_{irr} = 40$ min, the degradation of humic acid displayed a significant decrease in the UV-vis absorbances specifically in the visible region $\lambda > 400$ nm retaining the basic trend of exponential decay.

4.1.4.2. Fluorescence spectroscopic evaluation of raw humic acid during photocatalytic degradation. The emission scan (A) and synchronous scan (B) fluorescence spectra recorded for the photocatalytically treated humic acid samples in comparison to HA_r were displayed in Figure 4.21. The fluorescence spectra of the samples were recorded by excitation at $\lambda_{exc} = 350$ nm causing a major peak at the emission wavelength of $\lambda_{emis} = 455$ nm (Figure 4.21 A). Although an irradiation time dependent general increasing trend in fluorescence intensity could be visualized, the maximum fluorescence intensity was observed for $t_{irr} = 60$ minutes of irradiation time with reference to the raw humic acid revealing the possibility of formation of the new fluorophores upon irradiation of the humic moieties undergoing oxidative treatment.

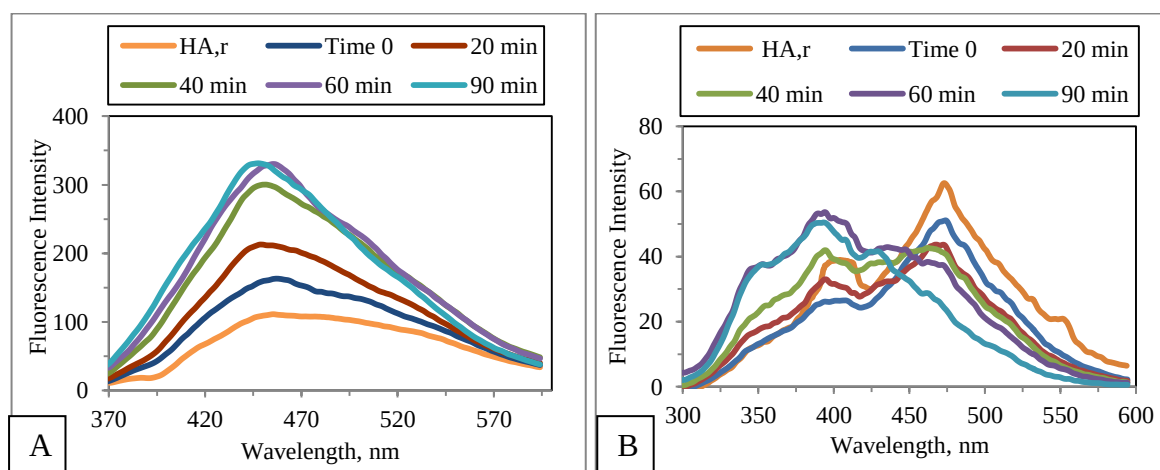


Figure 4.21. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid recorded for the photocatalytic degradation.

The synchronous scan fluorescence spectra for raw humic acid displayed a sharp peak around emission wavelength of $\lambda_{emis} = 470$ nm (Figure 4.21 B). A moderate peak around $\lambda_{emis} = 390$ nm emission wavelengths with a comparatively lower intensity could

also be noticed. The synchronous scan fluorescence spectra of the treated humic acid samples showed a generally decreasing intensity profiles with increasing photocatalytic irradiation time (Uyguner and Bekbolet, 2005a). Uyguner and Bekbolet (2005a) also reported that raw humic acid had a sharp peak around $\lambda_{\text{emis}} = 475$ nm and a moderate peak around $\lambda_{\text{emis}} = 400$ nm. Peuravuori and co-workers (2002) ascribed the peak around $\lambda_{\text{emis}} = 460$ nm wavelength to polycyclic aromatic moieties consisting of several fused benzene rings. The synchronous scan fluorescence spectra of the humic acid photodegradation led to a gradual decrease of FI in the region of $\lambda_{\text{emis}} = 470$ -600 nm emission wavelengths. It could be expressed by the degradation of the high molecular weight components of humic acids and formation of lower molecular size fractions of humic acid (Uyguner and Bekbolet, 2005a). After long irradiation periods, the characteristic sharp peak of raw humic acid at $\lambda_{\text{emis}} = 470$ nm emission wavelength completely disappeared. On the other hand, emergence of new peak at $\lambda_{\text{emis}} = 385$ nm emission wavelength was also noticed. After $t_{\text{irr}} = 60$ min irradiation time, the intensity of the observed peak at $\lambda_{\text{emis}} = 385$ nm sharply increased with reference to the shorter irradiation time periods as well as for raw and filtered humic acid (Figure 4.21 B). The spectral differences observed between the emission scan and synchronous scan fluorescence spectra could be attributed to the low resolution features of emission mode displaying an overlapping intensity profile.

Specified and specific UV-vis and fluorescence parameters and DOC contents of raw humic acid during photocatalytic degradation were given in Table 4.9. Photocatalytic degradation of humic acid was evaluated in terms of the changes observed for UV-vis parameters as expressed by Color_{436} , UV_{365} , UV_{280} and UV_{254} . In addition, Initial adsorptive removal of humic acid ($t = 0$) could also be assessed by the specified UV-vis parameters. The removal efficiencies expressing the TiO_2 surface adsorption attained at $t = 0$ condition were 43%, 40%, 37%, 36% and 31% for Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC respectively. While 59% of Color_{436} was removed in 20 minutes of irradiation, 80% removal was achieved after 60 minutes. In long irradiation periods such as 90 minutes, Color_{436} was detected as 0.030 cm^{-1} for humic acid that could be considered as an overall removal of the color forming moieties. For UV_{254} parameter, 46% removal was observed in 20 minutes of irradiation time. Similar to Color_{436} , UV_{254} was removed from the suspension in significant amounts as 62% and 71% after 60 and 90 minutes irradiation time periods, respectively.

Table 4.9. Specific and specified UV-vis and fluorescence parameters of humic acid recorded during photocatalytic degradation.

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm ⁻¹ DOC, mg L ⁻¹					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 475 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.18	96.93	62.35
HA,rf	0.200	0.411	0.947	1.098	16.48	121.80	106.51	56.486
Irradiation Time, min								
Time 0	0.135	0.280	0.658	0.766	11.80	162.42	132.38	51.12
20	0.099	0.216	0.542	0.644	10.45	211.56	156.86	43.20
40	0.069	0.160	0.446	0.539	10.34	297.98	216.23	40.76
60	0.048	0.122	0.369	0.453	9.182	330.30	238.18	36.68
90	0.030	0.080	0.278	0.349	7.583	323.38	233.68	23.80
Specific UV-vis and fluorescence parameters, m ⁻¹ mg ⁻¹ L								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
Irradiation Time, min								
Time 0	1.15	2.37	5.58	6.49	1376.43	1121.88	433.25	
20	0.95	2.07	5.19	6.16	2024.49	1501.05	413.37	
40	0.67	1.55	4.31	5.22	2881.78	2091.17	394.15	
60	0.52	1.33	4.02	4.93	3597.99	2594.52	399.51	
90	0.40	1.06	3.66	4.60	4266.18	3082.79	313.92	

Moreover, almost 74% and 64% degradation efficiencies were achieved in 60 minutes for UV₃₆₅ and UV₂₈₀, respectively. Upon prolonged irradiation periods (i.e. t_{irr} = 90

min), the removal percentages reached to 82% and 73% for UV₃₆₅ and UV₂₈₀, respectively. The removal efficiencies followed a basic decreasing trend of Color₄₃₆ > UV₃₆₅ > UV₂₈₀ > UV₂₅₄ irrespective of the irradiation time expressing that the color forming moieties were more susceptible to photocatalytic oxidation with respect to UV absorbing centers. DOC data presented a removal tendency displaying an overall decrease of approximately 9.5 mg L⁻¹ in dissolved organic carbon content at the end of 90 min reaction period. An initial adsorptive removal of 31% was followed by an incremental enhancement to 39% in $t_{irr} = 20$ minutes and reached to an almost stationary phase prevailing up to 40 min of irradiation time. Upon further irradiation periods, DOC removal expressed a rather slow removal regime reaching to 55% removal in $t_{irr} = 90$ minutes. Considering that SUVA parameter had been successfully used for the elucidation of the UV-vis parameters in accordance with the DOC removal, the respective specific parameters were also tabulated in Table 4.9. Filtration step did not significantly change SUVA₂₅₄ as was also observed in a similar degree of TiO₂ adsorptive effect (Tables 4.9). However, SUVA₂₅₄ gradually decreased to 4.60 during photocatalytic oxidation. Upon irradiation period of 90 min, following 71% removal of UV₂₅₄ and 55% removal of DOC, the remaining humic moieties still displayed a predominantly aromatic character since SUVA₂₅₄ > 4 represented the presence of aromatic moieties in humic structure (Edzwald et al., 1985). A similar trend was also attained for decolorization as expressed by SCoA₄₃₆ followed by the specific UV parameters as SUVA₃₆₅, and SUVA₂₈₀. However, no significant trend could be assessed by the specific SFI_{emis,455} and SFI_{emis,460} fluorescence parameters due to the inconsistency recorded for the fluorescence behavior of the humic moieties during photocatalytic oxidation. Likewise to the specific UV parameters, SFI_{syn,475} fluorescence parameter also decreased with increasing irradiation time.

4.1.5. Photocatalytic degradation of humic acid in the presence of montmorillonite

For the assessment of the photocatalytic degradation of humic acid in the presence of montmorillonite, TiO₂ photocatalyst loading was kept constant as 0.50 mg mL⁻¹ and Mt concentrations were chosen as 0.05 mg mL⁻¹, 0.10 mg mL⁻¹ and 0.20 mg mL⁻¹.

4.1.5.1. UV-vis spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.05 mg mL⁻¹ montmorillonite. Photocatalytically treated UV-vis spectra of humic acid in the presence 0.05 mg mL⁻¹ Mt showed a gradually declining trend with

respect to increasing wavelength in the 200-600 nm region similar to the humic acid degradation trend attained in the absence of Mt (Figure 4.8). Irradiation time dependent changes were also followed by spectroscopic properties during humic acid photocatalytic degradation starting with $t = 0$ min which was the initial titanium dioxide introduction to the humic acid and Mt binary system solution prior to irradiation. Initial adsorptive removal of humic acids could also be visualized by examining the UV-vis spectra with respect to the UV-vis spectra recorded humic acids under dark conditions (Figure 4.10). The adsorption capacity of humic acid in the presence of Mt increased as was also verified by the experiments performed under dark conditions. The photocatalytic degradation of humic acid displayed an enhancement in the presence of Mt under all irradiation time periods.

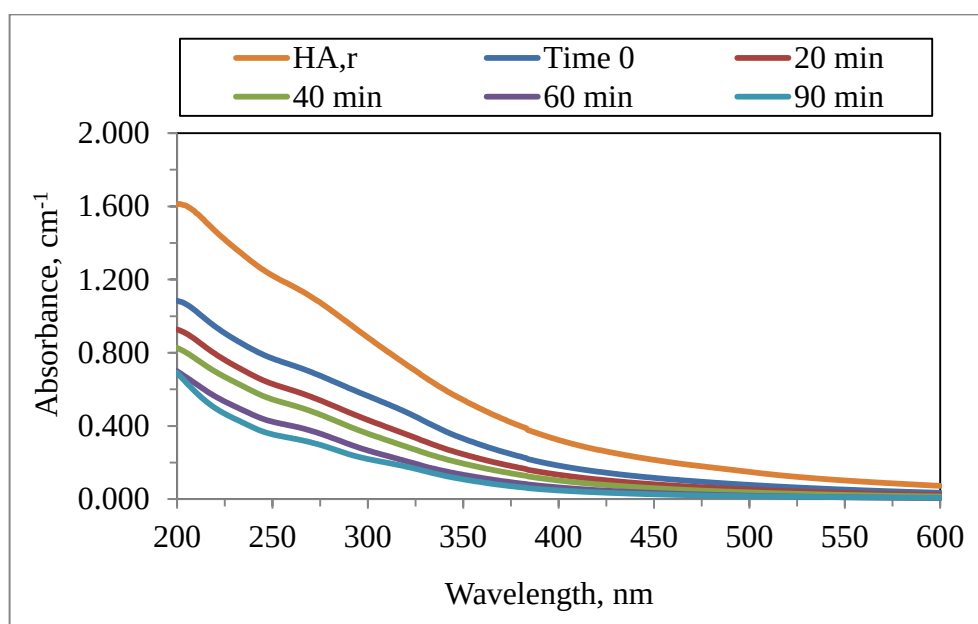


Figure 4.22. UV-vis spectra of humic acid recorded for the photocatalytic degradation in the presence of 0.05 mg mL^{-1} montmorillonite.

Similar results were also found with pillared clays specifically for montmorillonite displaying increased adsorption capacities leading to surface concentration of the substrates in very dilute solutions due to the mesoporous structures of TiO_2 (Ooka et al., 2003, Ooka et al., 2004). Additionally, the interlayer surface of pillared clays was generally hydrophobic which was an advantage in adsorbing and enriching diluted

hydrophobic organic compounds in water. Furthermore, TiO₂ pillared clays also showed photocatalytic activity owing to nano-sized TiO₂ pillars. Consequently, this would be one of the suitable materials exhibiting limited adsorptive capacity for photocatalysis in water. This case could be regarded as contrary to the use of humic acid as the substrate since humic acids express extensive surface coverage onto TiO₂. Moreover, initial adsorption of humic acids onto Mt could not be verified by the UV-vis/Fluorescence and DOC determinations displaying a removal tendency of 22%, 17%, 14% and 13% for Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄ respectively. No significant removal of DOC could be observed due to surface interaction of humic acid and Mt binary system upon introduction of TiO₂. Furthermore, photocatalytic degradation of humic acid in the presence of Mt was also evaluated in terms of DOC and UV-vis parameters as expressed by Color₄₃₆, UV₃₆₅, UV₂₈₀, and UV₂₅₄ parameters. Specified UV-vis and fluorescence parameters of humic acid in the presence of Mt during photocatalytic degradation were presented in Table 4.10.

4.1.5.2. Fluorescence spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.05 mg mL⁻¹ montmorillonite. Emission scan fluorescence spectra of photocatalytically treated humic acid in the presence of 0.05 mg mL⁻¹ Mt were displayed in Figure 4.23 A. In accordance with the conditions set forward for raw humic acid, the fluorescence spectra of the samples were also recorded by excitation at $\lambda_{\text{exc}} = 350$ nm which resulted in a major peak at emission wavelength of $\lambda_{\text{emis}} = 455$ nm (Figure 4.23 A).

The general increasing trend recorded in emission scan fluorescence intensity could be visualized with respect to the irradiation time periods and the maximum fluorescence intensity could be detected significantly for 90 minutes of irradiation time with reference to the raw humic acid. In relation to the fluorescence emission scan spectra recorded for humic acid, no distinct comparative evaluation could be deduced for the assessment of the effect of the Mt in binary system (Figures 4.6 A). However, the role of initial adsorptive interaction could still be visualized by the fluorescence emission scan spectra recorded for $t = 0$ condition for HA and Mt binary system.

Synchronous scan fluorescence spectra recorded for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL⁻¹ Mt were shown in Figure 4.23 B.

Synchronous scan fluorescence spectra for raw humic acid in the presence of 0.05 mg mL^{-1} Mt displayed a major sharp peak around emission wavelength of $\lambda_{\text{emis}} = 470 \text{ nm}$ and a moderate peak at $\lambda_{\text{emis}} = 390 \text{ nm}$ emission wavelength with a comparatively lower intensity. Under prolonged irradiation conditions (i.e. 90 min), the fluorescence intensity maxima recorded at $\lambda_{\text{emis}} = 470 \text{ nm}$ was completely removed and new fluorescence intensity maximum at $\lambda_{\text{emis}} = 350$ and $\lambda_{\text{emis}} = 375 \text{ nm}$ emission wavelengths were found to be evident with detectable intensity values. The shift of fluorescence maxima to lower wavelengths could be explained by the formation of new fluorophores during photocatalysis (Uyguner and Bekbolet, 2005a). Moreover, the observed wavelength shift was also found to be present in humic fluorescence spectra recorded in the absence of Mt. Therefore, the reason could only be attributed to the oxidative changes in humic structure rather than Mt and humic interactions prevailing during photocatalysis.

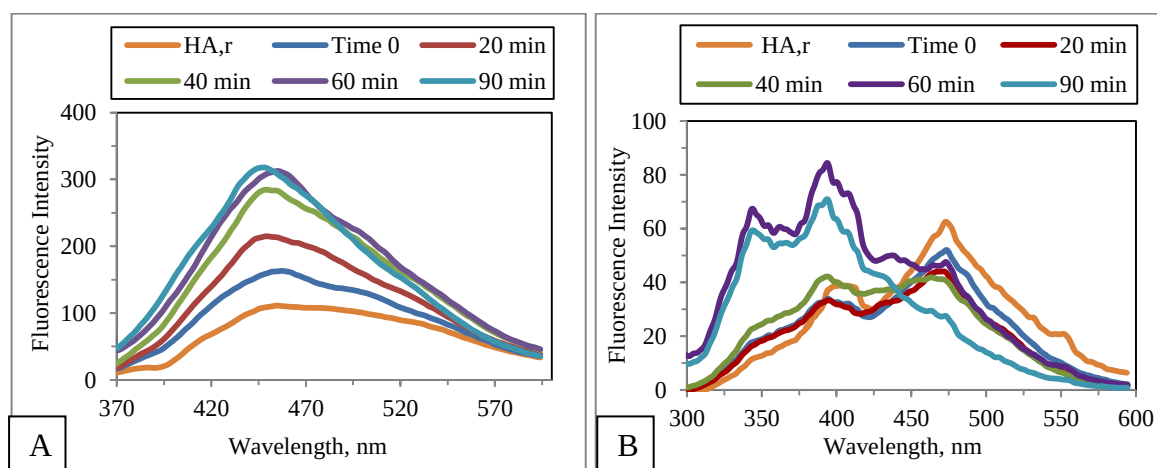


Figure 4.23. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.05 mg mL^{-1} montmorillonite recorded for the photocatalytic degradation.

Specified and specific UV-vis and fluorescence parameters of the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Mt given in Table 4.10. Initial adsorptive removals of humic acid were found to be 45%, 40%, 37%, 37% and 29% for Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC respectively. The presence of Mt did not significantly alter ($\leq 5\%$) the initial adsorptive removal of humic acid onto TiO_2 . In 20 minutes of irradiation time, all of the UV-vis parameters expressed more than 50%

removal efficiencies. On the other hand, DOC removal was 37%. While 61% of Color_{436} was removed in 20 minutes of irradiation, following photocatalysis 83% removal was achieved after 60 minutes. 49% removal was observed in 20 minutes irradiation time for UV_{254} . Similar with Color_{436} , UV_{254} was removed from the suspension by about 66% after 60 minutes of irradiation time. Comparatively lower removal efficiencies were expected for UV_{254} with reference to Color_{436} (Uyguner and Bekbolet, 2007; Uyguner and Bekbolet, 2010). In case of UV_{365} and UV_{280} parameters, 77% and 67% degradation efficiencies were achieved in 60 minutes, respectively. Complementary evaluation could also be presented by using the specific UV-vis and fluorescence parameters (Table 4.10). The decreasing trend of UV_{254} displayed the presence of aromatic structure for up to 90 min of irradiation time. With respect to the similar trend attained for the photocatalytic degradation of humic acid, the role of Mt could only be attributed to the preferential removal of humic moieties exhibiting aliphatic character (Uyguner and Bekbolet, 2005a).

Similar to the SUVA_{254} parameter of the photocatalytically treated humic acid samples, SUVA_{254} parameter for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Mt decreased with increasing irradiation time up to $t_{\text{irr}} = 90 \text{ min}$. SUVA_{254} value obtained for 90 min reaction time was found to be similar to the SUVA_{254} value for 60 min irradiation time for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Mt. However, lowest SCoA_{436} , SUVA_{365} , and SUVA_{280} values were obtained for 90 min irradiation time. Under all of the irradiation conditions, SUVA_{254} were found to be > 4 for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Mt.

Although a general trend could not be observed for $\text{SFI}_{\text{emis},455}$ and $\text{SFI}_{\text{emis},460}$ parameters, $\text{SFI}_{\text{syn},475}$ decreased with increasing irradiation time for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Mt. The reason could be attributed to the diversity of the observed FI trend with respect to a regular decreasing trend of DOC. While, lower $\text{SFI}_{\text{syn},475}$ were calculated for reaction period of 90 min with respect to the specific FI parameters, significantly higher $\text{SFI}_{\text{emis},455}$, $\text{SFI}_{\text{emis},460}$ values were attained for this reaction period of $t_{\text{irr}} = 90 \text{ min}$.

Table 4.10 Specific and specified UV-vis and fluorescence parameters of humic acid in the presence of 0.05 mg mL⁻¹ montmorillonite recorded during photocatalytic degradation.

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm ⁻¹ DOC, mg L ⁻¹					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 475 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.179	96.929	62.352
HA,rf	0.200	0.411	0.947	1.098	16.48	121.898	106.511	56.486
Irradiation Time, min								
Time 0	0.131	0.277	0.653	0.754	12.16	162.445	134.428	51.983
20	0.093	0.205	0.518	0.616	10.70	213.241	161.733	43.175
40	0.069	0.161	0.441	0.533	10.03	282.928	202.500	40.335
60	0.040	0.107	0.340	0.414	9.76	312.651	239.055	35.240
90	0.031	0.084	0.279	0.345	8.04	307.932	194.670	27.114
Specific UV-vis and fluorescence parameters, m ⁻¹ mg ⁻¹ L								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
Irradiation Time, min								
Time 0	1.08	2.28	5.37	6.20	1335.90	1105.50	427.49	
20	0.86	1.91	4.84	5.76	1992.91	1511.52	403.51	
40	0.69	1.60	4.40	5.31	2820.82	2018.95	402.14	
60	0.41	1.10	3.48	4.24	3203.39	2449.33	361.07	
90	0.38	1.05	3.47	4.29	3828.09	2420.07	337.07	

4.1.5.3. UV-vis spectroscopic evaluation humic acid during photocatalytic degradation in the presence of 0.10 mg mL⁻¹ montmorillonite. Photocatalytically treated UV-vis spectra of humic acid in the presence 0.10 mg mL⁻¹ Mt showed a gradually declining trend with

respect to increasing wavelength in the 200-600 nm region similar to the humic acid photocatalytic degradation trend in the absence Mt as well as in the presence of 0.05 mg mL⁻¹ Mt (Figure 4.22 and Figure 4.24). Increasing of the Mt dose to the 0.10 mg mL⁻¹ Mt did not lead to substantial changes in the degradation trend. Initial adsorptive removal of humic acid could also be visualized by examining the UV-vis spectra with respect to the UV-vis spectra recorded humic acids under dark conditions According to this examination, adsorption capacity of humic acid in the TiO₂-Mt ternary system increasing with increasing Mt dose as seen in the dark experiment time= 0 values (Figure 4.10).

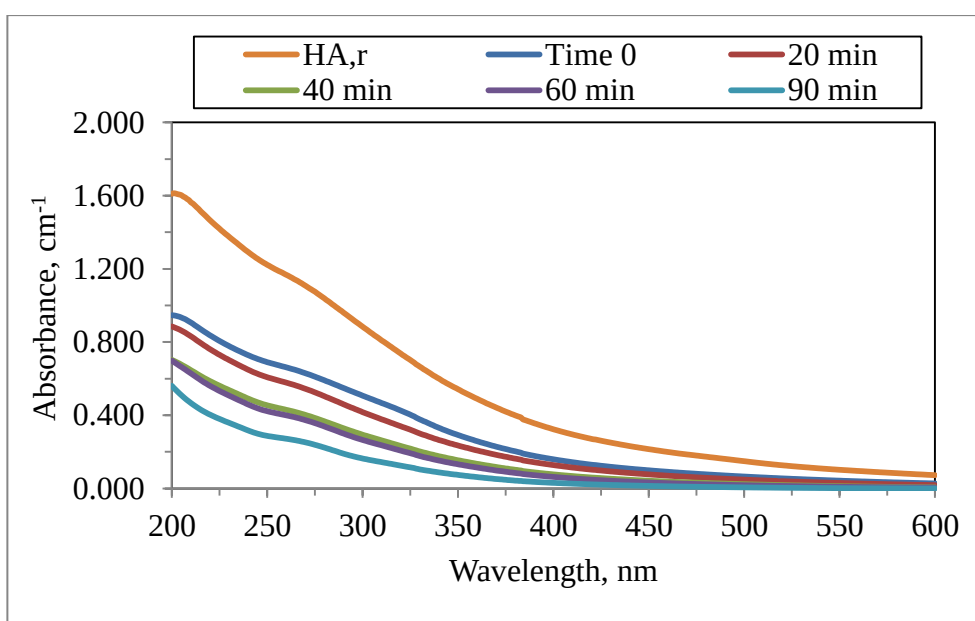


Figure 4.24. UV-vis spectra of humic acid recorded for the photocatalytic degradation in the presence of 0.10 mg mL⁻¹ montmorillonite.

4.1.5.4. Fluorescence spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.10 mg mL⁻¹ montmorillonite. Emission scan fluorescence spectra of photocatalytically treated humic acid in the presence of 0.10 mg mL⁻¹ Mt were also displayed in Figure 4.25 A. In accordance with the conditions set forward for raw humic acid, the fluorescence spectra of the samples were recorded by excitation at $\lambda_{\text{exc}} = 350$ nm which resulted in a major peak at the wavelength of $\lambda_{\text{emis}} = 455$ nm. A general increasing trend in emission fluorescence intensity could be visualized with respect to irradiation time and the maximum FI could be detected significantly for 60 minutes of irradiation time with reference to the raw humic acid (Figure 2.13A and 2.9A).

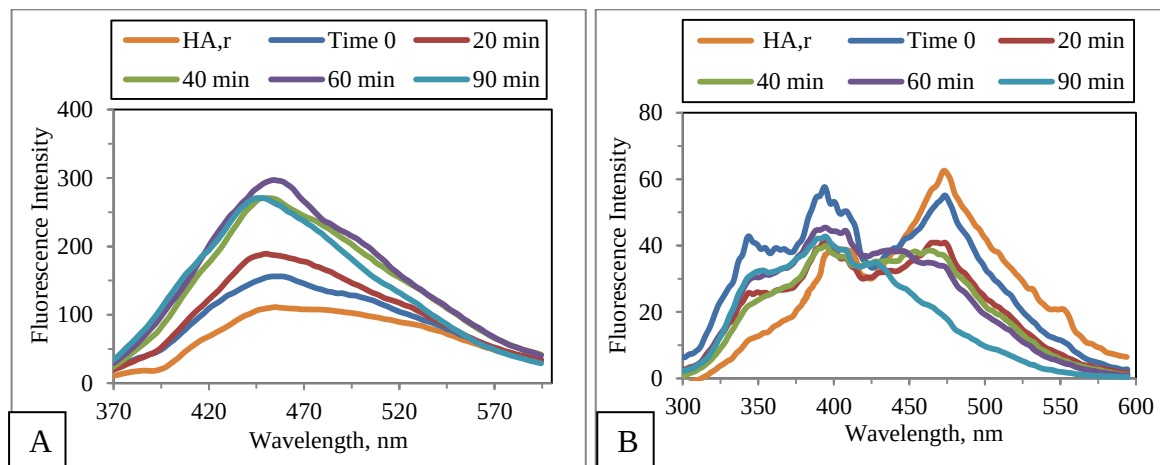


Figure 4.25. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.10 mg mL^{-1} montmorillonite recorded for the photocatalytic degradation.

Synchronous scan fluorescence spectra recorded for the photocatalytically treated humic acid in the presence of 0.10 mg mL^{-1} Mt were shown in Figure 4.25 B. Synchronous scan spectra trend for humic acid in the presence of 0.10 mg mL^{-1} Mt displayed a similar trend with humic acid in the presence of lower dose Mt as 0.05 mg mL^{-1} . There was also a moderate peak at $\lambda_{\text{emis}} = 390 \text{ nm}$ wavelength with a comparatively lower intensity. Under prolonged irradiation conditions (i.e. 90 min), the fluorescence intensity maxima at $\lambda_{\text{emis}} = 470 \text{ nm}$ was completely removed and new fluorescence intensity maxima at $\lambda_{\text{emis}} = 350$ and $\lambda_{\text{emis}} = 375 \text{ nm}$ were found to be evident with a detectable intensity value. The observed shift was also found to be present in the absence of Mt as well as in the presence of 0.05 mg mL^{-1} Mt. Specified and specific UV-vis and fluorescence parameters of the photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Mt were given in Table 4.11. Initial adsorptive removal of humic acid was found to be 53%, 47%, 43%, 43% and 34% for Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC respectively. In 20 minutes of irradiation time, the removal efficiencies of humic acid were 60%, 58%, 52% and 50% for Color_{436} , UV_{365} , UV_{280} , UV_{254} . On the other hand, DOC removal was found to be 41%. While 79% of Color_{436} was removed in 40 minutes of irradiation period, 93% removal was achieved after $t_{\text{irr}} = 90$ minutes expressing an almost complete removal of color forming moieties. 63% removal was observed in 40 minutes irradiation time for

UV₂₅₄. Similar with Color₄₃₆, 77% UV₂₅₄ was removed from the suspension after 90 minutes irradiation period representing a rather slower oxidation regime.

Table 4.11. Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of 0.10 mg mL⁻¹ montmorillonite recorded during photocatalytic degradation.

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm ⁻¹ DOC, mg L ⁻¹					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 475 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.179	96.929	62.352
HA,rf	0.200	0.411	0.947	1.098	16.48	121.898	106.511	56.486
Irradiation Time, min								
Time 0	0.112	0.243	0.591	0.679	11.17	156.070	126.817	55.000
20	0.088	0.196	0.504	0.596	10.11	187.033	141.787	40.811
40	0.050	0.126	0.367	0.444	9.82	269.038	188.306	36.563
60	0.039	0.106	0.339	0.413	8.66	296.784	225.119	33.523
90	0.018	0.057	0.223	0.281	7.24	262.406	194.670	18.277
Specific UV-vis and fluorescence parameters, m ⁻¹ mg ⁻¹ L								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
Irradiation Time, min								
Time 0	1.00	2.18	5.29	6.08	1397.22	1135.34	492.39	
20	0.87	1.93	4.98	5.89	1849.98	1402.44	403.67	
40	0.51	1.28	3.74	4.52	2739.69	1917.57	372.33	
60	0.45	1.23	3.91	4.76	3426.68	2599.22	387.06	
90	0.24	0.78	3.08	3.88	3624.39	2688.82	252.44	

A comparable decreasing trend for both $SUVA_{254}$ and $SUVA_{280}$ parameters for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Mt with the photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Mt was obtained with increasing irradiation time except that 60 min irradiation time. $SUVA_{254}$ and $SUVA_{280}$ values for 60 min irradiation time were found to be higher than the $SUVA_{254}$ and $SUVA_{280}$ values for 90 min irradiation time for photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Mt. Unlike to $SUVA_{254}$ and $SUVA_{280}$ parameters, lowest $SCoA_{436}$ and $SUVA_{365}$ values were obtained for 90 min irradiation time. As seen in Table 4.11, $SUVA_{254}$ for 90 minutes irradiation time was found to be 3.88 for the photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Mt.

Likewise to the $FI_{emis,455}$ and $SFI_{emis,460}$ parameters for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Mt, $FI_{emis,455}$ and $SFI_{emis,460}$ parameters for the photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Mt didn't not display a general altering trend. However, $SFI_{syn,475}$ parameter decreased with increasing irradiation time for the photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Mt, except that 60 min irradiation time. Even though, lower $SFI_{syn,475}$ was calculated for reaction period of $t_{irr} = 90 \text{ min}$ with respect to the specific FI parameters, considerably higher $SFI_{emis,455}$, $SFI_{emis,460}$ values were attained for this irradiation time.

4.1.5.5. UV-vis spectroscopic evaluation humic acid during photocatalytic degradation in the presence of 0.20 mg mL^{-1} montmorillonite. Photocatalytically treated UV-vis spectra of humic acid in the presence 0.20 mg mL^{-1} Mt showed a gradually declining trend with respect to increasing wavelength in the 200-600 nm region similar to the humic acid degradation trend in the presence of 0.05 and 0.10 mg mL^{-1} Mt (Figure 4.26, 4.22 and 4.24). Increasing of the Mt dose to the 0.20 mg mL^{-1} Mt did not lead to significant alterations in the degradation trend. However, adsorption capacity of humic acid in the presence of Mt onto TiO_2 increased with increasing Mt dose especially in the presence of 0.20 mg mL^{-1} Mt as could be visualized at $t = 0$ condition. The degradation of humic acid expressed by UV-vis parameters and DOC values were found to be slightly enhanced in the presence of 0.20 mg mL^{-1} Mt under all irradiation periods except 90 minutes of irradiation time.

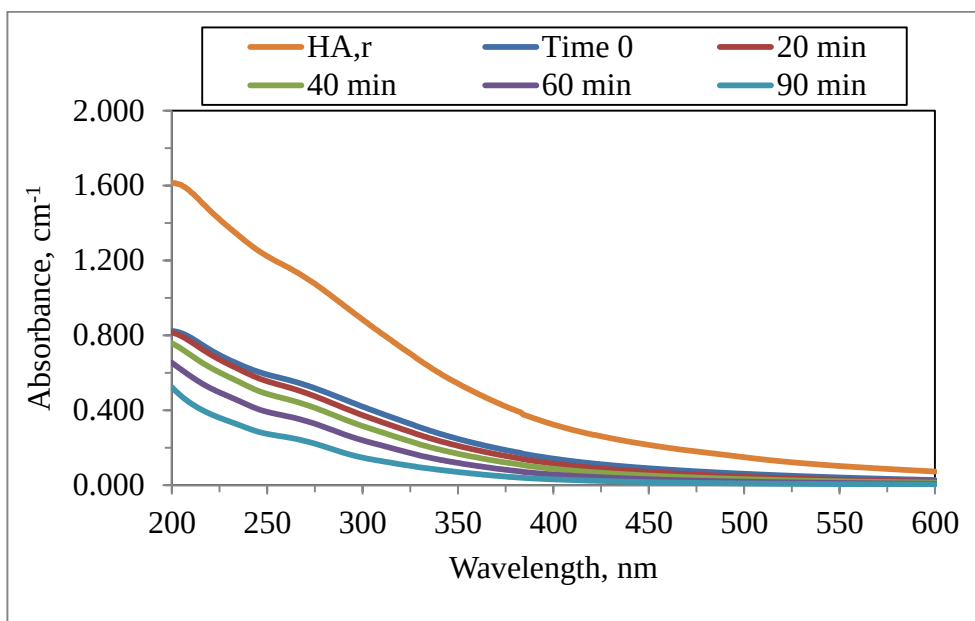


Figure 4.26. UV-vis spectra of humic acid during photocatalytic degradation in the presence of 0.20 mg mL^{-1} montmorillonite.

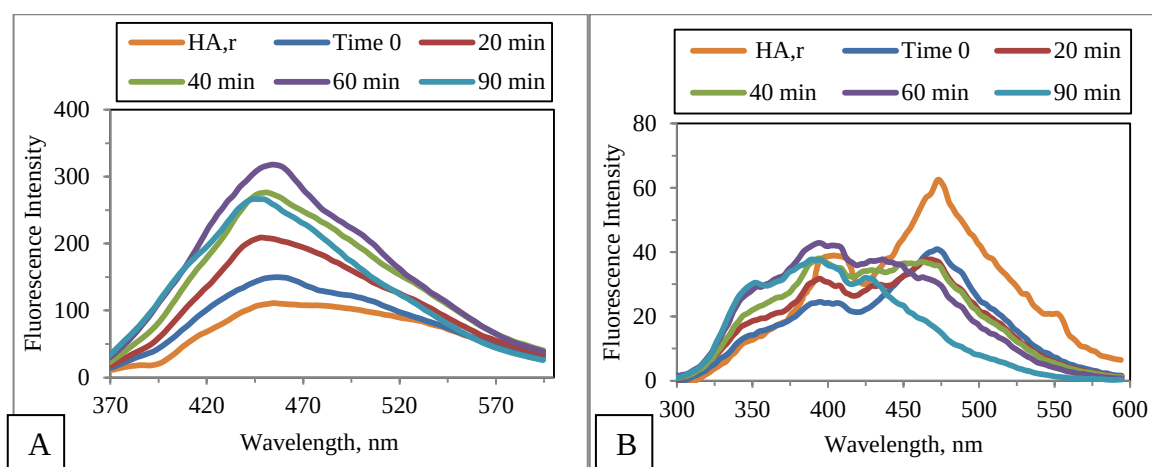


Figure 4.27. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.20 mg mL^{-1} montmorillonite during photocatalytic degradation.

4.1.3.6. Fluorescence spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.20 mg mL^{-1} montmorillonite. Emission scan (A) and synchronous scan (B) fluorescence spectra recorded for the photocatalytically treated humic acid in the presence of 0.20 mg mL^{-1} Mt were shown in Figure 4.27. The observed shift was also indicated to be present in the absence of Mt (Figure 4.21). In accordance

with the conditions set forward for raw humic acid, the fluorescence spectra of the samples were also recorded by excitation at $\lambda_{\text{exc}} = 350$ nm which resulted in a major peak at the emission wavelength of $\lambda_{\text{emis}} = 455$ nm. The fluorescence intensities displayed an increasing trend with respect to increasing irradiation period from time = 0 to 60 minutes. While the trend observed for the emission scan fluorescence spectra of humic acid and Mt binary system at $t = 0$ min condition displayed the lowest fluorescence intensity profile. The highest fluorescence intensities were obtained at $t_{\text{irr}} = 60$ minutes of reaction time expressing the formation of new highly fluorescent centers. Synchronous scan fluorescence spectral trend recorded for photocatalytically treated humic acid in the presence of 0.20 mg mL^{-1} Mt displayed a similar trend with humic acid in the presence of lower doses of Mt. The moderate peak at $\lambda_{\text{emis}} = 390$ nm wavelength with a comparatively lower intensity was also observed. Under prolonged irradiation conditions (i.e. 60 min), the fluorescence intensity maxima at $\lambda_{\text{emis}} = 470$ nm was completely removed and a new fluorescence intensity maxima at $\lambda_{\text{emis}} = 350$ and $\lambda_{\text{emis}} = 375$ nm were found to be evident with a detectable intensity values. The synchronous scan fluorescence spectra recorded for the photocatalytically treated humic acid in the presence of Mt under treatment conditions indicated the presence of structural changes leading to the formation and removal of fluorescent centers during photocatalysis. The increase in the FI recorded following 60 minutes of irradiation time had been associated with the increasing content of C=O, aromatic C and COOH groups (Senesi, 1990).

Specified and specific UV-vis and fluorescence parameters of the photocatalytically treated humic acid samples in the presence of 0.20 mg mL^{-1} Mt were given in Table 4.12. Initial adsorptive removal efficiencies of humic acid in the presence 0.20 mg mL^{-1} Mt were found to be 58%, 55%, 52%, 52% and 47% for Color₄₃₆, UV₃₆₅, UV₂₈₀, UV₂₅₄ and DOC respectively. The presence of 0.20 mg mL^{-1} Mt altered the initial adsorptive removal of humic acid by approximately 15%. The removal percentage of humic acid in the presence of 0.20 mg mL^{-1} Mt was found to be higher than the case attained in the absence of Mt for shorter time periods, such as 20 minutes. 62% removal of UV₃₆₅ and 56% removal of UV₂₈₀ were also recorded at the end of 20 minutes. While 67% of Color₄₃₆ was removed in 20 minutes of irradiation period, 85% removal was achieved after 60 minutes. UV₂₅₄ was removed from the humic suspension about 55% and 68% after 20 and 60 minutes irradiation times respectively. Furthermore, at the end of 90 minutes of irradiation time, $\leq$

20% of humic acid was found to be present as expressed by all of the specified UV-vis parameters representing 54% remaining DOC.

Table 4.12. Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of 0.20 mg mL⁻¹ montmorillonite recorded during photocatalytic degradation.

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm ⁻¹ DOC, mg L ⁻¹					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	F _{emis} ₃₅₀ 455 nm	F _{emis} ₃₇₀ 460 nm	F _I _{syn} 475 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.179	96.929	62.352
HA,rf	0.200	0.411	0.947	1.098	16.48	121.898	106.511	56.486
Irradiation Time, min								
Time 0	0.101	0.209	0.499	0.580	8.97	149.678	118.307	40.589
20	0.080	0.175	0.455	0.542	9.23	206.738	153.248	36.570
40	0.059	0.138	0.394	0.475	9.16	272.832	195.344	35.539
60	0.037	0.095	0.310	0.382	8.72	317.839	234.658	29.920
90	0.019	0.054	0.206	0.266	7.84	257.652	187.902	15.311
Specific UV-vis and fluorescence parameters, m ⁻¹ mg ⁻¹ L								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
Irradiation Time, min								
Time 0	1.13	2.33	5.56	6.46	1668.65	1318.92	452.49	
20	0.87	1.90	4.93	5.88	2239.85	1660.32	396.21	
40	0.64	1.50	4.30	5.19	2978.19	2132.34	387.93	
60	0.42	1.09	3.55	4.38	3644.95	2691.04	343.12	
90	0.24	0.69	2.62	3.40	3286.38	2396.71	195.29	

In comparison to the SCoA_{436} , SUVA_{365} , SUVA_{280} and SUVA_{254} parameters attained for the photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Mt, no significant change was observed with respect to irradiation time for the photocatalytically treated humic acid samples in the presence of 0.20 mg mL^{-1} Mt. All of these parameters decreased with increasing irradiation time. Lowest SCoA_{436} , SUVA_{365} , SUVA_{280} and SUVA_{254} values were obtained for 90 min irradiation time. SUVA_{254} value was found to be 3.40 for the photocatalytically treated humic acid samples in the presence of 0.20 mg mL^{-1} Mt representing alterations in aromatic character achieved under 90 minutes of irradiation time.

Increasing of Mt dose from 0.10 to 0.20 mg mL^{-1} did not lead to significant changes on $\text{SFI}_{\text{emis},455}$ and $\text{SFI}_{\text{emis},460}$ and $\text{SFI}_{\text{syn},475}$ parameters. As expected, a general trend could not be assessed for $\text{SFI}_{\text{emis},455}$ and $\text{SFI}_{\text{emis},460}$ parameters, while $\text{SFI}_{\text{syn},475}$ decreased with increasing irradiation time for the photocatalytically treated humic acid samples in the presence of 0.20 mg mL^{-1} Mt. Lowest $\text{SFI}_{\text{syn},475}$ were calculated for reaction period of $t_{\text{irr}} = 90$ min with respect to the specific FI parameters, however, significantly higher $\text{SFI}_{\text{emis},455}$, $\text{SFI}_{\text{emis},460}$ values were attained for 90 min irradiation time.

4.1.6. Photocatalytic degradation of humic acid in the presence of kaolinite

For the evaluation of the photocatalytic degradation of humic acid in the presence of kaolinite TiO_2 photocatalyst loading was kept constant as 0.50 mg mL^{-1} and Kt concentrations were chosen as 0.05 mg mL^{-1} , 0.10 mg mL^{-1} and 0.20 mg mL^{-1} .

4.1.6.1. UV-vis Spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.05 mg mL^{-1} kaolinite. UV-vis spectra of photocatalytically treated humic acid in the presence 0.05 mg mL^{-1} Kt illustrated a gradually declining trend with respect to increasing wavelength in the 200-600 nm wavelength region similar to the humic acid degradation trend observed in the presence Mt (Figure 4.28). Irradiation time dependent changes could also be followed by spectroscopic properties during humic acid photocatalytic degradation starting with $t = 0$ min which was the initial titanium dioxide introduction to the humic acid and Kt binary system solution prior to irradiation. Initial adsorptive removal of humic acids could be visualized by examining the UV-vis

spectra with respect to the UV-vis spectra recorded humic acids under dark conditions (Figure 4.12).

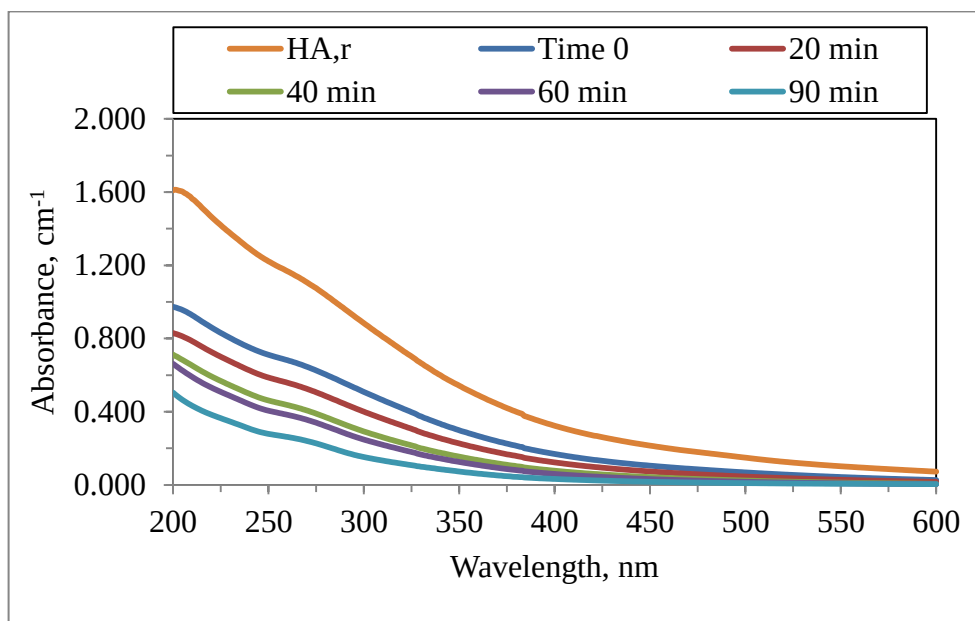


Figure 4.28. UV-vis spectra of humic acid during photocatalytic degradation in the presence of 0.05 mg mL^{-1} kaolinite.

The adsorption capacity of humic acid in the presence of Kt increased as was also verified by the experiments performed under dark conditions (Table 4.4). Similar to the photocatalytic degradation of humic acid in the presence of Mt, the photocatalytic degradation rate of humic acid displayed an enhancement in the presence of 0.05 mg mL^{-1} Kt under all irradiation times.

4.1.6.2. Fluorescence spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.05 mg mL^{-1} kaolinite. Emission scan fluorescence spectra of photocatalytically treated humic acid in the presence of 0.05 mg mL^{-1} Kt were displayed in Figure 4.29. In accordance with the conditions set forward for raw humic acid, the fluorescence spectra of the samples were also recorded by excitation at $\lambda_{\text{exc}} = 350 \text{ nm}$ which resulted in a major peak at the wavelength of $\lambda_{\text{emis}} = 455 \text{ nm}$ (Figure 4.29 A). The recorded general increasing trend in emission scan fluorescence intensity could be observed with respect to the irradiation time, the maximum fluorescence intensity could be

significantly detected for 60 minutes of irradiation time with reference to the raw humic acid. In relation to the fluorescence emission scan spectra recorded for humic acid, no distinct comparative evaluation could be deduced for the assessment of the effect of the Kt in binary system (Figures 4.7 A and 4.29 A).

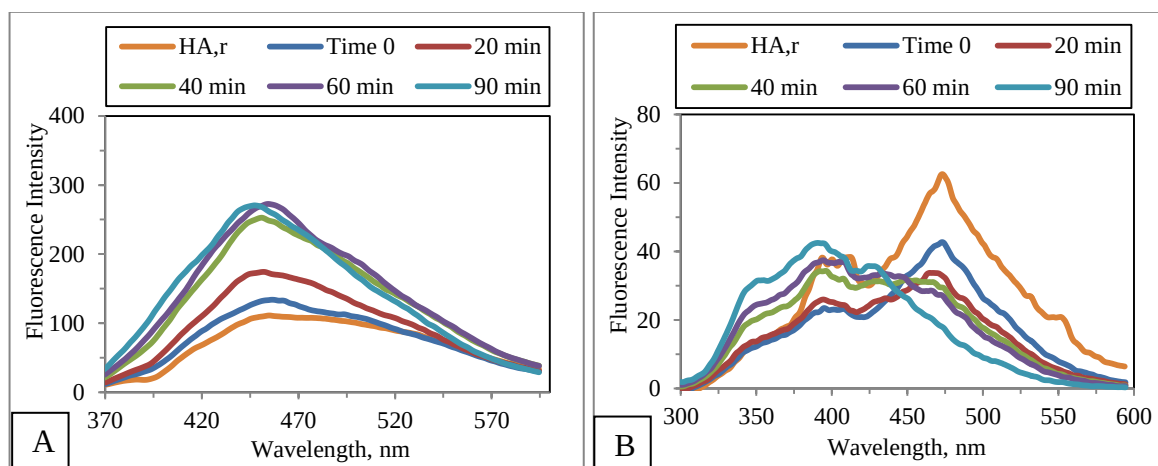


Figure 4.29. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.05 mg mL^{-1} kaolinite during photocatalytic degradation.

Synchronous scan fluorescence spectra recorded for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Kt were shown in Figure 4.29 B. Synchronous scan fluorescence spectra for humic acid in the presence of 0.05 mg mL^{-1} Kt displayed a major sharp peak around emission wavelength of $\lambda_{\text{emis}} = 475 \text{ nm}$ and a moderate peak at $\lambda_{\text{emis}} = 390 \text{ nm}$ wavelength with a comparatively lower intensity. Under prolonged irradiation conditions (i.e. 90 min), the fluorescence intensity maxima recorded at $\lambda_{\text{emis}} = 475 \text{ nm}$ was completely removed and new fluorescence intensity maximum at $\lambda_{\text{emis}} = 385 \text{ nm}$ emission wavelength was found to be evident with detectable intensity values. The shift of fluorescence maxima to lower wavelengths was previously explained by the formation of new fluorophores during photocatalysis (Uyguner and Bekbolet, 2005a). Furthermore, the observed wavelength shift was also found to be present in humic fluorescence spectra recorded in the absence of either Kt or Mt and humic fluorescence spectra recorded in the presence of Mt. Therefore, the reason could only be attributed to the oxidative changes in humic structure rather than Kt particles and humic fractions interactions prevailing during photocatalysis.

Specified and specific UV-vis and fluorescence parameters of the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Kt were given in Table 4.13. Initial adsorptive removals of humic acid were found to be 50%, 46%, 42%, 42% and 35% for Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC respectively. The presence of Kt did not alter significantly ($\leq 5\%$) the initial adsorptive removal of humic acid onto TiO_2 . However, the initial adsorptive removal of humic acid onto TiO_2 in the presence of 0.05 mg mL^{-1} Kt was found to be higher than the initial adsorptive removal of humic acid onto TiO_2 in the presence of 0.05 mg mL^{-1} Mt.

In 20 minutes of irradiation time, all of the UV-vis parameters expressed more than 50% removal efficiencies. On the other hand, 39% DOC removal was attained. While 65% of Color_{436} was removed in 20 minutes of irradiation, upon further irradiation conditions 84% removal was achieved after 60 minutes. 52% removal was observed in 20 minutes irradiation time for UV_{254} . Similar with Color_{436} , UV_{254} was removed from the suspension about 67% after 60 minutes of irradiation time. Comparatively lower removal efficiency was expected for UV_{254} with reference to Color_{436} (Uyguner and Bekbolet, 2007; Uyguner and Bekbolet, 2010). In case of UV_{365} and UV_{280} parameters, 78% and 69% degradation efficiencies were achieved in 60 minutes, respectively. Complementary evaluation could also be presented by using the specific UV-vis parameters. The decreasing trend of UV_{254} displayed the presence of aromatic structure for up to 90 min of irradiation time. With respect to the similar trend attained for the photocatalytic degradation of humic acid, the role of Kt could only be attributed to the preferential removal of humic moieties exhibiting aliphatic character.

Similar to SUVA_{254} parameter of the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Mt, SUVA_{254} parameter for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Kt decreased with increasing irradiation time. The lowest SCoA_{436} , SUVA_{365} , SUVA_{280} and SUVA_{254} values were attained for 90 min irradiation time. Under all of the irradiation conditions up to 60 min of irradiation period, SUVA_{254} was found to be > 4 for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Kt. However, upon prolonged irradiation conditions i.e. 90 minutes, SUVA_{254} decreased to 3.18 for the photocatalytically treated

humic acid samples in the presence of 0.05 mg mL⁻¹ Kt representing the oxidative degradation of aromatic core of humic acid.

Table 4.13. Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of 0.05 mg mL⁻¹ kaolinite recorded during photocatalytic degradation.

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm ⁻¹ DOC, mg L ⁻¹					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 475 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.18	96.93	62.351
HA,rf	0.200	0.411	0.947	1.098	16.48	121.80	106.51	56.486
Irradiation Time, min								
Time 0	0.119	0.252	0.603	0.699	11.03	133.614	107.420	42.577
20	0.084	0.189	0.485	0.575	10.35	172.119	128.665	32.618
40	0.050	0.126	0.370	0.451	9.32	248.286	176.669	29.382
60	0.038	0.101	0.321	0.397	8.58	272.506	203.260	26.790
90	0.020	0.057	0.211	0.272	8.56	261.183	195.482	17.718
Specific UV-vis and fluorescence parameters, m ⁻¹ mg ⁻¹ L								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
Irradiation Time, min								
Time 0	1.08	2.29	5.47	6.33	1211.37	973.89	386.01	
20	0.81	1.83	4.69	5.56	1662.99	1243.14	315.15	
40	0.54	1.35	3.97	4.84	2664.02	1895.59	315.25	
60	0.44	1.18	3.74	4.62	3176.06	2369.00	312.23	
90	0.24	0.66	2.47	3.18	3051.20	2283.67	206.98	

Although a general trend could not be assessed for $SFI_{emis,455}$ and $SFI_{emis,460}$ parameters, $SFI_{syn,475}$ decreased with increasing irradiation time for the photocatalytically treated humic acid samples in the presence of 0.05 mg mL^{-1} Kt. The reason could only be attributed to the diversity of the FI trend with respect to a regular decreasing trend of DOC. While, lower $SFI_{syn,475}$ was calculated for reaction period of $t_{irr} = 90 \text{ min}$ with respect to the specific FI parameters, significantly higher $SFI_{emis,455}$, $SFI_{emis,460}$ values were attained for this reaction period.

4.1.6.3. UV-vis spectroscopic evaluation humic acid during photocatalytic degradation in the presence of 0.10 mg mL^{-1} kaolinite. UV-vis spectra of photocatalytically treated humic acid in the presence of 0.10 mg mL^{-1} Kt showed a gradually declining trend with respect to increasing wavelength in the 200-600 nm wavelength regions similar to the humic acid degradation trend attained both in the absence as well as in the presence of 0.05 mg mL^{-1} Kt (Figure 4.28 and Figure 4.30).

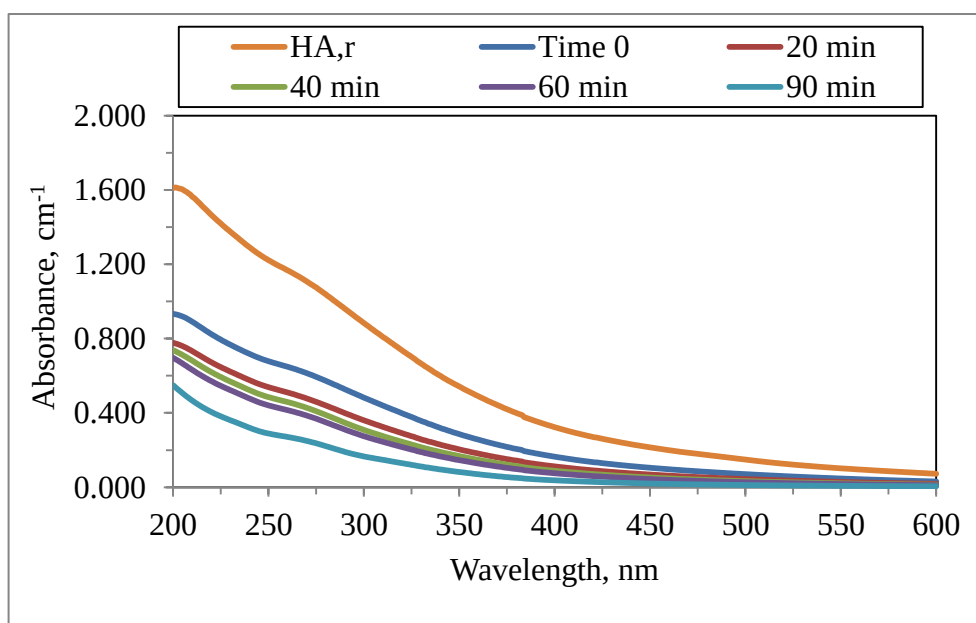


Figure 4.30. UV-vis spectra of humic acid during photocatalytic degradation in the presence of 0.10 mg mL^{-1} kaolinite.

Increasing of the Kt dose to 0.10 mg mL^{-1} did not lead to radical changes to the degradation trend of humic acid. Initial adsorptive removal of humic acid could also be

visualized by examining the UV-vis spectra with respect to the UV-vis spectra recorded humic acids under dark conditions (Figure 4.12). According to this examination, adsorption capacity of humic acid and Kt onto TiO_2 increased with increasing Kt dose as deduced by the dark experiments at time= 0 condition (Figure 4.12). The degradation efficiency of humic acid as expressed by the specified UV-vis parameters and DOC values was found to be slightly higher in the presence of 0.10 mg mL^{-1} Kt under all irradiation periods.

4.1.6.4. Fluorescence spectroscopic evaluation of humic acid during photocatalytic degradation in the presence of 0.10 mg mL^{-1} kaolinite. Emission scan fluorescence spectra of photocatalytically treated humic acid in the presence of 0.10 mg mL^{-1} Kt were displayed in Figure 4.31 A. In accordance with the specifications set forward for raw humic acid, the fluorescence spectra of the samples were also recorded by excitation at $\lambda_{\text{exc}} = 350 \text{ nm}$ which resulted in a major peak at the emission wavelength of $\lambda_{\text{emis}} = 455 \text{ nm}$. The general increasing trend in emission fluorescence intensity could be visualized with respect to irradiation time and the maximum fluorescence intensity could be detected significantly for 40 minutes and 60 minutes of irradiation times with reference to the raw humic acid (Figure 4.21 A and Figure 4.31 A).

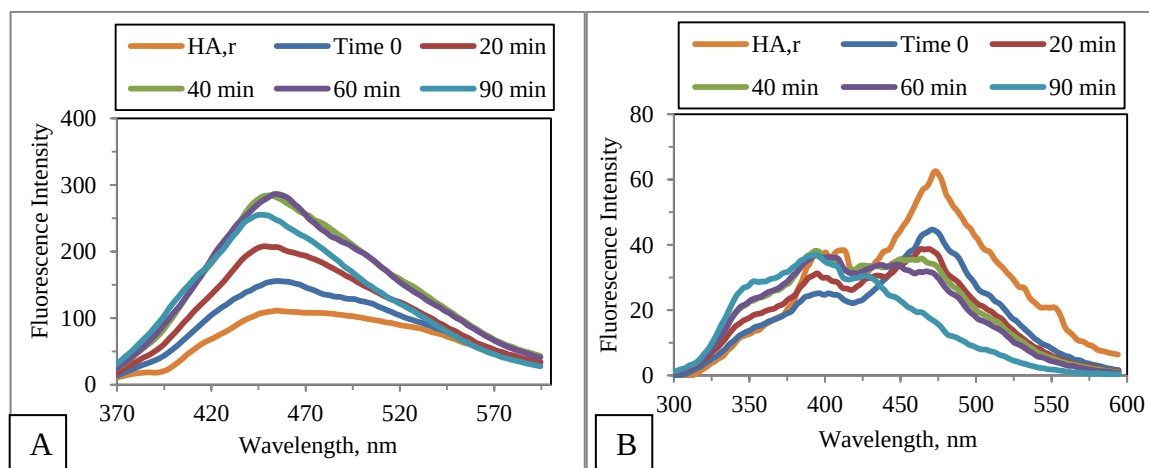


Figure 4.31. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.10 mg mL^{-1} kaolinite during photocatalytic degradation.

Synchronous scan fluorescence spectra recorded for the photocatalytically treated humic acid in the presence of 0.10 mg mL^{-1} Kt were shown in Figure 4.31 B. Synchronous scan spectra trend for humic acid in the presence of 0.10 mg mL^{-1} Kt displayed a similar trend with humic acid in the presence of lower dose Kt as 0.05 mg mL^{-1} . In a similar manner a moderate peak at $\lambda_{\text{emis}} = 390 \text{ nm}$ wavelength with a comparatively lower intensity was also observed. Under prolonged irradiation conditions (*i.e.* $t_{\text{irr}} = 90 \text{ min}$), the fluorescence intensity maxima at $\lambda_{\text{emis}} = 475 \text{ nm}$ was completely removed and new fluorescence intensity maxima at $\lambda_{\text{emis}} = 385 \text{ nm}$ was recorded with a detectable intensity value. The observed shift was also found to be present in the absence of Kt as well as in the presence of 0.05 mg mL^{-1} Kt.

Specified and specific UV-vis and fluorescence parameters of the photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Kt were given in Table 4.14 Initial adsorptive removals of humic acid were found to be 51%, 48%, 45%, 44% and 40% for Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC respectively. In 20 minutes of irradiation time, the oxidative removal efficiencies of humic acid were found to be 67%, 63%, 58% and 56% for Color_{436} , UV_{365} , UV_{280} and UV_{254} respectively. On the other hand, 46% DOC removal was achieved under 20 minutes of irradiation period. While 75% of Color_{436} was removed in 40 minutes of irradiation period 90% removal was achieved after 90 minutes. 61% removal of UV_{254} was attained in 40 minutes irradiation time. Considerably higher removal efficiencies as 77% for Color_{436} , and UV_{254} were attained from the suspension under 90 minutes of prolonged irradiation time period.

A similar decreasing trend for SCoA_{436} , SUVA_{365} , SUVA_{280} and SUVA_{254} parameters with increasing irradiation time was obtained for the photocatalytically treated both for the humic acid samples in the presence of 0.05 mg mL^{-1} Kt and 0.10 mg mL^{-1} Kt. As could be seen in Table 4.14., lowest SCoA_{436} , SUVA_{365} , SUVA_{280} and SUVA_{254} values were attained for 90 min irradiation time as 0.32, 0.85, 2.93 and 3.73, respectively. As expected, $\text{SFI}_{\text{emis},455}$ and $\text{SFI}_{\text{emis},460}$ parameters of the photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Kt did not show a general trend. However, $\text{SFI}_{\text{syn},475}$ parameter was found to be decreasing with respect to increasing irradiation time for the photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Kt. Although, lower $\text{SFI}_{\text{syn},475}$ was calculated for reaction period of 90 min

with respect to the other specific FI parameters, considerably higher $SFI_{emis,455}$, $SFI_{emis,460}$ values were attained for this irradiation time.

Table 4.14. Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of 0.10 mg mL^{-1} kaolinite recorded during photocatalytic degradation.

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm^{-1} DOC, mg L^{-1}					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 475 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.18	96.93	62.351
HA,rf	0.200	0.411	0.947	1.098	16.48	121.80	106.51	56.486
Irradiation Time, min								
Time 0	0.118	0.242	0.573	0.666	10.26	155.701	124.449	44.054
20	0.078	0.170	0.440	0.527	9.20	206.595	157.358	37.278
40	0.061	0.139	0.389	0.474	8.42	280.808	196.869	33.475
60	0.051	0.120	0.350	0.430	7.98	286.346	218.427	30.340
90	0.024	0.065	0.221	0.281	7.55	247.008	180.373	16.098
Specific UV-vis and fluorescence parameters, $\text{m}^{-1}\text{mg}^{-1}\text{L}$								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	$SFI_{emis,455}$	$SFI_{emis,460}$	$SFI_{syn,475}$	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
Irradiation Time, min								
Time 0	1.15	2.36	5.58	6.49	1517.55	1212.95	429.38	
20	0.85	1.85	4.78	5.73	2245.60	1710.41	405.20	
40	0.72	1.65	4.62	5.63	3335.01	2338.11	397.57	
60	0.64	1.50	4.38	5.39	3588.30	2737.18	380.20	
90	0.32	0.85	2.93	3.73	3271.63	2389.04	213.22	

4.1.6.5. UV-vis spectroscopic evaluation humic acid during photocatalytic degradation in the presence of 0.20 mg mL^{-1} kaolinite. UV-vis spectra of photocatalytically treated humic acid in the presence 0.20 mg mL^{-1} Kt showed a gradually declining trend with respect to increasing wavelength in the 200-600 nm wavelength region similar to the humic acid degradation trend observed both in the presence of 0.05 and 0.10 mg mL^{-1} Kt (Figures 4.28, 4.30 and 4.32). Increasing the dose of Kt to 0.20 mg mL^{-1} Kt, did not significantly alter the UV-vis absorption profile retaining the exponential decreasing trend. Initial adsorptive removal of humic acid in the presence of Kt onto oxide surface increased by addition of 0.20 mg mL^{-1} Kt as was also explained by the dark experiments for time= 0 condition (Figure 4.12). Since the highest adsorptive removal was achieved by addition of 0.10 mg mL^{-1} Kt (34% for DOC), no direct effect could be assessed. The degradation efficiency of humic acid expressed by the UV-vis parameters and DOC values slightly increased in the presence of 0.20 mg mL^{-1} Kt under all irradiation periods except that 90 minutes of irradiation time.

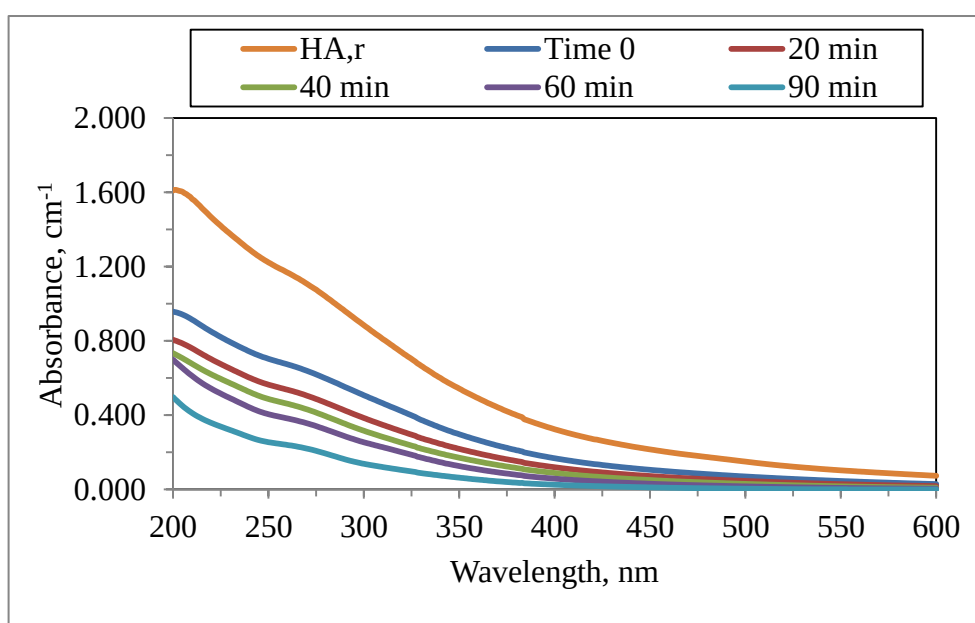


Figure 4.32. UV-vis spectra of humic acid during photocatalytic degradation in the presence of 0.20 mg mL^{-1} kaolinite.

Emission scan (A) and synchronous scan (B) fluorescence spectra recorded for the photocatalytically treated humic acid in the presence of 0.20 mg mL^{-1} Kt were shown in

Figure 4.33 A-B. The observed shift was also found to be present in the absence of Kt (Figure 4.21). As previously explained for raw humic acid, the fluorescence emission scan spectra of the humic samples were also recorded by excitation at $\lambda_{\text{exc}} = 350 \text{ nm}$, which resulted in a major peak at emission wavelength of $\lambda_{\text{emis}} = 455 \text{ nm}$. The fluorescence intensities displayed an increasing trend with respect to increasing irradiation periods from time = 0 to 60 minutes. Despite the observed trend for the emission scan fluorescence spectra of humic acid and Kt binary system, $t = 0 \text{ min}$ condition displayed the lowest fluorescence intensity profile. The highest fluorescence intensities were obtained at $t_{\text{irr}} = 60 \text{ min}$ of reaction time expressing the formation of new highly fluorescent centers proceeding through oxidative alterations.

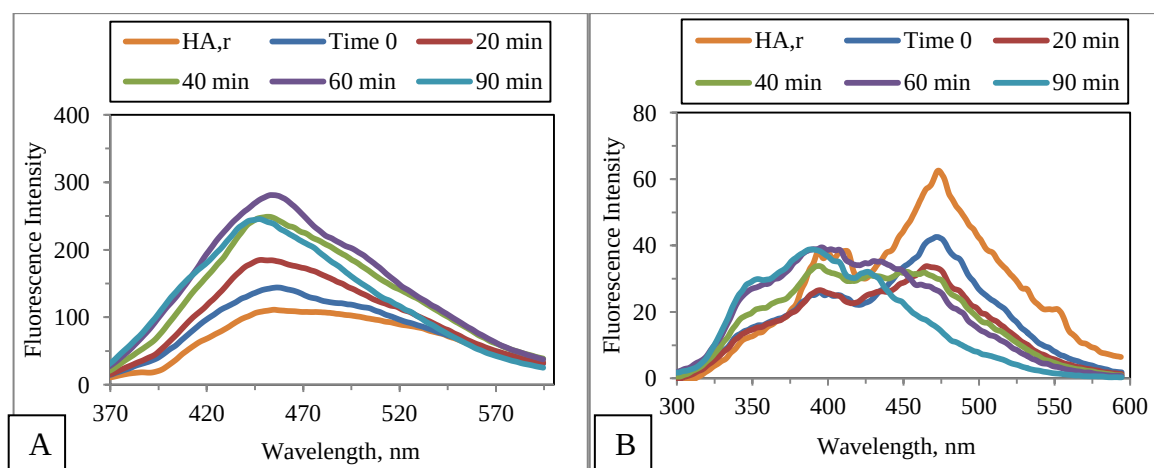


Figure 4.33. Emission scan (A) and synchronous scan (B) fluorescence spectra of humic acid in the presence of 0.20 mg mL^{-1} kaolinite during photocatalytic degradation.

Synchronous scan fluorescence spectral trend for photocatalytically treated humic acid in the presence of 0.20 mg mL^{-1} Kt displayed a similar trend with humic acid in the presence of lower doses Kt. The presence of a moderate peak at $\lambda_{\text{emis}} = 390 \text{ nm}$ emission wavelength with a comparatively lower intensity was also recorded. For longer irradiation conditions (*i.e.* $t_{\text{irr}} = 60 \text{ min}$), the fluorescence intensity maxima at $\lambda_{\text{emis}} = 475 \text{ nm}$ was completely removed and a new fluorescence intensity maxima at $\lambda_{\text{emis}} = 385 \text{ nm}$ was found to be evident with a detectable intensity value. The recorded synchronous scan fluorescence spectra of the photocatalytically treated humic acid in the presence of Kt under treatment conditions indicated the presence of structural changes leading to the

formation and removal of fluorescent centers during photocatalysis. The increase in the FI for 60 minutes irradiation time could be associated with the increasing content of C=O, aromatic C and COOH groups upon photocatalysis.

Specified and specific UV-vis and fluorescence parameters of the photocatalytically treated humic acid samples in the presence of 0.20 mg mL^{-1} Kt were given in Table 4.15. Initial adsorptive removal efficiencies of humic acid in the presence 0.20 mg mL^{-1} Kt were found to be 51%, 46%, 43%, 42% and 35% for Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC respectively. The removal percentage for photocatalytic degradation of humic acid in the presence of 0.20 mg mL^{-1} Kt was found to be higher than the case attained in the absence of Kt under all irradiation time periods. 61% removal of UV_{365} and 55% removal of UV_{280} were recorded at the end of 20 minutes. While 66% of Color_{436} was removed in 20 minutes of irradiation period, 85% removal was achieved after 60 minutes. UV_{254} was removed from the suspension about 54% and 67% after 20 and 60 minutes irradiation times respectively. Furthermore, at the end of 90 minutes of irradiation time, $\leq 20\%$ of humic acid was found to be present as expressed by all of the specified UV-vis parameters. Under similar conditions, DOC removal could only reach to 54% following a rather slow mineralization rate.

In comparison to the SCoA_{436} , SUVA_{365} , SUVA_{280} and SUVA_{254} parameters for the photocatalytically treated humic acid samples in the presence of 0.10 mg mL^{-1} Kt, no significant change was observed with respect to time in the presence of 0.20 mg mL^{-1} Kt. All of these parameters decreased with increasing irradiation time. Lowest SCoA_{436} , SUVA_{365} , SUVA_{280} and SUVA_{254} values were obtained for 90 min irradiation time as expected. SUVA_{254} value was found to be 3.65 for the photocatalytically treated humic acid samples in the presence of 0.20 mg mL^{-1} Kt under 90 minutes irradiation time. The reason could also be attributed to the oxidation induced structural changes rather than DOC removal.

Although, a general trend could not be observed for $\text{SFI}_{\text{emis},455}$ and $\text{SFI}_{\text{emis},460}$ parameters, $\text{SFI}_{\text{syn},475}$ decreased with increasing irradiation time for the photocatalytically treated humic acid samples in the presence of 0.20 mg mL^{-1} Kt. The lowest $\text{SFI}_{\text{syn},475}$ were calculated for reaction period of $t_{\text{irr}} = 90 \text{ min}$ with respect to the other specific FI

parameters, however, significantly higher $SFI_{emis,455}$, $SFI_{emis,460}$ values were attained for 90 min irradiation time.

Table 4.15. Specified and specific UV-vis and fluorescence parameters of humic acid in the presence of 0.20 mg mL^{-1} kaolinite recorded during photocatalytic degradation.

Specified UV-vis and fluorescence parameters and DOC								
	UV-vis Spectroscopic parameters, cm^{-1} DOC, mg L^{-1}					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 475 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.18	96.93	62.351
HA,rf	0.200	0.411	0.947	1.098	16.48	121.80	106.51	56.486
Irradiation Time, min								
Time 0	0.118	0.250	0.597	0.691	11.05	143.805	112.739	42.332
20	0.081	0.182	0.466	0.552	9.84	183.963	133.916	32.857
40	0.058	0.140	0.394	0.476	9.21	246.934	175.885	29.841
60	0.036	0.099	0.323	0.395	9.01	280.960	205.411	26.086
90	0.013	0.047	0.192	0.247	6.78	237.914	177.236	14.637
Specific UV-vis and fluorescence parameters, $\text{m}^{-1}\text{mg}^{-1}\text{L}$								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	$SFI_{emis,455}$	$SFI_{emis,460}$	$SFI_{syn,475}$	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
Irradiation Time, min								
Time 0	1.07	2.26	5.40	6.25	1301.40	1020.27	383.10	
20	0.83	1.85	4.74	5.61	1869.54	1360.94	333.91	
40	0.63	1.52	4.27	5.17	2681.15	1909.72	324.01	
60	0.40	1.10	3.58	4.38	3118.32	2279.82	289.52	
90	0.20	0.70	2.83	3.65	3509.05	2614.10	215.88	

4.1.7. Effect of Ca^{2+} on the photocatalytic degradation of humic acid and clay system

It was previously shown that the presence of Ca^{2+} ions in HA solution resulted in structural changes through bridging and re-conformation of humic moieties (Engebretson and von Wandruszka, 1998; Wall and Choppin 2003; Sutton and Sposito, 2006). Preliminary experiments designed in a sequential addition mode were performed for the understanding of the prevailing interactions and extent of coverage of the oxide surface. Considering that 31% DOC (43% Color_{436} , and 36% UV_{254}) was removed by the sole addition of TiO_2 , primary addition of Ca^{2+} to the HA solution prior to the introduction of TiO_2 caused an enhancement (58%) in the removal of DOC (88% Color_{436} , and 77% UV_{254}). However in case that, Ca^{2+} ions were added after addition of TiO_2 , electrostatic interactions prevailed primarily between humic sub-fractions and TiO_2 surface followed by successive interaction of Ca^{2+} ions and the remaining fraction of the negatively charged TiO_2 surface and humic moieties (<15% in all UV-vis parameters). In both cases, the question of whether Ca^{2+} acts as bridge between oxide surface and humic moieties or Ca-humate was directly attracted to the oxide surface remained to be solved.

Moreover, as a result of the dark interactions of HA, Mt, and TiO_2 , 34% DOC (53% Color_{436} , and 43% UV_{254}) was removed. In case that “HA and Ca^{2+} ” complex formed first and exposed to TiO_2 followed by addition of Mt, 63% DOC (85% Color_{436} , and 70% UV_{254}) removal was attained in a reasonable fashion to the addition sequence of HA and Ca^{2+} , TiO_2 and Mt. However, if Mt was introduced first to the HA solution followed by addition of TiO_2 and Ca^{2+} , 59% DOC (75% Color_{436} , and 53% UV_{254}) removal was attained. Moreover, upon introduction of TiO_2 to the HA solution followed by addition of Mt and Ca^{2+} resulted in removal of 47% DOC (58% Color_{436} , and 48% UV_{254}).

These results indicated that surface interactions of HA and TiO_2 was affected extensively (20%) by the addition of Mt and/or Ca^{2+} . Therefore, the presence of Ca^{2+} could significantly influence the HA reactivity in photocatalysis by acting as a cementing cation (Majzik and Tombácz, 2007a and 2007b). Similar interactions could also be assessed in a lesser degree in the presence of Kt. Based on these results; photocatalytic degradation experiments were performed by sequential addition of Ca^{2+} , Mt or Kt and TiO_2 to

the HA solution without any pre-equilibration period but maintaining sufficient surface coverage to fulfill the basic requirements of the surface oriented nature of photocatalysis.

To display a basis for comparison, Ca^{2+} loading effect on sole HA was also presented. For simplicity purposes pCa term defined as $\text{pCa} = -\log \text{Ca}^{2+}$ was used. Decreasing pCa resulted in an increasing trend in initial adsorptive uptake of HA as expressed by all of the specified UV-vis parameters ($> 30\%$) and DOC ($> 20\%$) (Figure 4.34 A-C). During the early stages of photocatalytic treatment (t_{irr} up to 20 min) at which an adsorption-desorption phase prevailed, significant enhancements in the removal percentages of all of the HA parameters (59% Color_{436} , 46% UV_{254} , and 35% DOC) were observed. Upon irradiation period of 60 minutes, considerably higher photocatalytic removal of HA was observed as expected (80% Color_{436} , 62% UV_{254} , and 46% DOC). A slight improvement was attained (i.e. $t_{\text{irr}} = 60$ minutes) as 90% Color_{436} , 74% UV_{254} , and 55% DOC in the presence of $\text{pCa} = 3.5$. However, no significant enhancement could be observed for the photocatalytic degradation of sole HA upon decreasing pCa.

In the presence of Mt, decreasing pCa resulted in an increasing trend in initial adsorptive uptake of HA as expressed by all of the specified UV-vis parameters ($> 10\%$) and DOC ($> 8\%$) being comparatively lower than the observed removal efficiencies attained for sole HA. During the early stages of the photocatalytic treatment ($t_{\text{irr}} = 20$ min), the presence of Mt slightly enhances the removal of HA as expressed by all of the specified parameters. Upon irradiation period of 60 minutes, considerably higher removal of HA was attained under all pCa conditions in the presence of Mt with respect to sole HA. The overall effect of decreasing pCa could be considered as a slight enhancement in the photocatalytic removal of HA. These results could also be considered in agreement with those findings achieved in a study performed for elucidation of interaction between HA and Mt in the presence of calcium ions (Majzik and Tombácz 2007a and 2007b).

A similar trend could also be visualized for the photocatalytic degradation of HA in the presence of Kt for varying pCa conditions. The removal efficiencies could be considered as comparable to those attained both in the presence of Mt and sole HA.

However, it could also be stated that under $pCa=3.5$ conditions, slight variations could be reported for UV-vis parameters upon irradiation period of 60 minutes in comparison to the results attained under adsorption-desorption phase prevailing for 20 minutes of irradiation period. An overall deviation in DOC removal could be presented as $\pm 4\%$ irrespective of the solution matrix and photocatalytic treatment conditions. Moreover, the removal of humic parameters followed the decreasing trend of $Color_{436} > UV_{254} > DOC$. The presence of Ca^{2+} ions in the specified concentration range slightly altered the photocatalytic degradation efficiency of HA.

The effect of Ca^{2+} ions could be evaluated through the pH dependent surface charge formation on the TiO_2 oxide surface as well as on the Mt and Kt surface groups with reference to the respective pH_{zpc} conditions (Table 3.1). Divalent cation-humic interaction occurring through chelation could also dominate over the Ca^{2+} - particle- particle interactions as verified by the respective DOC removal data. The resulting effect could be due to the partition of Ca^{2+} ions between the in-situ formed negatively charged species in the reaction medium. Considering the surface oriented nature of photocatalysis, as a prerequisite condition, the TiO_2 surface should be partially covered by humic fractions with a free space for sufficient light absorption leading to the formation of the reactive oxidizing species.

Moreover, under the photocatalytic degradation conditions, the reaction medium should be regarded as unsteady due to photoadsorption and photodesorption of both oxidized and native humic fractions. The successive utilization of the light intensity could lead to a comparatively higher degradation efficiency of HA in the presence of Ca^{2+} ions regardless of the type of the clay mineral. Ca loading effect should be considered as a slight enhancement irrespective of the type of the clay mineral. It should also be mentioned that the selected range of pCa would induced a solution matrix effect rather than leading to an effective coagulation and/or aggregation of the medium constituents (Majzik and Tombácz, 2007b). Therefore, the attained results could be attributed to the divalent cation induced alterations in humic conformational structures subjected to non selective oxidation.

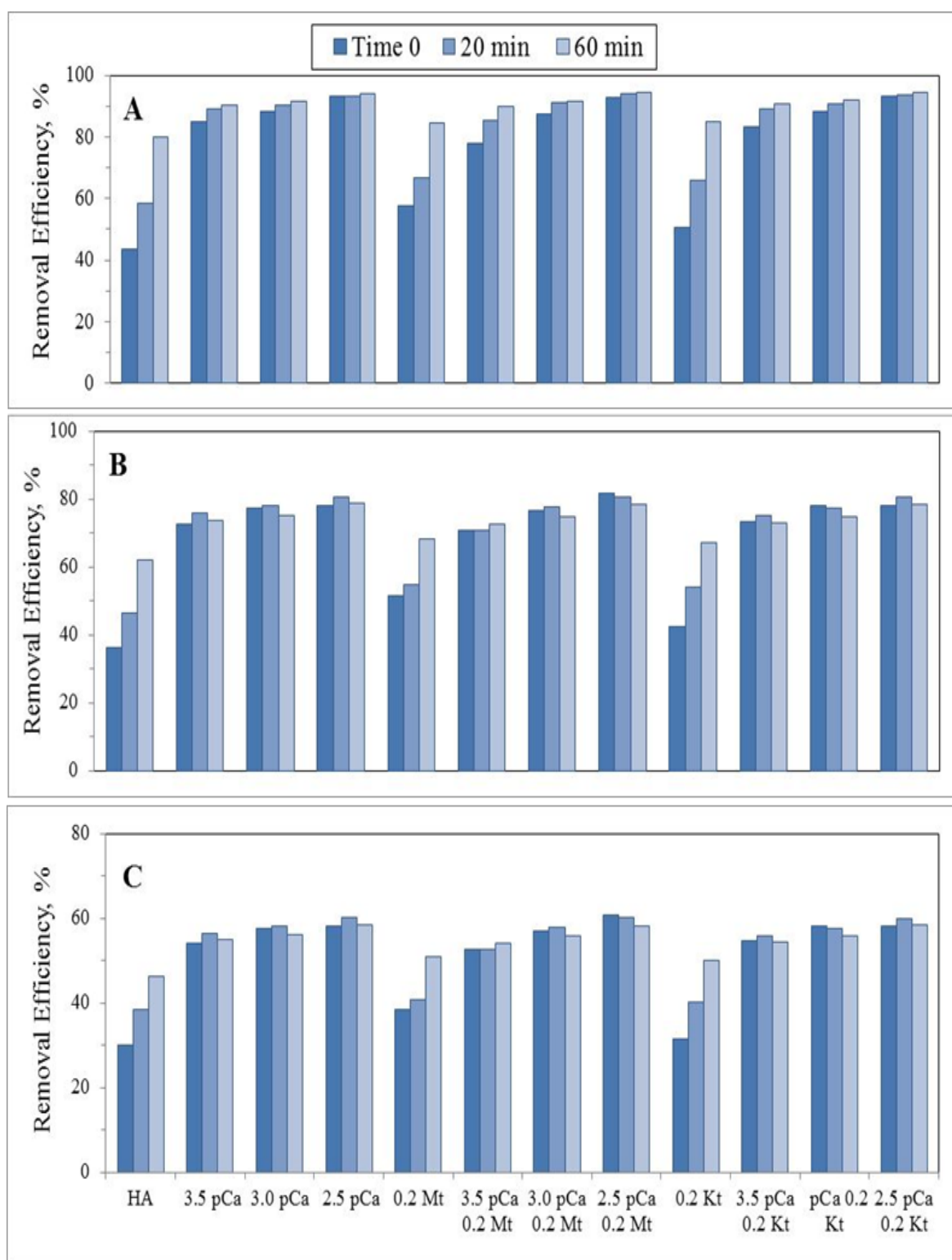


Figure 4.34. Effect of pCa (pCa: 3.5-2.5) on the photocatalytic removal efficiency of humic acid both in the presence and absence of clay minerals with respect to time (0.20 mg mL⁻¹ montmorillonite or kaolinite), A: Color₄₃₆, B: UV₂₅₄, and C: DOC.

4.1.8. Evaluation of humic acid photocatalytic oxidation by UV-vis absorption spectra

Under photocatalytic oxidation conditions, the UV-vis spectral properties of humic acid retained the basic declining features (Uyguner Bekbolet 2005a). For comparison purposes, the UV-vis spectra were displayed for sole HA (A) and HA in the presence of Mt (B) and Kt (C) under photocatalytic oxidation conditions (Figure 4.35 1A-C). In general, UV-vis spectra of humic acid retained the logarithmic declining trend being different in absorbance magnitudes and irrespective of the applied reaction conditions.

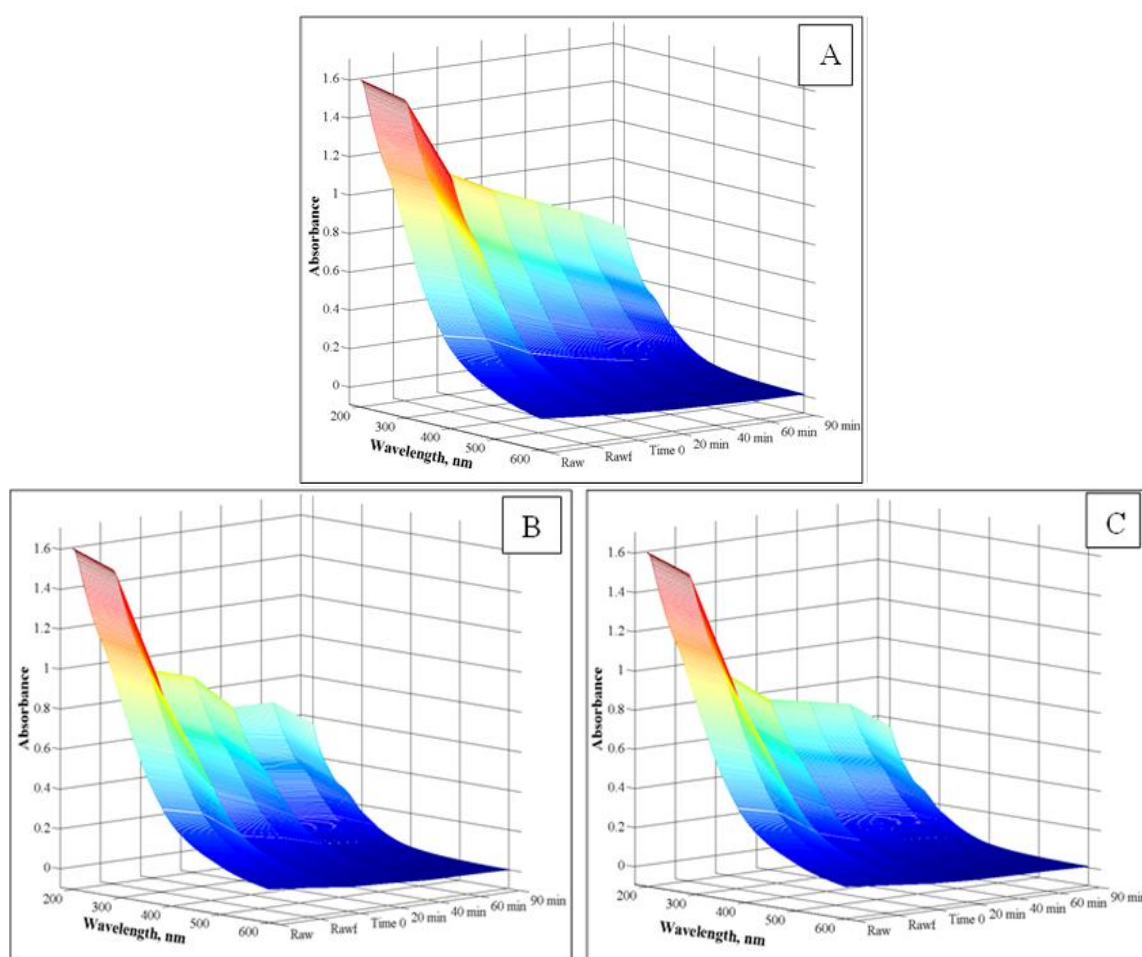


Figure 4.35. UV-vis absorption profiles of (A) humic acid (B) humic acid and montmorillonite, 0.1 mg mL⁻¹, (C) humic acid and kaolinite, 0.10 mg mL⁻¹. Prior to and after photocatalysis (PC, irradiation time: 0-60 min). For comparison purposes, samples were also presented followed by filtration through 0.45 μ m membrane filters (f). TiO₂ loading was kept constant as 0.50 mg mL⁻¹.

Bearing in mind that filtration through 0.45 μm membrane filters consisted the major step of sample preparation following photocatalytic treatment and prior to the characterization analyses, the UV-vis spectra of humic acid (raw) and filtered humic acid (Rawf) were also given (Figure 4.35 A-C). Followed by photocatalysis (e.g. irradiation period of 60 min), oxidized humic acids also retained the featureless declining trend. Since the figure covered only one single dose of clay mineral (0.10 mg mL^{-1}), it should be indicated that the UV-vis spectral shapes were under consideration rather than the extent of absorptivities that were obviously dose dependent. The consistency attained in the UV-vis spectral shapes indicated the possibility of the implementation of the specific as well as the fractional UV-vis parameters for the elucidation of the photocatalytic oxidation of humic acid under the specified experimental conditions.

4.1.8.1. Evaluation of humic acid photocatalytic oxidation by specific UV-vis absorbance parameters. As a basis to photocatalytic degradation, baseline and preliminary interactions were evaluated to express adsorptive interactions as well as photolytic removals. All of the specific UV-vis parameters displayed slight variations irrespective of the prevailing interaction mechanisms resulting from both preliminary and baseline interactions (Figure 4.36 A-B). Dark interactions of humic acid and either montmorillonite or kaolinite binary systems expressed lowest SCoA, and SUVA₃₆₅ whereas highest SUVA₂₈₀ and SUVA₂₅₄ were obtained upon dark interactions of humic acid and kaolinite binary system in the presence of TiO₂. Considerably higher SUVA₂₈₀ and SUVA₂₅₄ indicated the dominating aromatic character of the residual humic acid fractions. The binary and ternary surface interactions resulted in successive removal of color forming moieties rather than the counterpart inner structural core aromatic domains with respect to the removals of DOC under the specified experimental conditions. A plausible reason could be attributed to the prevailing electrostatic attractions between the charged humic functional groups and exposed surfaces of TiO₂, Mt and Kt.

Changes attained in the specific UV-vis parameters were also followed during photocatalytic degradation of humic acid both in the presence and absence of clay particles. It was observed that the removal of the specific UV-vis parameters revealed a logarithmic profile that could be successfully mimicked by a first order kinetic decay model ($r^2 > 0.80$) (Table 4.16). The possible role of the clay dose (0.05 mg mL^{-1} ,

0.10 mg mL⁻¹ and 0 mg mL⁻¹) due to the presence of expanded surface exposed to the humic fractions was also presented. The expected effect could possibly be related to the enhanced adsorptive interactions related to the increased surface area comprised of TiO₂ as well as Mt and Kt.

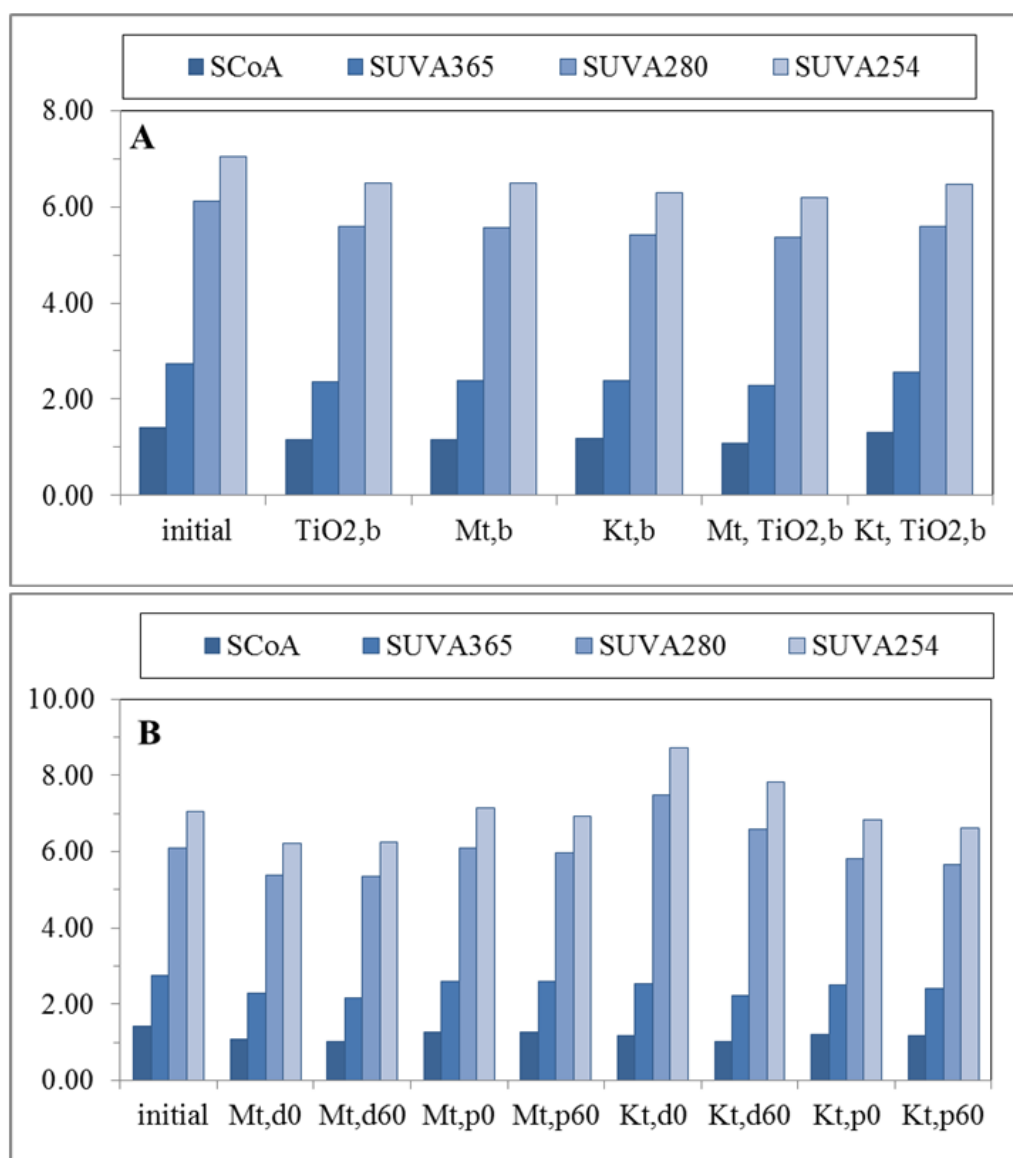


Figure 4.36. Removal of specific UV-vis parameters of humic acid by baseline (A) and preliminary interactions (B) both in the presence and absence of clay minerals i.e. montmorillonite/kaolinite. Humic acid: 50 mg mL⁻¹, montmorillonite: 0.10 mg mL⁻¹; kaolinite: 0.10 mg mL⁻¹, TiO₂: 0.5 mg mL⁻¹, b: baseline interactions, d: dark interactions (time, 0 and 60 min) and p: photolytic interactions (irradiation time; 0 and 60 min).

Table 4.16. Photocatalytic first order kinetic decay model rate constant ($k \times 10^{-3}$, min^{-1}) of the specific UV-vis parameters of HA both in the presence and absence of either montmorillonite or kaolinite.

Rate constant, $k \times 10^{-3}$, min^{-1}				
	SUVA ₂₅₄	SUVA ₂₈₀	SUVA ₃₆₅	SCoA
HA	4.78	5.68	10.53	13.94
Mt dose				
0.05 mg mL^{-1}	5.73	6.45	11.02	14.81
0.10 mg mL^{-1}	6.33	7.26	13.35	18.66
0.20 mg mL^{-1}	8.00	9.18	15.06	19.21
Kt dose				
0.05 mg mL^{-1}	8.17	9.35	14.93	18.87
0.10 mg mL^{-1}	6.24	7.23	11.70	15.07
0.20 mg mL^{-1}	7.09	8.23	14.83	21.25

Contrary to the effect observed in the presence of Kt, increasing Mt dose significantly affected the removal of the specific UV-vis parameters in a consistent trend. Regarding the different morphological properties of the clay minerals, it could be deduced that the mechanism of photocatalytic degradation proceeded through dissimilar pathways. On the other hand, photocatalytic degradation of sole humic acid displayed a consistent increasing trend for the removal of color forming groups being faster with respect to the removal of the UV absorbing centers in accordance with the DOC removals.

4.1.8.2. Evaluation of humic acid degradation by fractional UV-vis parameters. Absorption of UV light by HA is caused by π -electrons and expresses conjugated aromatic systems, whereas functional groups with quinoide structures and keto-enol-systems are more responsible for the visible light absorption (Uyguner and Bekbolet, 2005b). Various absorption wavelengths at 254, 280, 365, 436 and 465 nm as well as ratios like E2/E3 (e.g. $\text{UV}_{254}/\text{UV}_{365}$), E3/E4 (e.g. $\text{UV}_{365}/\text{UV}_{436}$) have been reported as suitable parameters the spectral differentiation of humic substances (Uyguner and Bekbolet, 2005a and 2005b). In

a similar manner, E_{254}/E_{365} ; E_{254}/E_{436} ; E_{280}/E_{365} ; E_{280}/E_{436} , and E_{365}/E_{436} parameters have been selected for the differentiation of the prevailing systems under various conditions (Figure 4.37).

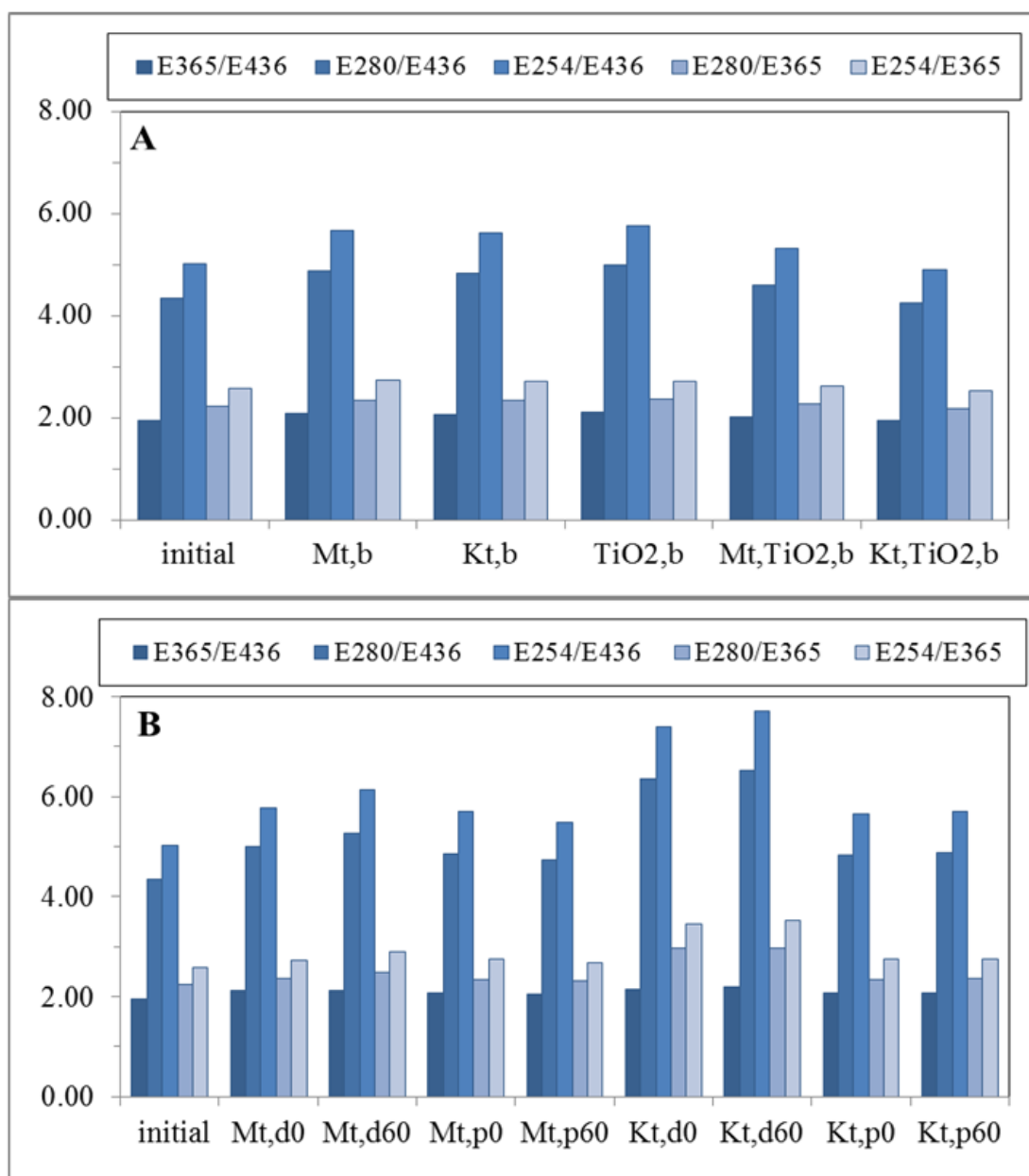


Figure 4.37. Removal of fractional UV-vis parameters of humic acid by baseline (A) and preliminary (B) interactions both in the presence and absence of clay minerals i.e. montmorillonite/kaolinite. HA: 50 mg mL⁻¹, Mt: 0.10 mg mL⁻¹; Kt: 0.10 mg mL⁻¹, TiO₂: 0.5 mg mL⁻¹, b: baseline interactions, d: dark interactions (time, 0 and 60 min) and p: photolytic interactions (irradiation time; 0 and 60 min).

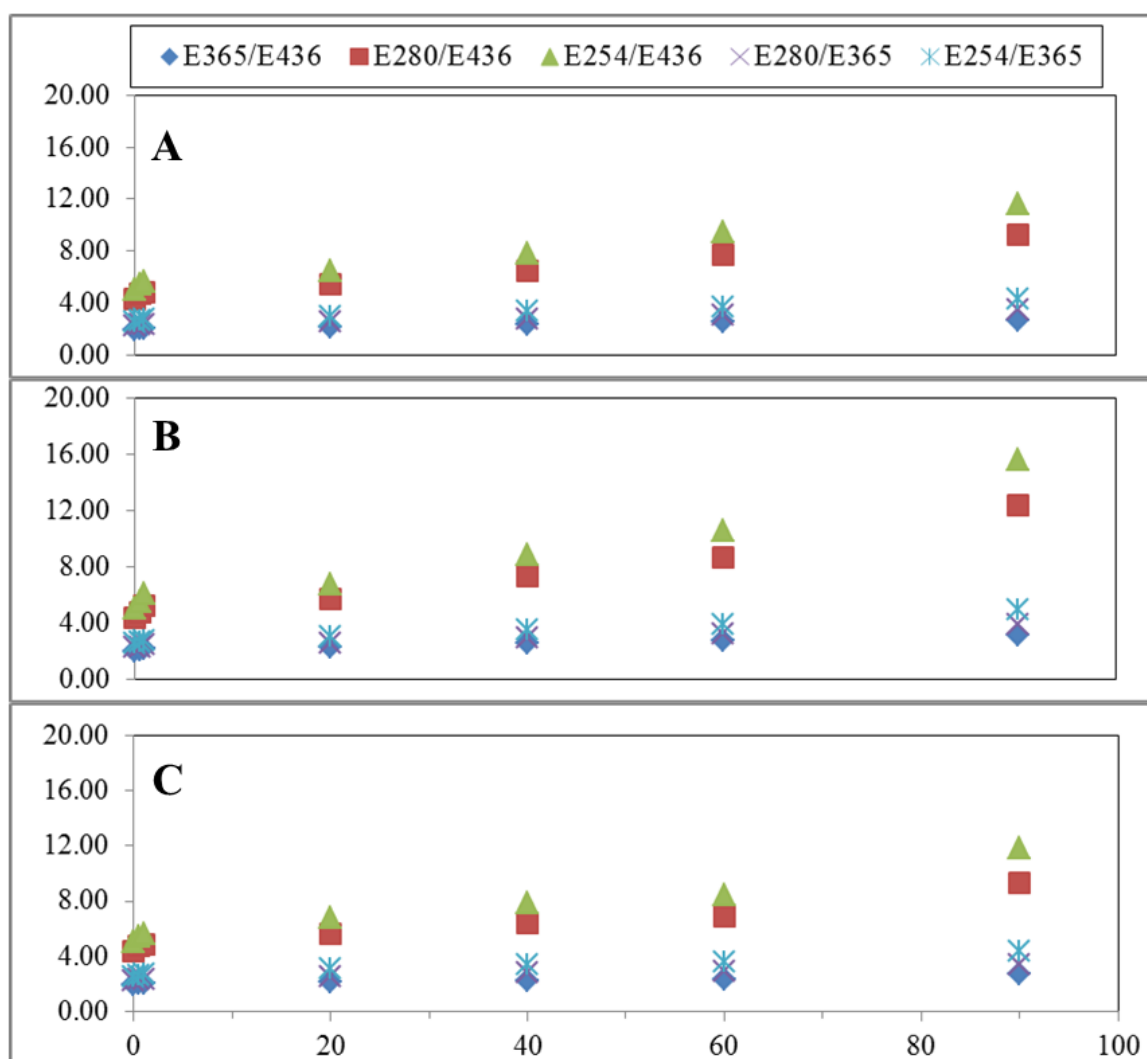


Figure 4.38. A-C. Change of fractional UV-vis parameters of humic acid with respect to irradiation time (x axis: irradiation time 0-90 min) both in the presence and absence of clay minerals i.e. montmorillonite/kaolinite. A: humic acid, B: humic acid and montmorillonite, and C: humic acid and kaolinite. Humic acid: 50 mg mL^{-1} , montmorillonite: 0.10 mg mL^{-1} , kaolinite: 0.10 mg mL^{-1} , TiO_2 : 0.5 mg mL^{-1} .

Figure 4.38 A demonstrated the changes attained in the fractional UV-vis parameters of HA. $\text{E}_{254}/\text{E}_{436}$ and $\text{E}_{280}/\text{E}_{436}$ ratios displayed the most significant variations under baseline conditions. The reason could be attributed to the predominant role of the aromatic domains represented by UV_{254} and UV_{280} parameters with respect to the color forming moieties (Color_{436}). Similar trend could also be visualized for the fractional UV-vis parameters of humic acid by preliminary experiments. Upon irradiation (t, 0-60 min) in the

absence of TiO_2 , comparatively similar changes in the fractional UV-vis parameters of humic acid were attained in the presence of either Mt or Kt expressing the sole photolytic behavior of humic acid irrespective of the aqueous medium constituents. However, due to the prevailing adsorption phenomena, time dependent changes in the humic fractional UV-vis parameters could be deduced being more significant in the presence of Kt with respect to the effect observed in the presence of Mt revealing the significant discriminative role of the surface properties of the clay minerals.

Furthermore, selected fractional UV-vis parameters were also followed with respect to irradiation time during photocatalysis (Figure 4.38 A-C). The most significant differences were attained for E_{254}/E_{436} and E_{280}/E_{436} revealing a differentiation between humic acid and humic acid-clay binary systems. The reason could be attributed to the prevailing competitive adsorption mechanism due to presence of TiO_2 and either Mt or Kt. Depending on the irradiation conditions, both the unoxidized as well as the oxidized humic fractions could possibly be attracted to the exposed oxide surfaces and further removed through filtration following photocatalytic treatment.

Although the presented figure (Figure 4.38 A-C) displays only one single dose of clay particles, in the presence of other doses of clay particles (0.05 mg mL^{-1} and 0.20 mg mL^{-1}), similar results were also attained. Correlation between fractional UV-vis and specific UV-vis parameters: UV-vis absorptions measured at 365 and 446 nm (E_3 and E_4 , respectively) and their ratio (E_3/E_4) were presented with respect to the changes attained in the respective specific UV-vis parameters as SCoA and SUVA_{365} . These two variables displayed the following tendency as the higher the specific absorption, the lower was the E_3/E_4 absorption ratio for humic acids (Artinger et al., 2000).

The observed phenomenon was attributed to a possible indication of an increasing aromaticity and molecular weight of humic acids. The overall evaluation would indicate the persistence of basic humic properties rather than the formation of lower molecular weight oxidized and more fulvic like structure with reference to the expected range of $E_{365}/E_{436} > 4$. The relationships were displayed where E_{365}/E_{436} and E_{254}/E_{436} were correlated with the respective specific UV-vis parameters as SCoA, SUVA_{365} and SUVA_{254} (Figure 4.39 A-B).

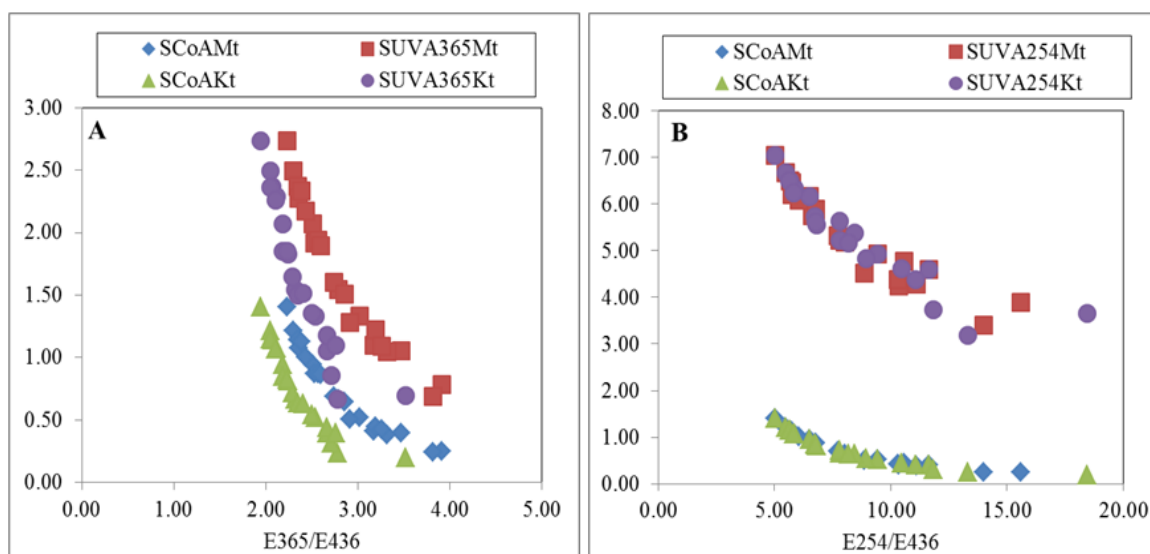


Figure 4.39. A: Specific SCoA and SUVA₃₆₅ variation with respect to E₃₆₅/E₄₃₆ ratio of humic acid and B: Specific SCoA and SUVA₂₅₄ variation with respect to E₂₅₄/E₄₃₆ ratio of humic acid in the presence of montmorillonite or kaolinite upon photocatalysis irrespective of clay dose and irradiation conditions.

E₃₆₅/E₄₃₆ ratio displayed a discriminative behavior with respect to SUVA₃₆₅ and SCoA values of the clay minerals either for Mt or Kt. However, the variations observed in SCoA and SUVA₂₅₄ with respect to E₂₅₄/E₄₃₆ did not reveal any significant difference from clay type point of view. Moreover, the attained data could well be modeled by a linear relationship irrespective of the clay type;

$$\text{SUVA}_{254} = -0.12 (\text{E}_{254}/\text{E}_{436}) + 1.81 \quad r^2 = 0.84 \quad (4.1)$$

$$\text{SCoA} = -0.11 (\text{E}_{254}/\text{E}_{436}) + 1.72 \quad r^2 = 0.80 \quad (4.2)$$

In the presence of montmorillonite, SCoA and SUVA₃₆₅ relationships with respect to E₃₆₅/E₄₃₆ could be expressed by the following equations (Equations 4.3 and 4.4)

$$\text{SCoA} = -0.65 (\text{E}_{365}/\text{E}_{436}) + 2.58 \quad r^2 = 0.89 \quad (4.3)$$

$$\text{SUVA}_{365} = -1.16 (\text{E}_{365}/\text{E}_{436}) + 4.95 \quad r^2 = 0.91 \quad (4.4)$$

In the presence of kaolinite, SCoA and SUVA₃₆₅ relationships with respect to E₃₆₅/E₄₃₆ could be expressed by the following equations (Equations 4.5 and 4.6)

$$\text{SCoA} = -0.85 (E_{365}/E_{436}) + 2.78 \quad r^2 = 0.80 \quad (4.5)$$

$$\text{SUVA}_{365} = -1.51 (E_{365}/E_{436}) + 5.28 \quad r^2 = 0.80 \quad (4.6)$$

Moreover, in the presence of montmorillonite, SCoA and SUVA₂₅₄ relationships with respect to E_{254}/E_{436} could be expressed by the following equations (Equations 4.7 and 4.8)

$$\text{SCoA} = -0.11 (E_{254}/E_{436}) + 1.64 \quad r^2 = 0.895 \quad (4.7)$$

$$\text{SUVA}_{254} = -0.32 (E_{254}/E_{436}) + 8.07 \quad r^2 = 0.91 \quad (4.8)$$

Also, in the presence of kaolinite, SCoA and SUVA₂₅₄ relationships with respect to E_{254}/E_{436} could be expressed by the following equations (Equations 4.9 and 4.10)

$$\text{SCoA} = -0.09 (E_{254}/E_{436}) + 1.54 \quad r^2 = 0.79 \quad (4.9)$$

$$\text{SUVA}_{254} = -0.29 (E_{254}/E_{436}) + 7.84 \quad r^2 = 0.82 \quad (4.10)$$

Regarding the close similarities of the coefficients of equations 4.7 and 4.9 and equations 4.8 and 4.10, the attained overall data could well be modeled by a linear relationship irrespective of the clay type as given in below equations 11 and 12.;

$$\text{SCoA} = -0.11 (E_{254}/E_{436}) + 1.72 \quad r^2 = 0.80 \quad (4.11)$$

$$\text{SUVA}_{254} = -0.32 (E_{254}/E_{436}) + 8.29 \quad r^2 = 0.84 \quad (4.12)$$

It is noteworthy to indicate that the correlation of SCoA and SUVA₂₅₄ parameters with respect to E_{254}/E_{436} did not reveal any significant difference from clay type point of view. Therefore, both SCoA and SUVA₃₆₅ parameters could well be correlated with E_{365}/E_{436} to express the discrimination of the effects of the different clay minerals. It should also be mentioned that neither irradiation period nor dose of the clay minerals contribute remarkably on the correlation. As a conclusive remark, color forming moieties (Color₄₃₆) as well as the UV absorbing centers at near visible wavelength (UV₃₆₅) as related to the DOC removals could serve as a differentiation factor for the assessment of the effects of the clay minerals on the photocatalytic degradation of humic acids.

4.1.9. Kinetic evaluation of the photocatalytic degradation of humic acid in the presence clay minerals

In relation to the UV-vis and fluorescence spectroscopic characterization presented under appropriate subheadings for humic acid both the presence and absence of clay minerals i.e. montmorillonite and kaolinite, photocatalytic degradation data were also processed using pseudo first order kinetic model. For the assessment of the photocatalytic degradation of humic acid (50 mg L^{-1}) photocatalyst loading was kept constant as 0.50 mg mL^{-1} in the presence of Mt and Kt concentrations of which were selected as 0.05 mg mL^{-1} , 0.10 mg mL^{-1} and 0.20 mg mL^{-1} .

It is very well documented that many organic compounds more specifically natural organic matter (humic acid) present in the illuminated titanium dioxide slurry undergo many chain and consecutive oxidation reactions. In an ideal case, all intermediate compounds are expected to be fully mineralized to carbon dioxide and water (Carp et al., 2004). However, under any specified experimental condition and irradiation period, the resultant solutions would contain a measurable amount of organic content either expressed by UV-vis parameters or by DOC. Photocatalytic degradation of humic acid displayed a logarithmic decay profile as explained in detail in the previous part. Moreover, photocatalytic degradation of humic substances is reported to obey pseudo first order kinetic model (Bekbolet et al., 1998; Bekbolet et al., 2002).

Pseudo first order kinetic model is expressed by the following equation;

$$R = -dC/dt = k C \quad (4.13)$$

The terms represent the following meanings;

R: Pseudo first order rate in terms of the specified UV-vis parameters ($\text{m}^{-1} \text{ min}^{-1}$) or DOC ($\text{mg L}^{-1} \text{ min}^{-1}$).

C: Specified UV-vis parameters i.e. Color_{436} , UV_{365} , UV_{280} and UV_{254} (m^{-1}) or DOC (mg L^{-1})

t: Irradiation period (min) and

k: Pseudo first order reaction rate constant (min^{-1}).

The related half life, $t_{1/2}$ (min) values could also be assessed by the Equation (4.14);

$$t_{1/2} = 0.693/k \quad (4.14)$$

According to the data obtained by the photocatalytic degradation experiments, pseudo first order reaction rate constants, half-life values and rates are calculated and presented with the related correlation coefficients ($r^2 \geq 0.70$) in respective tables (Tables 2.9-2.11).

4.1.9.1. Kinetic modeling of photocatalytic degradation of raw humic acid. Photocatalytic removal data attained both for UV-vis parameters and DOC of raw humic acid displayed the expected declining profile with respect to the applied irradiation periods (Figure 4.40) (Bekbolet, 1996). The kinetic evaluation of the experimental data achieved up to 60 min for the photocatalytic degradation of raw humic acid revealed the following pseudo first order kinetic model (Equation 2.1) parameters for Color_{436} , UV_{365} , UV_{280} and UV_{254} as presented in Table 4.17.

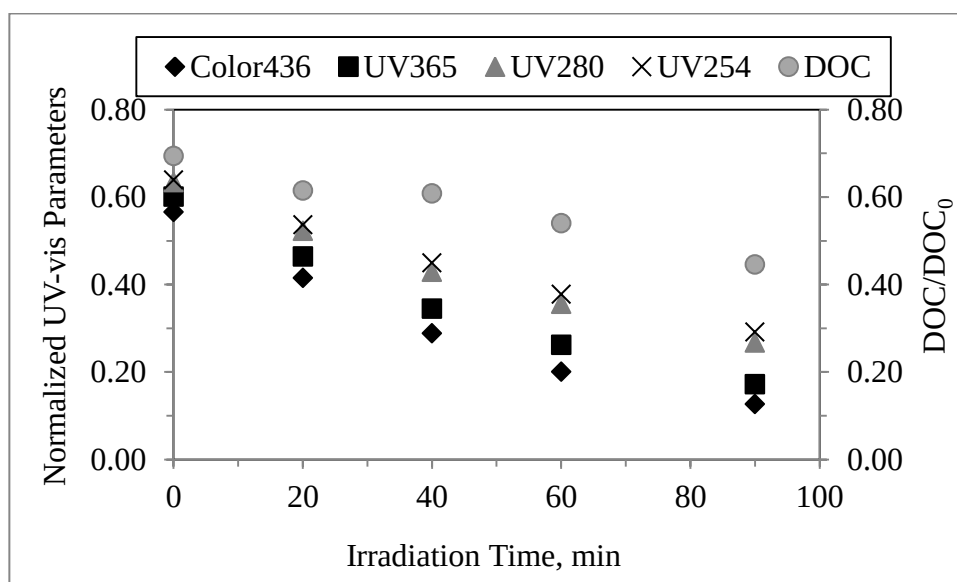


Figure 4.40. Photocatalytic degradation of humic acid illustrated by normalized specified UV-vis spectroscopic parameters (Color_{436} , UV_{365} , UV_{280} and UV_{254}) correlated with DOC removal.

Table 4.17. Pseudo first order kinetic model parameters for the photocatalytic degradation of humic acid.

Kinetic parameters	Specified UV-vis parameters				DOC
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	
k, $\times 10^{-2}$, min^{-1}	2.49	1.83	1.35	1.09	0.841
$t_{1/2}$, min	28	38	51.5	64	82.5
R^* , $\text{m}^{-1}\text{min}/\text{mg L}^{-1} \text{min}^{-1}$	0.595	0.850	1.40	1.31	0.143

R^* calculated for humic acid; Color₄₃₆: 0.239 cm^{-1} , UV₃₆₅: 0.465 cm^{-1} , UV₂₈₀: 1.038 cm^{-1} , UV₂₅₄: 1.199 cm^{-1} and DOC: 17.00 mg L^{-1} .

Pseudo first order degradation rate constants (k , min^{-1}) were found to be 2.49×10^{-2} , 1.83×10^{-2} , 1.35×10^{-2} and 1.09×10^{-2} for the UV-vis parameters specified as Color₄₃₆, UV₃₆₅, UV₂₈₀, and UV₂₅₄. Considerably lower rate constant (k , min^{-1}) as 0.841×10^{-2} for DOC was calculated. The removal of color forming moieties (Color₄₃₆) was found to be relatively faster than the UV absorbing centers ($\sim > 30\%$) as expressed by UV₂₈₀ and UV₂₅₄. (Uyguner and Bekbolet 2005a), studied several model humic acids and presented the pseudo first order rate constants k (min^{-1}) for HA humic acid removal to be decreasing in the range of 2.98×10^{-2} to 2.01×10^{-2} for specified UV-vis parameters of Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄. The observed trend could be regarded as in accordance with the previously reported findings of Bekbolet and co-workers (Uyguner and Bekbolet 2005a and 2005b).

The corresponding half-life ($t_{1/2}$, min) values were found to be in the range of 28-82.5 min. As could be deduced both by the pseudo first order kinetic model rate constants and the related half-life conditions, DOC removal was found to be significantly slower than the UV-vis spectroscopic parameters. The reason could be attributed to the structural and conformational changes in humic moieties attained by photocatalytic degradation however, the condition might not successively lead to oxidative mineralization as

expressed by DOC contents. Moreover, photocatalytic degradation rates (R , $\text{m}^{-1} \text{min}^{-1} // \text{mg L}^{-1} \text{min}^{-1}$) were calculated by using the kinetic rate equation (4.13) and expressed by the decreasing order of $\text{UV}_{280} > \text{UV}_{254} > \text{UV}_{365} > \text{Color}_{436} > \text{DOC}$. The trend observed in photocatalytic degradation rates should be cautiously interpreted due to the effect of the initial contents of the respective parameters that were used in calculations.

4.1.9.2. Kinetic modeling of photocatalytic degradation of raw humic acid in the presence of montmorillonite. The kinetic evaluation of the experimental data for the photocatalytic oxidation of raw humic acid in the presence of $0.05\text{--}0.20 \text{ mg mL}^{-1}$ Mt revealed the degradation profiles with respect to irradiation periods as presented in Figures 4.41–4.43. The exponential decreasing trends attained for the studied binary systems signified a similar reaction mechanism prevailing under all conditions. Application of the pseudo first order kinetic model could possibly lead to a comparative evaluation of the photocatalytic degradation efficiencies for the elucidation of effect of the montmorillonite. Referring to the previously presented photocatalytic degradation kinetic model parameters of raw humic, the following table presents the kinetic model parameters attained in the presence of Mt (Tables 4.18)

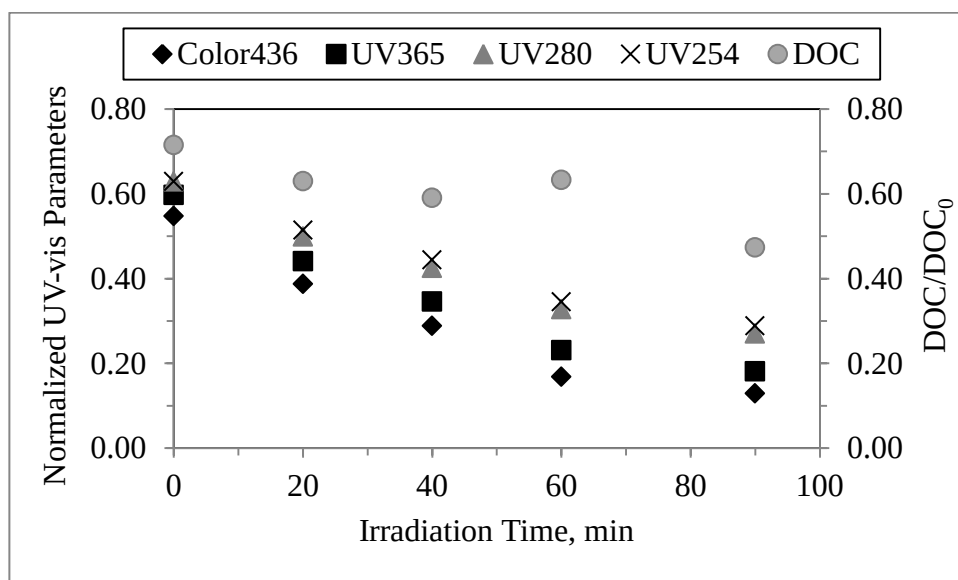


Figure 4.41. Photocatalytic degradation of humic acid in the presence of 0.05 mg mL^{-1} montmorillonite illustrated by normalized specified UV-vis spectroscopic parameters (Color_{436} , UV_{365} , UV_{280} and UV_{254}) correlated with DOC removal.

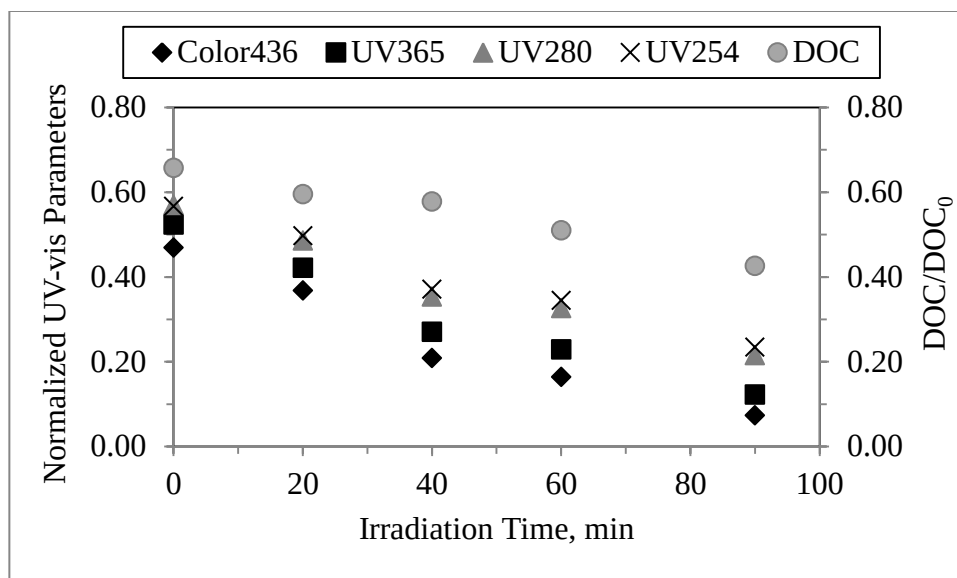


Figure 4.42. Photocatalytic degradation of humic acid in the presence of 0.10 mg mL⁻¹ montmorillonite illustrated by normalized specified UV-vis spectroscopic parameters (Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄) correlated with DOC removal.

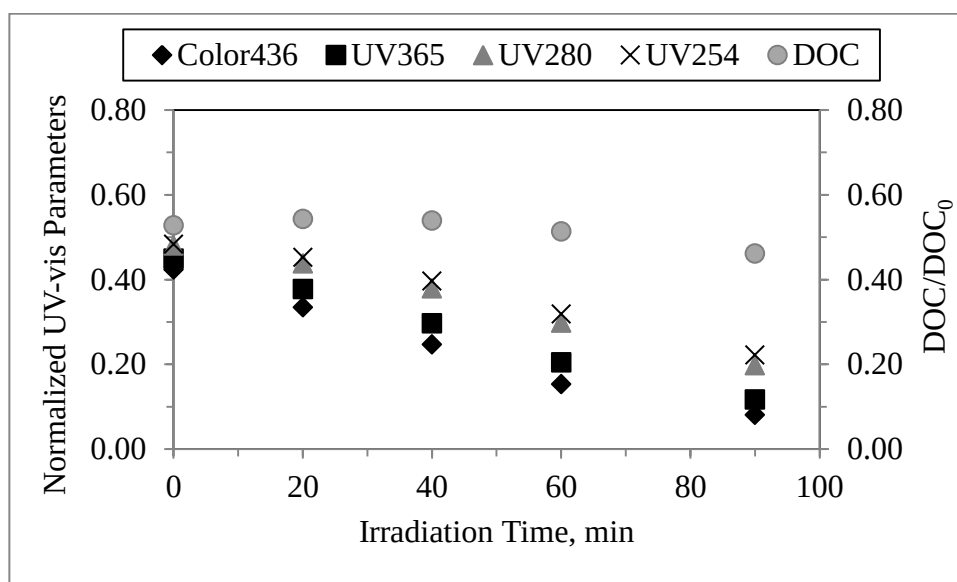


Figure 4.43. Photocatalytic degradation of humic acid in the presence of 0.20 mg mL⁻¹ montmorillonite illustrated by normalized specified UV-vis spectroscopic parameters (Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄) correlated with DOC removal.

In the presence of 0.05 mg mL^{-1} Mt, pseudo first order degradation rate constants (k , min^{-1}) were found to be 2.19×10^{-2} , 1.81×10^{-2} , 1.35×10^{-2} , 1.28×10^{-2} and 0.672×10^{-2} for the UV-vis parameters specified as Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC, respectively. The corresponding half life ($t_{1/2}$, min) values were found to be in the range of 32-103.5 min. Photocatalytic degradation rates (R , $\text{m}^{-1} \text{ min}^{-1}$) were calculated by using the rate equation (2.1) expressed by removals in the decreasing order of $\text{UV}_{254} > \text{UV}_{280} > \text{UV}_{365} > \text{Color}_{436} > \text{DOC}$.

Table 4.18. Pseudo first order kinetic model parameters for the photocatalytic degradation of humic acid in the presence of montmorillonite.

	UV-vis parameters				
Kinetic parameters	Color_{436}	UV_{365}	UV_{280}	UV_{254}	DOC
HA and 0.05 mg mL^{-1} Mt binary system					
$k, \times 10^{-2}, \text{min}^{-1}$	2.19	1.81	1.35	1.28	0.672
$t_{1/2}, \text{min}$	32	38.5	51.5	54	103.5
$R, \text{m}^{-1} \text{ min}^{-1} / \text{mg L}^{-1} \text{ min}^{-1}$	0.523	0.841	1.40	1.53	0.114
HA and 0.1 mg mL^{-1} Mt binary system					
$k, \times 10^{-2}, \text{min}^{-1}$	2.72	2.17	1.56	1.49	0.833
$t_{1/2}, \text{min}$	25.5	32	44.5	46.5	83.5
$R, \text{m}^{-1} \text{ min}^{-1} / \text{mg L}^{-1} \text{ min}^{-1}$	0.650	1.01	1.62	1.79	0.141
HA and 0.20 mg mL^{-1} Mt binary system					
$k, \times 10^{-2}, \text{min}^{-1}$	2.62	2.21	1.63	1.51	0.711
$t_{1/2}, \text{min}$	26.5	31.5	42.5	46	98
$R, \text{m}^{-1} \text{ min}^{-1} / \text{mg L}^{-1} \text{ min}^{-1}$	0.626	1.03	1.69	1.81	0.121

Humic acid; Color_{436} : 0.239 cm^{-1} , UV_{365} : 0.465 cm^{-1} , UV_{280} : 1.038 cm^{-1} , UV_{254} : 1.199 cm^{-1} and DOC: 17.00 mg L^{-1} .

Upon a substantial increase in the Mt concentration to 0.10 mg mL^{-1} photocatalytic degradation data revealed the pseudo first order degradation rate constants (k , min^{-1}) as 2.72×10^{-2} , 2.17×10^{-2} , 1.56×10^{-2} , 1.49×10^{-2} and 0.833×10^{-2} for the UV-vis parameters specified as Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC, respectively. The removal of color forming moieties was found to be relatively faster than the UV absorbing centers ($> 35\%$) as expressed by UV_{280} and UV_{254} . The corresponding half life ($t_{1/2}$, min) values were found to be in the range of 25.5-83.5 min. The effect of 0.10 mg mL^{-1} Mt on the photocatalytic degradation performance of humic acid could be regarded as significant for Color_{436} , UV_{365} , UV_{280} and UV_{254} whereas enhancement in the removal rate could not be indicated for DOC.

The kinetic evaluation of the experimental data for the photocatalytic degradation of humic acid in the presence of 0.20 mg mL^{-1} Mt revealed the following pseudo first order kinetic model parameters for Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC as presented in Table xxx. Pseudo first order degradation rate constants (k , min^{-1}) were found to be 2.62×10^{-2} , 2.21×10^{-2} , 1.63×10^{-2} , 1.51×10^{-2} and 0.711×10^{-2} for the UV-vis parameters specified as Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC, respectively. The corresponding half life ($t_{1/2}$, min) values were in the range of 26.5-98 min. Photocatalytic degradation rates (R , $\text{m}^{-1} \text{ min}^{-1}$) were calculated by using the rate equation (2.1) expressed by the decreasing order of $\text{UV}_{254} > \text{UV}_{280} > \text{UV}_{365} > \text{Color}_{436}$.

DOC removal rates could be expressed by the following order representing an inconsistent role of Mt concentration on the degradation rate of humic acid;

$$\text{HA} = \text{HA and } 0.10 \text{ mg mL}^{-1} \text{Mt} > \text{HA and } 0.2 \text{ mg mL}^{-1} \text{Mt} > \text{HA and } 0.05 \text{ mg mL}^{-1} \text{Mt}$$

Photocatalytic degradation rate constants calculated for the specified UV-vis parameters indicated similar relativities expressing the role of complexation resulting in conformational alterations. These changes in binary system structure might lead to the formation of new sites available to TiO_2 surface interactions. The effect of the presence of 0.20 mg mL^{-1} Mt on the photocatalytic degradation performance of humic acid could be considered as significant for UV-vis parameters whereas contributing 0.20 mg mL^{-1} Mt to the system lead to decreasing of rate constant for DOC.

4.1.9.3. Kinetic modeling of photocatalytic degradation of raw humic acid in the presence of kaolinite. The kinetic evaluation of the experimental data for the photocatalytic degradation of raw humic acid in the presence of $0.05\text{--}0.20\text{ mg mL}^{-1}$ Kt revealed the following decaying profiles with respect to irradiation periods as presented in Figures 4.44–4.46. The respective pseudo first order kinetic model parameters for Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC were presented in Table 4.19.

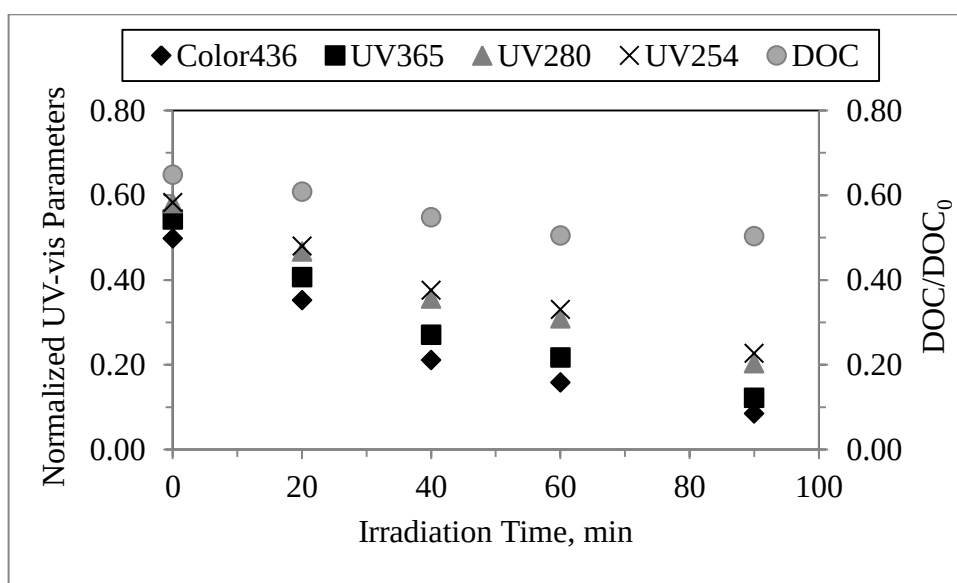


Figure 4.44. Photocatalytic degradation of humic acid in the presence of 0.05 mg mL^{-1} kaolinite illustrated by normalized specified UV-vis spectroscopic parameters (Color_{436} , UV_{365} , UV_{280} and UV_{254}) correlated with DOC removal.

In the presence of 0.05 mg mL^{-1} Kt pseudo first order degradation rate constants (k , min^{-1}) were found to be 2.57×10^{-2} , 2.17×10^{-2} , 1.60×10^{-2} , 1.50×10^{-2} and 0.683×10^{-2} for the UV-vis parameters specified as Color_{436} , UV_{365} , UV_{280} , UV_{254} and DOC, respectively.

The corresponding half life ($t_{1/2}$, min) values were in the range of 27–102 min. Photocatalytic degradation rates (R , $\text{m}^{-1}\text{ min}^{-1}$) were calculated by using the rate equation (2.1) expressed by removals in the decreasing order of $\text{UV}_{254} > \text{UV}_{280} > \text{UV}_{365} > \text{Color}_{436}$. Photocatalytic degradation rate of humic acid in the presence of 0.05 mg mL^{-1} Kaolinite $\text{DOC}_R = 0.114\text{ mg L}^{-1}\text{ min}^{-1}$ being lower than the rate attained for sole of humic acid $\text{DOC}_R = 0.143\text{ mg L}^{-1}\text{ min}^{-1}$.

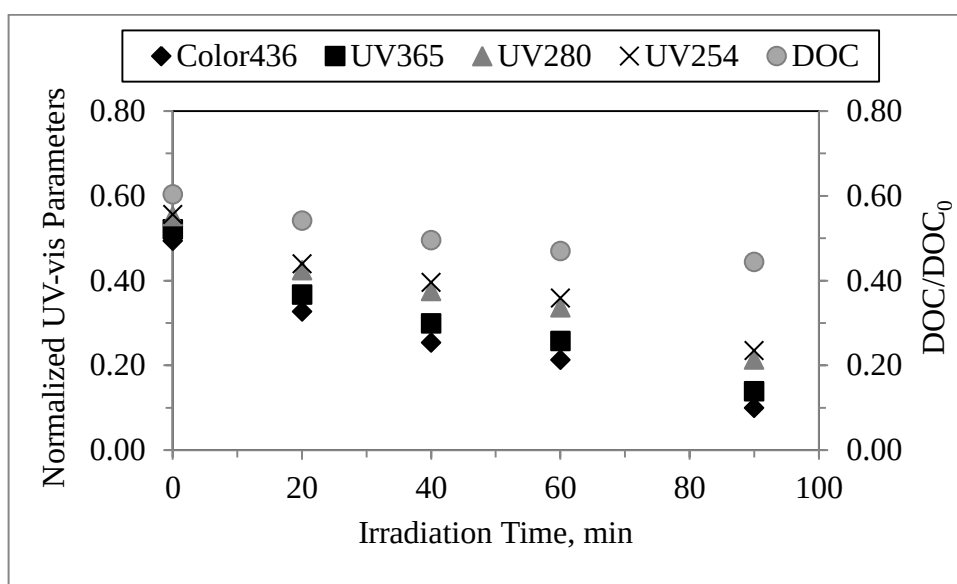


Figure 4.45. Photocatalytic degradation of humic acid in the presence of 0.10 mg mL⁻¹ kaolinite illustrated by normalized specified UV-vis spectroscopic parameters (Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄) correlated with DOC removal.

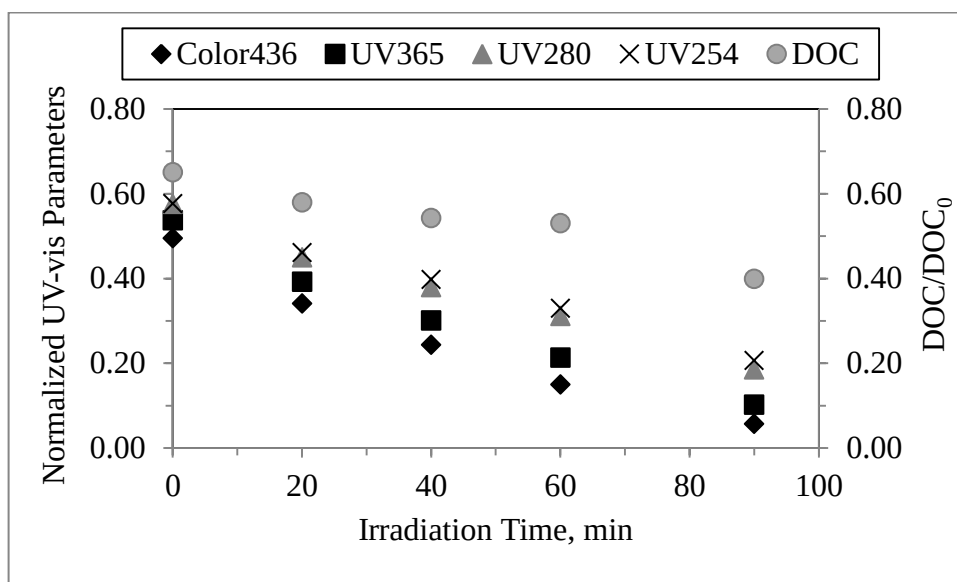


Figure 4.46. Photocatalytic degradation of humic acid in the presence of 0.20 mg mL⁻¹ kaolinite illustrated by normalized specified UV-vis spectroscopic parameters (Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄) correlated with DOC removal

Table 4.19. Pseudo first order kinetic model parameters for the photocatalytic degradation of humic acid in the presence of 0.05-0.20 mg mL⁻¹ kaolinite.

	UV-vis parameters				DOC
Kinetic parameters	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	
HA and 0.05 mg mL ⁻¹ Kt binary system					
k, x10 ⁻² , min ⁻¹	2.57	2.17	1.60	1.50	0.683
t _{1/2} , min	27	32	42	46	102
R, m ⁻¹ min//mg L ⁻¹ min ⁻¹	0.614	1.008	1.672	1.798	0.116
HA and 0.10 mg mL ⁻¹ Kt binary system					
k, x10 ⁻² , min ⁻¹	2.28	1.94	1.49	1.40	0.773
t _{1/2} , min	30	36	46.5	49.5	90
R, m ⁻¹ min//mg L ⁻¹ min ⁻¹	0.545	0.902	1.547	1.678	0.131
HA and 0.20 mg mL ⁻¹ Kt binary system					
k, x10 ⁻² , min ⁻¹	2.99	1.81	1.21	1.58	0.762
t _{1/2} , min	23	38	57	44	91
R, m ⁻¹ min//mg L ⁻¹ min ⁻¹	0.714	0.841	1.256	1.894	0.129

Humic acid; Color₄₃₆: 0.239 cm⁻¹, UV₃₆₅: 0.465 cm⁻¹, UV₂₈₀:1.038 cm⁻¹, UV₂₅₄: 1.199 cm⁻¹ and DOC: 17.00 mg L⁻¹.

Upon a substantial increase in the Kt concentration to 0.10 mg mL⁻¹ photocatalytic degradation data revealed the pseudo first order degradation rate constants (k, min⁻¹) as 2.28x10⁻², 1.94x10⁻², 1.49x10⁻², 1.40x10⁻² and 0.773x10⁻² for the UV-vis parameters specified as Color₄₃₆, UV₃₆₅, UV₂₈₀, UV₂₅₄ and DOC, respectively. The removal of color forming moieties was found to be relatively faster than the UV absorbing centers (> 35%) as expressed by UV₂₈₀ and UV₂₅₄. The corresponding half life (t_{1/2}, min) values were found to be in the range of 30-90 min. The effect of 0.10 mg mL⁻¹ Kt on the photocatalytic degradation performance of humic acid could be regarded as significant for Color₄₃₆,

UV₃₆₅, UV₂₈₀ and UV₂₅₄ whereas enhancement in the removal rate could not be indicated for DOC.

The kinetic evaluation of the experimental data for the photocatalytic degradation of humic acid in the presence of 0.20 mg mL⁻¹ Kt revealed the following pseudo first order kinetic model parameters for Color₄₃₆, UV₃₆₅, UV₂₈₀, UV₂₅₄ and DOC as presented in Table 4.19. Pseudo first order degradation rate constants (k, min⁻¹) were found to be 2.99x10⁻², 1.81x10⁻², 1.21x10⁻², 1.58x10⁻² and 0.762x10⁻² for the UV-vis parameters specified as Color₄₃₆, UV₃₆₅, UV₂₈₀, UV₂₅₄ and DOC, respectively. The corresponding half life (t_{1/2}, min) values were in the range of 23-91 min. Photocatalytic degradation rates (R, min⁻¹) were calculated by using the rate equation (4.13) expressed by the decreasing order of UV₂₅₄ > UV₂₈₀ > UV₃₆₅ > Color₄₃₆. DOC removal rates could be expressed by the following order representing an inconsistent role of Kt concentration on the degradation rate of humic acid;

$$HA = HA \text{ and } 0.10 \text{ mg mL}^{-1}Kt > HA \text{ and } 0.20 \text{ mg mL}^{-1}Kt > HA \text{ and } 0.05 \text{ mg mL}^{-1}Kt$$

Photocatalytic degradation rate constants calculated for the specified UV-vis parameters indicated similar relativities expressing the role of complexation resulting in conformational alterations. These changes in binary system structure might lead to the formation of new sites open to TiO₂ surface interactions. The effect of the presence of 0.20 mg mL⁻¹ Kt on the photocatalytic degradation performance of humic acid could be considered as significant for UV-vis parameters whereas contributing 0.20 mg mL⁻¹ Kt to the system lead to decreasing of rate constant for DOC.

4.1.9.4. Comparative evaluation of kinetic modeling of the photocatalytic oxidation of humic acid in the presence of clay minerals. The interactive systems composed of humic acid, TiO₂ and Mt/Kt were defined by binary systems i.e. “humic acid and Mt”; “humic acid and Kt”; “humic acid and TiO₂” and ternary systems i.e. “humic acid, Mt and TiO₂” and “humic acid, Kt and TiO₂”. Adsorptive interactions were assessed by baseline experiments performed under dark conditions (Section 4.1.1). Besides the removal of UV-vis parameters in a consistent trend of Color₄₃₆ > UV₃₆₅ > UV₂₈₀ > UV₂₅₄ irrespective of the system under consideration, DOC exhibited system dependent varying removal

efficiencies. An insignificant DOC removal as $< 6\%$ was attained due to exposure of humic acid with either Mt or Kt. However, upon instantaneous introduction of TiO_2 to humic acid solution (time = 0), DOC removal was 30% and in case of ternary systems due to the presence of clay particles slight variations were attained as $\pm 10\%$. Moreover, further time periods as 60 minutes did not significantly alter the DOC removal efficiencies. The reason could be attributed to the formation of coating layers of humic acid sub-fractions on both clay minerals and oxide surfaces as expected (Zhou et al., 1994). On the other hand, photolytic interactions revealed only $< 10\%$ removal of DOC both for sole HA and binary systems composed HA and Mt or Kt through the experiments performed in the absence of TiO_2 (Section 4.1.2). In a similar fashion, upon irradiation very slight removal was observed for the UV-vis parameters of humic acid. Moreover, the presence of clay minerals did not significantly alter the removal of UV-vis parameters through photolytic interactions.

Photocatalytic oxidation of humic acid obeys pseudo first order kinetic model under all solution matrix conditions as reported and reviewed by Bekbolet and co-workers (Uyguner-Demirel and Bekbolet, 2011). Photocatalytic degradation of humic acid could also be expressed by surface area normalized rates eliminating the effect of the surface area and to form a basis for a sound comparison in the presence of various oxide surfaces delivering excess surface area for the interaction of the humic sub-fractions (Bekbolet et al., 2002). For comparative purposes, assuming that clay particles, TiO_2 particles and humic molecular size fractions could co-exist in the form of a discrete colloidal consortium, pseudo first order rate; R , ($\text{m}^{-1}\text{min}^{-1}$ for specified UV-vis parameters and $\text{mg L}^{-1}\text{min}^{-1}$ for DOC) could also be expressed in terms of areal rate; AR ($\text{m}^{-1}\text{min}^{-1}\text{m}^{-2}$ for specified UV-vis parameters and $\text{mg L}^{-1}\text{min}^{-1}\text{m}^{-2}$ for DOC) and specific rate; SR ($\text{m}^{-1}\text{min}^{-1}\text{g}^{-1}$ for specified UV-vis parameters and $\text{mg L}^{-1}\text{min}^{-1}\text{g}^{-1}$ for DOC).

First order rate, $R = -dC/dt = kC$ where, C denotes UV-vis parameters or DOC,

Areal rate, $AR = R/\text{total exposed surface area of } \text{TiO}_2 \text{ and Mt/Kt,}$

Specific rate, $SR = R/\text{total loading mass of } \text{TiO}_2 \text{ and Mt/Kt}$

It was evident that pseudo first order kinetic rate constants of the specified humic acid parameters displayed a general decreasing order of $\text{Color}_{436} > \text{UV}_{365} > \text{UV}_{280} \geq \text{UV}_{254} > \text{DOC}$ (Figure 4.47A). Referring to the expressed distribution profiles of the first order rate constants, it could be visualized that the presence of neither Mt nor Kt did not exhibit a distinctly apparent trend. Removal of color forming moieties of humic acid (Color_{436}) was found to be significantly faster under all conditions representing the investigated dose range of clay minerals. UV_{365} removal rate constants were observed to display similar rates for “HA and 0.10 mg mL^{-1} Mt”, “HA and 0.20 mg mL^{-1} Mt” and “HA and 0.05 mg mL^{-1} Kt” binary systems in comparison to the Color_{436} removal rate constant of “HA and 0.05 mg mL^{-1} Mt” binary system. Moreover, in the presence of kaolinite, UV_{365} and UV_{280} parameters followed a dose dependent (0.05 mg mL^{-1} -0.20 mg mL^{-1}) decreasing profile contrary to the inconsistent effect observed for montmorillonite.

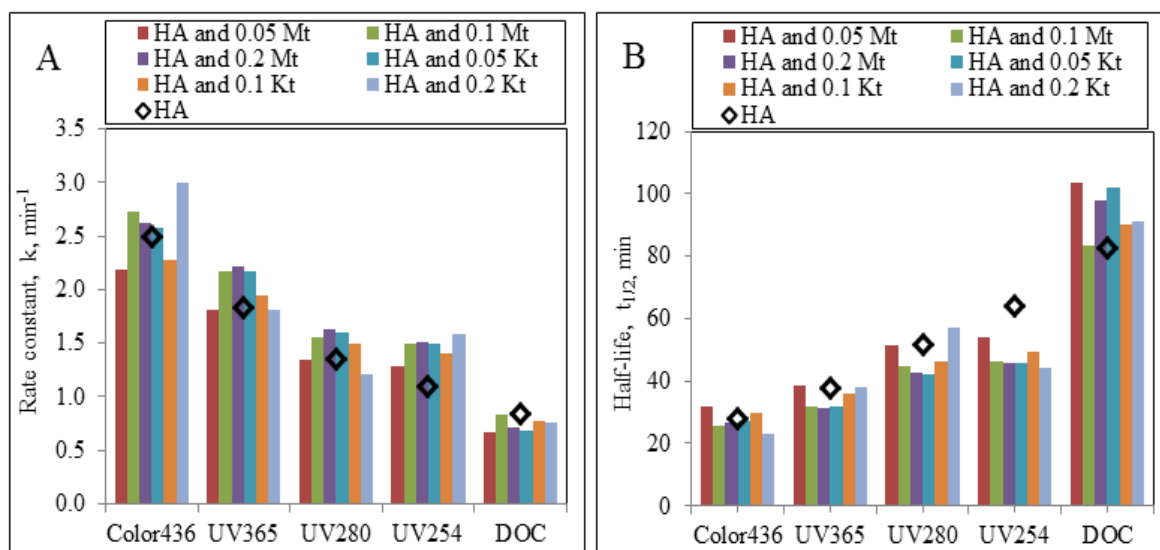


Fig. 4.47. Pseudo first order kinetic model parameters of photocatalytic degradation of humic acid in the presence of montmorillonite and kaolinite, A: rate constant, k (min^{-1}) and B: Half-life (min).

The highest kinetic rate constant was attained for Color_{436} ($k = 2.99 \times 10^{-2} \text{ min}^{-1}$) in the presence of 0.20 mg mL^{-1} Kt. Relatively similar kinetic pattern could be indicated for UV_{365} and UV_{280} in the presence of both montmorillonite and kaolinite. UV_{254} exhibited similar removal rate constants in the presence of higher doses of Mt and lower dose of Kt (0.05 mg mL^{-1}). The highest rate constant of UV_{254} was attained for “HA and 0.20

mg mL⁻¹ Kt” binary system. Furthermore, DOC removal rate constants could be visualized as almost similar under all conditions ($k_{av} = 0.752 \pm 0.8 \text{ min}^{-1}$) representing a plausible ineffective role of clay minerals on the photocatalytic degradation rate of humic acid. Correspondingly, half-life ($t_{1/2}$, min) conditions displayed similar pattern being most significantly higher for DOC of sole humic acid (Figure 4.4 7B). The lowest $t_{1/2}$ was attained for humic acid DOC ($t_{1/2} = 82.5 \text{ min}$) with respect to other conditions obtained for humic acid in the presence of both higher doses of Mt and also for all doses of Kt. From a general perspective, the effects of Mt and Kt on the photocatalytic degradation kinetics of humic acid could be visualized as very slight variations with no specific discrimination from clay type. It should also be stated that the results attained for the specified UV-vis parameters representing both the color forming moieties as well as the aromatic structural units of UV-absorbing centers should be regarded as significant insight information to the mineralization of the organic carbon contents.

By definition, first order kinetic rate is calculated by multiplication of the rate constant with the initial substrate concentration. As previously stated, degradation rates of UV-vis parameters of humic acid displayed an increasing trend by value with respect to the decreasing wavelength of the specified parameters i.e. 436 nm, 365 nm, 280 nm and 254 nm. Therefore, to present a sound basis of comparison, the effects of varying clay doses on the photocatalytic degradation rate of humic acid, UV-vis parameters were considered individually as Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄ in Figure 4.48 A, B, C, and D respectively. Photocatalytic mineralization rates (DOC) were also presented in Figure 4.48E. Referring to the differences in the surface area data of the clay specimens (Mt, BET surface area = $97 \text{ m}^2 \text{ g}^{-1}$ and Kt, BET surface area = $10 \text{ m}^2 \text{ g}^{-1}$), the respective areal rates (AR) and specific rates (SR) were discussed in comparison to the first order photocatalytic oxidation rates (R) (Figure 4.48 A-E).

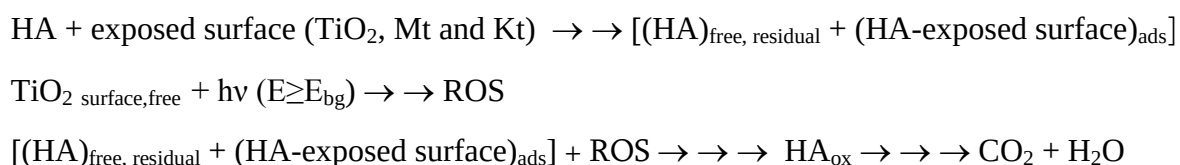
Highest Color₄₃₆ removal rate (R_{Color436}) was observed for humic acid in the presence of 0.20 mg mL^{-1} Kt and lower rate was achieved for “HA and 0.05 mg mL^{-1} Mt” binary system. Surface area normalized rates, AR_{Color436} displayed the highest case for “HA and 0.20 mg mL^{-1} Kt” binary system and the lowest for “HA and 0.20 mg mL^{-1} Mt” binary system. With respect to the loading mass of total solid surfaces, the highest specific rate (SR_{Color436}) was attained for “HA and 0.05 mg mL^{-1} Kt” binary system and the lowest

SR_{Color436} for “HA and 0.20 mg mL⁻¹ Mt” binary system. Removal rate of UV₃₆₅ (R_{UV365}) was observed to be higher for “HA and 0.20 mg mL⁻¹ Mt” binary system and the lowest attained rate was for both “HA and 0.05 mg mL⁻¹ Mt” and “HA and 0.20 mg mL⁻¹ Kt” binary systems. Areal rates (AR_{UV365}) were found to be comparatively higher for humic acid in the presence of varying doses of Kt with respect to the effect observed for humic in the presence of Mt. Moreover, SR_{UV365} displayed the highest rate for “HA and 0.05 mg mL⁻¹ Kt” binary system and the lowest also for “HA and 0.20 mg mL⁻¹ Kt” binary system. UV₂₈₀ removal (R_{UV280}) expressed almost equal rates for HA, “HA and 0.05 mg mL⁻¹ Mt” binary system and “HA and 0.20 mg mL⁻¹ Kt” binary system. Considerably similar rates ($\pm$ 5%) were also attained for “HA and 0.10 mg mL⁻¹ Mt” binary system, “HA and 0.20 mg mL⁻¹ Mt” binary system, “HA and 0.05 mg mL⁻¹ Kt” binary system, and “HA and 0.10 mg mL⁻¹ Kt” binary system. AR_{UV280} exhibited a similar trend with AR_{UV365} for all of the studied experimental conditions. Dose dependent variations were observed for SR_{UV280} of humic acid in the presence of Mt in comparison to the consistent decreasing profile of SR_{UV280} of humic acid in the presence of Kt. UV₂₅₄ removal rate (R_{UV254}) displayed an increasing trend as HA < “HA and 0.05 mg mL⁻¹ Mt” binary system < “HA and 0.10 mg mL⁻¹ Kt” binary system < “HA and 0.10 mg mL⁻¹ Mt” binary system $\leq$ “HA and 0.05 mg mL⁻¹ Kt” binary system $\leq$ “HA and 0.20 mg mL⁻¹ Kt” binary system and < “HA and 0.20 mg mL⁻¹ Kt” binary system. Lower doses of Mt as 0.05 mg mL⁻¹- 0.10 mg mL⁻¹ did not significantly affect the areal rate of HA (AR_{UV254}) whereas an inconsistent trend was observed for areal rate of UV₂₅₄ in the presence of varying doses of Kt. SR_{UV254} rates displayed a consistent decreasing trend with respect to increasing Kt doses. The lowest SR_{UV254} was attained in the presence of 0.20 mg mL⁻¹ Mt at which both the exposed surface and the amount of dose were significantly higher than the remaining conditions.

Photocatalytic mineralization rate (R_{DOC}) was found to be highest for sole HA and lowest for “HA and 0.05 mg mL⁻¹ Mt” binary system. Inconsistent trend could be expressed for the effect of Mt dose, however in increasing trend could be expressed for “HA and 0.05 mg mL⁻¹ Kt” binary system < “HA and 0.20 mg mL⁻¹ Kt” binary system $\leq$ “HA and 0.10 mg mL⁻¹ Kt” binary system. The lowest AR_{DOC} was attained for “HA and 0.20 mg mL⁻¹ Mt” binary system and the highest AR_{DOC} for sole HA. A slight retardation effect of Kt could also be regarded as dose independent with respect to the AR_{DOC} attained for sole HA. Highest removal of SR_{DOC} could be expressed for sole HA and the lowest for

“HA and 0.20 mg mL⁻¹ Mt” binary system. The presence of Kt affected the specific rate of DOC in the order of “HA and 0.20 mg mL⁻¹ Kt” binary system < “HA and 0.05 mg mL⁻¹ Kt” binary system < “HA and 0.10 mg mL⁻¹ Kt” binary system.

Generally, photocatalytic oxidation of humic acid could be discussed with reference to the aqueous medium pH, respective pH_{zpc} conditions and surface area of the photocatalyst oxides. It could be visualized that under neutral pH reaction medium, the overall effect due to the pH_{zpc} conditions of TiO₂, Mt and Kt displaying similar surface species properties could be considered as insignificant (Figure 4.48A-E). Moreover, with respect to the expressed surface area differences being Mt almost tenfold greater than Kt, the rate dependency could be explained through the active roles of the functional groups in surface interactions. The remaining deprotonated functional groups could simply be used in surface interactions prevailing between humic sub-fractions and TiO₂ oxide surface (Tertre et al., 2006; Tombácz and Szekeres, 2006; Bourg et al., 2007). Moreover, the extension of the surface coverage should also be appropriate for the light absorption leading to the successful formation of the reactive oxygen species (ROS).



Referring to the previous findings, the surface charge of the oxide surfaces covering the clay particles were primarily dominated by the charges originating from the pH dependent deprotonation of the oxide (Tombácz et al., 1999). Moreover, a partitioning process could also be operating between humic sub-fractions and the surfaces of the clay particles and TiO₂ prior to-and during photocatalytic treatment (Zhou et al., 1994; Kretzschmar et al., 1999). The role of post treatment-adsorption conditions could also be effective on the experimental step of filtration for the achievement of the successful elimination of the suspended particles from the reaction medium. Based on the illustration of the degradation rates, it could be concluded that the surface properties of neither Mt nor Kt displayed a dose dependent significantly consistent trend towards photocatalytic oxidation.

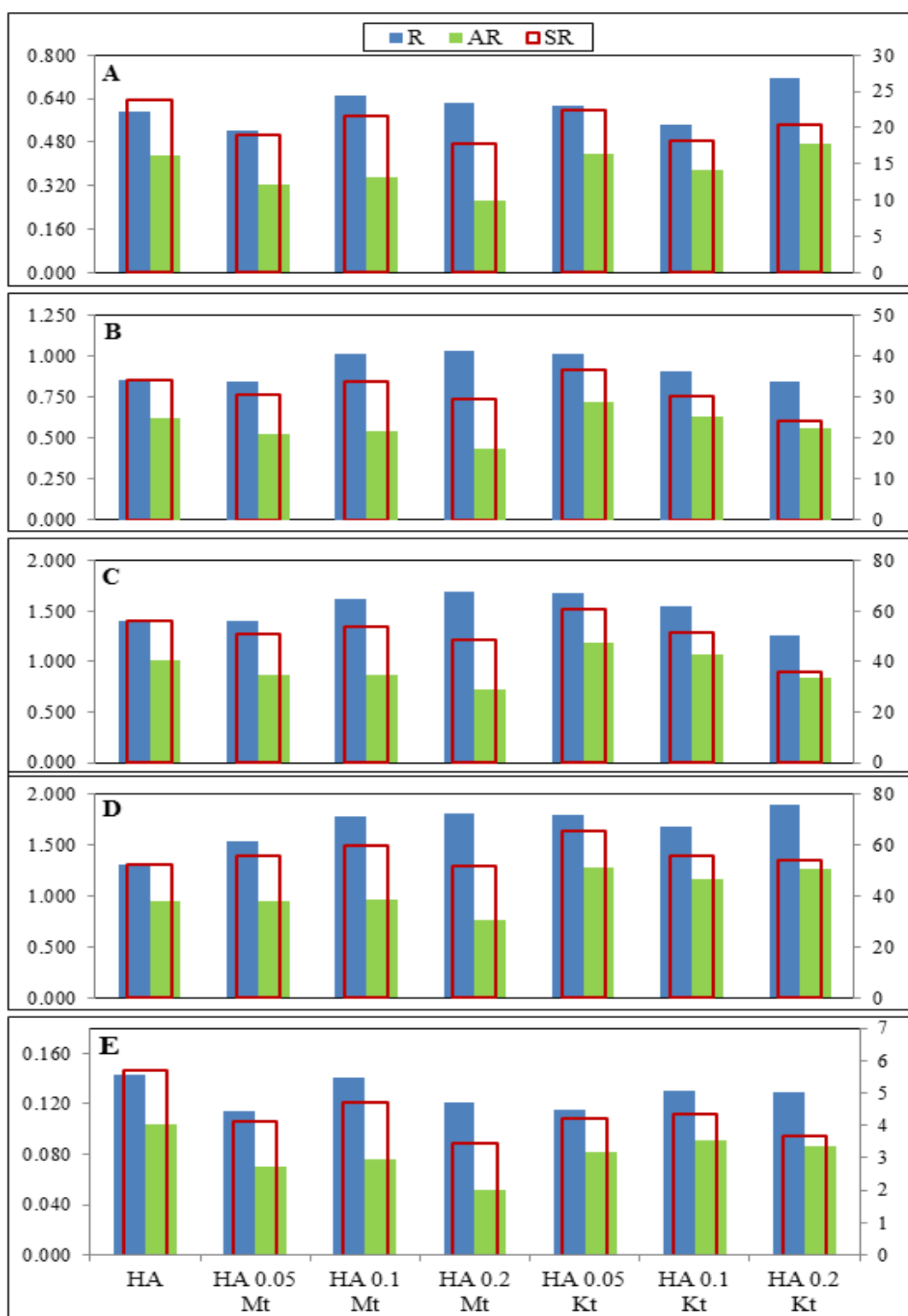


Figure 4.48. Comparative presentation of pseudo first order rates (R, left y-axis), areal rates (AR, left y-axis) and specific rates (SR, right y-axis) for the photocatalytic oxidation of humic acid in the presence and absence of montmorillonite and kaolinite A: Color₄₃₆, B: UV₃₆₅, C: UV₂₈₀, D: UV₂₅₄ and E: DOC.

4.1.10. SEM analysis prior to and following photocatalysis

Surface interactions of HA in binary and ternary systems could be assessed by SEM analysis performed on the samples attained under the indicated conditions (Figure 4.4 A-F). Sole TiO_2 particles displayed quite similar particles in size and shape as expected (Yalcin et al., 2010; Murcia-López et al., 2012). The SEM image obtained for “HA and TiO_2 ” displayed a structure composed of comparatively large embedded humic regions surrounded by TiO_2 particles (Figure 4.49 A and B) (Chen et al., 2007). Regarding the distinctly different surface morphologies of Mt and Kt, the corresponding EDX-analysis showed the presence of both clay particles as well as TiO_2 (Figure 4.49 C and D) (Wang et al., 2011).

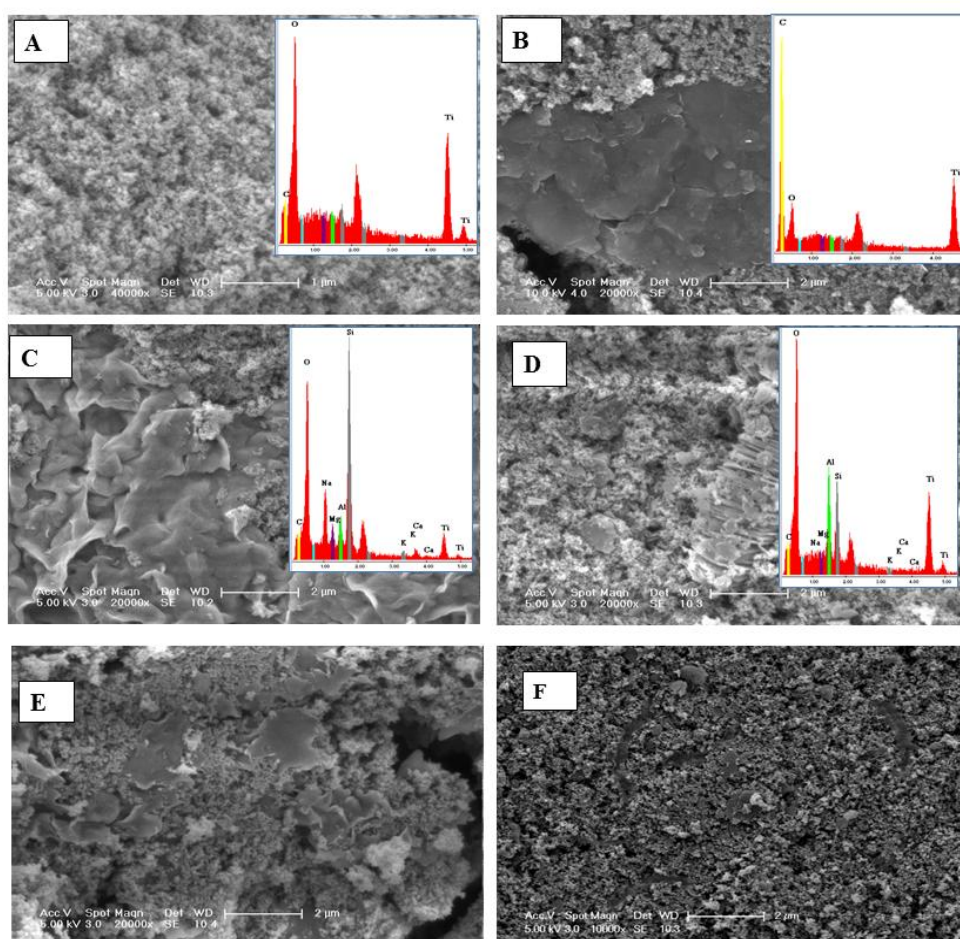


Figure 4.49. A-F SEM images of sole TiO_2 (A), TiO_2 and humic acid (B), TiO_2 and montmorillonite (C), TiO_2 and kaolinite (D), TiO_2 , montmorillonite and humic acid (E), TiO_2 , kaolinite and humic acid (F), Insert figures indicate EDX results.

In case of ternary systems, HA allocation in between the clay particles and extensive uptake of humic fractions by the TiO_2 , Mt and Kt surfaces could also be detected. (Figure 4.49 E-F) (Laird,2001; Žbik, and Frost, 2009). Following photocatalysis, residual humic sub-fractions could still be seen in SEM images obtained for TiO_2 surface, TiO_2 and Mt surfaces and TiO_2 and Mt surfaces were presented in Figure 4.50A-C respectively.

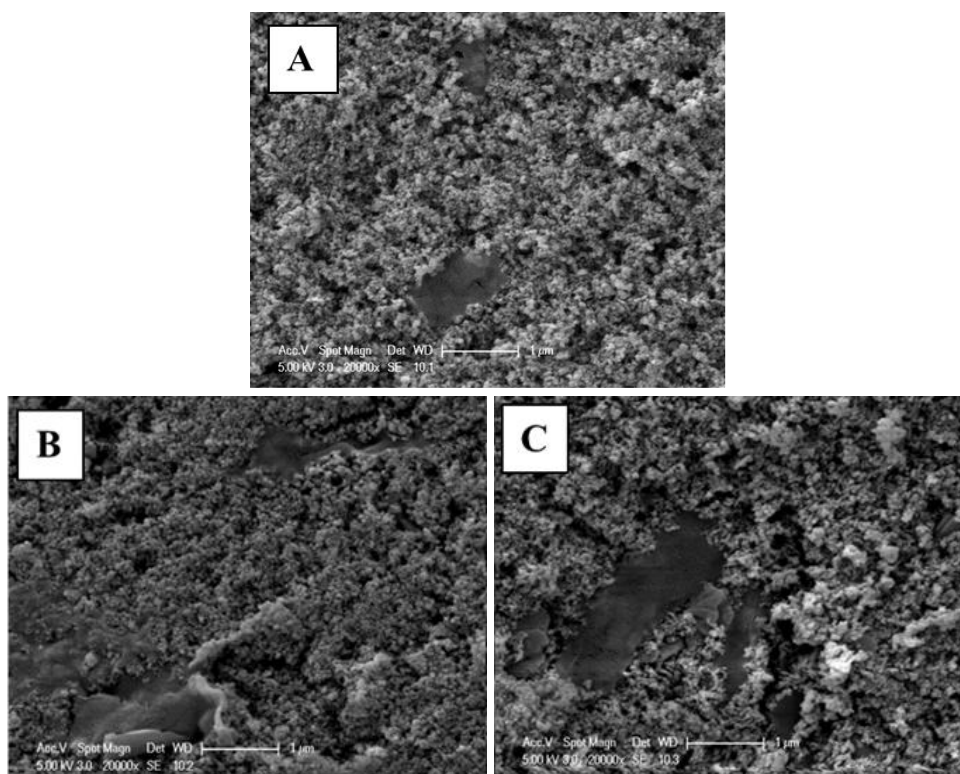


Figure 4.50. A-C SEM images of photocatalytically treated humic acid (A), photocatalytically treated HA in the presence of montmorillonite (B) and photocatalytically treated HA in the presence of kaolinite (C).

HA sub-fractions composed of photocatalytically oxidized and non-oxidized fractions could be visualized in between finely dispersed TiO_2 particles (Figure 4.50 A). It should be mentioned that 54% DOC still remained following $t_{\text{irr}} = 60$ min. Following a similar manner, untreated HA fractions as well as the oxidized humic moieties were located in between Mt/Kt particles embedded in TiO_2 matrix. Under the selected irradiation conditions, 51% DOC and 53% DOC were still existing in the presence of Mt and Kt respectively.

4.1.11. Molecular size fractionation of humic acid in the presence of clay minerals prior to and after photocatalysis

Molecular size fractionation of humic acid were employed for humic acid both in the presence and absence of clay minerals i.e. montmorillonite and kaolinite prior to and after photocatalytic degradation achieved by 60 min of irradiation period. The selected irradiation period displayed almost 50% removal of DOC and removals of 80% Color₄₃₆, 74% UV₃₆₅, 64% UV₂₈₀ and 62% UV₂₅₄.

4.1.11.1. Molecular size fractionation of humic acid prior to photocatalysis. Considering the polydisperse and heterogeneous nature of humic acids, molecular size fractionation was assessed through the application of the method outlined in Materials and Methods section. Following filtration through 0.45 μm membrane filters, humic acid samples were fractionated into different molecular size fractions such as 100 kDa, 30 kDa and 3kDa. The characterization of the humic acid and its molecular size fractions i.e. 0.45 μm filtered fraction, 100 kDa fraction, 30 kDa and 3kDa fractions were assessed with respect to their UV-vis and fluorescence spectroscopic properties. Fluorescence spectra were also recorded in both emission and synchronous scan modes. Besides the spectroscopic characterization, DOC contents of the raw humic acid and molecular size fractions were also determined.

The UV-vis spectra were recorded between 200-600 nm wavelength region. As indicated in the methodology section, selected absorbance values of all of the samples were recorded at 436 nm, 365 nm, 280 nm and 254 nm wavelengths for assessment of the specified parameters as Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄. All of the absorbance values of humic acid recorded at the spectral region were decreased with increasing wavelength revealing the basic characteristics of humic UV-vis spectra (Uyguner, 2005; Degirmenci-Ilhan, 2010).

In the Figure 4.51, it could be also easily observed that the absorbance values showed a gradually decreasing trend with decreasing molecular size fraction of humic acid. As expected, absorbance values of the raw and 0.45 μm filtered fraction of humic acid were very close to each other since humic acid was expected to pass completely through

0.45 μm membrane filter. The difference could be attributed to the possible aggregate formation and removal during pressure driven filtration step (Mallevialle et al., 1989). The recorded UV-vis absorbance values of 30 kDa fraction of humic acid were found to be significantly lower than other molecular size fractions at all wavelengths as shown in Figure 4.51. Moreover, 3 kDa fraction of humic acid exhibited very low absorbance values in the 200-350 nm wavelength region expressing the presence of very low color forming moieties by insignificant values in the 350-600 nm wavelength region. Molecular size fractions of humic acid as represented by the specified parameters followed a decreasing order; raw HA > 0.45 μm filtered fraction > 100 kDa fraction > 30 kDa fraction > 3 kDa fraction. As an indicator of organic carbon content, UV_{254} was found to be 1.199 cm^{-1} for raw humic acid, 1.098 cm^{-1} for 0.45 μm filtered fraction, 0.875 cm^{-1} for 100 kDa fraction, 0.339 cm^{-1} for 30 kDa fraction and 0.072 cm^{-1} for 3 kDa fraction. On the other hand, DOC (mg L^{-1}) contents were determined as 17.00, 16.48, 12.03, 5.253, and 2.052 for the raw humic acid, 0.45 μm filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction. As expected the DOC contents of raw and 0.45 μm filtered fraction of HA displayed a minor difference as $\leq 3\%$ that could also be considered as experimental error.

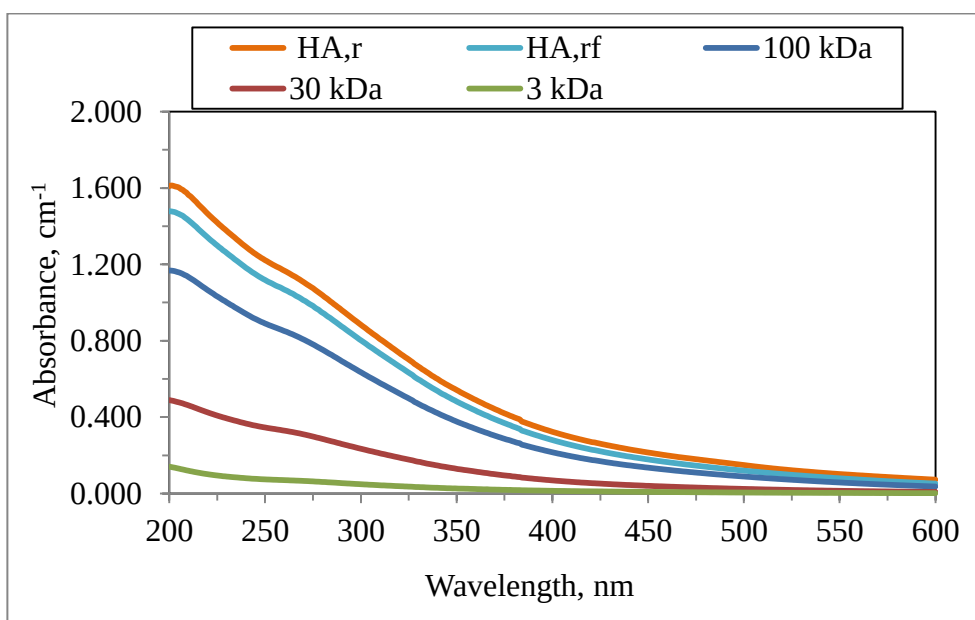


Figure 4.51. UV-vis spectra of raw, 0.45 μm filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction of humic acid.

It was reported that while UV-vis absorbance values displayed a decreasing order, the contents of carbon, hydrogen, nitrogen, and sulfur should also decrease with decreasing molecular weight of the fraction. On the other hand, the oxygen contents should increase. Carboxylic and phenolic carbon contents of the humic acid molecular size fractions tended to increase with decreasing molecular weight that could not be evaluated by the UV-vis spectroscopic features (Christl and Kretzschmar, 2001).

The emission scan (A) and synchronous scan (B) fluorescence spectra of raw, 0.45 μm filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction of humic acid were displayed in Figure 4.52 A-B. The emission fluorescence scan spectra were scanned in the emission wavelength range of 360-600 nm at a constant excitation wavelength of $\lambda_{\text{exc}} = 350$ nm. In Figure 4.52 A, the emission scan spectra gave increasing emission fluorescence intensities with decreasing molecular size fractions for raw, 0.45 μm filtered fraction, 100 kDa fraction and 30 kDa fraction of humic acid. However, 3 kDa fraction of humic acid displayed the lowest emission intensity, due to significantly lower organic content. A characteristic peak at $\lambda_{\text{emis}} = \sim 455$ nm wavelength was found to be evident for raw, 0.45 μm filtered fraction, 100 kDa fraction and 30 kDa fraction of humic acid. However, no distinctive peak for 3 kDa fraction of humic acid could be observed probably due to the low content of fluorophoric groups that should also be related to the low detection limits of the fluorescence measurement instrument. Up to about 420 nm emission wavelength, an overlapping trend was observed for raw humic acid, 0.45 μm filtered fraction, 30 kDa fraction and 3 kDa fraction of humic acid. On the other hand, 100 kDa fraction of humic acid gave the highest fluorescence intensities in spectra throughout the scanned emission wavelength range.

Synchronous spectra was recorded in the range of 200-600 nm excitation wavelength by using the bandwidth of $\Delta\lambda = 18$ nm between the excitation and emission monochromators. On the other hand, the synchronous scan fluorescence spectra was presented in the range of 300-600 nm emission wavelength because of very low absorbance values at the region below $\lambda_{\text{emis}} = 300$ nm emission wavelength.

Synchronous scan fluorescence spectra displayed decreasing fluorescence intensities with respect to decreasing molecular size fractions (Figure 4.52 B). Two main peaks were

observed at 400 and 470 nm emission wavelengths. While raw, 0.45 μm filtered fraction, 100 kDa and 30 kDa fraction of humic acid exhibited similar fluorescence intensities with small changes, 3 kDa fraction of humic acid had very low fluorescence intensities. In addition, for 3 kDa fraction of humic acid, the peaks detected as emission wavelengths of 400 nm and 470 nm were found to be nearly indistinguishable.

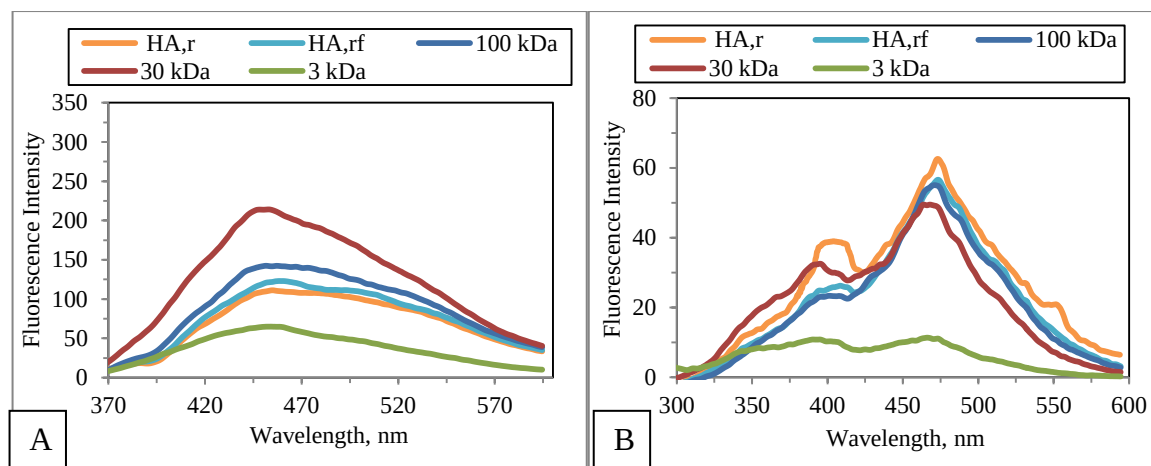


Figure 4.52. Emission scan (A) and synchronous scan (B) fluorescence spectra of raw, 0.45 μm filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction of humic acid.

With respect to the above presented UV-vis (Figure 4.51 and fluorescence (Figure 4.52 A-B) spectral features, the specified UV-vis parameters of the humic acid molecular size fractions were compiled and presented in Table 4.20. As explained previously, by definition humic acid was supposed to pass through 0.45 μm filter, therefore raw (HA_r) and 0.45 μm filtered fraction (HA_{rf}) of humic acid displayed very close absorbance values as illustrated in Table 4.20. The specified UV-vis parameters as Color₄₃₆, UV₃₆₅, UV₂₈₀, and UV₂₅₄ of 100 kDa fraction of humic acid decreased by 36%, 31%, 28%, and 27% respectively. Moreover, 29% decrease was attained for DOC of 100 kDa fraction of humic acid. On the other hand, the specified UV-vis parameters of 30 kDa fraction of humic acid were found to be less than approximately 70% of the raw humic acids' specified UV-vis parameters as Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄. Similar trend was also accounted for DOC. Moreover, 3 kDa fraction of humic displayed significantly lower organic content as expressed by the specified UV-vis parameters.

Table 4.20. Specified and specific UV-vis and fluorescence parameters of raw, 0.45 μ m filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction of humic acid.

	UV-vis Spectroscopic parameters, cm ⁻¹ DOC, mg L ⁻¹					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 474 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.179	96.929	62.352
HA,rf	0.200	0.411	0.947	1.098	16.48	121.898	106.511	56.486
100 kDa	0.153	0.320	0.753	0.875	12.03	141.760	120.723	54.596
30 kDa	0.046	0.108	0.286	0.339	5.253	213.216	163.429	48.325
3 kDa	0.010	0.022	0.060	0.072	2.052	64.832	46.710	10.983
Specific UV-vis and fluorescence parameters, m ⁻¹ mg ⁻¹ L								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
100 kDa	1.27	2.66	6.26	7.27	1178.39	1003.51	453.83	
30 kDa	0.88	2.05	5.44	6.46	4058.94	3111.16	919.95	
3 kDa	0.47	1.07	2.94	3.52	3159.43	2276.34	535.24	

Although no significant trend could be assessed for both of the FI_{emis350} recorded at 455 nm and FI_{emis370} recorded at 460 nm for higher molecular size fractions, 3 kDa fraction displayed significantly lower FI values. Moreover, the maximum synchronous scan fluorescence intensity, FI_{syn} recorded at λ_{emis} = 474 nm revealed a decreasing trend with respect to decreasing molecular size fraction of humic acid. The reason could be attributed to the plausible structural changes during ultrafiltration process as well as to the diversity of the fluorophores in different molecular size fractions.

For the elucidation of the specific UV-vis parameters, the respective terms were also presented in Table 4.20. From a broader perspective, it could be expressed that 100 kDa fraction expressed considerably higher $SCoA_{436}$, $SUVA_{365}$, $SUVA_{280}$ and $SUVA_{254}$. Since $SUVA_{254} > 4.0$ represents comparatively higher aromatic nature, the lowest molecular size fraction as 3 kDa displayed rather lower aromaticity ($SUVA_{254} = 3.52 \text{ m}^{-1}\text{mg}^{-1}\text{L}$). Moreover, specific fluorescence intensity values displayed an inconsistent trend with respect to decreasing molecular size fractions as could also be deduced by the variations of the respective values of the parameters. While, lower $SFI_{emis,455}$, $SFI_{emis,460}$ and $SFI_{syn,475}$ were calculated for raw, 0.45 μm filtered fraction of humic acid with respect to the specific FI parameters, significantly higher $SFI_{emis,455}$, $SFI_{emis,460}$ and $SFI_{syn,475}$ values were attained for 100 kDa fraction, 30 kDa fraction and 3 kDa fraction of humic acid. The reason could be attributed to the relatively low DOC contents with respect to the presence of high amount of fluorophoric groups residing on the humic molecular fractions.

4.1.11.2. Molecular size distribution of humic acid followed by photocatalytic degradation.

The molecular size fractionation of the photocatalytically oxidized humic substances were performed after 60 min irradiation period by using ultrafiltration stirred cell according to the methods outlined in Materials and Methods section. Following filtration through 0.45 μm membrane filters for the successive removal of photocatalyst particles, humic acid samples were also subjected to fractionation into particular molecular size fractions such as 100 kDa, 30 kDa and 3kDa. The characterization of the photocatalytically treated humic acid and its molecular size fractions i.e. 0.45 μm filtered fraction, 100 kDa fraction, 30 kDa and 3 kDa fractions were performed with respect to their UV-vis spectroscopic parameters, emission scan and synchronous scan fluorescence spectroscopic properties and DOC contents. For the characterization of the humic acid solutions, absorbance values of the samples were recorded at 436 nm, 365 nm, 280 nm and 254 nm wavelengths for the assessment of the specified parameters as $Color_{436}$, UV_{365} , UV_{280} and UV_{254} . The absorbance values of the oxidized humic acid samples displayed an exponential decay profile irrespective of the molecular size dependent properties (Figure 4.53).

For comparison purposes, HA,r and HA,r,f were also displayed since filtration through 0.45 μm membrane filter is the most crucial experimental step that should be performed followed by photocatalysis for the removal of TiO_2 from the aqueous medium. Therefore, the significant decrease observed in the UV-vis spectra recorded for the HA,ft demonstrates the removal of the UV-vis absorbing moieties followed by photocatalysis. It should also be pointed out that the lower molecular size fractions expressed distinctly lower absorbance values due to the achieved photocatalytic mineralization under irradiation period of 60 min. Under this experimental condition, 80% Color_{436} , 74% UV_{365} , 64% UV_{280} , 62% UV_{254} and 46% DOC removals were achieved (Table 4.21 and Figure 4.53).

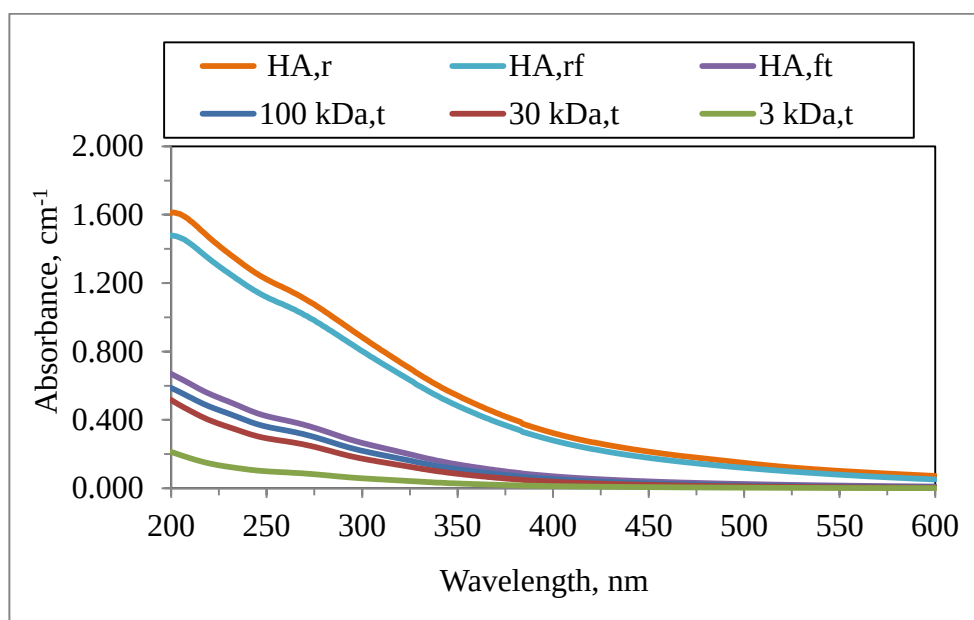


Figure 4.53. UV-vis spectra of raw, 0.45 μm filtered fraction, treated 0.45 μm filtered fraction, 100 kDa,t fraction, 30 kDa,t fraction and 3 kDa,t fraction of humic acid. t: denotes treatment.

Substantial differences among the fractions of different molecular sizes point out the importance of characterizing the size fractions properly to better understand the spectroscopic properties of oxidized humic substances. The structural as well as the conformational changes occurring in humic sub units would be better assessed in view of the absorbance ratios (Uyguner and Bekbolet, 2005a).

The emission scan (A) and synchronous scan (B) fluorescence spectra of molecular size fractions of oxidized humic acid samples *i.e.* 0.45 μm filtered fraction, 100 kDa,t fraction, 30 kDa,t and 3 kDa,t fractions were presented in Figure 4.54 A-B. The emission scan spectra were scanned in the range of 360-600 nm at a constant excitation wavelength of $\lambda_{\text{exc}} = 350$ nm. As presented in Figure 4.54 A, the emission scan spectra offered increasing emission fluorescence intensity with respect to molecular size fractions for raw, 0.45 μm filtered fraction, 100 kDa fraction and 30 kDa fraction of humic acid. Similar fluorescence intensities were recorded for 0.45 μm filtered fraction, 100 kDa fraction and 30 kDa fraction of humic acid probably due to the considerably lower remaining organic content. The photocatalytically treated samples of 0.45 μm filtered fraction, 100 kDa,t fraction and 30 kDa,t fraction of humic acid displayed an peak at emission wavelength of $\lambda_{\text{emis}} = 455$ nm that could be regarded as broad and featureless in shape. Moreover 3 kDa,t fraction of humic acid displayed the lowest emission intensity displayed by a nonsymmetrical broad peak.

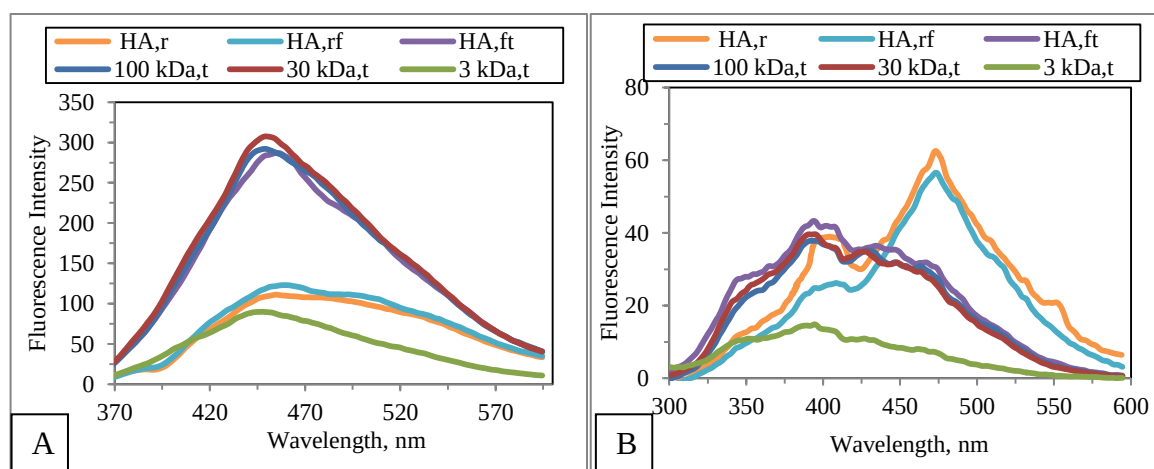


Figure 4.54. Emission scan (A) and synchronous scan (B) fluorescence spectra of raw, 0.45 μm filtered fraction, photocatalytically treated humic acid 0.45 μm filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid.

The synchronous scan fluorescence recorded in the range of 300-600 nm emission wavelength were presented in Figure 4.54 B. The synchronous scan fluorescence spectra showed decreasing fluorescence intensities with respect to decreasing molecular size fractions. Two main peaks were observed at 400 and 470 nm emission wavelengths for

raw, 0.45 μm filtered fraction as reported previously. However, treated 0.45 μm filtered fraction, 100 kDa,t and 30 kDa,t fraction of humic acid did not show any peak around $\lambda_{\text{emis}} = 470 \text{ nm}$ expressing the removal of fluorophoric moieties. Emergence of a new peak at 375 nm emission wavelength for treated 0.45 μm filtered fraction, 100 kDa,t and 30 kDa,t fraction was observed. Moreover, 3 kDa fraction of treated humic acid did not show any distinguishable peak displaying a continuum of fluorescence intensity throughout the emission wavelength range. Furthermore, referring to the above presented UV-vis (Figure 4.53) and fluorescence (Figure 4.54 A-B) spectral features, the specified and specific UV-vis and fluorescence parameters of the humic acid molecular size fractions were compiled and presented in Table 4.21.

UV-vis absorbance values of the particular fractions of the treated humic acids characterized by the specified parameters followed a decreasing order as Raw HA > 0.45 μm filtered fraction > treated 0.45 μm filtered fraction > 100 kDa,t fraction > 30 kDa,t fraction > 3 kDa,t fraction. As a surrogate parameter of organic carbon content, UV_{254} was found to be 1.199 cm^{-1} for raw humic acid, 1.098 cm^{-1} for 0.45 μm filtered fraction, 0.412 for treated 0.45 μm filtered fraction, 0.351 cm^{-1} for 100 kDa,t fraction, 0.285 cm^{-1} for 30 kDa,t fraction and 0.097 cm^{-1} for 3 kDa,t fraction. As expected, DOC values of molecular size fractions of oxidized humic acid samples were correlated with UV_{254} values i.e. 17.00 mg L^{-1} for raw humic acid, 16.48 mg L^{-1} for 0.45 μm filtered fraction, 7.60 mg L^{-1} for treated 0.45 μm filtered fraction, 6.43 mg L^{-1} for 100 kDa,t fraction, 5.34 mg L^{-1} for 30 kDa,t fraction and 2.22 mg L^{-1} for 3 kDa,t fraction. Referring to the fluorescence spectral features displayed in Figure 4.54 A-B, the FI recorded at the specific emission wavelengths exhibited an irregular decreasing trend with respect to decreasing molecular size. Accordingly, a non-specific trend could also be deduced from data for the specific fluorescence as $\text{SFI}_{\text{emis},455}$, $\text{SFI}_{\text{emis},460}$ and $\text{SFI}_{\text{syn},475}$.

From a broader perspective 100 kDa fraction expressed considerably higher specific UV-vis parameters as i.e. SCoA_{436} , SUVA_{365} , SUVA_{280} and SUVA_{254} . Since $\text{SUVA}_{254} > 4.0$ represents comparatively higher aromatic nature, the lowest molecular size fraction as 3 kDa displayed rather lower aromaticity ($\text{SUVA}_{254} = 4.36 \text{ m}^{-1}\text{mg}^{-1}\text{L}^{-1}$) ((Edzwald et al., 1985). Although a general decreasing trend was observed for all of the specific UV-vis

parameters, the role of oxidative treatment could be significantly expressed for 3 kDa fraction of humic acid in terms of $SUVA_{280}$ and $SUVA_{254}$ (Table 4.20 and Table 4.21).

Table 4.21. Specified and specific UV-vis and fluorescence parameters of 0.45 μ m filtered fraction, photocatalytically treated humic acid 0.45 μ m filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid.

	UV-vis Spectroscopic parameters, cm^{-1} DOC, $mg\ L^{-1}$					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 474 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.179	96.929	62.352
HA,rf	0.200	0.411	0.947	1.098	16.48	121.898	106.511	56.486
HA,ft	0.046	0.1142	0.336	0.412	7.60	286.954	207.503	30.327
100 kDa,t	0.034	0.090	0.283	0.351	6.43	287.108	206.038	27.557
30 kDa,t	0.023	0.067	0.228	0.285	5.34	303.323	212.110	25.604
3 kDa,t	0.008	0.022	0.077	0.097	2.22	87.217	59.711	7.037
Specific UV-vis and fluorescence parameters, $m^{-1}mg^{-1} L$								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
HA,ft	0.62	1.50	4.42	5.42	3775.71	2730.30	399.04	
100 kDa,t	0.53	1.40	4.41	5.46	4465.13	3204.33	428.57	
30 kDa,t	0.45	1.27	4.28	5.34	5680.21	3972.10	479.48	
3 kDa,t	0.37	1.02	3.50	4.36	3928.69	2689.67	316.97	

General trend could not be observed for $SFI_{emis,455}$, $SFI_{emis,460}$ and $SFI_{syn,475}$ parameters with decreasing molecular size fractions for raw, 0.45 μ m filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction of humic acid samples (Table 4.20).

Whereas, lower $SFI_{emis,455}$ $SFI_{emis,460}$ and $SFI_{syn,475}$ were calculated for raw, 0.45 μ m filtered fraction of humic acid, significantly higher $SFI_{emis,455}$ $SFI_{emis,460}$ and $SFI_{syn,475}$ values were attained for treated 0.45 μ m filtered fraction, 100 kDa fraction, 30 kDa fraction and 3 kDa fraction of humic acid.

4.1.11.3. Molecular size distribution of humic acid followed by photocatalytic degradation in the presence of montmorillonite. The molecular size fractionation of the photocatalytically oxidized humic acid in the presence of 0.20 mg mL⁻¹ Mt were performed after 60 min irradiation period by using ultrafiltration stirred cell according to the methods outlined in Materials and Methods section. Following filtration through 0.45 μ m membrane filters, humic acid samples were fractionated into particular molecular size fractions such as 100 kDa, 30 kDa and 3 kDa. The characterization of the treated humic acid and its molecular size fractions i.e. 0.45 μ m filtered fraction, 100 kDa fraction, 30 kDa and 3kDa fractions were evaluated with respect to their UV-vis spectroscopic parameters, fluorescence spectroscopic properties and DOC contents. Based on the previous findings, under this experimental condition, 85% Color₄₃₆, 80% UV₃₆₅, 70% UV₂₈₀, 68% UV₂₅₄ and 49% DOC removals were achieved (Table 4.22 and Figure 4.55).

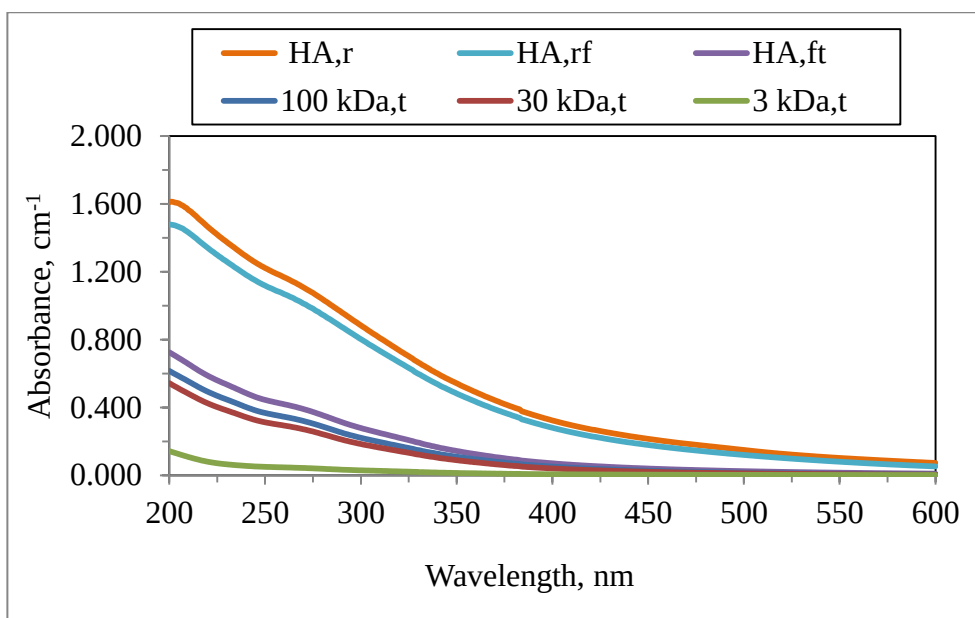


Figure 4.55. UV-vis spectra of raw, 0.45 μ m filtered fraction, treated 0.45 μ m filtered fraction, 100 kDa,t fraction, 30 kDa,t fraction and 3 kDa,t fraction of humic acid in the presence of 0.20 mg mL⁻¹ montmorillonite.

UV-vis absorbance spectra of the photocatalytically treated humic acid in the presence of Mt were recorded between 200-600 nm wavelength region (Figure 3.5) As was presented previously for the photocatalytically treated humic acid in the absence of Mt, oxidized humic acid in the presence of 0.20 mg mL^{-1} Mt, displayed UV-vis absorbance values in a decreasing order with respect to the decreasing molecular size filtration fraction (Figure 4.55). From a general perspective, the presence of Mt did not led to drastic changes in the UV-vis spectral trend of humic acid molecular size fractions.

The emission scan (A) and synchronous scan (B) fluorescence spectra of molecular size fractions of oxidized humic acid samples i.e. $0.45 \mu\text{m}$ filtered fraction, 100 kDa,t fraction, 30 kDa,t fraction and 3 kDa,t fraction were presented in Figure 4.56 A-B. The emission scan spectra were scanned in the range of 360-600 nm at a constant excitation wavelength of 350 nm. As presented in Figure 4.56 A, the emission scan spectra offered almost similar emission fluorescence intensity value for $0.45\mu\text{m}$ treated filtered fraction, 100 kDa,t fraction and 30 kDa,t fraction of humic acid. However, 3 kDa,t fraction of humic acid displayed lowest emission intensity in a broad and featureless style. A distinctive peak at emission wavelength of 455 nm was observed for treated $0.45\mu\text{m}$ filtered fraction, 100 kDa,t fraction and 30 kDa,t fraction of humic acid.

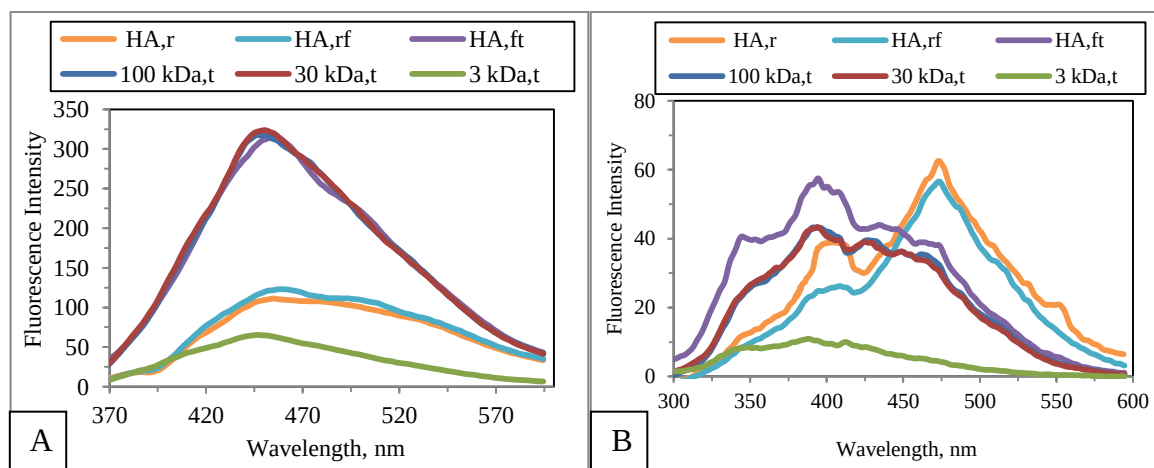


Figure 4.56. Emission scan (A) and synchronous scan (B) fluorescence spectra of raw, $0.45\mu\text{m}$ filtered fraction, photocatalytically treated humic acid $0.45\mu\text{m}$ filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid in the presence of 0.20 mg mL^{-1} montmorillonite.

The synchronous scan fluorescence spectra were recorded in the range of 300-600 nm emission wavelength and presented in Figure 4.56 B. Similar to the other studied humic acid systems, the synchronous scan fluorescence spectra showed decreasing fluorescence intensities with respect to decreasing molecular size fractions. Two main peaks were observed at $\lambda_{\text{emis}} = 400$ and $\lambda_{\text{emis}} = 470$ nm for raw and 0.45 μm filtered fraction of humic acid. After photocatalytic treatment of humic acid performed in the presence of Mt for an irradiation period of 60 min, treated 0.45 μm filtered fraction, 100 kDa_t and 30 kDa_t fractions of humic acid did not illustrate any peak around $\lambda_{\text{emis}} = 470$ nm. Emergence of a new peak was observed at 375 nm emission wavelength for treated 0.45 μm filtered fraction, 100 kDa_t and 30 kDa_t fractions, however 3 kDa fraction of humic acid did not exhibit any distinguishable peak at any emission wavelength.

Furthermore, referring to the above presented UV-vis (Figure 4.55) and fluorescence (Figure 4.56 A-B) spectral features, the specified and specific UV-vis and fluorescence parameters of the humic acid molecular size fractions were compiled and presented in Table 3.3. Similar to the trend observed for the results attained by oxidation of humic acid in the absence of Mt, specified UV-vis parameters of 0.45 μm filtered fraction of humic acid illustrated a radical decreasing manner. Following 0.45 μm filtered fraction of humic acid, 100 kDa_t fraction and 30 kDa_t fraction of humic acid exhibited a rather slow decreasing fashion with respect to decreasing molecular size fraction. Whereas, the absorbance spectra of 3 kDa_t fraction of humic acid in the presence of Mt showed significantly lower spectral features as seen in Figure 4.55. UV-vis absorbance assessment of the particular molecular size fractions of the treated humic acids in the presence of Mt as differentiated by the specified parameters followed an order of raw > 0.45 μm filtered fraction > treated 0.45 μm filtered fraction > 100 kDa_t fraction > 30 kDa_t fraction > 3 kDa_t fraction

Specified UV-vis parameter i.e., UV_{254} was found to be 1.199 cm^{-1} for raw humic acid, 1.098 cm^{-1} for 0.45 μm filtered fraction, 0.434 for treated 0.45 μm filtered fraction, 0.358 cm^{-1} for 100 kDa_t fraction, 0.304 cm^{-1} for 30 kDa_t fraction and 0.048 cm^{-1} for 3 kDa_t fraction. Except for 3 kDa_t fraction of humic acid, it could be specified that UV_{254} value of 0.45 μm filtered fraction of humic acid, 100 kDa_t fraction and 30 kDa_t fraction of humic acid increased with the addition of Mt in to aqueous medium. DOC values of the

photocatalytically treated humic acids in the presence of Mt were established to be 17.00 mg L⁻¹ for raw humic acid, 16.48 mg L⁻¹ for 0.45 µm filtered fraction, 8.46 mg L⁻¹ for treated 0.45 µm filtered fraction, 7.48 mg L⁻¹ for 100 kDa,t fraction, 6.64 mg L⁻¹ for 30 kDa,t fraction and 1.99 mg L⁻¹ for 3 kDa,t fraction.

Table 4.22. Specified UV-vis and fluorescence parameters of 0.45µm filtered fraction, photocatalytically treated humic acid 0.45µm filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid in the presence of 0.20 mg mL⁻¹ montmorillonite.

	UV-vis Spectroscopic parameters, cm ⁻¹ DOC, mg L ⁻¹					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 474 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.179	96.929	62.352
HA,rf	0.200	0.411	0.947	1.098	16.48	121.898	106.511	56.486
HA,ft	0.046	0.116	0.354	0.434	8.46	315.084	230.381	37.822
100 kDa,t	0.032	0.087	0.287	0.358	7.48	312.398	225.967	32.069
30 kDa,t	0.025	0.070	0.242	0.304	6.64	319.756	227.575	30.169
3 kDa,t	0.004	0.011	0.038	0.048	1.99	63.079	43.895	4.297
Specific UV-vis and fluorescence parameters, m ⁻¹ mg ⁻¹ L								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
HA,ft	0.54	1.37	4.18	5.12	3724.39	2723.18	447.07	
100 kDa,t	0.43	1.16	3.84	4.78	4176.44	3020.94	428.73	
30 kDa,t	0.37	1.06	3.65	4.58	4815.61	3427.33	454.36	
3 kDa,t	0.21	0.54	1.92	2.43	3169.81	2205.79	215.91	

SCoA₄₃₆, SUVA₃₆₅, SUVA₂₈₀ and SUVA₂₅₄ parameters of the partially oxidized humic acid in the presence of Mt were decreased with decreased molecular size fractions. The lowest SCoA₄₃₆, SUVA₃₆₅, SUVA₂₈₀ and SUVA₂₅₄ values were obtained for 3 kDa_t fraction. SUVA₂₅₄ values were found to be 2.43 for 3 kDa_t fraction of the partially oxidized humic acid in the presence of Mt (Table 4.22). Referring to the fluorescence spectral features displayed in Figure 4.56 A-B, the FI recorded at the specific emission wavelengths exhibited an irregular decreasing trend with respect to decreasing molecular size. Accordingly, a non-specific trend could also be deduced from the data for the specific fluorescence parameters as SFI_{emis,455}, SFI_{emis,460} and SFI_{syn,475} for the partially oxidized humic acid in the presence of Mt.

4.1.11.4. Molecular size distribution of humic acid followed by photocatalytic degradation in the presence of kaolinite. The molecular size fractionation of the photocatalytically oxidized humic acid in the presence of 0.20 mg mL⁻¹ Kt were performed followed by treatment for 60 min of irradiation time by using ultrafiltration stirred cell method according to the methods outlined in Materials and Methods section. Following filtration through 0.45 µm filter, humic acid samples were fractionated into particular molecular size fractions such as 100 kDa, 30 kDa and 3 kDa.

The characterization of the photocatalytically related humic acid and its molecular size fractions i.e. 0.45 µm filtered fraction, 100 kDa fraction, 30 kDa and 3kDa fractions were evaluated with respect to their UV-vis spectroscopic parameters, fluorescence spectroscopic properties and DOC contents. Fluorescence spectra were recorded in both emission and synchronous scan modes. Under this experimental condition, 85% Color₄₃₆, 79% UV₃₆₅, 69% UV₂₈₀, 67% UV₂₅₄ and 47% DOC removals were achieved (Table 4.23 and Figure 4.57).

UV-vis absorbance spectra of the photocatalytically treated humic acid in the presence of Kt were recorded between 200-600 nm wavelength regions. For the humic acid solutions in the presence of 0.20 mg mL⁻¹ Kt, UV-vis absorbance values were recorded at 436 nm, 365 nm, 280 nm and 254 nm wavelengths for the assessment of the specified UV-vis parameters as Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄ (Figure 4.57). As was presented for the photocatalytically oxidized humic acid in the absence of Kt, treated humic acid in the

presence of 0.20 mg mL^{-1} Kt presented UV-vis absorbance values to be following a decreasing order with respect to the decreasing molecular size filtration fraction (Figure 3.1). From a general perspective, the presence of Kt did not lead to drastic changes in the UV-vis spectra trend of humic acid.

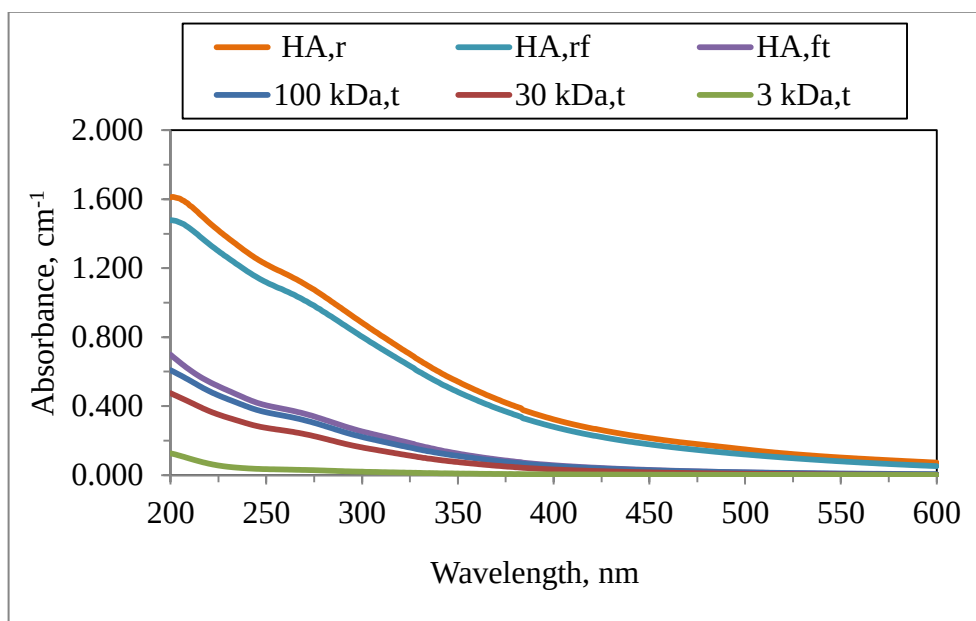


Figure 4.57. UV-vis spectra of raw, $0.45\mu\text{m}$ filtered fraction, treated $0.45\mu\text{m}$ filtered fraction, 100 kDa,t fraction, 30 kDa,t fraction and 3 kDa,t fraction of humic acid in the presence of 0.20 mg mL^{-1} kaolinite.

Emission scan fluorescence spectra of molecular size fractions of the oxidized humic acid samples i.e. $0.45 \mu\text{m}$ filtered fraction, 100 kDa,t fraction, 30 kDa,t fraction and 3 kDa,t fraction were presented in Figure 4.58 A-B. Emission fluorescence spectra were scanned in the range of $\lambda_{\text{emis}} = 360\text{--}600 \text{ nm}$ at a constant excitation wavelength of 350 nm. As displayed in Figure 4.58 A, the emission scan spectra offered almost similar emission fluorescence intensities for $0.45\mu\text{m}$ treated filtered fraction, 100 kDa,t fraction and 30 kDa,t fraction of humic acid. However, 3 kDa,t fraction of humic acid displayed the lowest emission fluorescence intensity in a broad and featureless style. A distinctive peak at $\lambda_{\text{emis}} = 455 \text{ nm}$ emission wavelength was observed for photocatalytically treated $0.45\mu\text{m}$ filtered fraction, 100 kDa,t fraction and 30 kDa,t fraction of humic acid. Moreover, 3 kDa,t fraction of humic acid followed a rather smooth fluorescence intensity profile.

The synchronous scan fluorescence spectra were recorded in the range of 300-600 nm wavelength and presented in Figure 4.58 B. Similar to the previously reported humic acid systems, the synchronous scan fluorescence spectra expressed decreasing fluorescence intensities with respect to decreasing molecular size fractions (Figure 4.54-4.56). Two major peaks were observed at 385 and 475 nm emission wavelengths for raw and 0.45 μm filtered fraction of humic acid. Followed by photocatalytic treatment of humic acid performed in the presence of Kt for an irradiation period of 60 min, treated 0.45 μm filtered fraction, 100 kDa,t and 30 kDa,t fractions of humic acid did not demonstrate any recordable peak around 475 nm emission wavelength. Emergence of a new peak was observed at 385 nm emission wavelength for treated 0.45 μm filtered fraction, 100 kDa,t and 30 kDa,t fractions, however 3 kDa fraction of humic acid did not exhibit any distinguishable peak at any emission wavelength.

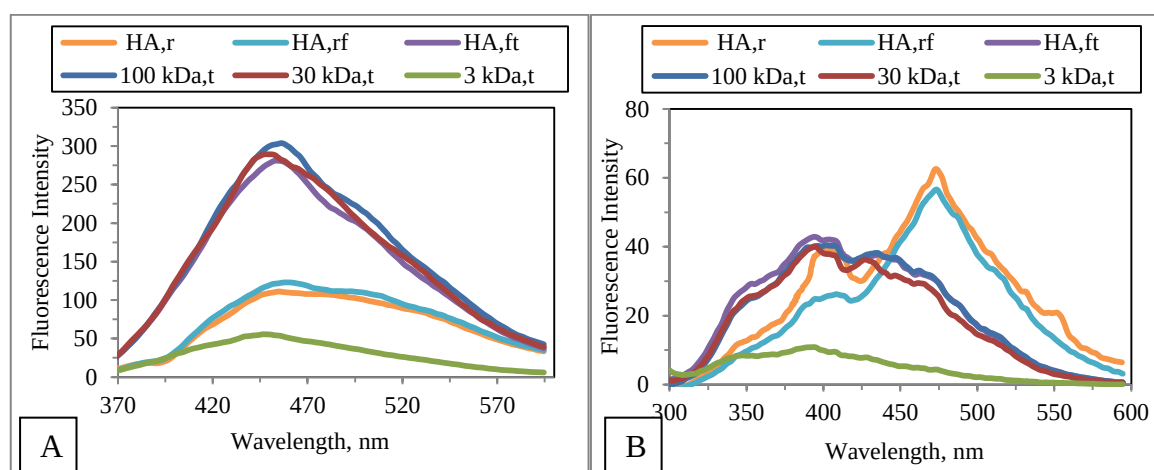


Figure 4.58. Emission scan (A) and synchronous scan (B) fluorescence spectra of raw, 0.45 μm filtered fraction, photocatalytically treated humic acid 0.45 μm filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid in the presence of 0.20 mg mL^{-1} kaolinite.

Furthermore, referring to the above presented UV-vis (Figure 4.57) and fluorescence (Figure 4.58) spectral features, the specified and specific UV-vis parameters of the humic acid and Kt system molecular size fractions were compiled and presented in Table 4.23.

Table 4.23. Specified UV-vis and fluorescence parameters of 0.45 μ m filtered fraction, photocatalytically treated humic acid 0.45 μ m filtered fraction 100 kDa fraction and 30 kDa fraction of humic acid in the presence of 0.20 mg mL⁻¹ kaolinite.

	UV-vis Spectroscopic parameters, cm ⁻¹ DOC, mg L ⁻¹					Fluorescence spectroscopic parameters		
	Color ₄₃₆	UV ₃₆₅	UV ₂₈₀	UV ₂₅₄	DOC	FI _{emis350} 455 nm	FI _{emis370} 460 nm	FI _{syn} 475 nm
HA,r	0.239	0.465	1.038	1.199	17.00	111.179	96.929	62.352
HA,rf	0.200	0.411	0.947	1.098	16.48	121.898	106.511	56.486
HA,ft	0.036	0.099	0.323	0.395	9.01	280.960	205.411	29.920
100 kDa,t	0.033	0.089	0.287	0.355	6.94	303.310	221.114	29.908
30 kDa,t	0.019	0.059	0.212	0.267	5.26	284.309	204.861	26.030
3 kDa,t	0.003	0.007	0.027	0.034	1.87	53.882	37.509	4.332
Specific UV-vis and fluorescence parameters, m ⁻¹ mg ⁻¹ L								
	SCoA ₄₃₆	SUVA ₃₆₅	SUVA ₂₈₀	SUVA ₂₅₄	SFI _{emis,455}	SFI _{emis,460}	SFI _{syn,475}	
HA,r	1.41	2.73	6.11	7.05	653.99	570.17	366.77	
HA,rf	1.21	2.49	5.74	6.66	739.67	646.30	342.76	
HA,ft	0.40	1.10	3.58	4.38	3118.32	2279.82	332.08	
100 kDa,t	0.48	1.28	4.13	5.12	4370.46	3186.08	430.95	
30 kDa,t	0.37	1.12	4.04	5.08	5405.11	3894.69	494.86	
3 kDa,t	0.16	0.39	1.43	1.80	2881.37	2005.81	231.66	

Similar to the trend observed for the results attained by oxidation of humic acid in the absence of Kt, specified UV-vis parameters of 0.45 μ m filtered fraction of humic acid illustrated a drastic decreasing trend (Table 4.23). Following 0.45 μ m filtered fraction of humic acid, 100 kDa,t and 30 kDa,t fractions of humic acid exhibited a rather slow decreasing fashion with respect to the decreasing molecular size fraction. Whereas, the absorbance spectra of 3 kDa,t fraction of humic acid in the presence of Kt displayed

significantly lower spectral features as seen in Figure 4.57. UV-vis absorbance assessment of the particular molecular size fractions of the treated humic acids in the presence of Kt as differentiated by the specified UV-vis parameters followed an order of raw > 0.45 μ m filtered fraction > treated 0.45 μ m filtered fraction > 100 kDa,t fraction > 30 kDa,t fraction > 3 kDa,t fraction

Specified UV-vis parameter value i.e., UV_{254} was found to be 1.199 cm^{-1} for raw humic acid, 1.098 cm^{-1} for 0.45 μ m filtered fraction, 0.395 for treated 0.45 μ m filtered fraction, 0.355 cm^{-1} for 100 kDa,t fraction, 0.267 cm^{-1} for 30 kDa,t fraction and 0.034 cm^{-1} for 3 kDa,t fraction. Excluding 3 kDa,t fraction of humic acid, it could be specified that UV_{254} value of 0.45 μ m filtered fraction of humic acid, 100 kDa,t fraction and 30 kDa,t fraction of humic acid increased with the addition of Kt to aqueous medium. DOC values of the photocatalytically treated humic acid in the presence of Mt were established to be 17.00 mg L^{-1} for raw humic acid, 16.48 mg L^{-1} for 0.45 μ m filtered fraction, 9.01 mg L^{-1} for treated 0.45 μ m filtered fraction, 6.94 mg L^{-1} for 100 kDa,t fraction, 5.26 mg L^{-1} for 30 kDa,t fraction and 1.87 mg L^{-1} for 3 kDa,t fraction.

$SCoA_{436}$, $SUVA_{365}$, $SUVA_{280}$ and $SUVA_{254}$ parameters of the partially oxidized humic acid in the presence of Kt were decreased with respect to decreasing molecular size fractions, except that treated 0.45 μ m filtered fraction. The lowest $SUVA_{254}$ values were obtained for 3 kDa,t fraction and found to be 1.80 $\text{m}^{-1}\text{mg}^{-1}\text{L}^{-1}$ (Table 4.23). Referring to the fluorescence spectral features displayed in Figure 4.58, the FI recorded at the specific emission wavelengths exhibited an irregular decreasing trend with respect to decreasing molecular size. Accordingly, a non-specific trend could also be deduced from data for the specific fluorescence as $SFI_{\text{emis},455}$, $SFI_{\text{emis},460}$ and $SFI_{\text{syn},475}$ for the partially oxidized humic acid in the presence of Kt

4.1.11.5. Comparative evaluation. Molecular size distribution profile of untreated sole HA displayed DOC contents as 71% 100 kDa, 31% 30 kDa and 12% 3 kDa fractions. Prior to and following photocatalysis, filtration through 0.45 μ m membrane filter constituted the main step of HA sample preparation in reaching a complete removal of the suspended particles i.e. TiO_2 , Mt and Kt. Therefore, molecular size distribution data were evaluated by normalization of the individual results to the corresponding 0.45 μ m filtered HA data.

Figure 4.59 A-C covered information regarding the molecular size distribution patterns attained by photocatalytic oxidation ($t_{irr} = 60$ min) in relation to the data achieved under non-oxidative conditions. From a general point of view, under dark conditions, the observed differences in clay type dependent surface reactivities were more pronounced for UV-vis parameters of HA for 0.45 μm filtered fraction of HA in binary and ternary systems. For ternary interactions; 100 kDa and 3 kDa fractions displayed a more consistent trend for humic UV-vis parameters. Upon photocatalytic treatment, higher molecular size fractions as 0.45 μm filtered fraction and 100 kDa fraction exhibited non-discriminative differences with regard to clay type. A decreasing trend with respect to UV-vis parameters as $UV_{254} > \text{Color}_{436}$ was observed for 100 kDa fraction for sole HA and HA in the presence of either Mt or Kt.

Under non-oxidative conditions, presence of TiO_2 significantly affected the Color_{436} content of 0.45 μm filtered fraction of HA (25%) with reference to the insignificant removals attained in the presence of either Mt or Kt. In the case of the ternary systems, further decreases were attained being more pronounced in the presence of Mt (43%) rather than Kt (37%). Moreover, followed by photocatalytic treatment of either sole HA or “HA and Mt” binary system, by successful elimination of Color_{436} of 0.45 μm filtered fraction of HA, similar contents (23%) were displayed in comparison to lower content attained for “HA and Kt” binary system (18%). 100 kDa fraction exhibited a considerably higher removal (34%) in the presence of Mt in comparison to the presence of Kt (9%) under dark conditions.

As expected, the presence of TiO_2 effectively removed Color_{436} of 100 kDa fraction (34%) followed by further decreases due to the presence of either Mt (43%) or Kt (41%). However by photocatalytic treatment of HA in the presence of clay particles, significant removal of Color_{436} could be assessed although no discriminative changes (78%) could be stated. Through a similar trend, revealing under dark conditions, upon photocatalysis, 100 kDa fraction of HA expressed almost equal Color_{436} removals under all medium conditions. In a similar fashion under dark conditions, 30 kDa fraction displayed a considerably higher removal in the presence of Mt in comparison to the presence of Kt both for binary and ternary systems. However, by photocatalytic treatment of HA performed in the presence Kt, slightly higher removal of Color_{436} was attained with respect

to the removal of sole HA. Moreover, Color₄₃₆ of the lowest molecular size fraction (3 kDa) displayed variable trends with respect to the systems under consideration, as 85% for sole HA, 42% for “HA and Mt” and 30% for “HA and Kt”. The effect observed in the presence of Kt via photocatalysis could be considered as non-significant with respect to the removal of Color₄₃₆ of the “HA, Kt, and TiO₂” ternary system under non-oxidative conditions.

In a similar fashion to Color₄₃₆, by dark interactions, the presence of TiO₂ significantly affected the UV₂₅₄ content of 0.45 µm filtered fraction of HA (~25%) with reference to the observed “no-effect” due to the presence of either Mt or Kt. In the case of the ternary systems, further decreases were attained being slightly higher in the presence of Mt (40%) in comparison to Kt (35%). Moreover followed by photocatalytic treatment, sole HA expressed slightly higher UV₂₅₄ content of 0.45 µm filtered fraction of HA (39%) with respect to the indifferent effect of either Mt or Kt (36%). Although different removal efficiencies were attained under dark conditions prior to photocatalysis, following degradation of HA, similar contents of 100 kDa fraction (41%) were found for sole HA and HA in binary systems. In a similar fashion obtained under dark conditions, 30 kDa (79%) and 3 kDa (47%) fractions of binary systems were found to be considerably lower than sole HA as 90% and 67% respectively. The resultant effect could be expressed by the formation of lower molecular size fractions through various pathways comprised of oxidative degradation as well as surface interactive fractionation (Goldstone et al., 2002; Kerc et al., 2004; Liu et al., 2008). A closer look to the profile of the 3 kDa molecular size fraction signified a photocatalytic route continuously and simultaneously occurring through a removal and formation pathway of lower molecular size humic fraction. It should also be emphasized that the attained molecular size distribution profiles of HA were determined followed by 60 minutes of irradiation time representing approximately 50% remaining DOC (photocatalytic degradation kinetic parameters of the respective systems were presented in Figure 4.59).

Besides UV-vis parameters, DOC based evaluation of the system displayed completely different tendencies with respect to the studied experimental conditions. The role of the adsorptive surface interactions leading to removals could be expressed as TiO₂ > Kt > Mt for 0.45 µm filtered fraction, TiO₂ > Mt > Kt for 100 kDa fraction, Kt > TiO₂ > Mt

for 30 kDa fraction and $K_t \geq \text{TiO}_2 > \text{Mt}$ for 3kDa fraction. The presence of ternary systems completely altered the interactive DOC removal trends whereas followed by photocatalysis, a shift to lower molecular size fractions was observed irrespective of the composition of the solution. By definition DOC represents the organic carbon content of the 0.45 μm filtered fraction of HA therefore; the data attained for this fraction could be discussed in relation to the photocatalytic degradation rates presented in Figure 4.59 C.

Under the specified experimental conditions, the first order removal rates were attained in the decreasing order of $\text{HA} > \text{“HA and Kt” binary system} > \text{“HA and Mt” binary system}$ displaying an inconsistent trend from exposed surface area point of view. The data presented in Figure 4.59 for DOC contents of the 0.45 μm filtered fraction of HA represented the removal efficiencies as being very close to each other upon irradiation period of 60 minutes. Although the photocatalytic removal rates were found to be considerably different, only a very slight change in DOC contents of 0.45 μm filtered fraction of HA was attained. It should also be mentioned that the DOC removal of 0.45 μm filtered fraction of HA should not be interpreted as explaining the “real” DOC consortium of the humic sub-fractions.

Measurement of the bulk properties of humic substances such as organic carbon content and UV-vis light absorptivity could provide important knowledge regarding their chemical reactivity during water treatment. In particular, due to the polydisperse nature of humic substances, assessment of the molecular weight and/or size distribution profiles could also bring site specific information (Chin et al., 1994). Moreover, polydispersity of humic substances displays diversity as a result of prevailing physical-chemical interactions i.e. adsorptive interactions with various oxide surfaces and also with respect to the oxidation conditions. Molecular size fractionation profiles of various HAs under oxidative and non-oxidative conditions have been presented previously (Uyguner and Bekbolet, 2005a; Kerc et al., 2004; Liu et al., 2008). Basically, the decreasing profile of the UV-vis parameters of sole HA with respect to the decreasing molecular size could be attributed mainly to the decreasing organic carbon contents of the respective fractions.

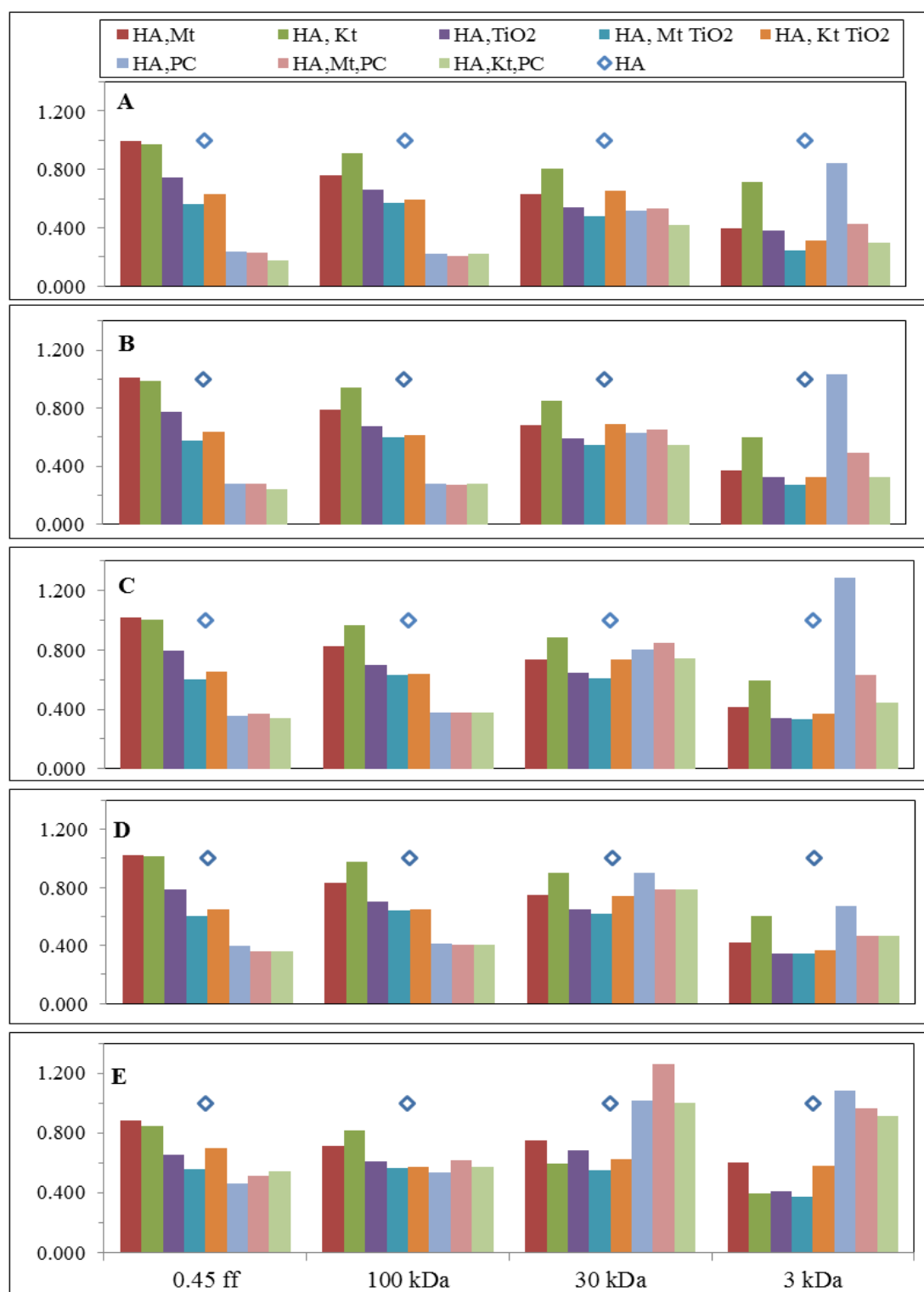


Figure 4.59. Molecular size distribution pattern of humic acid both in the presence and absence of montmorillonite and kaolinite under oxidative and non-oxidative conditions, A: Color₄₃₆, B: UV₃₆₅, C: UV₂₈₀, D: UV₂₅₄, and E: DOC y-axis represents normalized fractions of the respective parameters.

Through photocatalysis, the observed consistent trend could also be explained by the removal of the organic carbon fractions with functional groups mostly responsible from color forming moieties composed of units with lone pair electrons as well as conjugated systems. These groups pertaining from the inner carbon skeleton could also be responsible for surface interactions and could be removed faster through oxidative degradation. Besides the effective removal of higher molecular size fractions (100 kDa and 30 kDa fractions), transformation to lower molecular size fractions (<3kDa) was more pronounced for sole HA rather than HA in the presence of either Mt or Kt. In light of the presented information, it could be visualized that the photocatalytic treatment of the natural colloidal consortium composed of “humic acid and clay particles” could be a plausible treatment option.

4.1.12. Excitation–emission matrix (EEM) fluorescence spectra to monitoring the photocatalytic degradation of humic acid in the presence of clay particles

Natural organic matter is a major concern in drinking water treatment due to well documented disadvantages including undesirable sensory properties. Dissolved organic matter (DOM) is a heterogeneous mixture of diverse organic compounds being aromatic and aliphatic in nature. Oxygen, nitrogen and sulfur containing functional groups (e.g. carboxyl, phenol, enol, alcohol, carbonyl, amine and thiol groups) act as bridges between the organic groups as well as protude from the aromatic skeleton. With reference to the illdefined complex nature of natural organic matter primarily composed of humic substances (humic and fulvic acids) organic matter contents are expressed by dissolved organic carbon contents (DOC). Moreover, several non-destructive spectroscopic analytical techniques are also employed for the chemical characterization of the organic matrix present in natural waters. Besides UV-vis spectroscopic features, DOM exhibits fluorescence properties via absorption of high-energy photons and re-emission of lower-energy photons at longer wavelengths (Her et al., 2003). Excitation-emission matrix (EEM) produces fluorescence spectra at many different excitation wavelengths providing an overall view of all features existing within a selected spectral range (Baker, 2001). This technique has been widely used to differentiate the origin of the organic matter in natural environments (Parlanti et al., 2000; Chen et al., 2003a and 2003b; Sierra et al., 2005; Bieroza et al., 2009a; Carstea et al., 2010; Halim et al., 2013; Stedmon et al., 2011).

Recently, this technique found an application area in describing the behaviour of organic fluorophores during various treatment schemes (Hambly et al., 2010; Bagthoth et al., 2011; Sanchez et al., 2013; Valencia et al., 2013).

4.1.12.1. Removal efficiencies of unoxidized and photocatalytically oxidized humic acid in the presence of clay minerals. In relation to the maximum fluorescence emission intensities measured both for excitation-emission fluorescence spectra ($FI_{emis350}$ λ_{max} 455 nm) and synchronous fluorescence spectra (FI_{syn} λ_{max} 474 nm), fluorescence excitation–emission fluorescence spectra (EEM) were given in a comparative order with respect to the untreated conditions (Figure 4.60 A-F), and photocatalytically treated conditions for sole HA (Figure 4.61 A-D), HA in the presence of Mt (Figure 4.62 A-D) and HA in the presence of Kt (Figure 4.63 A-D) under irradiation periods of t_{irr} = 20 min, 60 min, 120 min and 180 min. Photocatalytic degradation and adsorptive removal efficiencies of HA expressed by the descriptive spectroscopic parameters under the indicated conditions were given in Table 4.24.

Under unoxidized conditions, adsorptive interactions resulted in removals of UV-vis parameters in an inconsistent trend. The most significant effect was attained in the presence of both TiO_2 and Kt revealing 34% DOC. With reference to the irradiation periods, removal efficiencies of HA displayed a consistent trend in a decreasing order of $Color_{436} > UV_{280} > UV_{280} > UV_{254}$ irrespective of the reaction conditions. During the early stages of photocatalytic treatment i.e. t_{irr} = 20 min, removals of $\geq 46\%$, upon further irradiation conditions i.e. t_{irr} = 60 min, removals of $\geq 62\%$ were attained for the specified UV-vis parameters. However, under these conditions DOC removal was $<50\%$ indicating the presence of significant amounts of organic carbon composed of mostly dense aromatic skeleton with decreasing degrees of color forming chromophoric groups.

EEM fluorescence spectra of humic acid under pre photocatalytic treatment conditions: Intrinsic fluorescence of humic acids covers information relating to structure, conformation, and heterogeneity of organic matter as well as dynamical properties related to intramolecular and intermolecular interactions (Mobed et al., 1996). Humic structural units express fluorescence properties generally described by fluorescence intensities recorded by emission or synchronous modes (Hudson et al., 2007; Uyguner and Bekbolet,

2005a). Since fluorescent organic matter exhibits discrete intensity peaks at known wavelengths, fluorescence centers could be detected by inspection of the EEM data (Baker, 2001).

Table 4.24. Descriptive UV-vis spectroscopic parameters and DOC for unoxidized and photocatalytically oxidized humic acid in the presence of clay minerals (t_{irr} : 0, 20 min, 60 min, 120 min and 180 min).

	UV-vis parameters			DOC mg L ⁻¹
	Color ₄₃₆ m ⁻¹	UV ₂₈₀ m ⁻¹	UV ₂₅₄ m ⁻¹	
HA, initial	23.9	46.5	119.9	17.00
Unoxidized conditions, Removal, %				
HA and TiO ₂	44	40	36	31
HA and Mt	22	17	13	5
HA and Kt	21	18	17	16
HA, Mt, TiO ₂	45	40	37	29
HA, Kt, TiO ₂	39	38	40	34
Photocatalytic treatment, irradiation time: 20 min, Removal, %				
HA	58	48	46	39
HA and Mt	66	56	55	46
HA and Kt	66	55	54	42
Photocatalytic treatment, irradiation time: 60 min, Removal, %				
HA	80	64	62	46
HA and Mt	85	70	68	49
HA and Kt	85	69	67	47
Photocatalytic treatment, irradiation time: 120 min, Removal %				
HA	91	66	83	64
HA and Mt	92	63	81	58
HA and Kt	92	63	82	60
Photocatalytic treatment, irradiation time: 180 min, Removal, %				
HA	93	84	92	78
HA and Mt	96	86	93	73
HA and Kt	98	95	97	75

According to the pioneering work of Senesi and colleagues, the occurrence of fluorescence bands and peaks with high relative intensity at short wavelengths is associated with the presence of simple structural components of wide molecular heterogeneity and

small molecular weight, small degree of aromatic polycondensation, small level of conjugated chromophores. The prevalence of fluorescence bands with high relative intensity at long wavelengths may be ascribed to the presence of extended, linearly-condensed aromatic ring networks and other unsaturated conjugated bond systems representing large molecular weight units (Senesi et al., 1990; Senesi et al., 1991).

Humic substances typically express fluorescence in the excitation range of $\lambda_{\text{exc}} \sim 300 - 400$ nm and the emission range of $\lambda_{\text{emis}} \sim 400 - 500$ nm. Moreover, Coble ascribed these fluorophoric centers as humic-like fluorescence (peak A, fluorescence excited between λ_{exc} 220 and 250 nm, and emitted between λ_{emis} 400 and 460 nm), fulvic-like fluorescence (peak C, fluorescence excited between λ_{exc} 300 and 340 nm, and emitted between λ_{emis} 400 and 460 nm), and protein-like (tryptophan and tyrosine) fluorescence (peak T, fluorescence excited between λ_{exc} 270 and 280 nm and emitted between λ_{emis} 330 and 370 nm) (Coble, 1996). Although these groups have attributed to the origin of the organic matter, their variability could also be ascribed to the oxidative degradation and formation of new fluorophores.

Under dark conditions, interactions of HA with TiO_2 surface and clay minerals either Mt or Kt distinctly affected the EEM fluorescence spectra expressing comparatively higher intensities (Figure 4.60 A-F). The most significant effect was observed in the presence of Kt displaying the significant role of the fluorophoric groups in the binding sites of HA and the respective surfaces. Upon inspection of the EEM spectral features of sole HA, both humic-like and fulvic-like fluorophoric regions could be visualized. Regarding the prevailing adsorptive interactions, humic fluorophores were distinctly evident both for binary and ternary systems. Introduction of TiO_2 to HA resulted to a regional separation of humic fluorophores in excitation wavelengths of λ_{exc} 320nm and 410nm with emission wavelengths of λ_{emis} 430 nm and 520 nm respectively (Figure 4.60 B). The presence of either Mt or Kt exerted a more pronounced effect on fulvic-like fluorophoric region as represented by differing fluorescence intensities (Figure 1 C and D). Moreover, in the presence of both TiO_2 and Mt, humic fluorophores displayed close similarities (Figure 4.60 E). On the other hand, in the presence of both TiO_2 and Kt, fulvic-like fluorophores were more affected in comparison to the aforementioned cases (Figure 4.60 F).

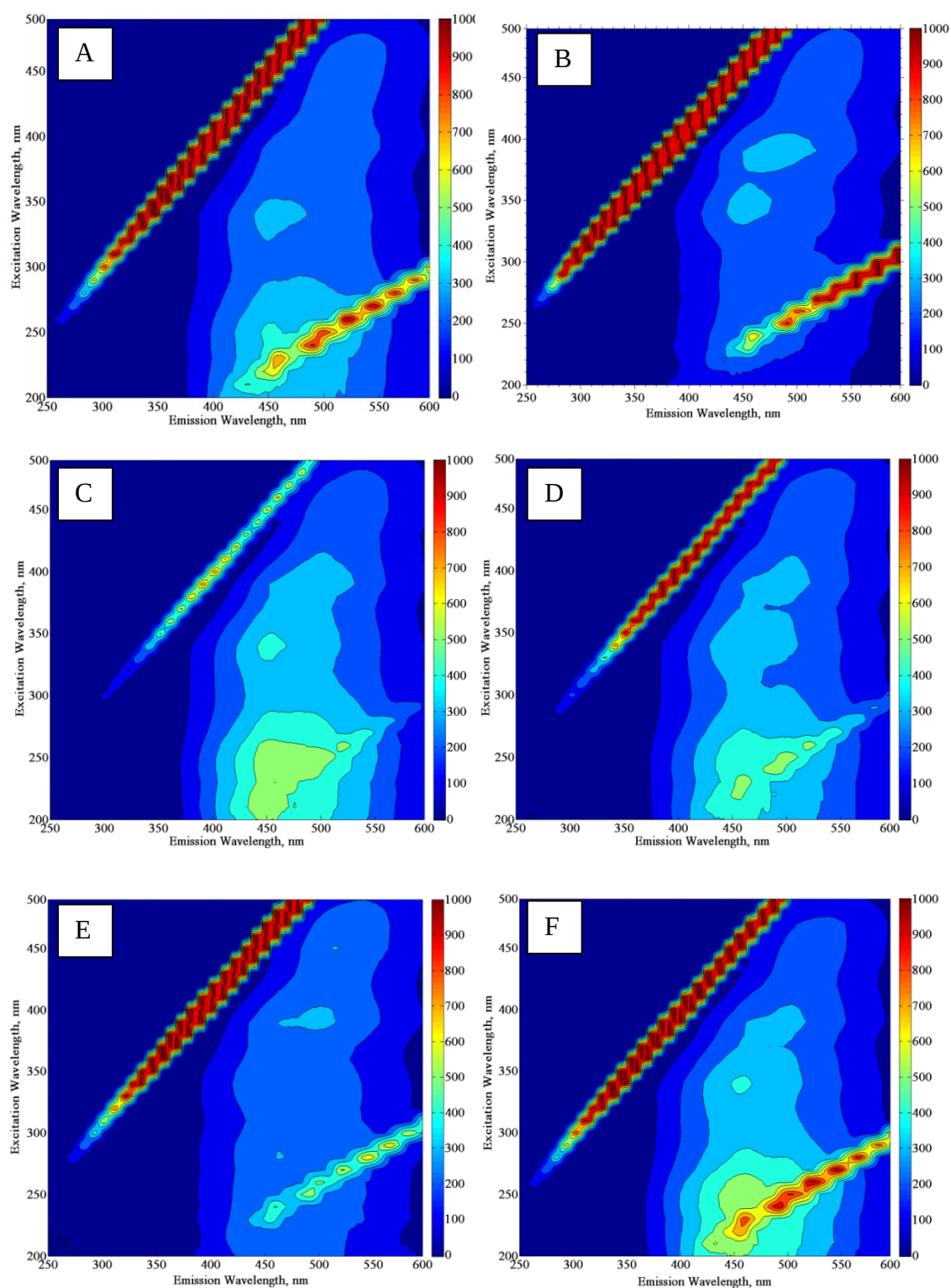


Figure 4.60. EEM fluorescence spectra of humic acid (A), humic acid in the presence of TiO_2 (B), humic acid in the presence of montmorillonite (C), humic acid in the presence of kaolinite (D), humic acid in the presence of TiO_2 and montmorillonite (E), humic acid in the presence of TiO_2 and kaolinite (F).

4.1.12.2. EEM matrices of humic acid under post photocatalytic oxidation conditions.

Irradiation time dependent EEM fluorescence spectra of photocatalytically oxidized sole HA were presented in Figure 4.61 A-D.

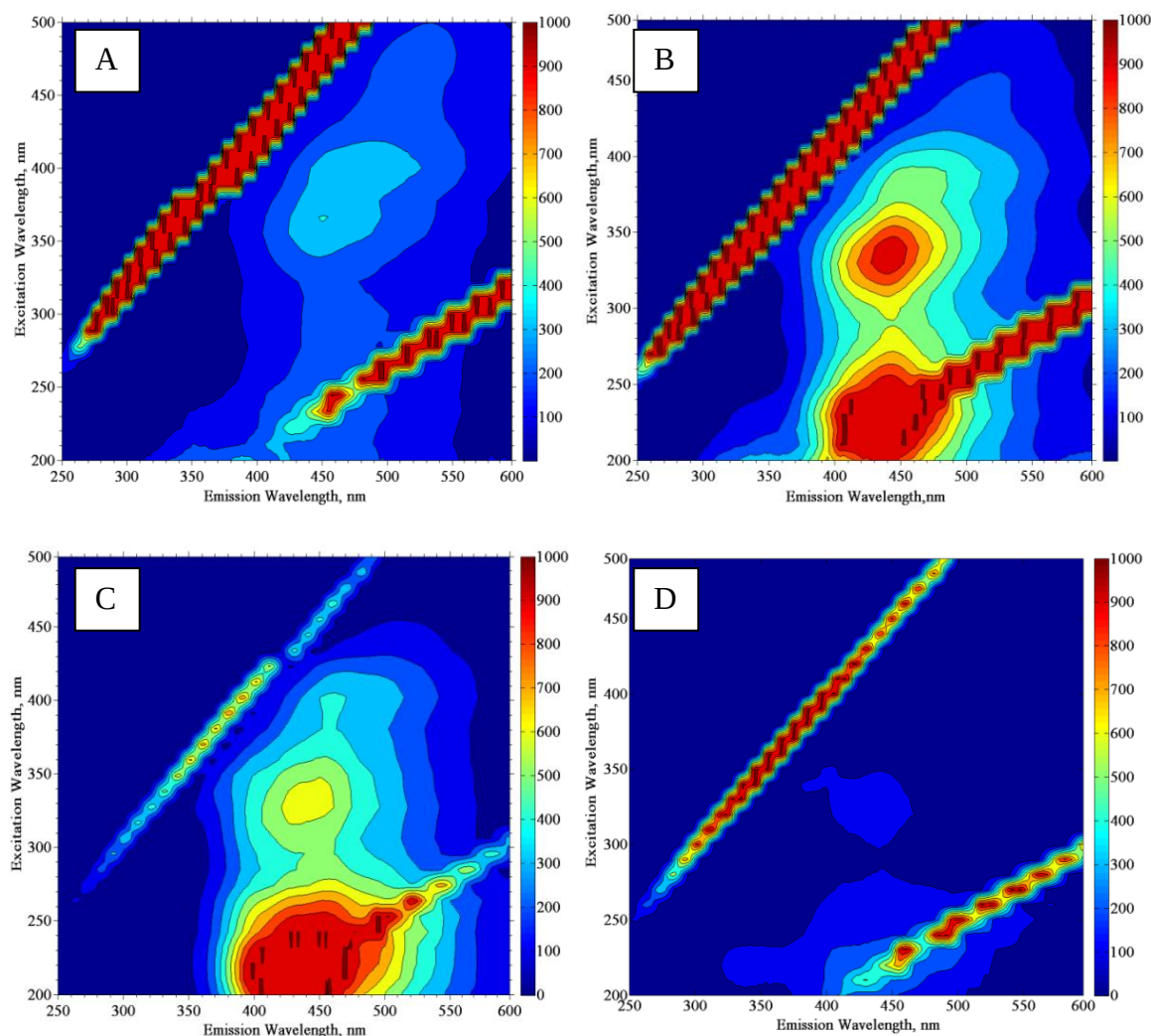


Figure 4.61. Irradiation time dependent EEM fluorescence spectra of humic acid A: 20 min, B: 60 min, C: 120 min, D: 180 min.

EEM fluorescence spectra of sole HA (Figure 4.61 A) and HA following pre-adsorption phase (Figure 4.61 B) displayed the presence of both humic-like and fulvic-like fluorophores. During early stages of irradiation (t_{irr} = 20 min) humic-like fluorophores were evident (Figure 4.61 A). Moreover, upon further irradiation periods, intensities of both humic-like and fulvic-like fluorophores increased although 46% DOC was removed under these conditions of photocatalysis (Figure 4.61 B). Under prolonged irradiation conditions,

i.e. $t_{irr} = 120$ min, removal of humic-like fluorophores were more evident than the removal of fulvic-like fluorophores (Figure 4.61 C). Upon 180 min of irradiation, both humic-like and fulvic-like fluorophores were removed substantially in accordance with almost 80% DOC removal (Table 4.24). The remaining humic acid fractions could possibly be expressing fulvic-like properties.

EEM fluorescence spectral features of photocatalytically oxidized HA in the presence of Mt are presented in Figure 4.62A-D.

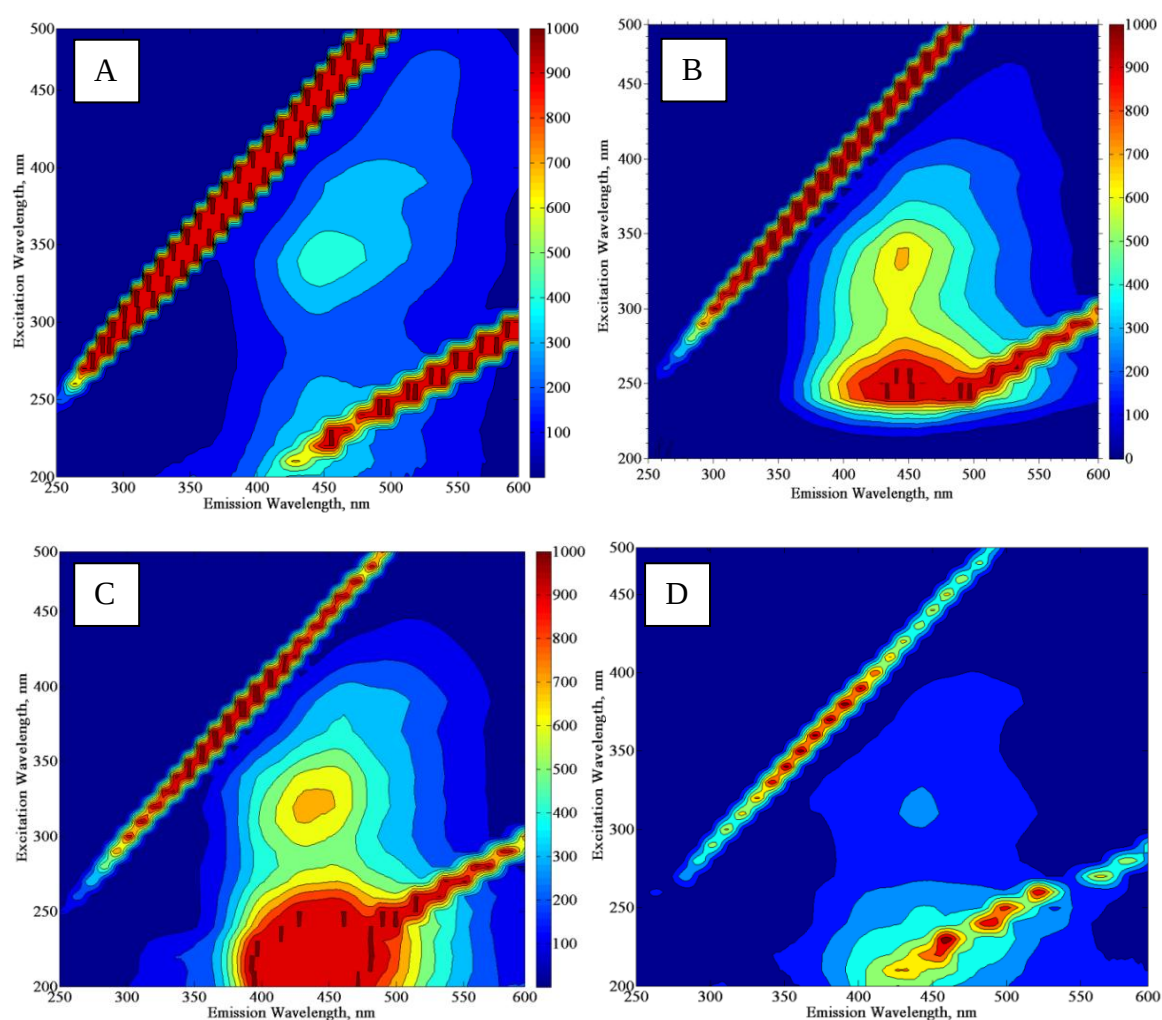


Figure 4.62. Irradiation time dependent EEM fluorescence spectra of humic acid in the presence of montmorillonite, A: 20 min, B: 60 min, C: 120 min, D: 180 min.

EEM fluorescence spectra of sole HA (Figure 4.60 A) and HA in the presence of both TiO_2 and Mt (Figure 4.60 E) predominantly reflected the presence of humic-like

fluorophores. Regional separation of fluorophoric groups could be visualized even under early stages of irradiation, $t_{irr}= 20$ min (Figure 6.62 A). Further irradiation conditions ($t_{irr}= 60$ min) displayed the emergence of oxidized humic fractions exhibiting a transition to fulvic-like fluorophoric character with higher fluorescence intensities (Figure 4.62 B). Moreover, upon irradiation of $t_{irr}= 120$ min, fulvic-like fluorophores were distinctly evident in the excitation wavelength region of λ_{exc} 280nm-200nm with an emission wavelength region of λ_{emis} 360nm-550nm (Figure 62 C). Furthermore, upon prolonged irradiation period of $t_{irr}= 180$ min, HA fluorophores were still recorded in good accordance with 73% DOC removal (Figure 4.62 D, Table 4.24).

EEM fluorescence spectral features of photocatalytically oxidized HA in the presence of Kt are presented in Figure 4.63 A-D. Regarding the EEM fluorescence spectra of sole HA (Figure 4.60 A) and HA in the presence of both TiO_2 and Kt (Figure 4.60 F), HA could be visualized as possessing more fulvic-like fluorophores prone to photocatalysis. Even under early stages of irradiation i.e. $t_{irr}= 20$ min, fulvic-like fluorophores were more evident displaying higher intensities (Figure 4.63 A). Upon irradiation period of 60 min, oxidized humic fluorophores were more intensely visualized in the excitation wavelength region of λ_{exc} 290 nm-370 nm with an emission wavelength region of λ_{emis} 400 nm-520 nm (Figure 4.63 B). Further irradiation conditions resulted in transformation to fulvic-like character through removal of humic-like fluorophores (Figure 4.63 C).

Through photocatalytic oxidation achieved by irradiation for 180 min, both humic-like and fulvic-like fluorophores were removed significantly in good accordance with 75% DOC removal (Table 4.24). Moreover, under the specified long irradiation periods, the organic matrix would be highly oxidized, hydroxylated, less aromatic in character therefore resembling more fulvic like properties. Since fulvic-like fluorophores were also removed in relation to the removal of humic-like fluorophores, the reason could be attributed to the formation of the lower molecular weight fractions as expressed previously (Sen-Kavurmaci and Bekbolet, 2013a). Besides the effective removal of higher molecular size fractions (100 kDa and 30 kDa fractions), transformation to lower molecular size fractions (<3kDa) was more pronounced for sole HA rather than HA in the presence of either Mt or Kt as presented in Figure 4.59.

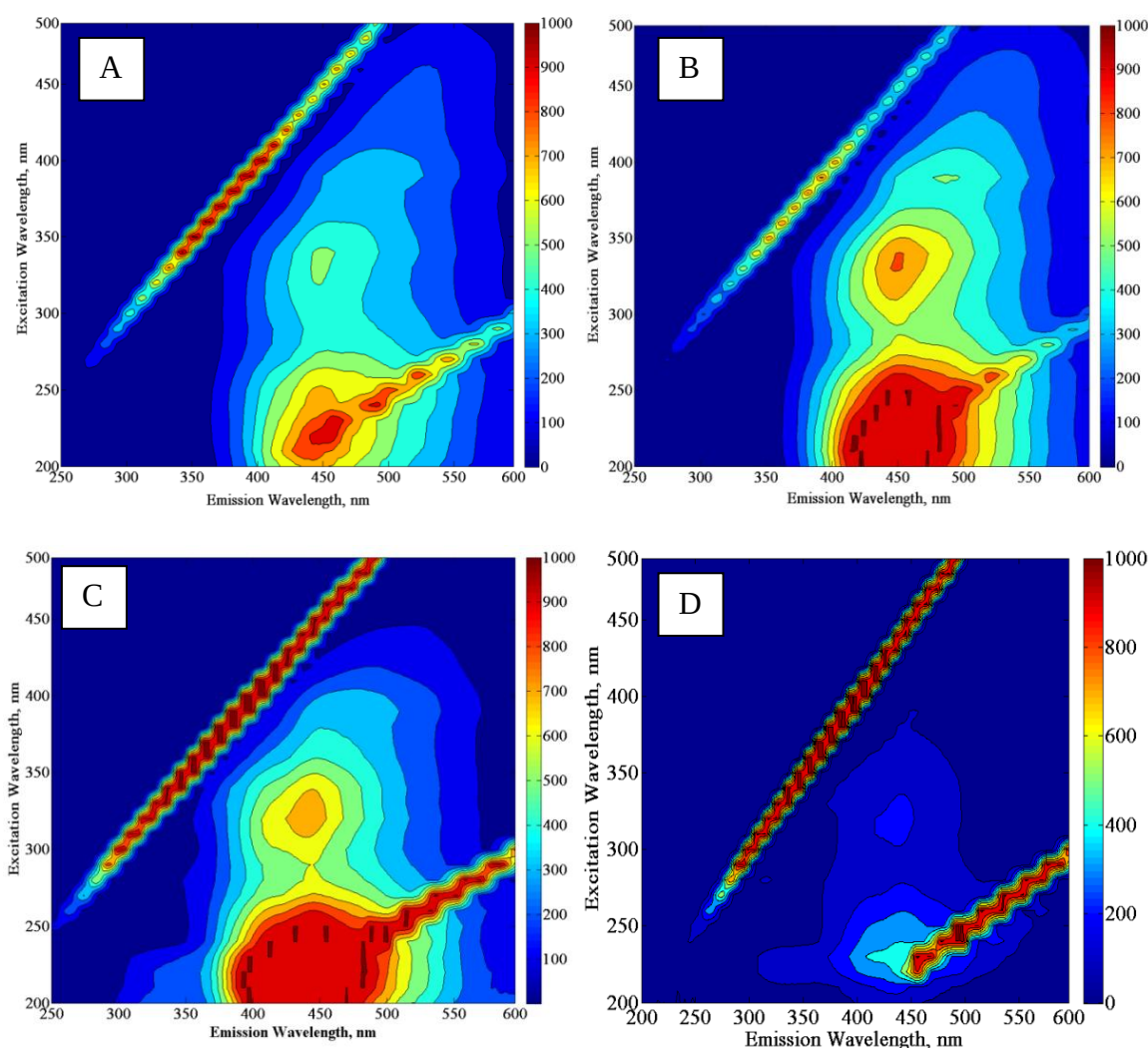


Figure 4.63. Irradiation time dependent EEM fluorescence spectra of humic acid in the presence of kaolinite, A: 20 min, B: 60 min, C: 120 min, D: 180 min.

4.1.12.3. Role of Ca^{2+} ions on the EEM fluorescence spectral features of photocatalytically oxidized HA in the presence of either montmorillonite or kaolinite. Calcium ion as an ubiquitous common cation in natural waters could bind to the deprotonated carboxyl and phenolic groups of humic acid that are present in close proximity to each other. The presence of Ca^{2+} ions also exert an ionic strength effect resulting in reconfiguration of humic sub-fractions through intra- and inter-bridging mechanism. Consequently, conformational changes resulting from electrostatic interactions result in the alterations of the adsorptive properties of humic acid onto both TiO_2 and clay minerals. Moreover, it was previously shown that the presence of divalent cations enhanced the photocatalytic removal of humic acid (Uyguner and Bekbolet, 2010). Fluorescence quenching has been

reported as a promising tool for investigating the binding behavior of humic fluorophores with metal ions (Kumke et al., 2005; Zhang et al., 2010; Wu et al., 2012). Therefore, the role of Ca^{2+} ions on the EEM fluorescence features of photocatalytically oxidized HA in the presence of either Mt or Kt are evaluated as presented in Figure 4.64 A-I.

Ca^{2+} effect ($\text{pCa}^{2+} = 3.5$) on humic acid fluorophores could be regarded as more significant with respect to the effects observed due to the presence of either Mt or Kt (Figure 4.64 A-C). Although no further DOC removal was attained upon irradiation period of 20 min (~55%), EEM fluorescence spectra displayed fluorophoric changes both in humic-like and fulvic-like regions (Figure 4.64 D-F). Upon irradiation period of $t_{\text{irr}} = 60$ min, a transition to fulvic-like fluorophoric region could be visualized through inspection of the humic-like fluorophores (Figure 4.64 G-I). Following 180 min of irradiation time, in accordance with almost complete mineralization of humic acid, EEM represented no significant fluorescence features resembling a blank water EEM. It should also be mentioned that the dose dependent pCa^{2+} effect could also be visualized in the EEM of photocatalytically treated HA. Increasing Ca^{2+} ion concentration resulted in substantial increases in the fulvic like fluorophores of HA upon photocatalytic treatment for 60 min of irradiation period.

With reference to the presented EEM fluorescence spectral features of the HA treated under non-oxidative as well as oxidative conditions, regional speciation depending on the excitation-emission bands were presented in Table 4.25. Fluorescence intensity strength was indicated by a symbol (+). Besides the aforementioned fulvic-like (Region III) and humic-like fluorophores (Region V), Region I and Region II signified the fluorophores resembling aromatic proteins and Region IV represented fluorophores attributed to the microbial byproducts mainly composed of amino acid like structures (tryptophan and tyrosine like). The emergence of Region I could be slightly visualized for photocatalytically oxidized sole humic acid ($t_{\text{irr}} = 60$ min) and humic acid in the presence of either Mt or Kt upon irradiation period of 120 min. Region II could only be specified under certain conditions especially for prolonged irradiation periods in the presence of either Mt or Kt. Region IV could be detected more significantly in the presence of Ca^{2+} ions under both non-oxidative as well as oxidative conditions.

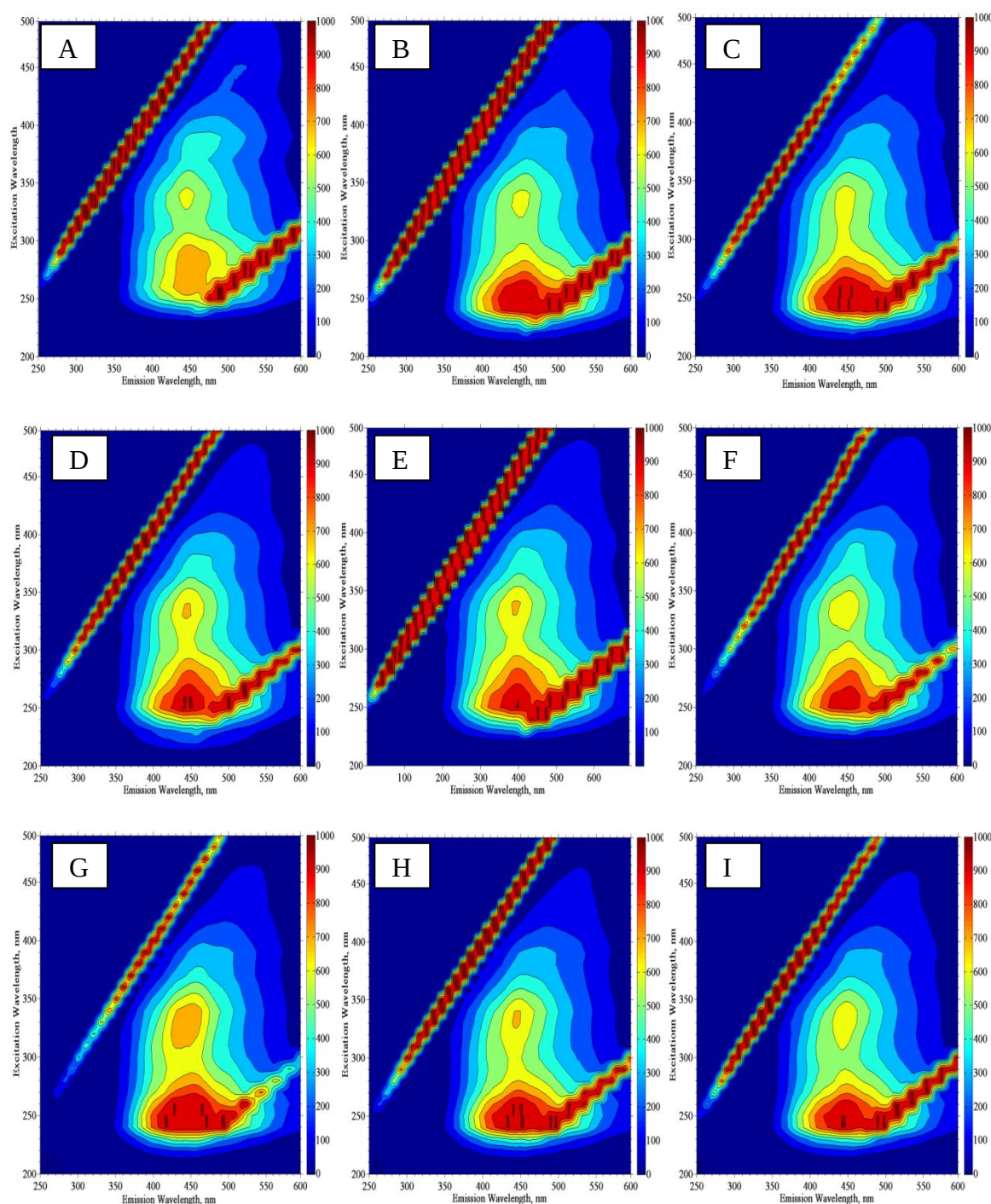


Figure 4.64. Ca^{2+} effect on EEM fluorescence spectra of humic acid in the presence of either montmorillonite or kaolinite, A: $t_{\text{irr}} = 0$ for sole humic acid, B: $t_{\text{irr}} = 0$ for HA in the presence of montmorillonite, C: $t_{\text{irr}} = 0$ for humic acid in the presence of kaolinite, D: $t_{\text{irr}} = 20$ min for sole humic acid, E: $t_{\text{irr}} = 20$ min for humic acid in the presence of montmorillonite, F: $t_{\text{irr}} = 20$ min for humic acid in the presence of kaolinite, G: $t_{\text{irr}} = 60$ min for sole humic acid, H: $t_{\text{irr}} = 60$ min for humic acid in the presence of montmorillonite, I: $t_{\text{irr}} = 60$ min for humic acid in the presence of kaolinite.

Table 4.25. Regional speciation of the EEM fluorescence spectral features of the humic acid treated under non-oxidative as well as oxidative conditions.

System	Region I Aromatic Proteins I $\lambda_{\text{exc}}220-250$ $\lambda_{\text{emis}}280-332$	Region II Aromatic Proteins II $\lambda_{\text{exc}}220-250$ $\lambda_{\text{emis}}332-380$	Region III Fulvic acid- like $\lambda_{\text{exc}}220-250$ $\lambda_{\text{emis}}380-580$	Region IV Microbial byproducts $\lambda_{\text{exc}}250-470$ $\lambda_{\text{emis}}280-380$	Region V, Humic acid- like $\lambda_{\text{exc}}250-470$ $\lambda_{\text{emis}}380-580$
HA	---	---	++++	---	+++
Unoxidized conditions					
HA,TiO ₂	---	-	+++	---	+++
HA,Mt	---	-	++++	--	+++
HA,Kt	---	+	+++	---	+++
HA,Mt,TiO ₂	---	-	++	---	+++
HA,Kt,TiO ₂	---	-	++++	---	+++
Photocatalytic treatment					
HA, 20 min	---	+	++	---	+++
HA, 60 min	+	++	+++++	+	++++++
HA,120 min	---	+++	+++++	++	+++++
HA,180 min	---	+	++	---	+
Mt, 20 min	---	+	++	+	++++
Mt, 60 min	---	++	+++++	+	+++++
Mt,120 min	+	+++	+++++	+	++++++
Mt,180 min	---	+	+++	---	++
Kt, 20 min	---	+	+++++	+	+++++
Kt, 60 min	---	+	+++++	---	++++++
Kt,120 min	+	+++	+++++	+	+++++
Kt,180 min	---	---	----	-----	----
pCa effect					
pCa t= 0	---	---	++	+	++++++
pCa, 20 min	---	+	++++	++	++++++

Table 4.25 Continued.

pCa,60 min	---	+	++++	++	++++++
pCaMt,t= 0	---	+	++++	++	++++++
pCaMt,20 min	---	+	++++	++	++++++
pCaMt,60 min	---	+	++++	++	++++++
pCaKt, t= 0	---	+	++++	++	++++++
pCaKt,20 min	---	+	++++	++	++++++
pCaKt,60 min	---	+	++++	++	++++++

4.1.11.4. Quantification approach. In drinking water treatment, organic matter removal results in substantial decreases in fluorescence intensity along the treatment train starting from raw to clarified water samples. In particular, the decrease in fluorescence intensity between raw and clarified water was correlated with the measured decrease in total organic carbon contents ($r^2 = 0.91$) (Bieroza et al., 2009b). A number of different methods were presented for interpreting fluorescence data covering peak detection to complex numerical modeling schemes like Parallel Factor Analysis (Coble, 1996; McKnight et al., 2001; Murphy et al., 2008). Fluorescence-derived index defined as Fluorescence Intensity (FI) was represented by the ratio of the emission intensity at $\lambda_{\text{emis}} = 450$ nm to that at $\lambda_{\text{emis}} = 500$ nm, following excitation at $\lambda_{\text{exc}} = 370$ nm (McKnight et al., 2001). An inverse relationship was elucidated between FI and aromaticity of humic matter. Moreover, $\text{FI} \leq 1.4$ represented humic fluorophores of forganic matter originating from terrestrial sources whereas $\text{FI} \geq 1.9$ mainly attributed to microbially derived organic material.

Therefore, fluorescence intensity (FI) could well be correlated with the specified UV parameters i.e. UV_{254} and UV_{280} . In comparison with fluorescence spectroscopy, UV absorbance measurements represented either as UV_{254} or UV_{280} has been reported to express lower selectivity and higher applicability to a wide range of organic molecules representing diverse chemical properties, i.e. natural organic matter (Marhaba et al., 2003).

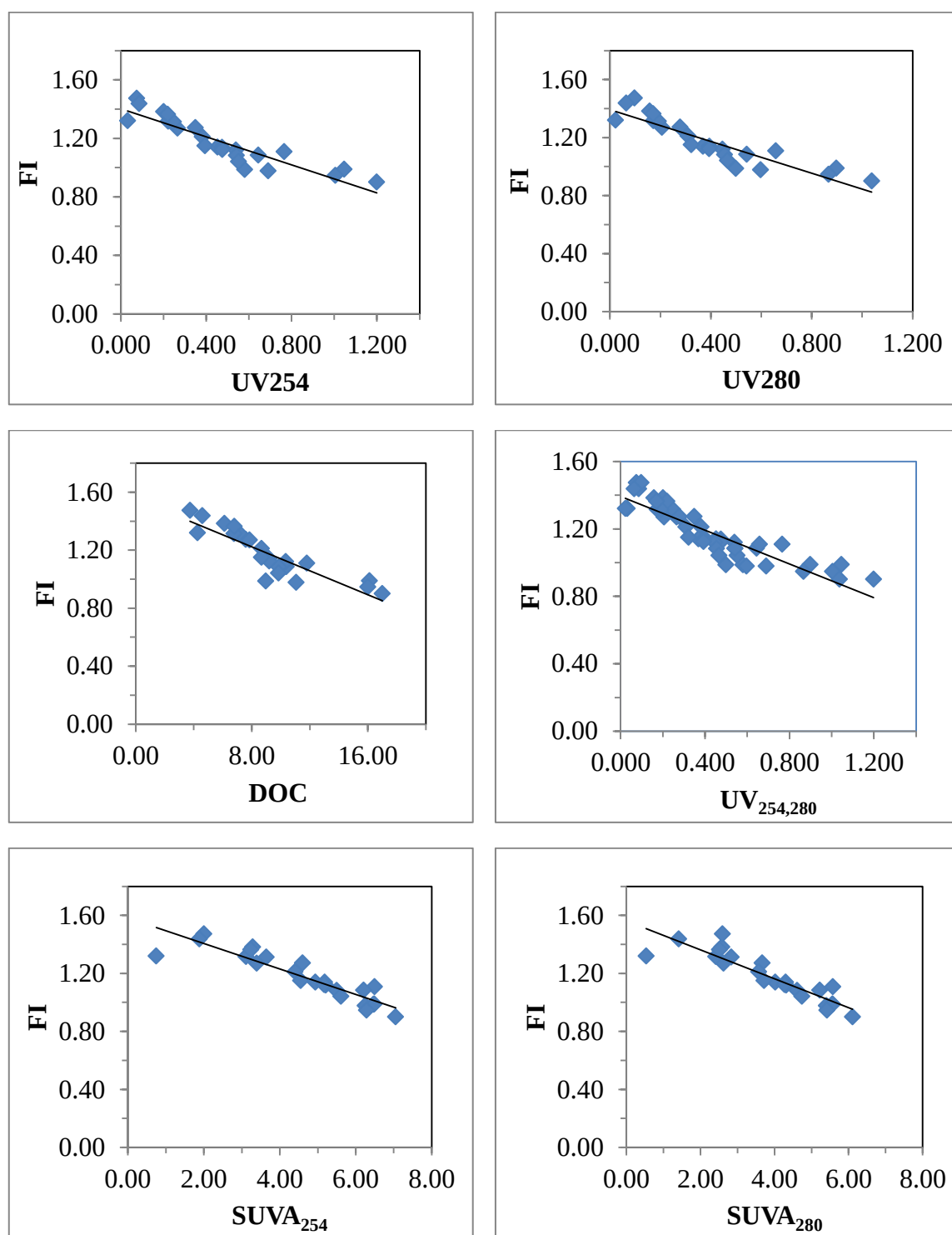


Figure 4.65. Correlations between FI and specified and specific humic parameters recorded under non-oxidative (dark) and oxidative (photocatalytic) conditions.

Below presented linear regression equations were derived from the data achieved by photocatalytic treatment of sole humic acid and “humic acid and clay binary systems” also

covering pre-treatment conditions as expressed by preliminary experiments indicating initial adsorption phase ($r^2 > 0.80$) (Section 4.1.1). It should also be mentioned that under non-irradiation conditions, adsorptive interactions could result in alterations in aromaticity without causing any significant change in FI as verified by the previously reported experimental results (McKnight et al., 2001).

$$FI = -0.480 \cdot UV_{254} + 1.402 \quad \text{and} \quad FI = -0.547 \cdot UV_{280} + 1.392 \quad (4.15)$$

Considering the close similarities attained in the regression equation coefficients, the data were merged to a single regression equation. Moreover, DOC degradation data also displayed an inverse relationship ($r^2 = 0.78$) with FI.

$$FI = -0.500 \cdot UV_{254/280} + 1.392 \quad \text{and} \quad FI = -0.041 \cdot DOC + 1.554 \quad (4.16)$$

Considering the significance of specific UV-vis parameters, FI variations were correlated with $SUVA_{254}$ and $SUVA_{280}$ ($r^2 > 0.82$) (Sen Kavurmaci and Bekbolet, 2013b).

$$FI = -0.088 \cdot SUVA_{254} + 1.583 \quad \text{and} \quad FI = -0.100 \cdot SUVA_{280} + 1.562 \quad (4.17)$$

EEM fluorescence spectral features were evaluated for the elucidation of the photocatalytic degradation of sole humic acid and humic acid in the presence of clay minerals either as montmorillonite or kaolinite. The role of Ca^{2+} ions was also visualized through EEM under the specified conditions. EEM features reflected the irradiation time dependent transformation of the humic like fluorophores to fulvic like fluorophores in accordance with the photocatalytic removal of humic acid. Upon photocatalytic treatment, the role of Mt was more pronounced with respect to the effects observed in the presence of Kt in comparison to the results achieved for sole humic acid. Upon prolonged irradiation conditions (180 min) almost complete removal of fluorophoric groups were detected in relation to a substantial degree of mineralization ($> 75\%$ removal of DOC). As a quantification approach, Fluorescence-derived index defined as Fluorescence Intensity (FI) as represented by the ratio of the emission intensity at $\lambda_{emis} = 450$ nm to that at $\lambda_{emis} = 500$ nm, following excitation at $\lambda_{exc} = 370$ nm was successfully correlated to UV_{254} and UV_{280} revealing an inverse relationship. Moreover, through normalization of the specified UV parameters to DOC contents, $SUVA_{254}$ and $SUVA_{280}$ could also be successfully correlated to FI.

4.2. Adsorption of Humic Acid onto TiO₂ in the Presence of Clay Minerals

Adsorption of humic acid onto sole TiO₂ and TiO₂ in the presence of clay minerals either as montmorillonite or kaolinite were assessed by batch adsorption experiments. Adsorption properties of humic acid onto sole TiO₂ and TiO₂ in the presence of clay minerals either as montmorillonite or kaolinite were evaluated in terms of the specified UV-vis parameters as well as DOC. Adsorption isotherms of Color₄₃₆, UV₂₅₄ and DOC were presented as figures within the text, whereas the isotherms related to UV₃₆₅ and UV₂₈₀ parameters were presented in Appendix A. Adsorption isotherms were evaluated in terms of the adsorption isotherm types (Types S, L, H and C) classified by Giles (Giles et al., 1960, Sposito, 1984). Adsorption data of the indicated humic parameters were further modeled by Freundlich adsorption isotherm model (Equation 2.3) and the calculated model coefficients were compiled in respective tables (Tables 2.4).

4.2.1. Humic acid adsorption onto sole TiO₂

In order to evaluate the adsorption properties of humic acid onto sole TiO₂, equilibrium adsorption experiments were carried out using 50 mg L⁻¹ humic acid (DOC_i= 17.00 mgL⁻¹) and TiO₂ as the adsorbate in the range from 0.10 mg mL⁻¹ to 1.0 mg mL⁻¹. Referring to the adsorption isotherm parameters, C_e (concentration of the adsorbate remaining in solution) values were correlated with q_A (adsorbed amount of adsorbate per mass of adsorbent). Adsorption isotherms attained for Color₄₃₆, UV₂₅₄ and DOC parameters of humic acid were given in the Figure 4.66, Figure 4.67, and Figure 4.68, respectively. Moreover, adsorption isotherms attained for UV₃₆₅ and UV₂₈₀ were presented in Appendix A.

Figure 4.66 indicated that C_e values of Color₄₃₆ varied between 13.02 – 20.96 m⁻¹ depending on the amount of TiO₂ present in solution. The corresponding q_A values were found to be in the range of 293 – 752 m⁻¹g⁻¹. As could be seen in Figure 4.2, C_e values of UV₂₅₄ varied between 64.8– 110.6 m⁻¹ and the values of q_A were in the range of 1559 – 3304 m⁻¹g⁻¹ correspondingly. Figure 4.68 represented that the values of C_e varied from 6.64 to 15.06 mg L⁻¹ for DOC. The corresponding q_A values varied in between 247– 788 mg L⁻¹g⁻¹.

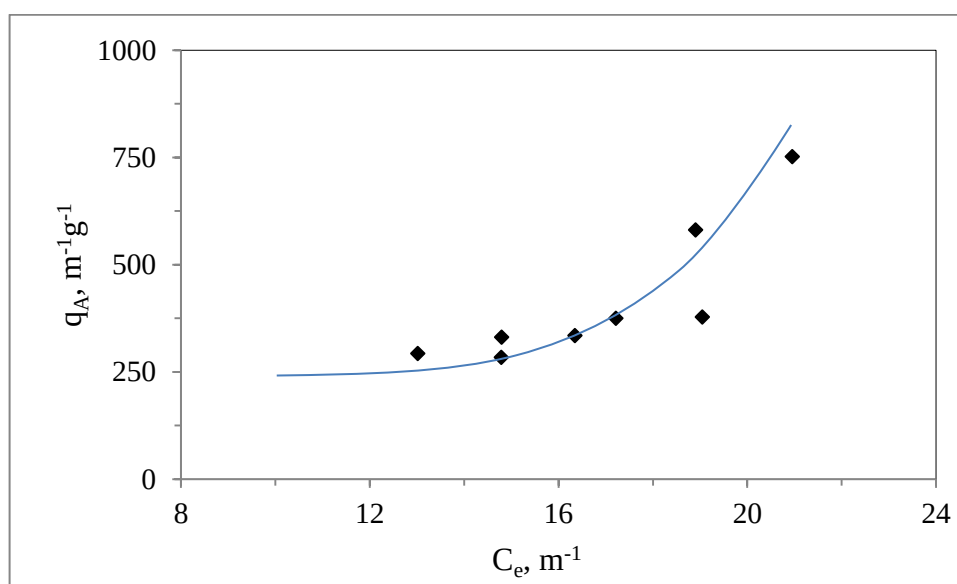


Figure 4.66. Color₄₃₆ adsorption isotherm of humic acid adsorption onto TiO₂.

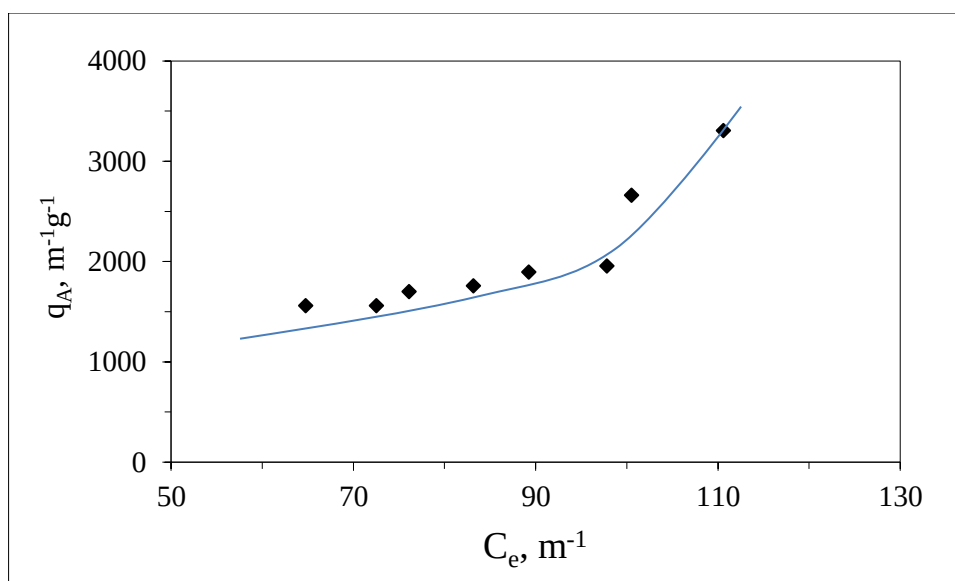


Figure 4.67. UV₂₅₄ adsorption isotherm of humic acid adsorption onto TiO₂.

As could be seen from Figure 4.66 and Figure 4.67 given above, the adsorption mg Isotherms showed similar trends both in terms of Color₄₃₆ and UV₂₅₄ parameters. This exhibited trend would have agreed well with the S-curve type isotherm. DOC adsorption isotherm also expressed the S-type adsorption isotherm shape representing an initial small slope followed by a rather steep increase in q_A .

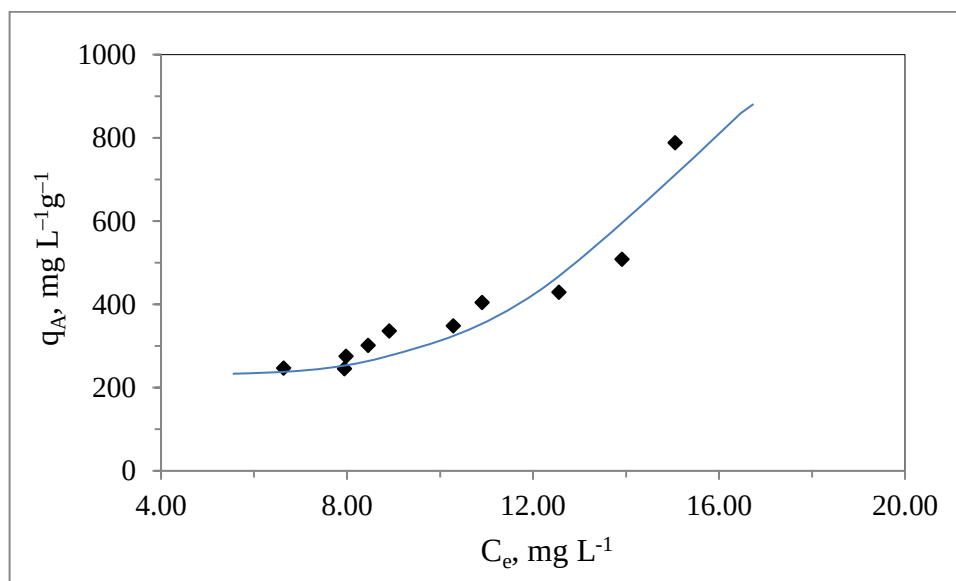


Figure 4.68. DOC adsorption isotherm of humic acid adsorption onto TiO₂.

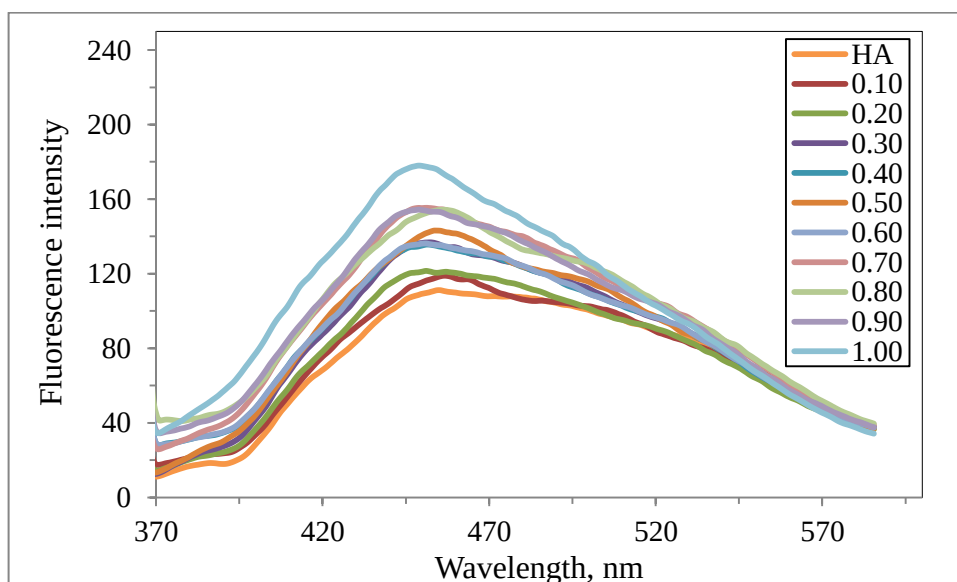
ΔC_e and Δq_A values of Color₄₃₆ for humic acid were 7.94 m⁻¹ and 460 m⁻¹g⁻¹ respectively. ΔC_e and Δq_A of UV₂₅₄ were 45.84 m⁻¹ and 1745 m⁻¹g⁻¹, respectively. DOC isotherm for humic acid gave a ΔC_e of 8.42 mg L⁻¹ where Δq_A was 541 mg L⁻¹g⁻¹. The value of q_A changes markedly with small changes in C_e .

The adsorption isotherm data attained for the specified humic parameters were modeled by Freundlich adsorption isotherm model ($R^2 \geq 0.80$). According to Table 4.26, adsorption capacity constant for Color₄₃₆ was found to be lowest (2.18) with respect to the K_F values calculated for the other humic parameters (4.66-6.39). UV- absorbing centers of humic acid as expressed by UV₃₆₅, UV₂₈₀ and UV₂₅₄ parameters displayed quite similar K_F values in comparison to the K_F obtained through adsorption of organic fractions as expressed by the dissolved organic carbon contents. Adsorption intensity, $1/n$ values for all of the UV-vis parameters *i.e.* Color₄₃₆, UV₃₆₅, UV₂₅₄ as well as DOC were found to be greater than 1, indicating that the adsorption bond would be weak possibly leading to surface precipitation. It should also be stated in cases that $1/n > 1$, adsorption should also be considered as proceeding through multi-layer formation. Adsorption intensity, $1/n$ values followed a decreasing order of Color₄₃₆ > UV₃₆₅ = UV₂₅₄ > DOC > UV₂₈₀. Adsorption capacity, K_F values followed a decreasing order of DOC > UV₃₆₅ > UV₂₅₄ > UV₂₈₀ > Color₄₃₆.

Table 4.26. Freundlich isotherm model coefficients of humic acid adsorption onto TiO_2 .

	K_f	$1/n$
Color ₄₃₆	2.18	1.84
UV ₃₆₅	6.39	1.33
UV ₂₈₀	4.66	1.34
UV ₂₅₄	5.82	1.31
DOC	19.7	1.27

Moreover, fluorescence spectral features were also evaluated to provide further information on the adsorption of humic acid onto TiO_2 . Emission and synchronous scan fluorescence spectra of humic acid were illustrated in Figure 4.69 and Figure 4.70, respectively. A continuously increasing trend in fluorescence intensity at emission wavelength of $\lambda_{\text{max}} = 450 \text{ nm}$ was observed with respect to the increasing TiO_2 dose. The reason could be attributed to the formation of new fluorophoric groups upon adsorption of humic fractions onto TiO_2 . Moreover, it could be also regarded that the initially present humic fluorophores might not take part in adsorptive interactions.

Figure 4.69. Emission scan fluorescence spectra of humic acid: Humic acid adsorption onto TiO_2 .

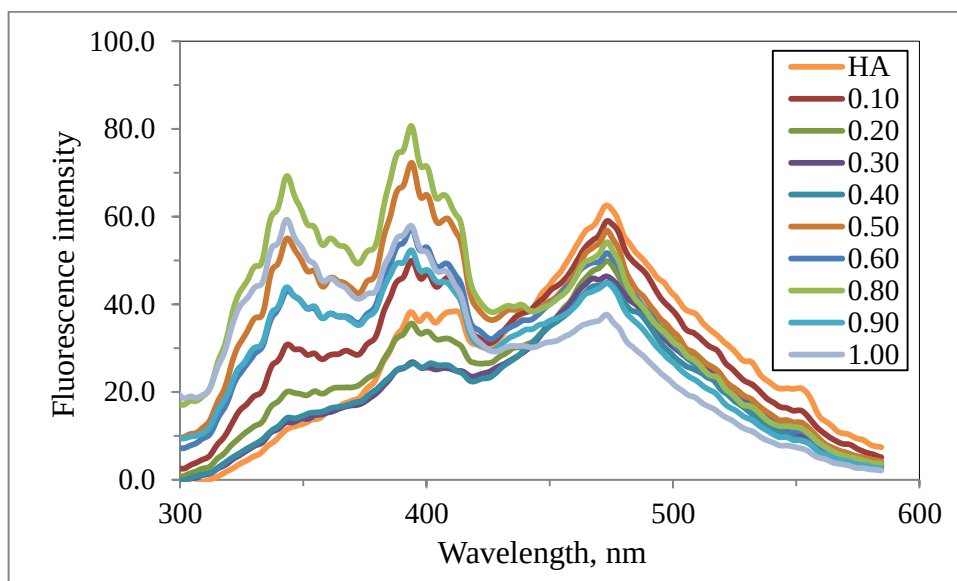


Figure 4.70. Synchronous scan fluorescence spectra of humic acid: Humic acid adsorption onto TiO_2 .

Adsorption dependent fluorescence intensities recorded at synchronous scan emission wavelength of λ_{max} (470 nm) displayed a decreasing trend with respect to increased TiO_2 dose (Figure 4.70). On the other hand, double peaks observed at approximately emission wavelengths of $\lambda_{\text{emis}} = 345$ nm and 395 nm displayed non-specific variations with respect to the TiO_2 dose. The fluorescence intensities recorded at emission wavelengths of $\lambda_{\text{emis}} = 345$ nm and $\lambda_{\text{emis}} = 395$ nm exhibited considerably higher values with respect to the fluorescence intensities recorded at emission wavelength of $\lambda_{\text{max}} = 470$ nm. It should also be mentioned that raw humic acid did not exhibit any considerable peak formation at this emission wavelengths of $\lambda_{\text{emis}} = 345$ nm and $\lambda_{\text{emis}} = 395$ nm.

4.2.2. Humic acid adsorption onto montmorillonite

In order to investigate the role of montmorillonite on the adsorption phenomena of humic acid, batch adsorption experiments were carried out using montmorillonite ($1.0 \text{ mg mL}^{-1} - 14.0 \text{ mg mL}^{-1}$). Adsorption isotherms attained for Color_{436} , UV_{254} and DOC parameters of humic acid were given in the Figure 4.71, Figure 4.72, and Figure 4.73, respectively. The isotherms related to the UV_{365} and UV_{280} parameters were presented in Appendix A.

Figure 4.71 indicated that C_e values varied between 16.41 – 20.04 m^{-1} for Color_{436} depending on the amount of montmorillonite present in solution. The corresponding values of q_A were in the range of 24.4 – 123 $\text{m}^{-1}\text{g}^{-1}$. As it could be seen in Figure 4.72, C_e values varied between 93.34-117.86 m^{-1} for UV_{254} . The values of q_A calculated were in the range of 84.43-370 $\text{m}^{-1}\text{g}^{-1}$ correspondingly.

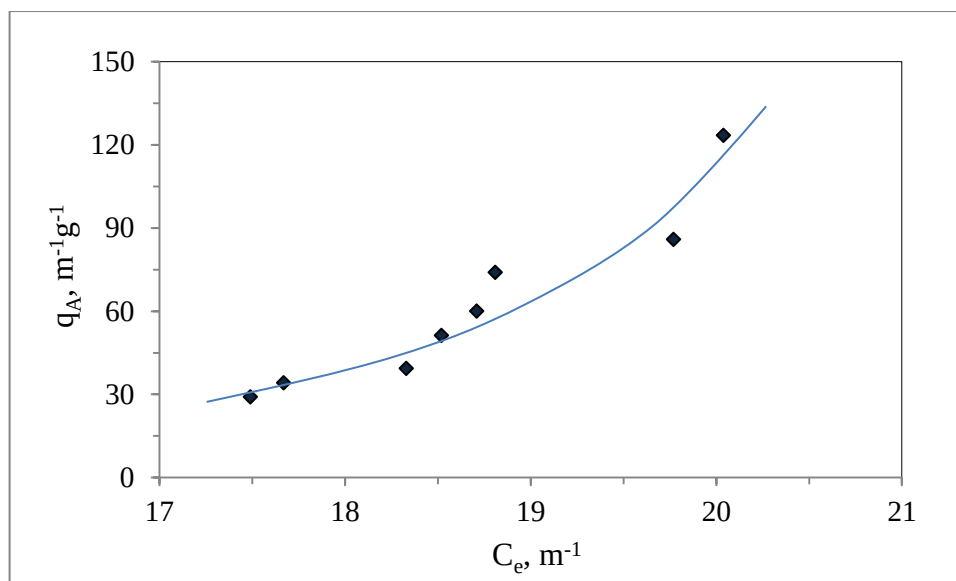


Figure 4.71. Color_{436} adsorption isotherm of humic acid adsorption onto montmorillonite.

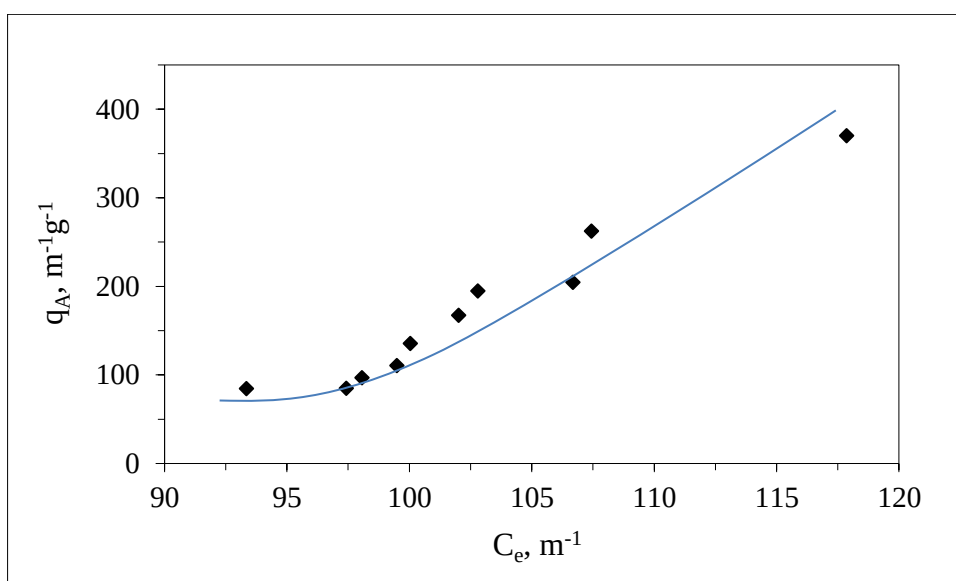


Figure 4.72. UV_{254} adsorption isotherm of humic acid adsorption onto montmorillonite.

Figure 4.73 represented that the values of C_e varied from 14.62 -20.84 mg L^{-1} for DOC. The calculated q_A values of DOC varied in between 24.6-115 $\text{mg L}^{-1} \text{g}^{-1}$.

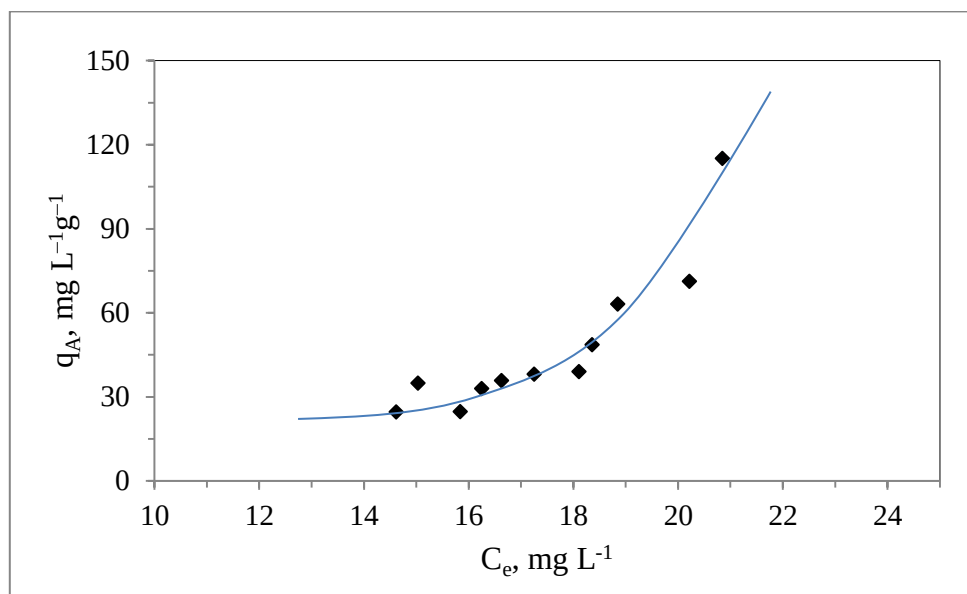


Figure 4.73. DOC adsorption isotherm of humic acid adsorption onto montmorillonite.

It could clearly be seen from Figures 4.68 and 4.73 that the DOC isotherm showed a quite different pattern with respect to Color_{436} and UV_{254} isotherms. Color_{436} isotherm of humic acid, (Figure 4.71) was distributed in a narrow C_e range ($\Delta C_e = 3.63 \text{ m}^{-1}$) and Δq_A was calculated as $98.9 \text{ m}^{-1} \text{g}^{-1}$. The UV_{254} isotherm (Figure 4.72) gave $286 \text{ m}^{-1} \text{g}^{-1}$ for Δq_A and 24.52 m^{-1} for ΔC_e . Moreover, Δq_A and ΔC_e for DOC isotherm (Figure 4.73) were $90.4 \text{ mg L}^{-1} \text{g}^{-1}$ and 6.23 mg L^{-1} , respectively. Despite the observed differences in the shapes of the indicated isotherms, they could all be characterized by an S type isotherm shape. In a similar manner, surface complexation could result in surface accumulation of the humic fractions through strong humic–humic interactions. Referring to the adsorption isotherms attained for humic acid adsorption onto TiO_2 , montmorillonite and TiO_2 acting as adsorbents could possibly expressed similar surface sites for humic acid functional groups (figures representing TiO_2 and Mt).

The application of the Freundlich adsorption isotherm model revealed adsorption capacity, K_f , and adsorption intensity, $1/n$, for humic acid adsorption onto montmorillonite as listed in Table 4.27.

Table 4.27. Freundlich isotherm model coefficients of humic acid adsorption onto montmorillonite.

	K_f	$1/n$
Color ₄₃₆	9.51×10^{-7}	7.70
UV ₃₆₅	1.25×10^{-9}	6.84
UV ₂₈₀	2.52×10^{-13}	7.64
UV ₂₅₄	2.90×10^{-13}	7.32
DOC	1.09×10^{-3}	3.71

According to Table 4.27, adsorption capacity (K_F) values attained for all of the humic parameters in the presence of montmorillonite were found to be lower than the adsorption capacities of humic acid adsorption onto TiO_2 (Table 4.27). K_f values for UV-vis parameters and DOC were found to be significantly low. It indicated that humic acid adsorption onto montmorillonite could be regarded as insignificant. However, K_f value for DOC was slightly higher than that attained for humic acid and TiO_2 binary system and $1/n$ value was found to be 3.71 (Table 4.27). Adsorption intensity values were found to be greater than one indicating a favorable adsorption profile irrespective of the specified humic parameter. Adsorption intensity values exhibited a decreasing order of $\text{Color}_{436} > \text{UV}_{280} > \text{UV}_{254} > \text{UV}_{365} > \text{DOC}$. Adsorption capacity values displayed a decreasing order of $\text{DOC} > \text{Color}_{436} > \text{UV}_{365} > \text{UV}_{254} > \text{UV}_{280}$.

Emission and synchronous scan fluorescence spectra of humic acid were illustrated in Figure 4.74 and Figure 4.75 respectively. From a general perspective, in the presence of varying doses of montmorillonite, an inconsistent trend was observed both for synchronous and emission scan fluorescence intensity spectra with respect to the increasing Mt dose. Emission scan fluorescence features of humic acid followed the same spectral shape in an overlapping trend (Figure 4.74). A slight difference was observed in fluorescence intensities recorded at maximum emission wavelength of $\lambda_{\text{max}} = 450\text{nm}$ ($\Delta\text{FI} = 20$).

Moreover, synchronous scan fluorescence spectral features also displayed an almost similar fluorescence intensity values at maximum emission wavelength of $\lambda_{\text{max}} = 450\text{nm}$

with an overlapping trend for all montmorillonite doses being considerably lower than the FI recorded for sole humic acid (Figure 4.75).

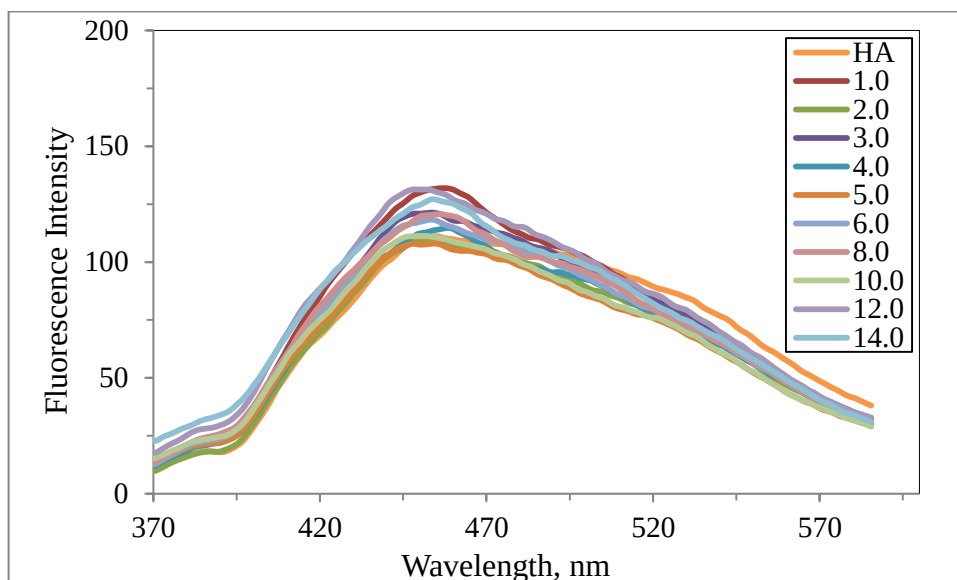


Figure 4.74. Emission scan fluorescence spectra of humic acid; Humic acid adsorption onto montmorillonite.

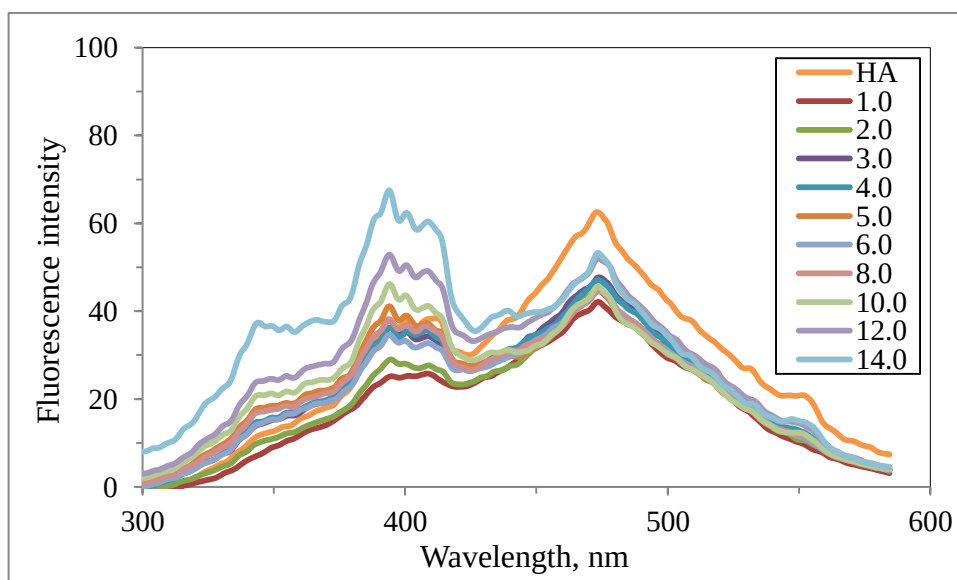


Figure 4.75. Synchronous scan fluorescence spectra of humic acid; Humic acid adsorption onto montmorillonite.

In the presence of montmorillonite and in the fluorescence emission wavelength range of $\lambda_{\text{emis}} = 325 \text{ nm}$ to 425 nm , synchronous scan fluorescence spectral features of humic acid displayed a comparatively different trend with respect to the observed fluorescence features of sole humic acid (Figure 4.75). The disappearance of the fluorophoric groups observed at emission wavelength region around $\lambda_{\text{emis}} = 435 \text{ nm}$ could be attributed to the possible role of these fluorophoric groups in adsorptive interactions prevailing between humic moieties and montmorillonite surface groups.

4.2.3. Humic acid adsorption onto kaolinite

With the purpose of evaluation of the adsorption properties of humic acid onto kaolinite, batch adsorption experiments were carried out using 50 mg L^{-1} humic acid and kaolinite ($1.0 \text{ mg mL}^{-1} - 14.0 \text{ mg mL}^{-1}$). Freundlich adsorption isotherms of humic acid for Color_{436} , UV_{254} and DOC were given in the Figure 4.76, Figure 4.77 and Figure 4.78, respectively. The isotherms related to the UV_{365} and UV_{280} parameters were presented in Appendix A.

As seen in Figure 4.76, C_e values varied between $5.28 - 16.52 \text{ m}^{-1}$ for Color_{436} depending on the amount of kaolinite present in solution. The calculated values of q_A were in the range of $48.6\text{-}328.00 \text{ m}^{-1}\text{g}^{-1}$ correspondingly. Figure 4.77 illustrated that the C_e values varied between $39.4\text{-}94.32 \text{ m}^{-1}$ for UV_{254} . The corresponding values of q_A calculated to be in the range of $204 - 1063 \text{ m}^{-1}\text{g}^{-1}$ for the corresponding C_e values. C_e values for DOC varied from 8.86 to 17.5 mg L^{-1} . The calculated q_A values for DOC varied in between $25.4\text{-}60.0 \text{ mg L}^{-1}\text{g}^{-1}$ (Figure 4.78).

While Δq_A and ΔC_e of Color_{436} were found to be $279 \text{ m}^{-1}\text{g}^{-1}$ and 11.24 m^{-1} , respectively, Δq_A and ΔC_e values for UV_{254} was found to be $860 \text{ m}^{-1}\text{g}^{-1}$ for Δq_A and 54.92 m^{-1} for ΔC_e . DOC isotherm for humic acid provided ΔC_e of 8.64 mg L^{-1} where Δq_A was $34.65 \text{ mg L}^{-1}\text{g}^{-1}$. It could be seen that the isotherms of DOC exhibited very narrow ΔC_e and Δq_A regions than the ΔC_e and Δq_A values of UV_{254} parameter. Regarding the isotherms presented for Color_{436} and UV_{254} an S type-isotherm is evident contrary to linear isotherm representing C-type isotherm attained for DOC. Although similar adsorption isotherm shapes were attained, humic acid structural features as expressed by the specified UV-vis

parameters could display significant differences in affinities towards the exposed kaolinite surfaces. Moreover, since DOC contents indicated the reactivities of the humic organic carbon moieties towards kaolinite adsorption sites, different adsorption isotherm shapes could be attained.

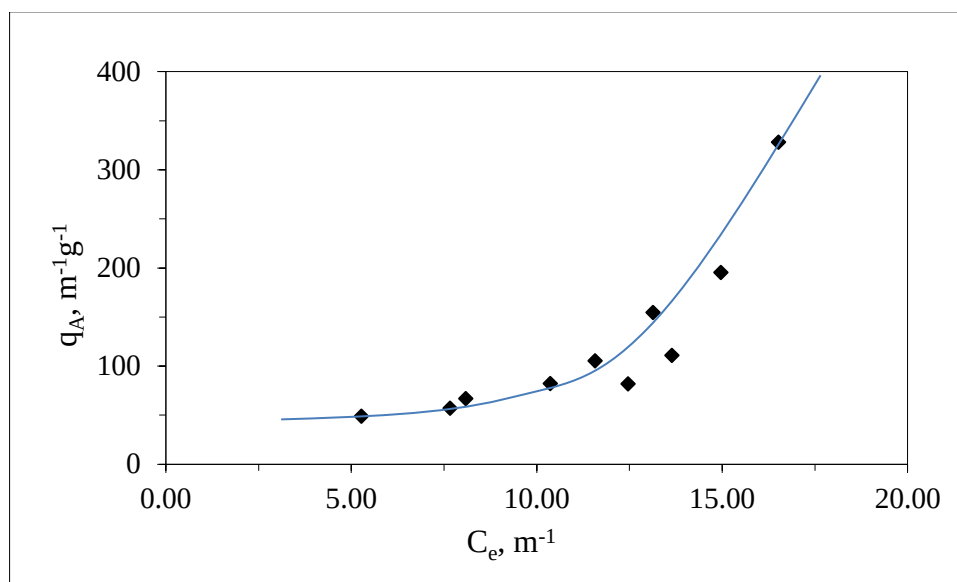


Figure 4.76. Color₄₃₆ adsorption isotherm of humic acid adsorption onto kaolinite.

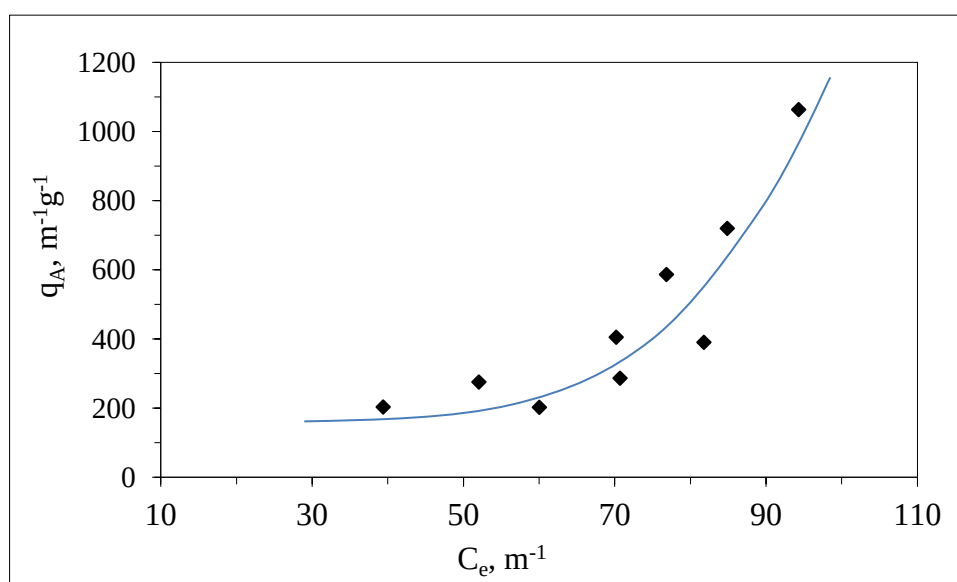


Figure 4.77. UV₂₅₄ adsorption isotherm of humic acid adsorption onto kaolinite.

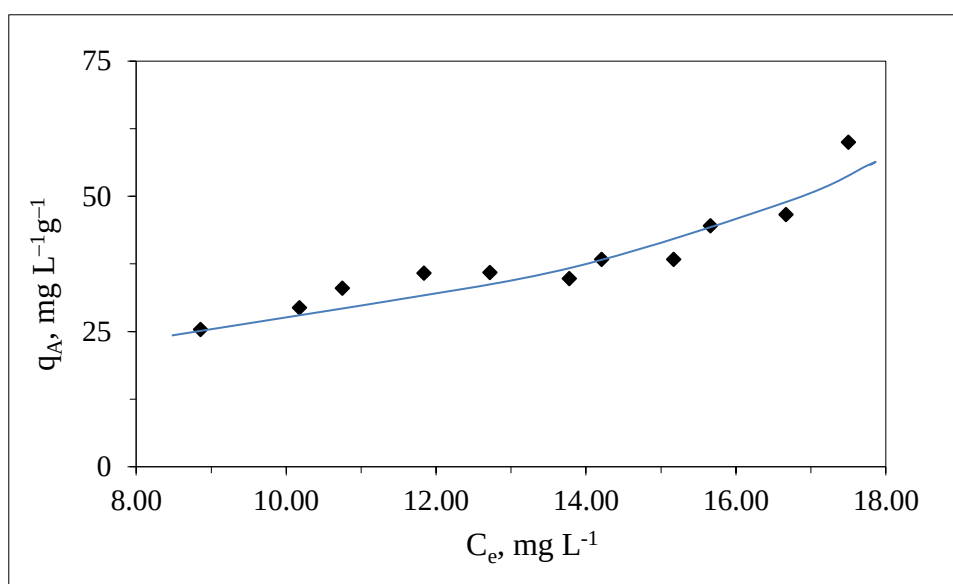


Figure 4.78. DOC adsorption isotherm of humic acid adsorption onto kaolinite.

The Freundlich adsorption model parameters as the adsorption capacity, K_f , and adsorption intensity, $1/n$, for humic acid adsorption onto kaolinite were listed in Table 4.28 ($r^2 > 0.80$).

Table 4.28. Freundlich isotherm model coefficients of humic acid adsorption onto kaolinite.

	K_f	$1/n$
Color ₄₃₆	3.17	1.47
UV ₃₆₅	1.71	1.48
UV ₂₈₀	0.306	1.73
UV ₂₅₄	0.394	1.63
DOC	2.93	0.989

According to Table 4.28, adsorption capacity constants for both of the UV absorbing centers and the color forming chromophoric groups were found to be different to each other. Adsorption intensity, $1/n$ values were found to be greater than one for all of the specified UV-vis parameters; however $1/n$ value for DOC was found to be equal to 0.989 representing an almost linear trend. Adsorption intensity values displayed a decreasing

order of $UV_{280} > UV_{254} > UV_{365} \geq Color_{436} > DOC$, whereas adsorption capacity values followed a decreasing order of $Color_{436} > DOC > UV_{365} > UV_{254} > UV_{280}$.

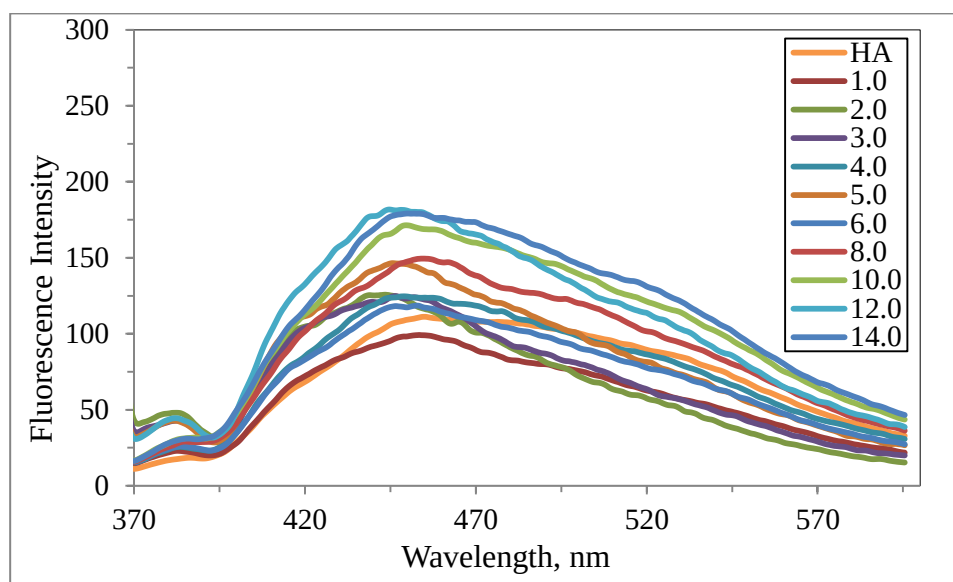


Figure 4.79. Emission scan fluorescence spectra of humic acid; Humic acid adsorption onto kaolinite.

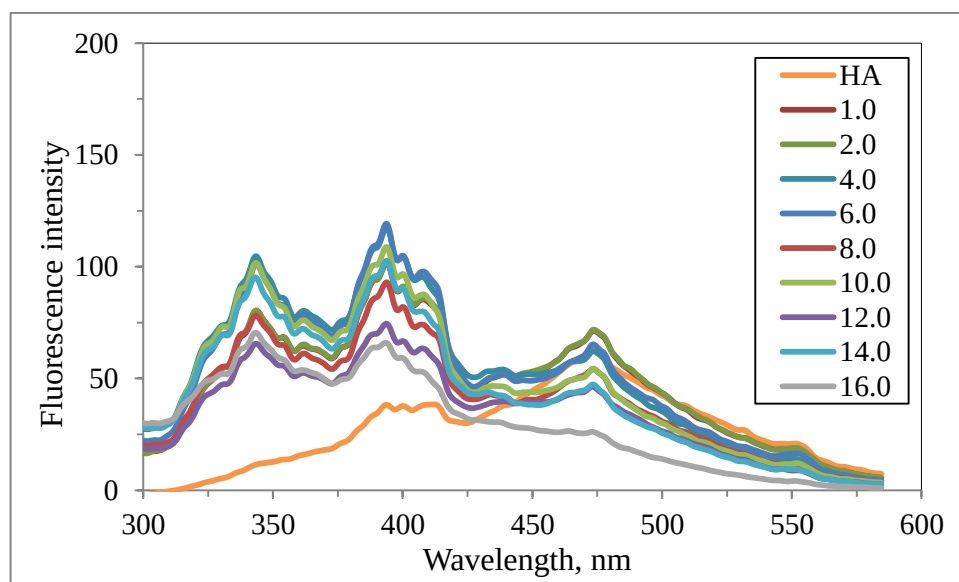


Figure 4.80. Synchronous scan fluorescence spectra of humic acid; Humic acid adsorption onto kaolinite.

For the assessment of the fluorescence spectroscopic features of humic acid attained under post adsorption conditions, emission scan fluorescence spectra were scanned in the range of 360-600 nm at a constant excitation wavelength of $\lambda_{\text{exc}} = 350$ nm (Figure 4.79). It could be visualized that a continuously increasing trend in emission scan fluorescence intensity at emission wavelength of $\lambda_{\text{max}} = 450$ nm was observed with respect to increasing kaolinite dose except that recorded for humic acid in the presence of 4.0 mg L^{-1} kaolinite dose. Displaying a non-overlapping behavior, emission scan fluorescence spectral features of humic acid recorded in case that kaolinite served as the adsorbent, could be visualized more significantly different from the ones recorded for sole humic acid (Figure 4.69) and humic acid in the presence of montmorillonite (Figure 4.74). Synchronous scan fluorescence spectra recorded for sole humic acid displayed a main peak around emission wavelength of $\lambda_{\text{max}} = 475$ nm and a moderate peak at emission wavelength of $\lambda_{\text{emis}} = 385$ nm with a comparatively lower intensity as explained previously. In the presence of various doses of kaolinite (1.0 mg mL^{-1} - 14.0 mg mL^{-1}), the main peak detected at emission wavelength of $\lambda_{\text{max}} = 475$ nm was evident. However, in the presence of 16.0 mg mL^{-1} synchronous scan fluorescence spectral features of humic displayed the removal of the fluorophores exhibiting emission at wavelength of $\lambda_{\text{max}} = 475$ nm. On the other hand, raw humic acid displayed a continuously increasing trend for synchronous scan fluorescence intensities up to emission wavelength of $\lambda_{\text{emis}} = 425$ nm. In the presence of kaolinite, fluorescence intensities increased displaying two peaks at emission wavelengths of $\lambda_{\text{emis}} = 345 \text{ nm}$ and 395 nm with increasing kaolinite doses. It should also be indicated that the synchronous scan fluorescence intensities of humic acid expressed a decreasing trend with respect to increasing kaolinite doses.

4.2.4. Humic acid adsorption onto TiO_2 in the presence of montmorillonite

With the aim of examining the interactive adsorption behavior of humic acid onto TiO_2 , batch adsorption experiments were also carried out with 50 mg L^{-1} humic acid in the presence of montmorillonite. In batch adsorption experiments, monmorillonite dose was kept constant as 0.20 mg L^{-1} and varied amount of TiO_2 doses (0.10 - 1.0 mg mL^{-1}) were applied. Adsorption isotherms of humic acid parameters as Color_{436} , UV_{254} and DOC were shown in Figures 4.81, Figures 4.82 and Figures 4.83, respectively. The isotherms related to the UV_{365} and UV_{280} parameters were presented in Appendix A.

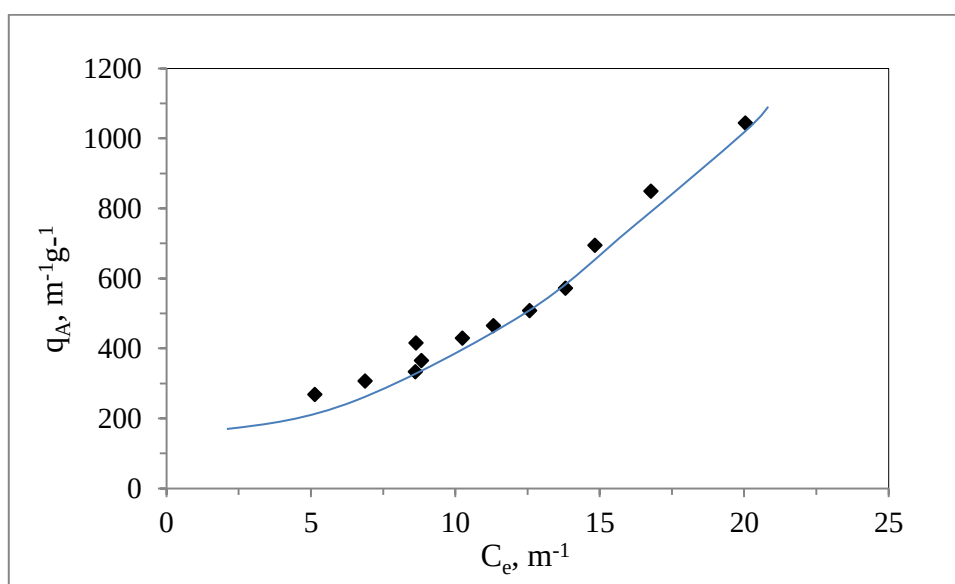


Figure 4.81. Color₄₃₆ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of montmorillonite.

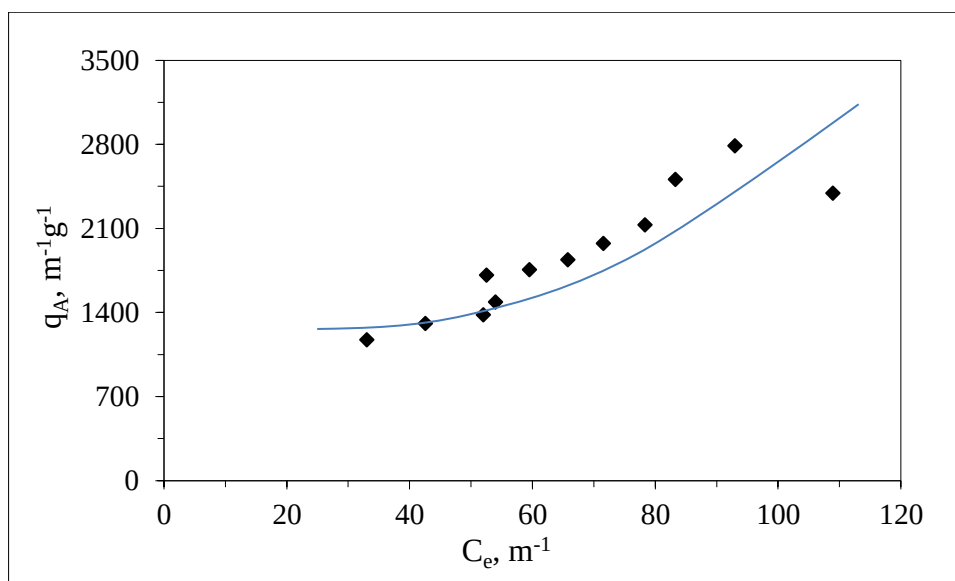


Figure 4.82. UV₂₅₄ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of montmorillonite.

Figure 4.81 indicated that C_e values of Color₄₃₆ varied between 5.14-20.04 m^{-1} depending on the amount of TiO₂ present in solution. The values of q_A calculated were in the range of 268-1044 $m^{-1} g^{-1}$ correspondingly. As it could be seen in Figure 4.82, C_e values

of UV_{254} , varied between 33.03 – 108.91 m^{-1} . The corresponding values of q_A were in the range of 1171 – $2390\text{ m}^{-1}\text{g}^{-1}$. Figure 4.83 showed that the values of C_e varied from 1.60 to 2.50 mg L^{-1} for DOC. Correspondingly, the calculated q_A values varied in between 35.4 – $142\text{ mg L}^{-1}\text{g}^{-1}$. ΔC_e and Δq_A values of $Color_{436}$ were found to be 14.90 m^{-1} and $776\text{ m}^{-1}\text{g}^{-1}$ respectively and ΔC_e and Δq_A for UV_{254} were 75.88 m^{-1} and $1219\text{ m}^{-1}\text{g}^{-1}$ respectively. As expected, the adsorption isotherm for $Color_{436}$ had a narrow ΔC_e and Δq_A range than the ΔC_e of UV_{254} . DOC adsorption isotherm of humic acid offered a ΔC_e of 11.65 mg L^{-1} whereas Δq_A was found to be equal to $306\text{ mg L}^{-1}\text{g}^{-1}$. With respect to the isotherm shapes presented in Figures 4.81–4.83, it could be indicated that the isotherms of the specified UV-vis parameters followed a rather smooth S type curve; DOC adsorption isotherm displayed a distinct S-type shape expressing a trend of multilayer adsorption model.

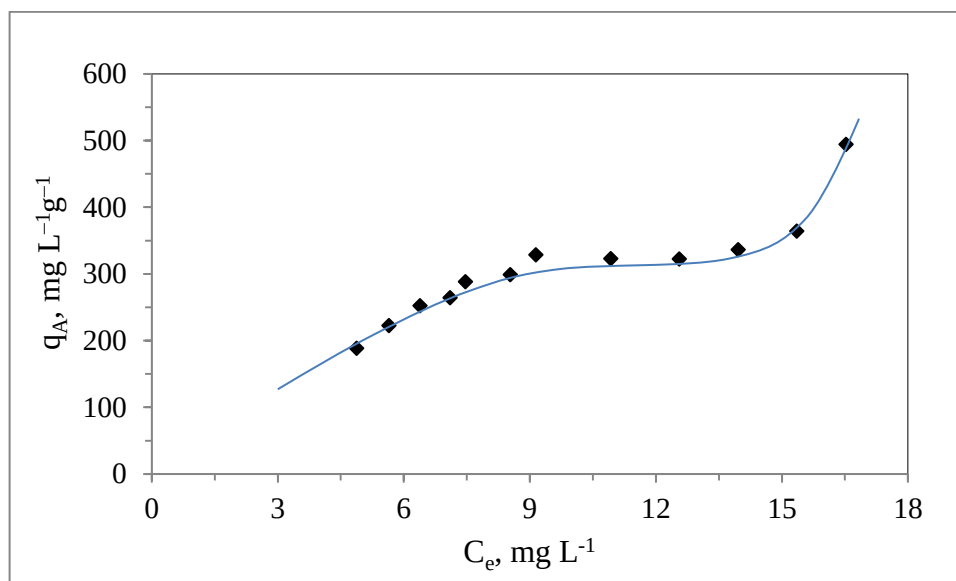


Figure 4.83. DOC adsorption isotherm of humic acid adsorption onto TiO_2 in the presence of montmorillonite.

The data attained for the adsorption isotherms of the specified humic parameters as well as DOC were fitted to the Freundlich adsorption model ($R^2 \geq 0.80$). Model coefficients as adsorption capacity K_f , and adsorption intensity $1/n$ calculated for the humic acid adsorption onto TiO_2 in the presence of montmorillonite were listed in Table 4.29.

Table 4.29. Freundlich isotherm model coefficients of humic acid adsorption onto TiO_2 in the presence of montmorillonite.

	K_f	$1/n$
Color_{436}	41.7	1.03
UV_{365}	55.8	0.852
UV_{280}	90.5	0.710
UV_{254}	76.9	0.762
DOC	84.8	0.567

According to Table 4.29, adsorption capacities, K_f , of UV_{254} and DOC were found to be 76.9 and 84.8, respectively. Moreover, the adsorption intensity for UV_{254} and DOC were found to be 0.762 and 0.567, respectively. These values indicated very weak concentration dependency. Except that of Color_{436} , $1/n$ values were lower than one. Adsorption intensity values displayed a decreasing order of $\text{Color}_{436} > \text{UV}_{365} > \text{UV}_{254} > \text{UV}_{280} > \text{DOC}$ whereas adsorption capacity values followed a decreasing order of $\text{UV}_{280} > \text{DOC} > \text{UV}_{254} > \text{UV}_{365} > \text{Color}_{436}$.

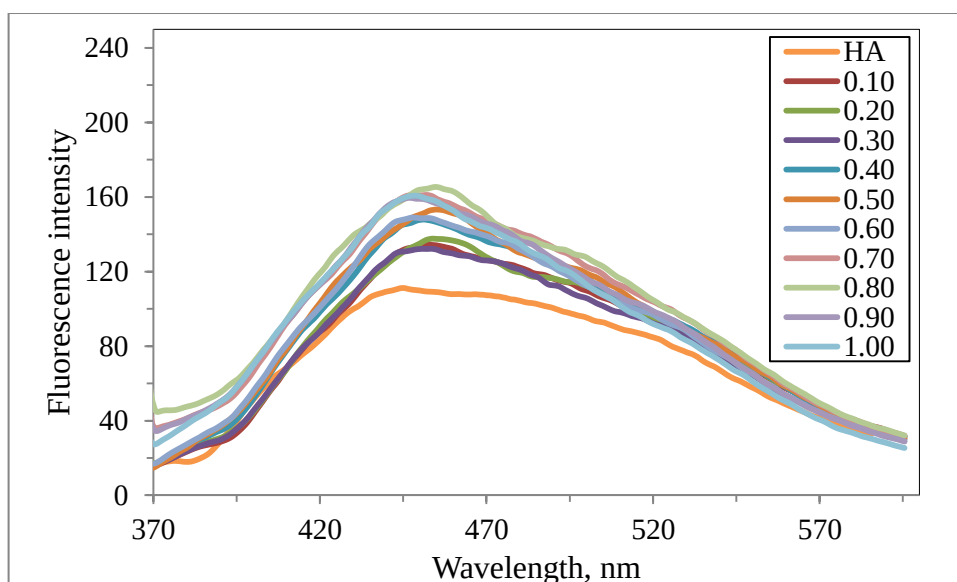


Figure 4.84. Emission scan fluorescence spectra of humic acid: Humic acid adsorption onto TiO_2 in the presence of montmorillonite.

Moreover, regarding the fluorescence spectroscopic properties, both emission scan and synchronous scan fluorescence spectra of humic acid recorded under post adsorption conditions were presented in Figures 4.84 and 4.85.

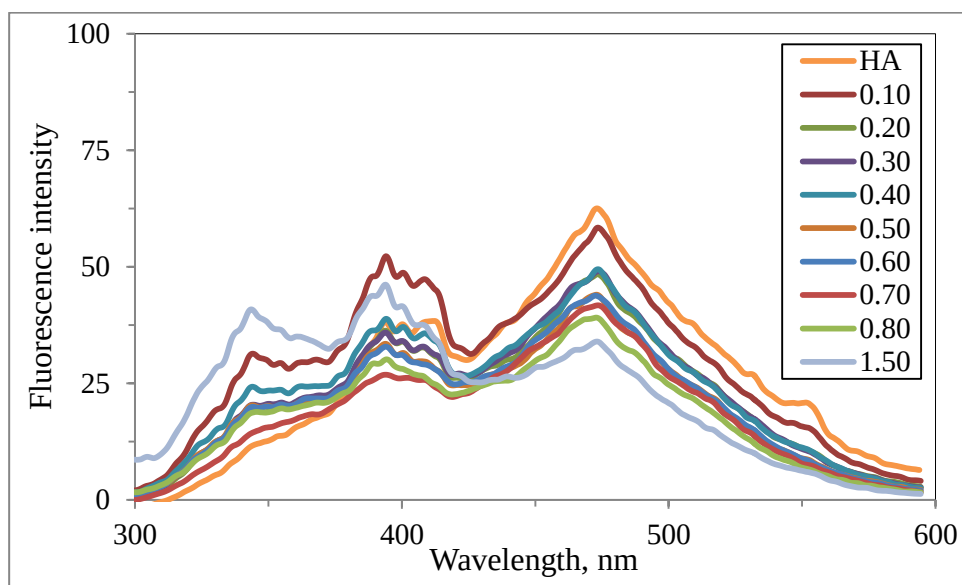


Figure 4.85. Synchronous scan fluorescence spectra of humic acid; Humic acid adsorption onto TiO_2 in the presence of montmorillonite.

A continuously increasing trend was observed in the fluorescence intensity recorded at emission wavelength of $\lambda_{\text{max}} = 450 \text{ nm}$ with respect to increasing TiO_2 dose (Figure 4.84). Although similar emission scan fluorescence spectral patterns were observed for sole humic acid (Figure 4.69) and humic acid in the presence of montmorillonite (Figure 4.84), fluorescence intensities decreased due to the adsorptive interactions prevailing between humic functional groups and exposed surfaces of TiO_2 as well as montmorillonite with respect to the fluorescence behavior observed in the presence of sole TiO_2 . However, in the presence of sole montmorillonite considerably lower fluorescence intensity difference was observed with respect to the fluorescence intensity differences attained both in the presence of sole TiO_2 and binary system composed of TiO_2 and montmorillonite (Figure 4.84). It should also be stated that the fluorescence intensity increases attained relative to the increasing active surfaces were found to be TiO_2 dose independent in the presence of a fixed amount of montmorillonite.

With reference to the synchronous scan fluorescence spectra of sole humic acid displaying a sharp peak around wavelength of $\lambda_{\text{max}} = 475 \text{ nm}$ (Figure 4.70), and humic acid spectra recorded in the presence of sole montmorillonite (Figure 4.75) through adsorption of humic acid onto TiO_2 in the presence of montmorillonite, similar peaks were also observed (Figure 4.85). It should also be mentioned that the synchronous scan fluorescence spectral features of humic acid displayed TiO_2 dose independent variations in fluorescence intensities recorded for minor peaks at emission wavelengths of $\lambda_{\text{emis}} = 435 \text{ nm}$ and $\lambda_{\text{emis}} = 390 \text{ nm}$.

4.2.5. Humic acid adsorption onto TiO_2 in the presence of kaolinite

Batch adsorption experiments were also carried out using humic acid, in the presence of 0.20 mg mL^{-1} kaolinite with increasing amount ($0.10\text{-}1.0 \text{ mg mL}^{-1}$) of TiO_2 . The adsorption isotherms of Color_{436} , UV_{254} and DOC were shown in Figure 4.86, Figure 4.87 and Figure 4.88, respectively. The isotherms related to the UV_{365} and UV_{280} parameters were presented in Appendix A.

Visual inspection of the adsorption isotherms presented for humic UV-vis parameters as well DOC displayed an S type isotherm shape expressing a smooth stabilization of the humic moieties on the exposed oxide surfaces. It should also be indicated that S type isotherms signified a strong adsorbate-adsorbate interactions on the adsorbent. Therefore, interactions prevailing between humic fractions should be considered as more significant leading to clustering followed by adsorption onto exposed surfaces composed of TiO_2 and kaolinite. The prevailing mechanism could well be explained by all of the specified humic parameters. C_e values for Color_{436} varied between $10.55 - 18.57 \text{ m}^{-1}$ depending on the amount of TiO_2 present in solution. The values of q_A calculated were in the range of $283\text{-}1230 \text{ m}^{-1}\text{g}^{-1}$ correspondingly (Figure 4.86). As presented in Figure 4.87, C_e values of UV_{254} varied between $74.61\text{-}104.39 \text{ m}^{-1}$ and the corresponding q_A were in the range of $925\text{-}3294 \text{ m}^{-1}\text{g}^{-1}$. Figure 4.88 displayed that the C_e values of DOC varied from 9.57 to 14.29 mg L^{-1} . The calculated q_A values varied in between $149\text{-}271 \text{ mg L}^{-1}\text{g}^{-1}$ correspondingly. ΔC_e and Δq_A values of Color_{436} were found to be 8.02 m^{-1} and $947 \text{ m}^{-1}\text{g}^{-1}$ respectively. The isotherm for Color_{436} had a narrow ΔC_e range (4.72 mg L^{-1}) whereas Δq_A of DOC was 122

$\text{mg L}^{-1}\text{g}^{-1}$. The highest ΔC_e and Δq_A values of UV_{254} were found to be 29.71 m^{-1} and $2369 \text{ m}^{-1}\text{g}^{-1}$, respectively.

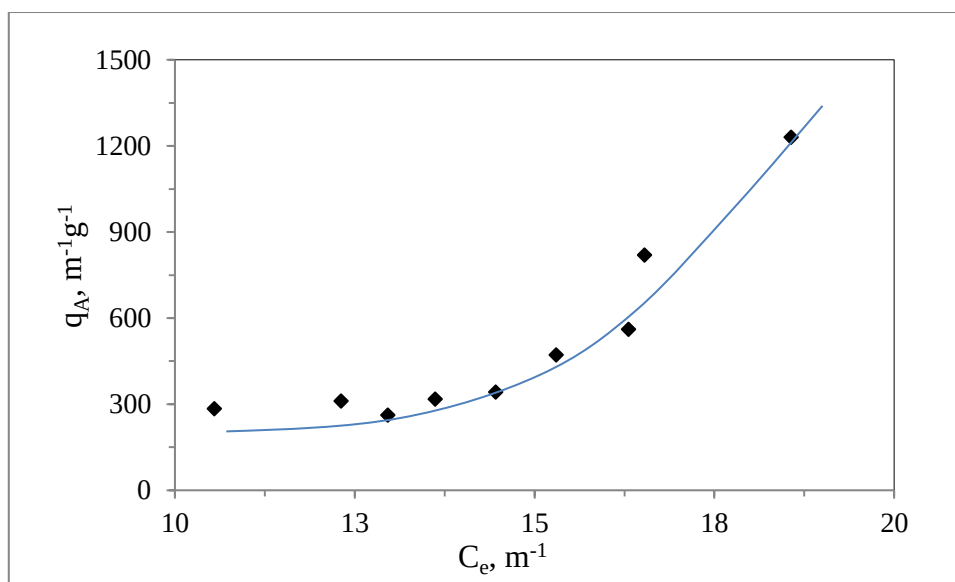


Figure 4.86. Color_{436} adsorption isotherm of humic acid adsorption onto TiO_2 in the presence of kaolinite.

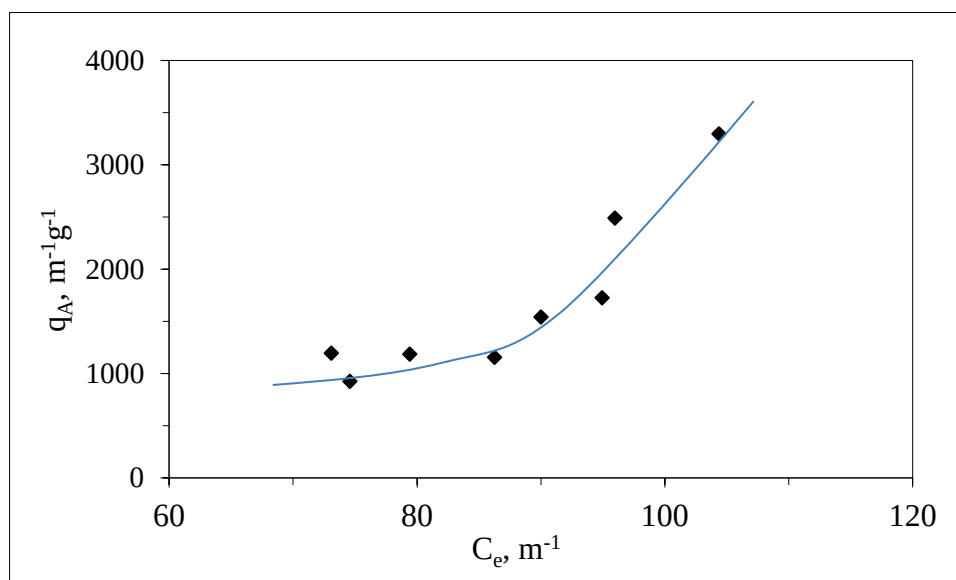


Figure 4.87. UV_{254} adsorption isotherm of humic acid onto adsorption TiO_2 in the presence of kaolinite.

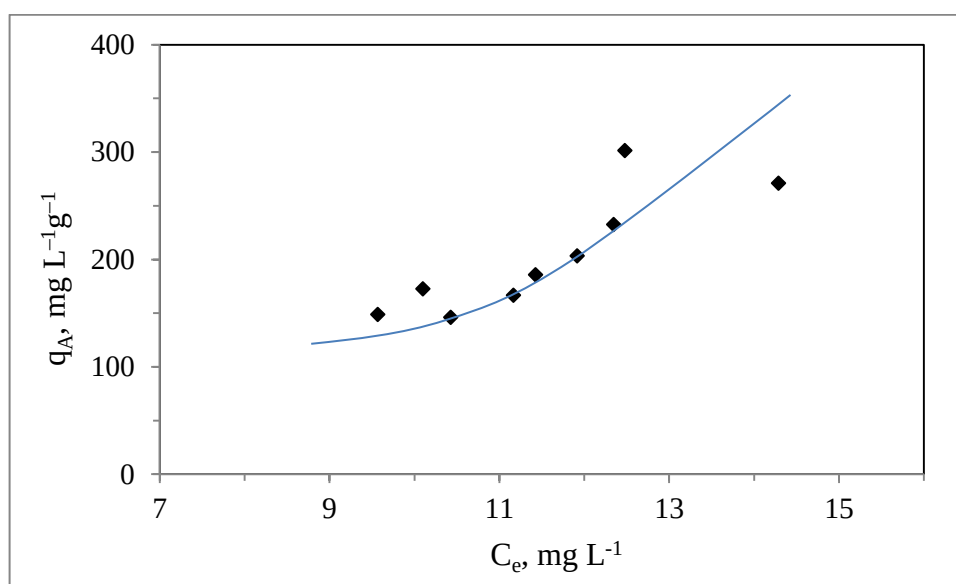


Figure 4.88. DOC adsorption isotherm of humic acid adsorption onto TiO_2 in the presence of kaolinite.

Table 4.30. Freundlich isotherm model coefficients of humic acid onto TiO_2 in the presence of kaolinite.

	K_f	$1/n$
Color ₄₃₆	0.327	2.71
UV ₃₆₅	0.104	2.59
UV ₂₈₀	3.24×10^{-3}	2.99
UV ₂₅₄	2.16×10^{-3}	3.03
DOC	2.33	1.82

The adsorption data were fitted to the Freundlich adsorption isotherm model. The adsorption capacity, K_f , and adsorption intensity $1/n$, for humic acid adsorption onto TiO_2 in the presence of kaolinite were listed in Table 4.5 ($R^2 \geq 0.80$). According to Table 4.30, the adsorption capacity constant for Color₄₃₆ ($K_F = 0.327$) was found to be higher than the adsorption capacities attained for all of the other UV-vis parameters. Moreover, adsorption capacity constant for DOC was found to be highest as $K_F = 2.33$. On the other hand, adsorption intensity values of the UV-vis parameters were higher than the adsorption

intensity of DOC. $1/n$ values of all the specified humic parameters were found to be higher than 1 indicating strong concentration dependency.,

Adsorption intensity values displayed a decreasing order of $UV_{254} \geq UV_{280} > Color_{436} > UV_{365} > DOC$ whereas adsorption capacity values followed a decreasing order of $DOC > Color_{436} > UV_{365} > UV_{280} > UV_{254}$.

Fluorescence spectra recorded in emission scan mode displayed a quite narrow fluorescence intensity band at emission wavelength of $\lambda_{max} = 470$ nm in comparison to the emission scan fluorescence spectra attained for sole humic acid adsorption onto TiO_2 (Figure 4.69) and humic acid adsorption onto kaolinite (Figure 4.89). Moreover, it could also be indicated that a continuously increasing trend in FI at $\lambda_{max} = 450$ nm was observed with respect to increasing TiO_2 dose (Figure 4.89). Synchronous scan fluorescence spectra of humic acid as illustrated by Figure 4.90 gave a major peak around emission wavelength of $\lambda_{max} = 470$ nm in accordance with the previously recorded fluorescence features. However peak recorded at around emission wavelength of $\lambda_{max} = 395$ nm increased with increasing TiO_2 doses in the presence of fixed dose of kaolinite.

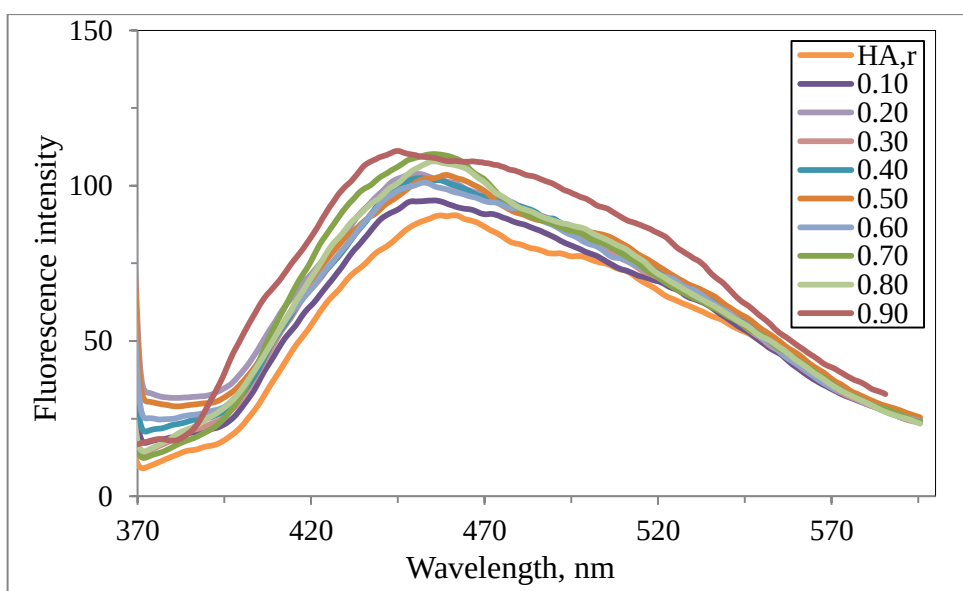


Figure 4.89. Emission scan fluorescence spectra of humic acid: Humic acid adsorption onto TiO_2 in the presence of kaolinite.

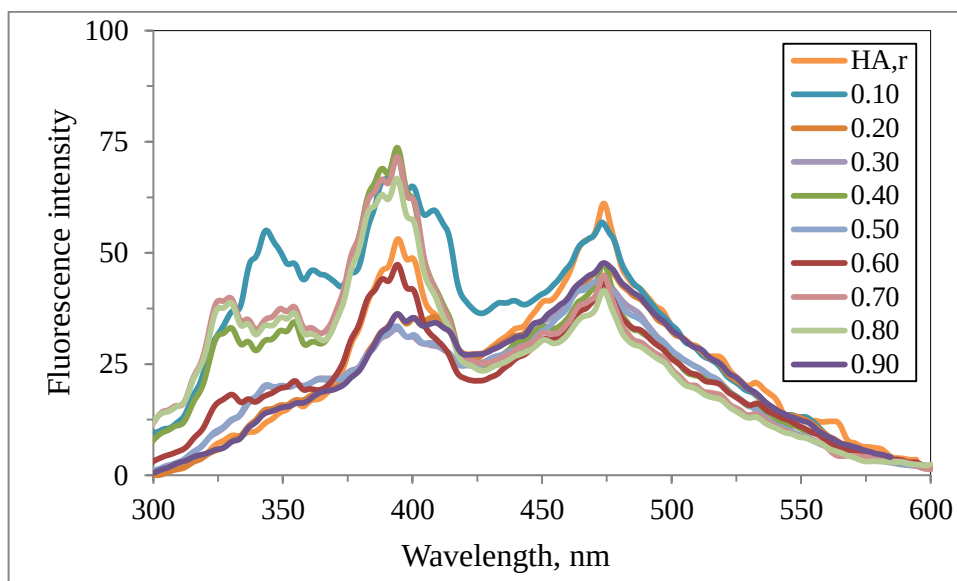


Figure 4.90. Synchronous scan fluorescence spectra of humic acid: Humic acid adsorption onto TiO_2 in the presence of kaolinite.

Furthermore, fluorescence intensity variations recorded at emission wavelength region of 300 nm - 400 nm displayed a level-off behavior for humic acid in the presence of 0.90 mg mL^{-1} TiO_2 dose thereby exhibited the lowest fluorescence intensity as presented in Figure 4.90. Comparison of synchronous scan fluorescence spectra recorded for humic acid in the presence of sole kaolinite (Figure 4.80) revealed the predominant contribution of TiO_2 surface interactions.

4.2.6. Humic acid adsorption onto TiO_2 in the presence of Ca^{2+}

With the aim of examining the adsorption behavior of humic acid in the presence of Ca^{2+} ion, batch adsorption experiments were also carried out using 50 mg L^{-1} humic acid with varying doses of TiO_2 (0.10 - 1.0 mg L^{-1}). The adsorption isotherms of Color_{436} , UV_{254} and DOC parameters were shown in Figure 4.91, Figures 4.92 and Figures 4.93, respectively. The isotherms related to the UV_{365} and UV_{280} parameters were presented in Appendix A.

Figure 4.91 indicated that C_e values of Color_{436} varied between 1.71 - 3.62 m^{-1} depending on the amount of TiO_2 present in solution. The values of q_A calculated to be in

the range of 460-4220 $\text{m}^{-1}\text{g}^{-1}$ correspondingly. C_e values of UV_{254} varied between 21.46-33.33 m^{-1} as presented in the Figure 4.92. The corresponding values of q_A were found to be in the range of 2070-18332 $\text{m}^{-1}\text{g}^{-1}$. Moreover, C_e values of DOC varied from 4.88 to 17.53 mg L^{-1} as illustrated in Figure 4.93. The calculated q_A values for DOC varied in between 202-494 $\text{mg L}^{-1}\text{g}^{-1}$ correspondingly. ΔC_e and Δq_A values of Color_{436} were 1.91 m^{-1} and 3760 $\text{m}^{-1}\text{g}^{-1}$ respectively. ΔC_e and Δq_A of UV_{254} were calculated as 11.87 m^{-1} and 16261 $\text{m}^{-1}\text{g}^{-1}$ respectively.

Considerably high Δq_A as 292 $\text{mg L}^{-1}\text{g}^{-1}$ and low C_e range as 12.65 mg L^{-1} were attained for dissolved organic carbon contents as depicted from DOC isotherm (Figure 4.93). A close inspection of the adsorption isotherms of the specified humic parameters revealed an S type shape for both Color_{436} and UV_{254} whereas an L type shape was attained for DOC. In comparison to the DOC adsorption isotherm obtained for humic acid adsorption onto TiO_2 (Figure 4.68), the presence of Ca^{2+} significantly altered the adsorption mechanism leading to a Langmuirian type adsorption. It could be indicated that monolayer coverage could be attained by bridging of Ca^{2+} ions between deprotonated humic functional and negatively charged oxide surface sites (Figure 2.1).

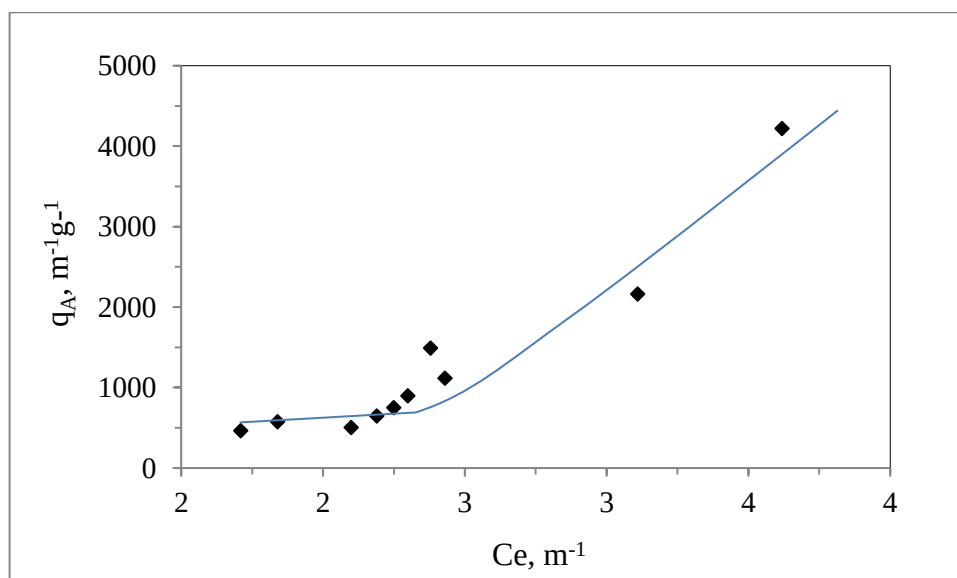


Figure 4.91. Color_{436} adsorption isotherm of humic acid adsorption onto TiO_2 in the presence of Ca^{2+} .

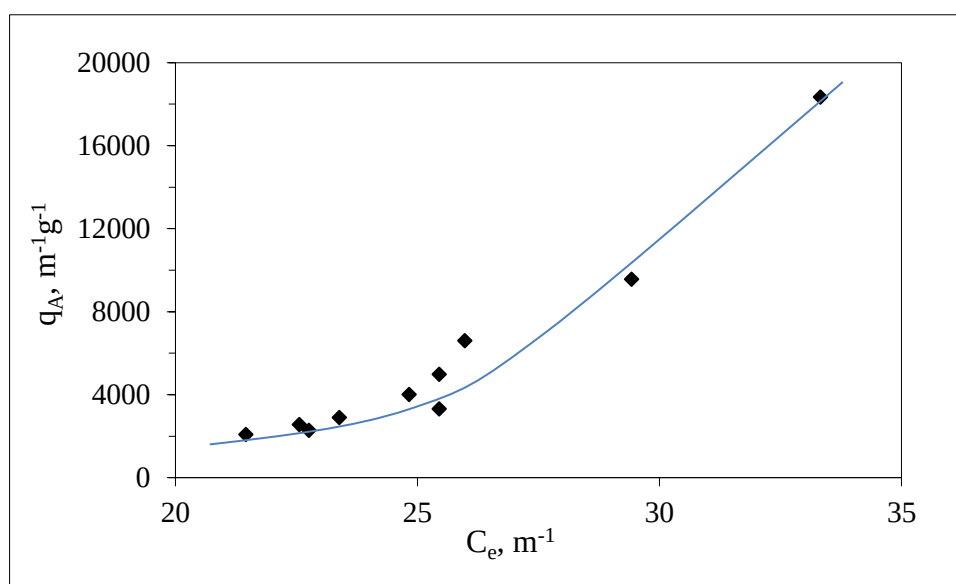


Figure 4.92. UV₂₅₄ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of Ca²⁺.

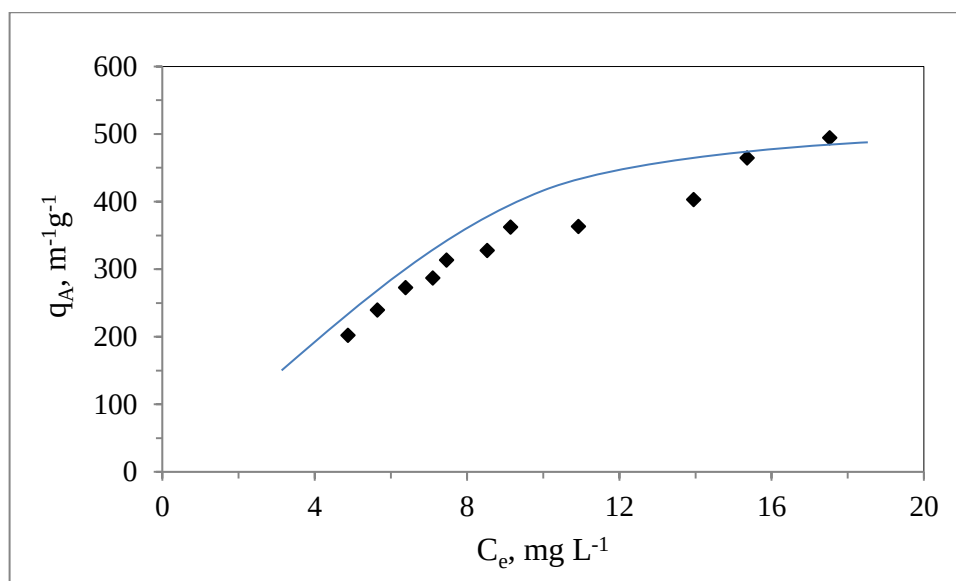


Figure 4.93. DOC adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of Ca²⁺.

The data attained for specified humic parameters were fitted to the Freundlich adsorption isotherm model. The adsorption capacity, K_f , and adsorption intensity $1/n$, for

humic acid adsorption onto TiO_2 in the presence of Ca^{2+} were presented in Table 4.31 ($R^2 \geq 0.80$).

Table 4.31. Freundlich isotherm model coefficients of humic acid adsorption onto TiO_2 in the presence of Ca^{2+} .

	K_f	$1/n$
Color ₄₃₆	75.5	3.03
UV ₃₆₅	6.41	3.30
UV ₂₈₀	2.67×10^{-4}	5.07
UV ₂₅₄	2.66×10^{-4}	5.15
DOC	81.4	0.634

According to Table 4.31, the adsorption capacity constant for Color₄₃₆ ($K_f = 75.5$) was found to be higher than the adsorption capacities of other humic parameters in the presence of Ca^{2+} ion. However, adsorption capacity constant for UV₂₈₀ and UV₂₅₄ were found to be almost equal to each other. $1/n$ values for Color₄₃₆, UV₃₆₅ and UV₂₅₄ were found to be higher than 1, indicating a weak adsorptive behavior. On the other hand, $1/n$ values for DOC were found to be 0.579. Adsorption intensity values displayed a decreasing order of $\text{UV}_{254} \geq \text{UV}_{280} > \text{UV}_{365} > \text{Color}_{436} > \text{DOC}$, whereas adsorption capacity values followed a decreasing order of $\text{DOC} > \text{Color}_{436} > \text{UV}_{365} > \text{UV}_{280} \geq \text{UV}_{254}$.

According to the spectral features of the emission scan fluorescence spectra, a continuously increasing trend in fluorescence intensity at emission wavelength of $\lambda_{\text{max}} = 450$ nm was observed with respect to increasing TiO_2 dose in the presence of Ca^{2+} . A close similarity could be visualized between the emission scan fluorescence spectra of humic acid adsorption onto sole TiO_2 (Figure 4.69) indicating insignificant role of Ca^{2+} . Moreover, no distinct trend with respect to increasing dose of TiO_2 could be indicated for both of the cases. As it could be seen in Figure 4.95, synchronous scan fluorescence spectra of humic acid obeyed the TiO_2 dose dependent continuous decreasing trend for both of the emission wavelengths of λ_{max} as 395 nm and 470 nm. A sharp decrease in synchronous scan fluorescence intensity at emission wavelength of $\lambda_{\text{max}} = 470$ nm was observed by introduction of TiO_2 in the presence of Ca^{2+} ion. However slight differences

of fluorescence intensities at $\lambda_{\text{max}} = 450 \text{ nm}$ was detected with respect to increasing TiO_2 dose for humic acid in the presence of Ca^{2+} ion.

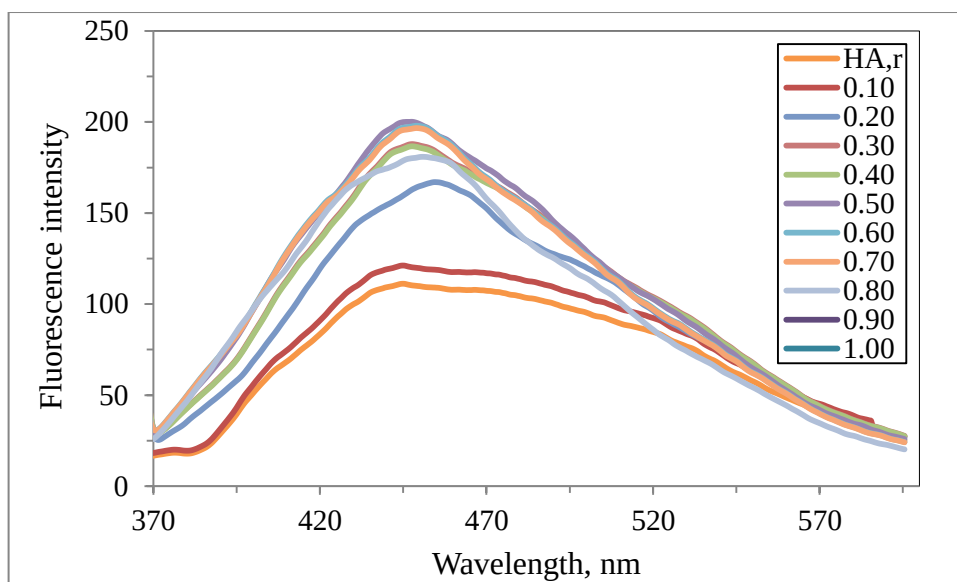


Figure 4.94. Emission scan fluorescence spectra of humic acid adsorption onto TiO_2 in the presence of Ca^{2+} .

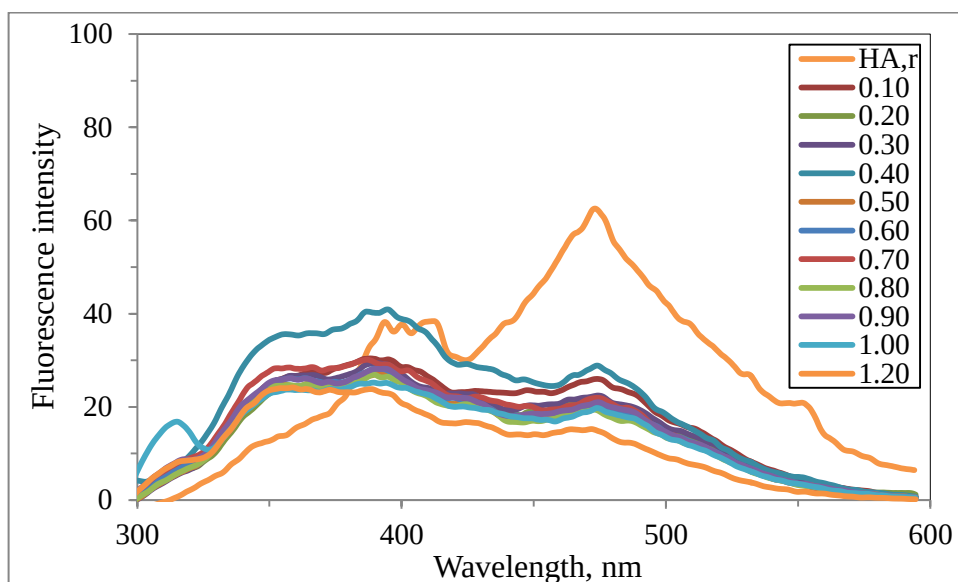


Figure 4.95. Synchronous scan fluorescence spectra of humic acid adsorption onto TiO_2 in the presence of Ca^{2+} .

4.2.7. Humic acid adsorption onto montmorillonite in the presence of Ca^{2+}

In order to examine the adsorption behavior of humic acid onto montmorillonite in the presence of Ca^{2+} , batch adsorption experiments were conducted under identical experimental conditions. Adsorption isotherms of Color_{436} , UV_{254} and DOC were shown in Figure 4.96, Figure 4.97 and Figure 4.98, respectively. The isotherms related to the UV_{365} and UV_{280} parameters were presented in Appendix A.

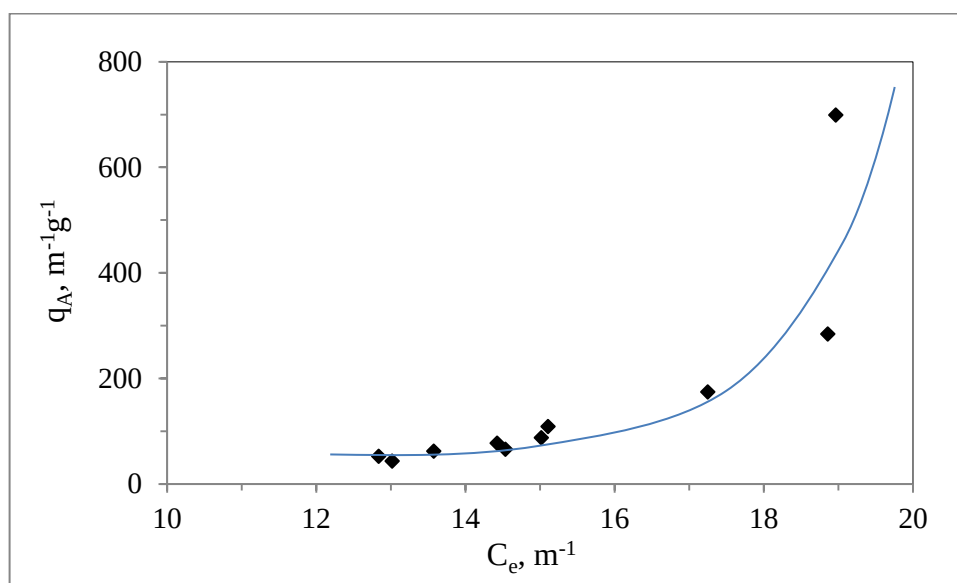


Figure 4.96. Color_{436} adsorption isotherm of humic acid adsorption onto montmorillonite in the presence of Ca^{2+} .

As it could be seen in Figure 4.96, C_e values varied between 13.02-18.97 m^{-1} for Color_{436} depending on the amount of montmorillonite present in solution. The values of q_A were calculated in the range of 43.13-699 $\text{m}^{-1}\text{g}^{-1}$ for the corresponding C_e values. C_e values of UV_{254} varied between 73.86-103.12 m^{-1} . The values of q_A were in the range of 157-1774 $\text{m}^{-1}\text{g}^{-1}$ correspondingly (Figure 4.97). Figure 4.98 showed that the values of C_e varied from 12.02 to 17.84 mg L^{-1} for DOC. The calculated q_A values varied in between 26.6-86.00 $\text{mg L}^{-1}\text{g}^{-1}$. ΔC_e and Δq_A values of humic acid were 5.95 m^{-1} and 656 $\text{m}^{-1}\text{g}^{-1}$ respectively for Color_{436} . ΔC_e and Δq_A for UV_{254} were 29.26 m^{-1} and 1617 $\text{m}^{-1}\text{g}^{-1}$, respectively. Furthermore, Δq_A was 59.4 $\text{mg L}^{-1}\text{g}^{-1}$ and C_e range was 5.83 mg L^{-1} for DOC. An S type adsorption isotherm shape was evident for all of the adsorption isotherms

obtained for the specified humic parameters (Figure 4.96-4.98). A comparison with the isotherms attained for sole humic acid indicated a rather steep curve profile for humic acid adsorption onto montmorillonite in the presence of Ca^{2+} ions (Figure 4.66-4.68).

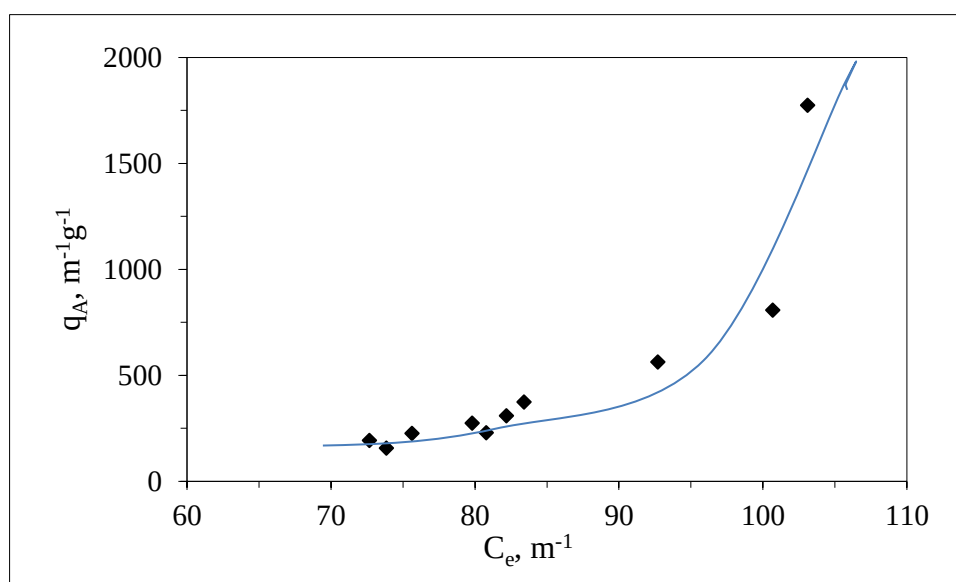


Figure 4.97. UV_{254} adsorption isotherm of humic acid adsorption onto montmorillonite in the presence of Ca^{2+} .

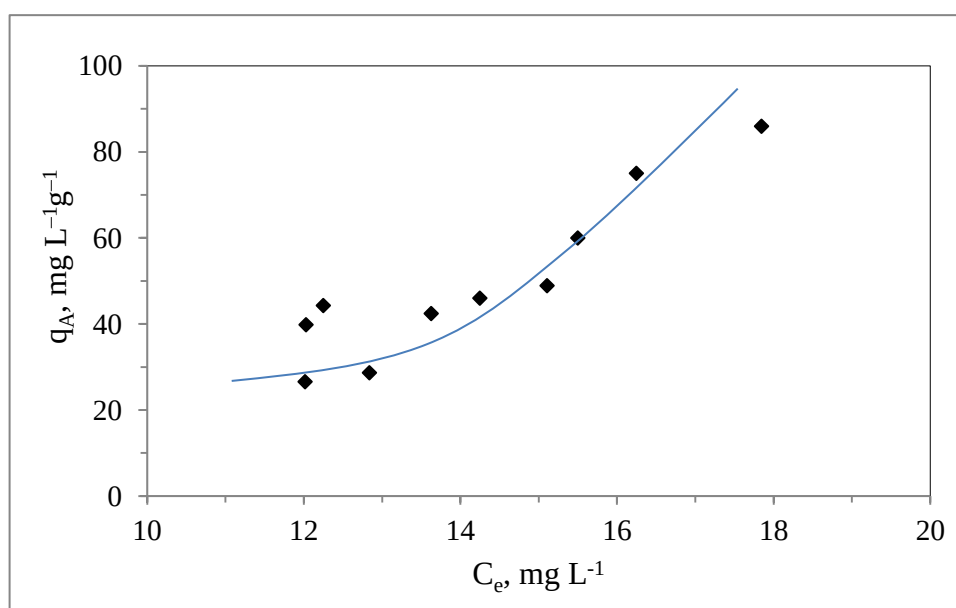


Figure 4.98. DOC adsorption isotherm of humic acid adsorption onto montmorillonite in the presence of Ca^{2+} .

The attained adsorption data were evaluated through modeling by Freundlich adsorption isotherm model and the calculated coefficients were presented in Table 4.32. ($R^2 \geq 0.80$).

Table 4.32. Freundlich isotherm model coefficients of humic adsorption onto montmorillonite in the presence of Ca^{2+} .

	K_f	$1/n$
Color_{436}	1.54×10^{-5}	5.79
UV_{365}	1.41×10^{-6}	5.43
UV_{280}	2.03×10^{-8}	5.52
UV_{254}	2.62×10^{-9}	5.79
DOC	8.01×10^{-2}	2.41

According to Table 4.32, adsorption capacities of humic acid adsorption onto montmorillonite in the presence of Ca^{2+} ion were found to be low for the specified humic UV-vis parameters. It should be indicated that montmorillonite in the presence of Ca^{2+} ions had no significant adsorptive interaction with humic acid. Moreover, K_f value for DOC was slightly higher than the other parameters and $1/n$ value was found to be 2.41. Adsorption intensity values displayed a decreasing order of $\text{UV}_{254} = \text{Color}_{436} > \text{UV}_{280} > \text{UV}_{365} > \text{DOC}$, whereas adsorption capacity values followed a decreasing order of $\text{DOC} > \text{Color}_{436} > \text{UV}_{365} > \text{UV}_{280} > \text{UV}_{254}$. A comparison to the Freundlich adsorption model parameters calculated for sole humic acid adsorption onto montmorillonite (Table 4.27) displayed a stronger adsorption capacity of humic acid in the presence of Ca^{2+} . However, no distinct difference could be accounted for adsorption intensities achieved for both of the cases.

Emission scan and synchronous scan fluorescence spectral features of humic acid adsorption onto montmorillonite in the presence of Ca^{2+} ions were presented in Figures 4.99 and 4.100 respectively. As expected, according to the emission scan fluorescence spectra of humic acid recorded under post-adsorption conditions lead to continuously increasing trend in fluorescence intensities at emission wavelength of $\lambda_{\text{max}} = 450 \text{ nm}$ with respect to increasing montmorillonite dose in the presence of Ca^{2+} ions (Figure 4.99).

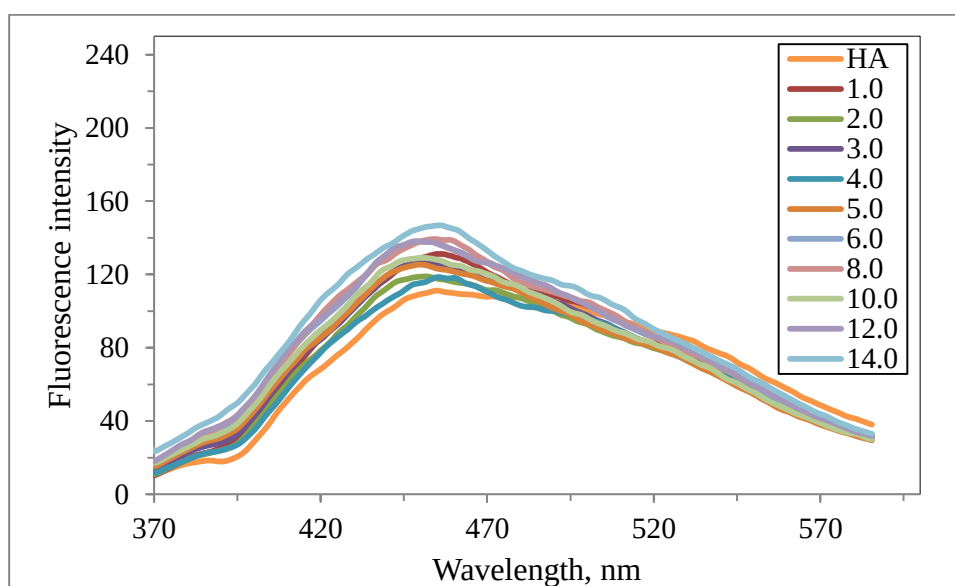


Figure 4.99. Emission scan fluorescence spectra of humic acid adsorption onto montmorillonite in the presence of Ca^{2+} .

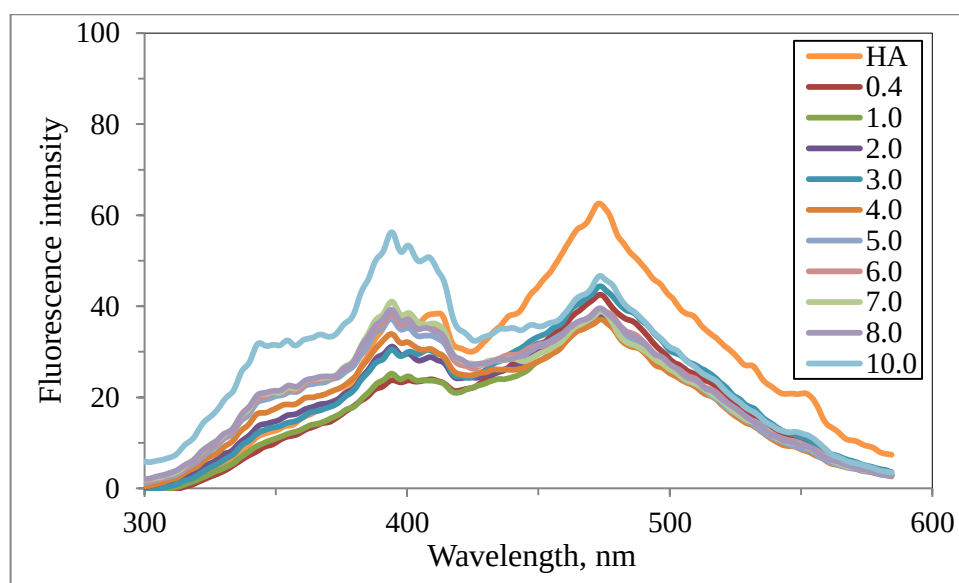


Figure 4.100. Synchronous scan fluorescence spectra of humic acid adsorption onto montmorillonite in the presence of Ca^{2+} .

Synchronous scan fluorescence spectra for raw humic acid displayed a sharp peak around emission wavelength of $\lambda_{\text{max}} = 475$ nm and a moderate peaks at emission wavelengths of $\lambda_{\text{emis}} = 345$ nm and $\lambda_{\text{emis}} = 385$ nm with a comparatively different

intensities. As explained previously (Figure 4.100) upon adsorption onto montmorillonite, the synchronous scan fluorescence spectra of humic acid retained the sharp weak and emergence of new fluorophoric groups at lower emission wavelengths were noticed. In a similar fashion, in the presence of montmorillonite and Ca^{2+} ions, continuously increasing smooth trend was observed for synchronous scan fluorescence intensities up to emission wavelength of 400 nm with increasing montmorillonite doses. However, for longer wavelengths $\lambda_{\text{emis}} > 450$ nm, fluorescence intensity values decreased with increasing montmorillonite doses.

4.2.8. Humic acid adsorption onto kaolinite in the presence of Ca^{2+} .

Batch adsorption experiments were also carried out using humic acid as the adsorbate and kaolinite as the adsorbent in the presence of Ca^{2+} ion. The adsorption isotherms of Color_{436} , UV_{254} and DOC were shown in Figure 4.101, Figure 4.102 and Figure 4.103, respectively. The isotherms related to the UV_{365} and UV_{280} parameters were presented in Appendix A.

Figure 4.101 indicated that C_e values of Color_{436} varied between 0.77-10.35 m^{-1} depending on the amount of kaolinite present in the solution. The values of q_A were calculated as 79.83-606 $\text{m}^{-1}\text{g}^{-1}$ correspondingly. As it could be seen in Figure 4.102, C_e values of UV_{254} varied between 11.58– 67.35 m^{-1} with corresponding q_A values in the range of 324 – 2140 $\text{m}^{-1}\text{g}^{-1}$. Figure 4.103 showed that the values of C_e varied from 2.24 to 10.56 mg L^{-1} for DOC. The calculated q_A values varied in between 59.04-257.6 $\text{mg L}^{-1}\text{g}^{-1}$ correspondingly.

ΔC_e and Δq_A values of Color_{436} were 9.58 m^{-1} and 526 $\text{m}^{-1}\text{g}^{-1}$ respectively. ΔC_e and Δq_A for UV_{254} were 55.77 m^{-1} and 1776 $\text{m}^{-1}\text{g}^{-1}$, respectively. Humic acid resulted in steep curves with high Δq_A of 198 $\text{mg L}^{-1}\text{g}^{-1}$ in a short C_e range of 8.32 mg L^{-1} for DOC isotherm. Referring to the adsorption isotherm shapes, it could be visualized that all of the specified humic parameters displayed an S type isotherm. It should be indicated that the adsorption isotherms of UV-vis parameters of humic acid also displayed an S type-isotherm contrary to the linear isotherm shape attained for DOC in the absence of Ca^{2+} ion (Figures 4.78). The presence of Ca^{2+} ions distinctly affected the adsorptive behavior of

humic fractions onto kaolinite. The observed role Ca^{2+} ions could mainly be attributed to the bridging effect through electrostatic attractions between oppositely charged species present at adsorbate /adsorbent surfaces.

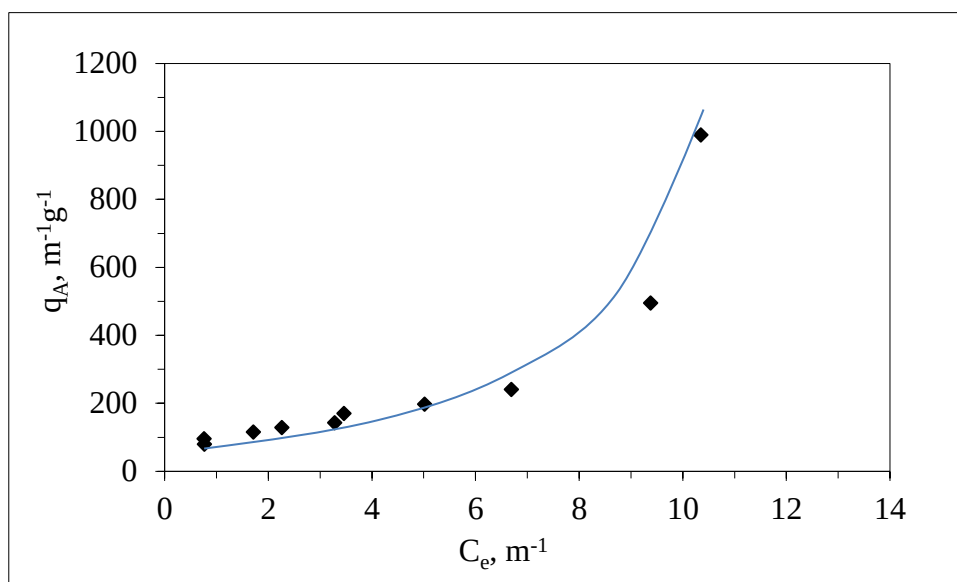


Figure 4.101. Color₄₃₆ adsorption isotherm of humic acid adsorption onto kaolinite in the presence of Ca^{2+} .

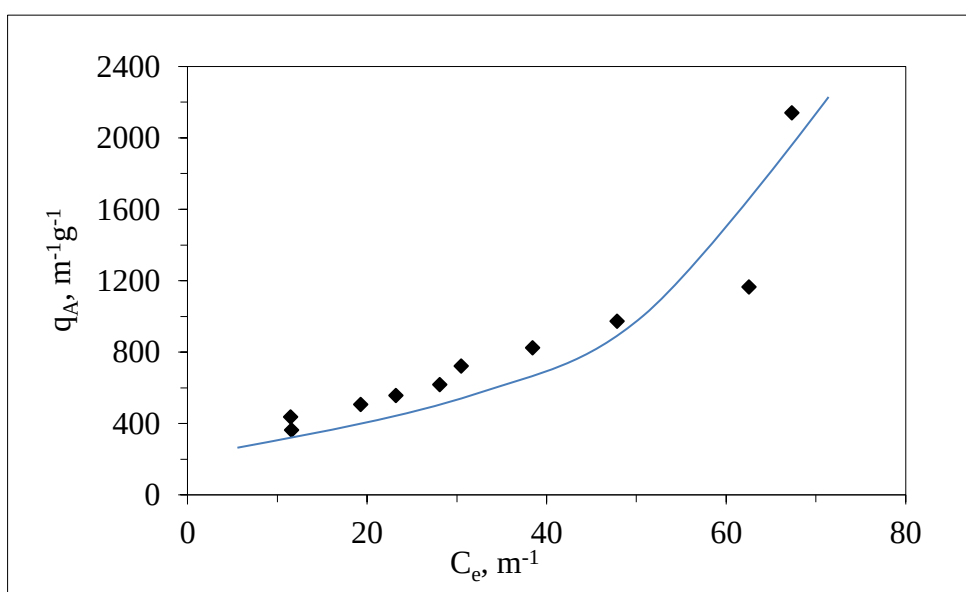


Figure 4.102. UV₂₅₄ adsorption isotherm of humic acid adsorption onto kaolinite in the presence of Ca^{2+} .

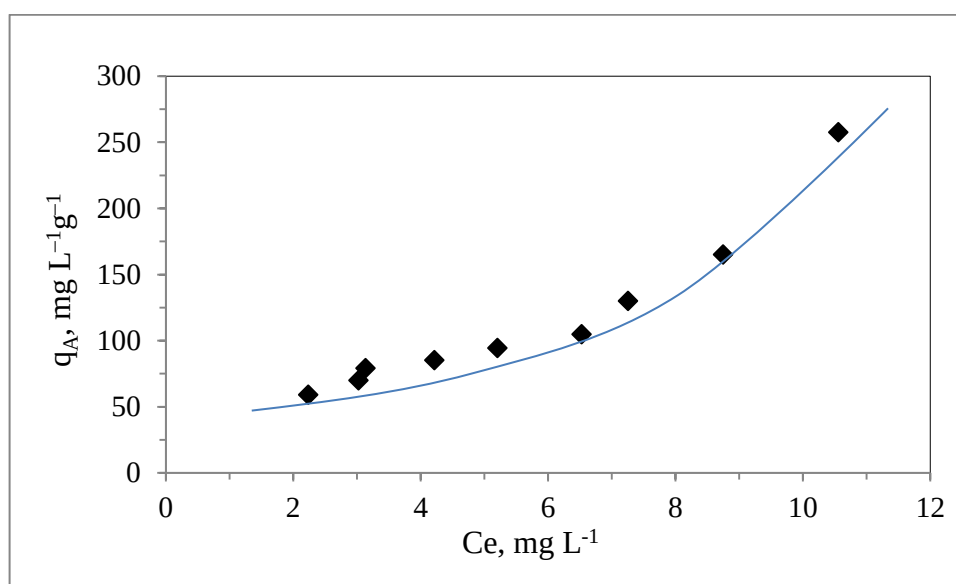


Figure 4.103. DOC adsorption isotherm of humic acid adsorption onto kaolinite in the presence of Ca^{2+} .

Adsorption isotherm modeling of the above presented data using Freundlich model revealed the following isotherm coefficients as tabulated in Table 4.33.

Table 4.33. Freundlich isotherm model coefficients of humic acid adsorption onto kaolinite in the presence of Ca^{2+} .

	K_f	$1/n$
Color ₄₃₆	85.8	0.662
UV ₃₆₅	85.0	0.634
UV ₂₈₀	57.5	0.761
UV ₂₅₄	52.7	0.780
DOC	27.7	0.823

According to Table 4.33, an adsorption capacity constant for UV₃₆₅ is found to be higher than the adsorption capacities of other humic parameters in the presence of Ca^{2+} ion. However, adsorption capacity constant for UV₂₈₀ and UV₂₅₄ were found to be very close to each other. $1/n$ values for Color₄₃₆, UV₃₆₅, UV₂₅₄ and DOC parameters were found to be lower than 1 indicating a comparatively less concentration dependency. Adsorption

intensity values displayed a decreasing order of $\text{DOC} > \text{UV}_{254} > \text{UV}_{280} > \text{Color}_{436} > \text{UV}_{365}$, whereas adsorption capacity values followed a decreasing order of $\text{Color}_{436} > \text{UV}_{365} > \text{UV}_{280} > \text{UV}_{254} > \text{DOC}$. Although no significant difference was attained for adsorption intensity of DOC in the presence of Ca^{2+} ions (Table 4.33), $1/n$ values of the UV-vis parameters were significantly lower. Moreover, the specified humic parameters displayed distinctly higher adsorption capacities.

The emission scan fluorescence spectra and synchronous scan fluorescence spectra recorded for the adsorption experiments of humic acid onto kaolinite in the presence of Ca^{2+} ions were displayed in Figure 4.104 and Figure 4.105, respectively. Retaining the basic mono peak trend, the emission scan fluorescence spectral features displayed a rather steep increase in shape in comparison to the spectra recorded for humic acid adsorption onto kaolinite (Figure 4.79). In the presence of Ca^{2+} ions, emission scan fluorescence intensities of humic acid displayed inconsistent variations with respect to the increasing kaolinite doses. An overlapping behavior was more evident in the presence of Ca^{2+} ions specifically at the emission wavelength region $\lambda_{\text{emis}} > 520$ nm expressing lower fluorescence intensities with respect to the fluorescence emission spectra of sole humic acid.

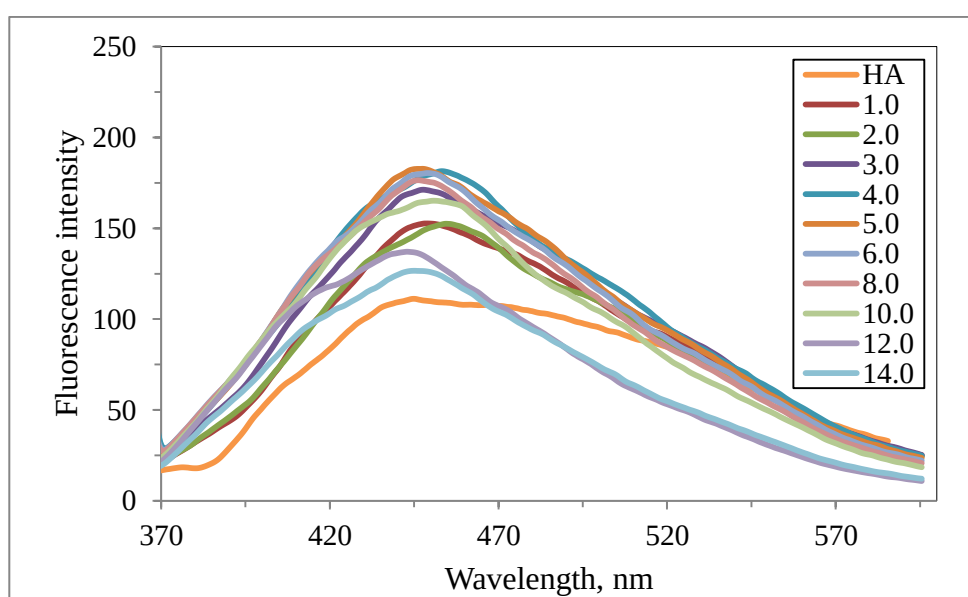


Figure 4.104. Emission scan fluorescence spectra of humic acid adsorption onto kaolinite in the presence of Ca^{2+} .

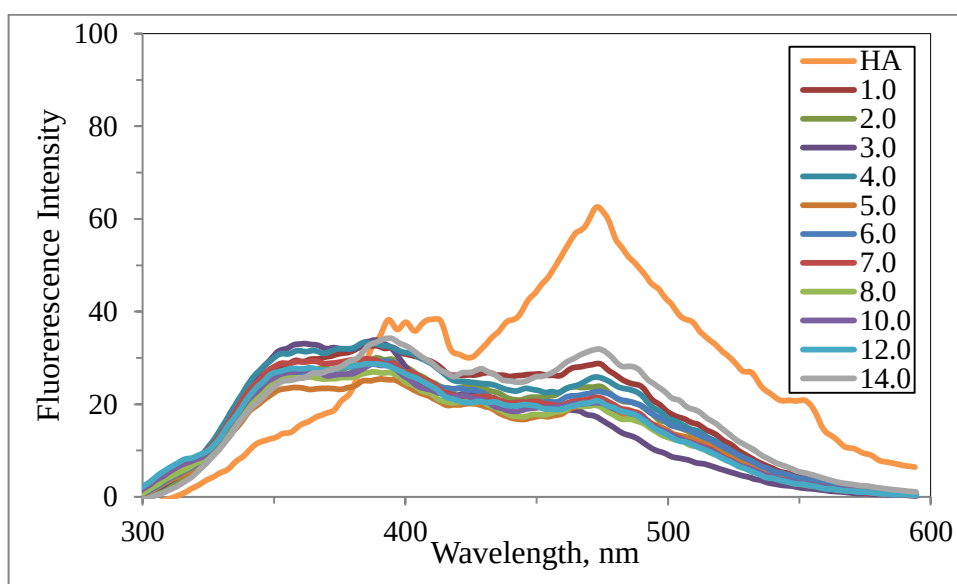


Figure 4.105. Synchronous scan fluorescence spectra of humic acid adsorption onto kaolinite in the presence of Ca^{2+} .

With reference to the synchronous scan fluorescence spectra of raw humic acid displaying a sharp peak around emission wavelength of $\lambda_{\text{max}} = 475$ nm, by adsorption of humic acid onto kaolinite in the presence of Ca^{2+} ions, minor increases were observed for fluorescence intensities up to emission wavelength of $\lambda = 390$ nm (Figure 4.105). For longer emission wavelengths $\lambda_{\text{emis}} > 450$ nm, fluorescence intensity values displayed a decreasing trend by introducing various doses of kaolinite in the presence of Ca^{2+} ions. The reason could be explained by the possible structural and conformational changes in the fluorophoric groups mainly due to the presence of Ca^{2+} ions exerting an ionic strength effect.

4.2.9. Humic acid adsorption onto TiO_2 in the presence of montmorillonite and Ca^{2+}

In order to elucidate the effect of Ca^{2+} ions on the adsorption behavior of humic acid onto TiO_2 in the presence of montmorillonite, batch adsorption experiments were also carried out. The adsorption isotherms of Color_{436} , UV_{254} and DOC parameters were shown in Figures 4.106, Figures 4.107 and Figures 4.108, respectively. The isotherms related to the UV_{365} and UV_{280} parameters were presented in Appendix A.

Figure 4.106 indicated that C_e values of Color_{436} varied between 0.72-6.24 m^{-1} depending on the amount of TiO_2 present in solution. The corresponding values of q_A were found to be in the range of 480-3696 $\text{m}^{-1}\text{g}^{-1}$. As it could be seen in Figure 4.107, C_e values varied between 9.68-46.50 m^{-1} for UV_{254} . The values of q_A calculated were in the range of 2224-14872 $\text{m}^{-1}\text{g}^{-1}$ correspondingly. Figure 4.108 showed that the values of C_e varied from 1.36 to 4.23 mg L^{-1} for DOC. The adsorbed amount of DOC onto adsorbent varied in between 313-2554 $\text{mg L}^{-1}\text{g}^{-1}$. ΔC_e and Δq_A values for humic acid were 5.52 m^{-1} and 3216 $\text{m}^{-1}\text{g}^{-1}$ respectively at Color_{436} . ΔC_e and Δq_A for UV_{254} were 36.82 m^{-1} and 12648 $\text{m}^{-1}\text{g}^{-1}$, respectively. humic acid resulted in steep curves with high Δq_A of 2241 $\text{mg L}^{-1}\text{g}^{-1}$ in a short C_e range of 2.87 mg L^{-1} for DOC isotherm.

The inspection of the adsorption isotherms of the UV-vis parameters as presented in Figures 4.106 and 4.107 revealed a linear trend representing C type isotherm. However, adsorption isotherm of DOC exhibited a distinct S type isotherm. Although a similarity could be visualized in between the isotherms attained for UV-vis parameters both in the presence and absence of Ca^{2+} , DOC isotherm distinctly reflected the role of Ca^{2+} on the adsorptive interactions prevailing among the humic functional groups and the oppositely charged surface groups.

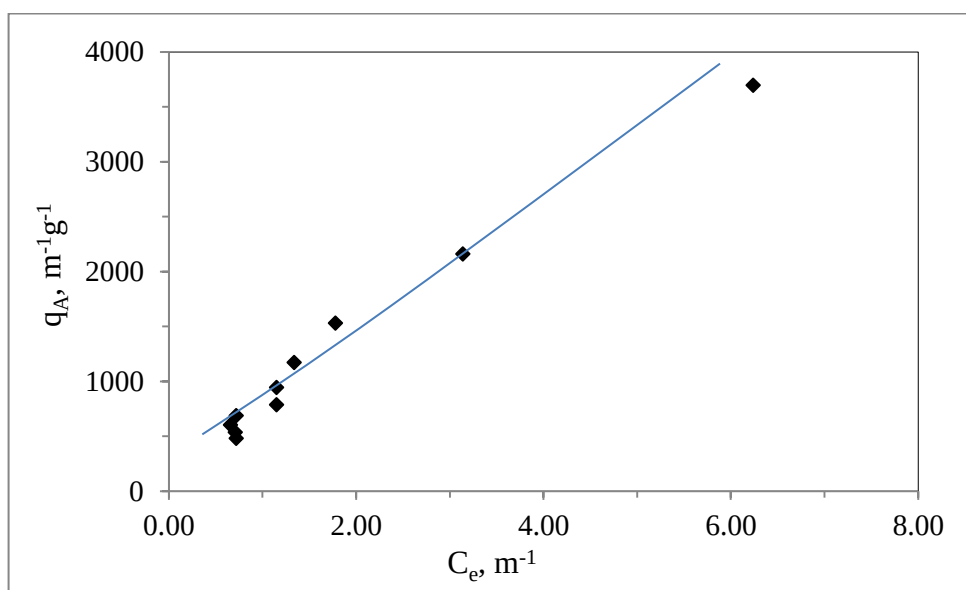


Figure 4.106. Color_{436} adsorption isotherm of humic acid adsorption onto TiO_2 in the presence of montmorillonite and Ca^{2+} .

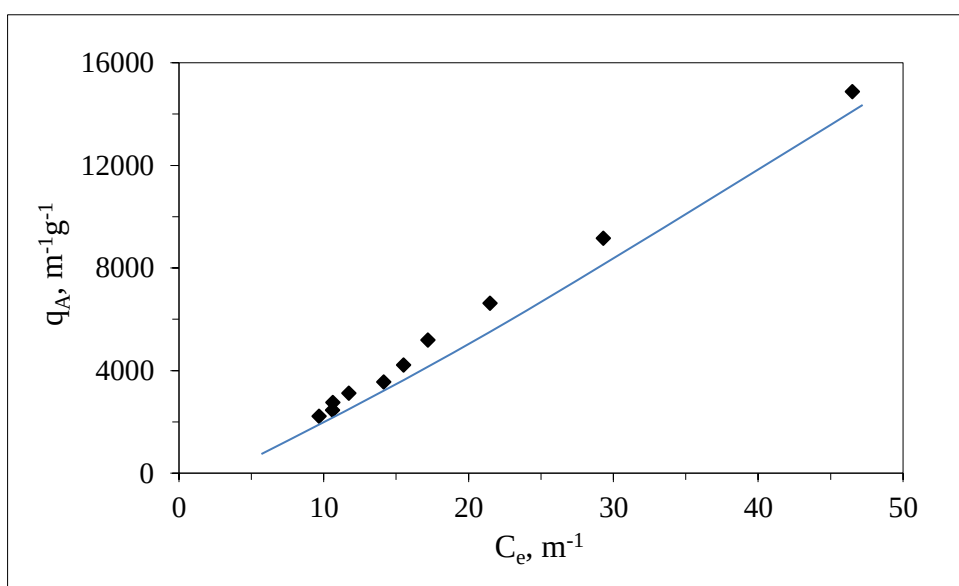


Figure 4.107. UV₂₅₄ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of montmorillonite and Ca²⁺.

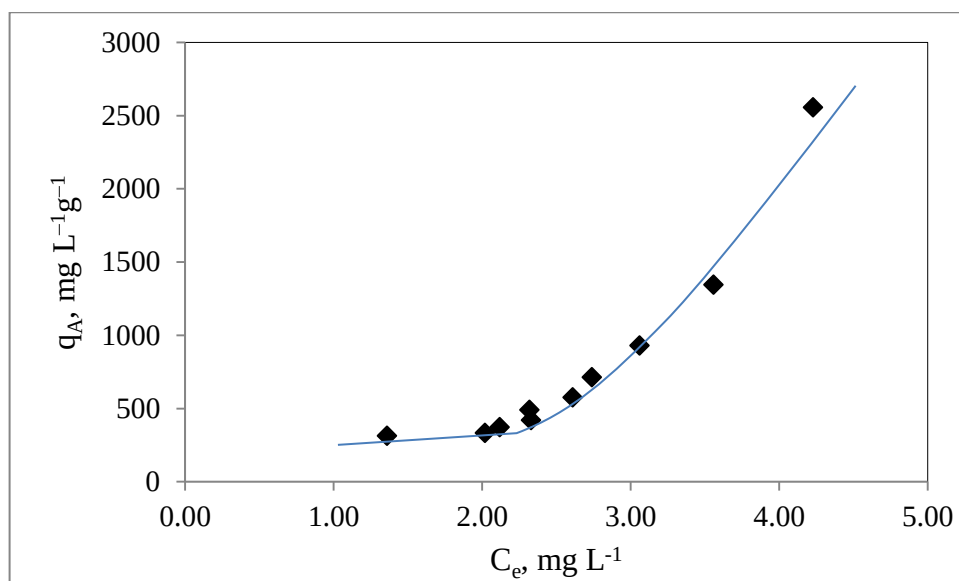


Figure 4.108. DOC adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of montmorillonite and Ca²⁺.

In a similar manner, adsorption data attained for humic acid adsorption onto TiO₂ in the presence of montmorillonite and Ca²⁺ ions were modeled by Freundlich isotherm model and the calculated model coefficients were presented in Table 4.34.

Table 4.34. Freundlich isotherm model coefficients of humic acid adsorption onto TiO₂ in the presence of montmorillonite and Ca²⁺.

	K _f	1/n
Color ₄₃₆	797	0.876
UV ₃₆₅	520	0.970
UV ₂₈₀	188	1.18
UV ₂₅₄	151	1.21
DOC	102	1.97

According to Table 4.34, adsorption capacities of humic parameters onto TiO₂ in the presence of montmorillonite and Ca²⁺ ions were found to be very high towards the functional groups of humic acid. Adsorption capacity constant for Color₄₃₆ (K_F= 797) was found to be higher than the adsorption capacities of other specified UV- parameters as well as DOC (K_F= 102). From a general perspective it should be indicated that the adsorption capacity of humic acid onto TiO₂ in the presence of montmorillonite and Ca²⁺ ions were significantly higher in comparison to the humic acid UV-vis parameters attained in the absence of Ca²⁺ ions (Table 4.29). However, no distinct difference could be attained for DOC due to the presence of Ca²⁺ ions. Adsorption intensity, 1/n values for Color₄₃₆ and UV₃₆₅ were found to be lower than 1. Contrary to the case reported for sole humic acid (Table 4.26), DOC had the highest 1/n value as 1.97. Adsorption intensity values displayed a decreasing order of DOC > UV₂₅₄ > UV₂₈₀ > UV₃₆₅ > Color₄₃₆ whereas adsorption capacity values followed a decreasing order in Color₄₃₆ > UV₃₆₅ > UV₂₈₀ > UV₂₅₄ > DOC.

Emission scan fluorescence spectra of humic acid onto TiO₂ in the presence of montmorillonite and Ca²⁺ ions lead to continuously decreasing trend in fluorescence intensities at emission wavelength of λ_{max} = 450 nm with respect to increasing TiO₂ doses (Figure 4.109). Fluorescence intensities recorded at emission wavelength of λ_{max} = 450 nm for all TiO₂ doses revealed that the fluorescence intensity of at λ_{max} = 450 nm of raw humic acid was significantly higher. Comparison of the emission scan fluorescence spectra of humic acid recorded in the absence of Ca²⁺ ions (Figure 4.69) expressed the disappearance of the overlapping trend at longer wavelength region (λ > 500nm). The reason could be

attributed to the release more intense fluorophoric groups upon adsorption onto TiO_2 in the presence of montmorillonite and Ca^{2+} ions.

The synchronous scan fluorescence spectra for raw humic acid displayed a sharp peak around emission wavelength of $\lambda_{\text{max}} = 475$ nm and a moderate peak at emission wavelength of $\lambda_{\text{emis}} = 385$ nm with a comparatively lower intensity as explained previously (Figure 4.110). Humic acid adsorption onto TiO_2 in the presence of both montmorillonite and Ca^{2+} ions, resulted in a continuously decreasing trend in synchronous scan fluorescence intensities up to emission wavelength of $\lambda_{\text{emis}} = 400$ nm with increasing TiO_2 doses except that 0.20 mg mL^{-1} TiO_2 dose. However, for longer wavelengths as emission wavelength of $\lambda_{\text{emis}} > 450$ nm, fluorescence intensity values decreased with increasing TiO_2 doses.

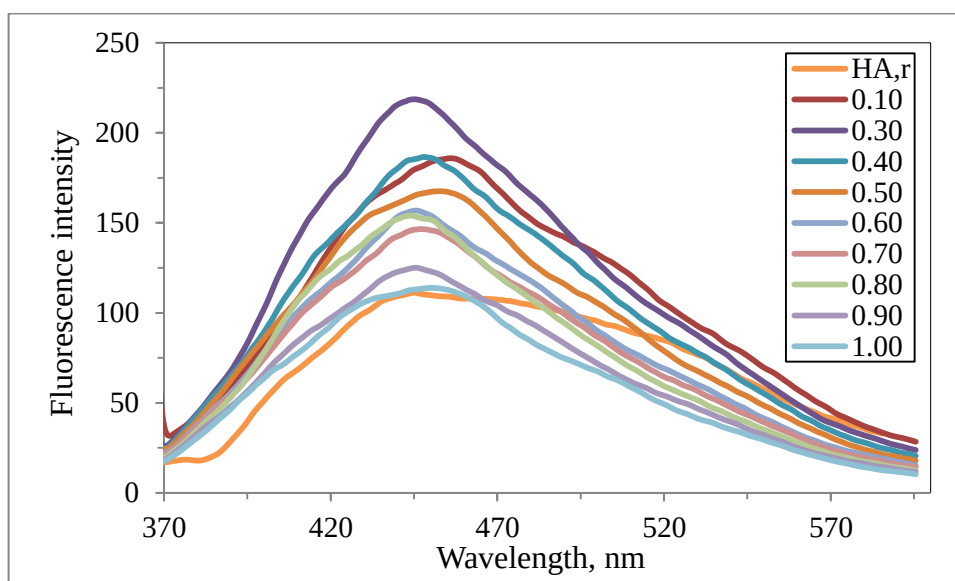


Figure 4.109. Emission scan fluorescence spectra of humic acid adsorption onto TiO_2 in the presence of montmorillonite and Ca^{2+} .

As explained for emission scan fluorescence spectra (Figure 4.109), the release of fluorophoric groups with higher intensities were also evident in the synchronous scan fluorescence spectra (Figure 4.110). However, no distinct trend could be indicated with respect to increasing TiO_2 dose in the presence of montmorillonite and Ca^{2+} ions. The

highest fluorescence intensity was recorded at emission wavelength of $\lambda_{\text{emis}} = 395$ nm in the presence of $0.20 \text{ mg mL}^{-1} \text{ TiO}_2$.

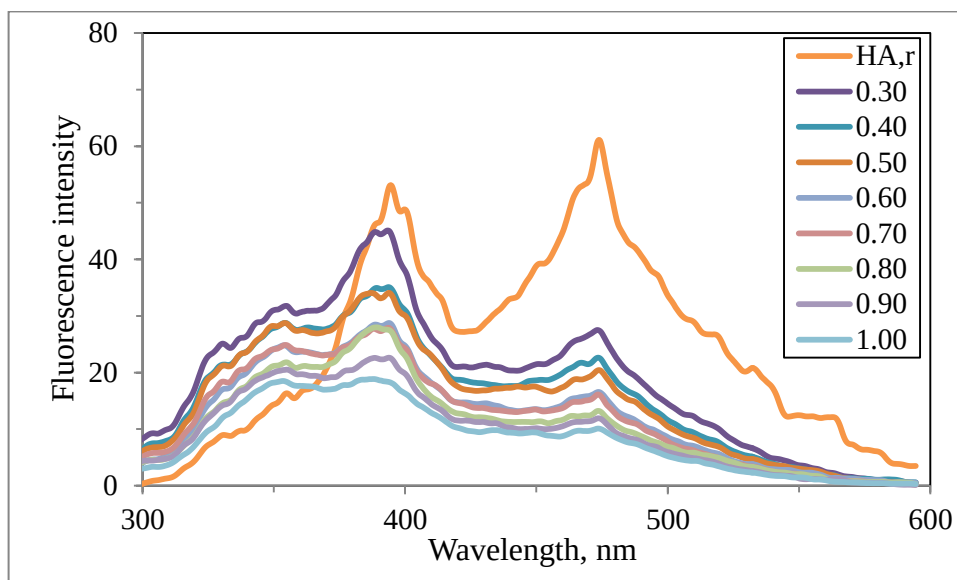


Figure 4.110. Synchronous scan fluorescence spectra of humic acid adsorption onto TiO_2 in the presence of montmorillonite and Ca^{2+} .

4.2.10. Humic acid adsorption onto TiO_2 in the presence kaolinite and Ca^{2+}

In order to elucidate the effect of Ca^{2+} ions on the adsorption behavior of humic acid onto TiO_2 in the presence of kaolinite, batch adsorption experiments were also carried out. The adsorption isotherms of Color_{436} , UV_{254} and DOC were shown in Figures 4.111, Figures 4.112 and Figures 4.113, respectively. The isotherms related to the UV_{365} and UV_{280} parameters were presented in Appendix A.

Figure 4.111 indicated that C_e values varied between $0.77\text{--}7.17 \text{ m}^{-1}$ for Color_{436} depending on the TiO_2 dose. The corresponding values of q_A calculated were in the range of $479\text{--}3510 \text{ m}^{-1}\text{g}^{-1}$. As it could be seen in Figure 4.112, C_e values varied between $10.98\text{--}50.37 \text{ m}^{-1}$ for UV_{254} with corresponding q_A values as $2198\text{--}14098 \text{ m}^{-1}\text{g}^{-1}$. Figure 4.113 showed that the values of C_e varied from 1.59 to 6.97 mg L^{-1} for DOC and the calculated q_A values varied in between $308\text{--}2006 \text{ mg L}^{-1}\text{g}^{-1}$ correspondingly.

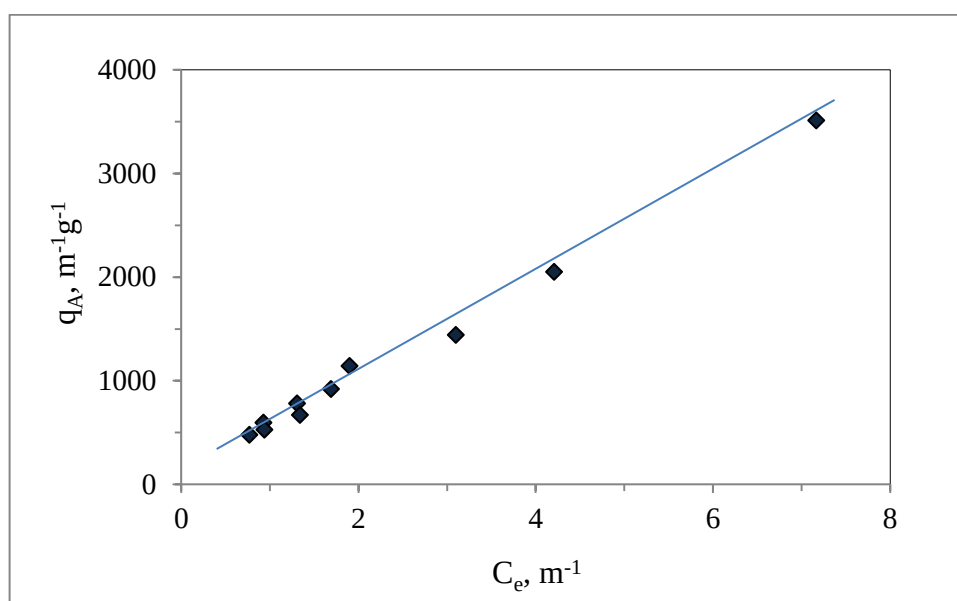


Figure 4.111. Color₄₃₆ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of kaolinite and Ca²⁺.

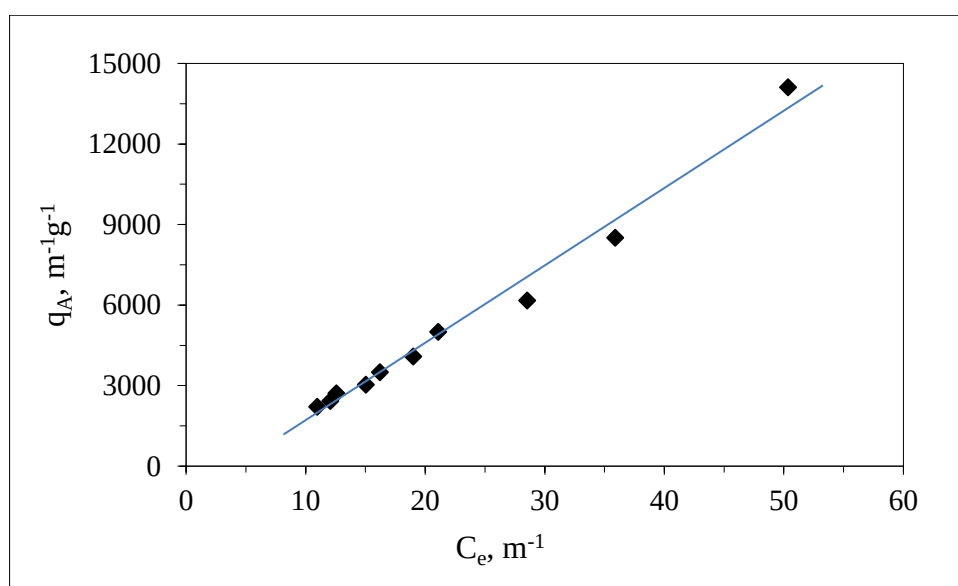


Figure 4.112. UV₂₅₄ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of kaolinite and Ca²⁺.

Upon inspection of the adsorption isotherms presented for UV-vis parameters of humic acid (Figures 4.111 and 4.112) revealed a linear trend representing C type isotherm. However, in the absence of Ca²⁺, S type adsorption isotherm shapes were expressed in

Figures 4.66 and 4.67. Adsorption isotherm of DOC also exhibited a S type isotherm shape prevailing among the humic functional groups and the oppositely charged surface groups. ΔC_e and Δq_A values for humic acid were calculated as 6.40 m^{-1} and $3031 \text{ m}^{-1}\text{g}^{-1}$ respectively at Color_{436} . ΔC_e and Δq_A for UV_{254} were 39.39 m^{-1} and $11900 \text{ m}^{-1}\text{g}^{-1}$, respectively. Moreover, humic acid adsorption onto TiO_2 in the presence of kaolinite and Ca^{2+} ions resulted in steep curves with high Δq_A of $1698 \text{ mg L}^{-1}\text{g}^{-1}$ in a short C_e range of 5.38 mg L^{-1} for DOC.

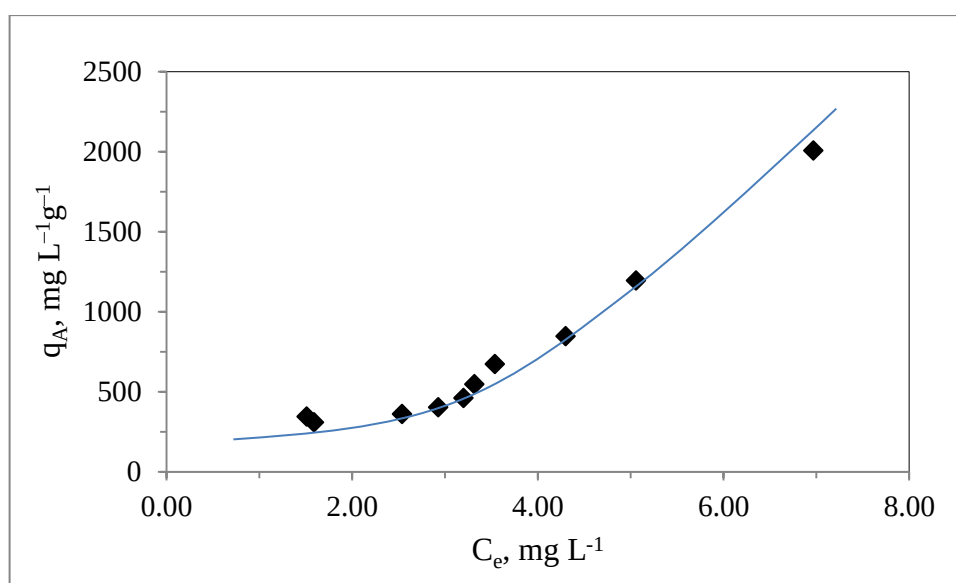


Figure 4.113. DOC adsorption isotherm of humic acid adsorption onto TiO_2 in the presence of kaolinite and Ca^{2+} .

Based on the attained adsorption data, Freundlich isotherm modeling revealed isotherm model coefficients as presented in Table 4.35 ($r^2 > 0.80$). According to Table 4.35, adsorption capacity constant for Color_{436} was found to be higher than the adsorption capacities of other parameters for humic acid adsorption onto TiO_2 in the presence of kaolinite and Ca^{2+} ions. However, adsorption capacity constant for UV_{280} and DOC were found to be very close each other. The lowest K_f value was calculated for UV_{254} parameter. $1/n$ values for Color_{436} and UV_{365} were found to be higher than 1. On the other hand, $1/n$ values for UV_{254} and DOC were almost equal to each other as 1.19 and 1.18 respectively. Adsorption intensity values displayed a decreasing order of $\text{DOC} = \text{UV}_{254} \geq \text{UV}_{280} > \text{UV}_{365}$.

$> \text{Color}_{436}$, whereas adsorption capacity values followed a decreasing order in $\text{Color}_{436} > \text{UV}_{365} > \text{UV}_{280} > \text{DOC} > \text{UV}_{254}$.

Table 4.35. Freundlich isotherm model coefficients of humic acid adsorption onto TiO_2 in the presence of kaolinite and Ca^{2+} .

	K_f	$1/n$
Color_{436}	587.3	0.880
UV_{365}	386.1	0.976
UV_{280}	155.2	1.15
UV_{254}	128.9	1.18
DOC	151.4	1.18

Emission scan fluorescence spectra of humic acid adsorption onto TiO_2 in the presence of kaolinite and Ca^{2+} ions lead to continuously decreasing trend in fluorescence intensities at emission wavelength of $\lambda_{\text{max}} = 450 \text{ nm}$ with respect to increasing TiO_2 doses (Figure 4.114). The highest fluorescence intensity was recorded in the presence of $0.10 \text{ mg mL}^{-1} \text{ TiO}_2$ and the lowest one was attained in the presence of $1.0 \text{ mg mL}^{-1} \text{ TiO}_2$.

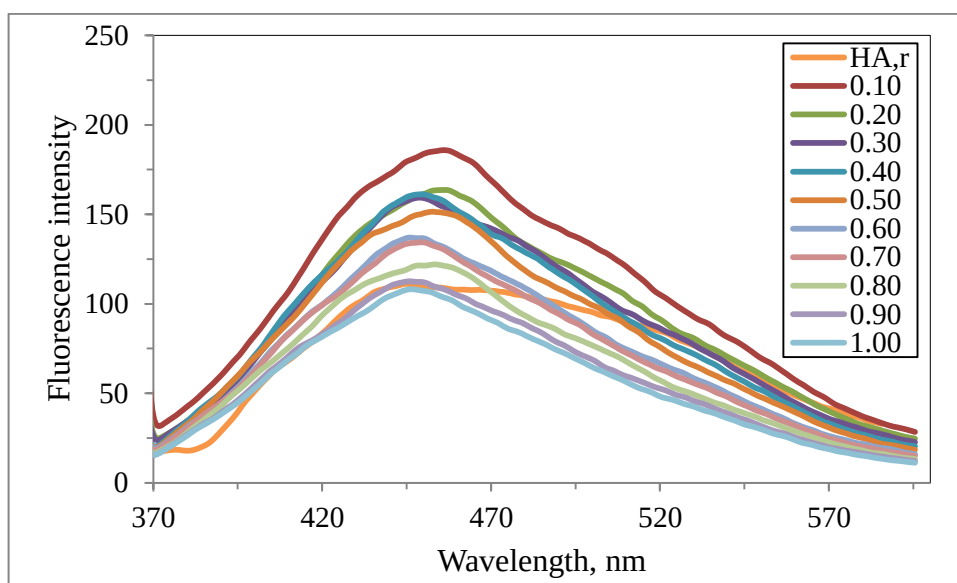


Figure 4.114. Emission scan fluorescence spectra of humic acid adsorption onto TiO_2 in the presence of kaolinite and Ca^{2+} .

A comparison to the previously recorded emission scan fluorescence spectra of humic acid in the absence of Ca^{2+} ions (Figure 4.79) revealed moderate increases in fluorescence intensities rather than a fluorescence quenching effect due to the presence of divalent cations (Cabaniss, 1992, Kumke et al., 2005, Shin et al., 2001).

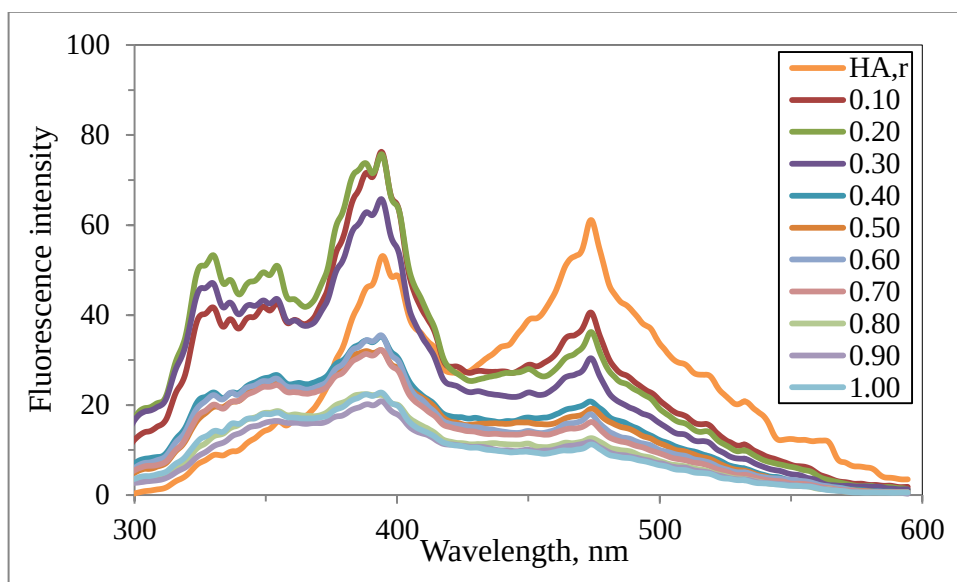


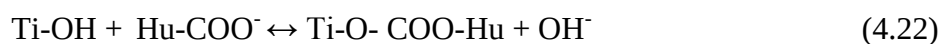
Figure 4.115. Synchronous scan fluorescence spectra of humic acid adsorption onto TiO_2 in the presence of kaolinite and Ca^{2+} .

Synchronous scan fluorescence spectra for raw humic acid displayed a sharp peak around emission wavelength of $\lambda = 475$ nm and a moderate peak at $\lambda = 385$ nm with a comparatively lower intensity as explained previously (Figure 4.115). In the presence of kaolinite and Ca^{2+} ions, a continuously decreasing trend was observed for synchronous scan fluorescence intensities up to emission wavelength of $\lambda_{\text{emis}} = 400$ nm with increasing TiO_2 doses except that recorded for 0.10, 0.20 and 0.3 mg mL^{-1} TiO_2 doses. However, for longer wavelengths $\lambda_{\text{emis}} > 450$ nm, fluorescence intensity values decreased with increasing TiO_2 doses. A comparison to the synchronous scan fluorescence spectra of humic acid recorded in the presence of TiO_2 and kaolinite and in the absence of Ca^{2+} indicated TiO_2 dose dependent variations being more significant in the shorter emission wavelengths. A plausible reason could be attributed to the release of new fluorophoric groups upon introduction of divalent cations followed by adsorption on both TiO_2 and kaolinite surfaces.

4.2.11. Evaluation of adsorption properties of humic acid onto TiO₂ and TiO₂ in the presence of clay minerals

Humic acid adsorption onto TiO₂ Degussa P-25 has been studied extensively by Bekbolet and colleagues since 2002 (Bekbolet et al., 2002, Uyguner et al., 2007). Therefore, the introductory part covered information to present a basis for further comparison of the humic adsorption data attained in the presence of sole clay minerals *i.e.* montmorillonite and kaolinite as well as TiO₂ in the presence of these clay minerals.

Humic acid adsorption onto sole TiO₂ (Degussa P-25) followed a S-type adsorption profile in accordance with the previously studied systems (Bekbolet et al., 2002). The major difference could be attributed to the type of the humic acid (allochthonous) as well as to the initial humic acid concentration (50 mg L⁻¹). It should also be mentioned that the adsorption properties of humic acid onto TiO₂ and the specified binary systems were studied in the range of 0.10-1.0 mg mL⁻¹ representing the photocatalytically active dose of the photocatalyst. Moreover, adsorption experiments were performed under natural pH solution conditions without any pH adjustment to mimic the photocatalytic degradation conditions as well as natural water systems. Under neutral pH conditions the surface of the TiO₂ is slightly acidic due to the deprotonation-protonation equilibria pertaining with respect to p*H*_{zpc} of TiO₂ (p*H*_{zpc} = 6.3, Kormann et al., 1991). Humic acid functional groups primarily expressed by the presence of carboxylic and phenolic (ph) groups could also be dissociated to express negatively charged carboxylate/phenolate groups (Christl and Kretzschmar, 2001). Therefore, electrostatic attractions prevailing in between these oppositely charged centers either in the form of attraction or repulsion resulted in adsorption of humic fractions (Hu) onto oxide surface.



As a result, the electrostatic forces resulting in surface complexation could possibly lead to the surface coverage that could also be successfully modeled by Langmuir adsorption isotherm model.

Humic acid adsorption onto clay minerals either montmorillonite (2:1 type) or kaolinite (1:1 type) revealed completely different trends with respect to the clay type characteristics. From a broader perspective, montmorillonite displayed a lower tendency to adsorb humic acid in comparison to the adsorption properties attained in the presence of kaolinite (Table 4.2 and Table 4.3). The prevailing mechanism could well be explained by the surface properties of the active clay specimens. Montmorillonite exhibited 2:1 type layer silicate structure and was composed of silica tetrahedral and alumina octahedral layers expressing permanent negative charge sites on the faces. Amphoteric Al–OH and Si–OH groups were reported to be situated at the broken edges of montmorillonite surfaces (Bourg et al., 2007; Tombácz and Szekeres, 2004). Therefore, these amphoteric surface hydroxyl groups present at the edges were responsible for the development of negative and positive charges. Moreover, montmorillonite had high permanent negative particle charge which was attributed to the isomorphous substitution of Si^{4+} by Al^{3+} and was pH independent (Tombácz et al., 1999). The following protonation and deprotonation equilibria could represent the charge formation on surface site, Al–OH as well as for SiOH;



The pH of zero proton charge (pH_{zpc}) of montmorillonite was reported as pH 6.5 by Tombácz and Szekeres (Tombácz and Szekeres, 2004). The pH of zero proton charge (pH_{zpc}) of kaolinite was reported as pH 5.3 (Meier et al., 1999).

Although the prevailing surface interactions between humic acid and oxide surfaces primarily could possibly be originated through electrostatic attractions, lateral interactions could also occur between the adsorbed humic macromolecules themselves and the steric

arrangements of the macromolecules (Vermeer et al., 1998). It could be pointed out that the hydrophobic properties humic acid might accumulate on surfaces because of their incompatibility with water, which was more polar than the surface (Lai and Chen, 2001). Moreover, under neutral pH conditions, humic acid could reduce electrostatic forces by aligning hydrophobic structures together in a core and aligning charged functional groups in the molecule towards solvating water molecules. Thus, it would be plausible to explain the adsorption properties of the humic acid in terms of UV-vis parameters expressing both the conjugated systems through color forming moieties (Color_{436}) and UV absorbing centers that were mainly aromatic in nature (UV_{365} , UV_{280} and UV_{254}) in accordance with DOC parameters.

Besides the pH_{zpc} condition of the adsorbents, surface area also played a significant role on the adsorption phenomena. Therefore, selected properties of TiO_2 , Mt and Kt were presented in Table 3.1.

Although montmorillonite exhibited comparatively larger surface area ($97.42 \text{ m}^2 \text{ g}^{-1}$) with respect to the other adsorbents i.e. TiO_2 ($55 \text{ m}^2 \text{ g}^{-1}$) and kaolinite ($10.05 \text{ m}^2 \text{ g}^{-1}$), Freundlich adsorption isotherm model parameters reflected a nonsignificant adsorption capacity for all of the specified humic parameters (Table 4.1, Table 4.2 and Table 4.3). The reason could be attributed to the presence of the significantly less charged surface sites located on montmorillonite in relation to the diverse surface morphologies of the adsorbent specimens. For the elucidation of the surface interactions, scanning electron micrographs accompanied by the Energy Dispersive X-ray analysis of the adsorbate-adsorbent systems were evaluated and presented by Sen-Kavurmaci and Bekbolet (Sen-Kavurmaci and Bekbolet, 2013c). SEM images of the sole TiO_2 particles displayed quite similar particles in size and shape as expected (Murcia-López et al., 2012, Yalcin et al., 2010). The SEM image obtained for “humic acid and TiO_2 ” displayed a structure composed of comparatively large embedded humic regions surrounded by TiO_2 particles (Chen et al., 2007). Regarding the distinctly different surface morphologies of Mt and Kt, the corresponding EDX-analysis showed the presence of both clay particles as well as TiO_2 (Wang et al., 2011). Furthermore, in ternary systems where humic adsorption onto TiO_2 in the presence of clay minerals was investigated, SEM images displayed the presence of humic aggregates located in between the surfaces of TiO_2 , montmorillonite or kaolinite.

In relation to the individual adsorption properties of humic acid onto TiO_2 , montmorillonite and kaolinite, adsorption of humic fractions onto TiO_2 in the presence of either montmorillonite or kaolinite were also elucidated (Table 4.27 and Table 4.28). Regarding the adsorption isotherms, an S type isotherm shape could be indicated for all of the specified UV-vis parameters. However, DOC isotherm data displayed quite different shapes with respect to the characteristics of the studied matrix expressing an L type isotherm shape. Therefore, DOC adsorption data were further modeled by Langmuir adsorption model and the calculated model parameters were presented in Table 4.37.

Langmuir adsorption isotherm model could be expressed by the following equation and through linearization of the equation, Langmuir model parameters could be calculated (Equation 2.4 and 2.5).

Table 4.36. Langmuir isotherm model parameters of DOC adsorption onto TiO_2 , montmorillonite and kaolinite.

Langmuir adsorption isotherm model parameters		
Humic acid adsorption onto	$q_{\max}, \text{mg g}^{-1} \text{L}^{-1}$	$K_L, \text{mg L}^{-1}$
TiO_2	2500	1.25×10^{-2}
Montmorillonite	18	4.00×10^{-2}
Kaolinite	625	4.81×10^{-3}
Montmorillonite and TiO_2	714	7.96×10^{-2}
Kaolinite and TiO_2	217	5.08×10^{-2}
Ca^{2+} ion effect		
TiO_2	1031	5.33×10^{-2}
Montmorillonite and TiO_2	1429	1.13×10^{-2}
Kaolinite and TiO_2	3333	6.3×10^{-3}

Langmuir adsorption model parameters of DOC adsorption onto TiO_2 , montmorillonite and kaolinite ($r^2 > 0.90$). Although the presence of Ca^{2+} ions significantly altered the adsorption properties of humic acid onto the specified adsorbents, Langmuir model could also be successfully applied ($r^2 > 0.90$).

The highest surface coverage condition was attained in the presence of sole TiO_2 ($q_{\text{max}} = 2500$). A decreasing order of q_{max} could be assessed for humic acid adsorption onto TiO_2 in the presence of montmorillonite $>$ TiO_2 in the presence of kaolinite. These results were in good accordance with the K_F attained by Freundlich adsorption isotherm model (Table 4.27 and Table 4.28). However, the variations attained in K_L could be explained by different conformational orientations of humic fractions prevailing during surface interactions.

Kaolinite has been reported to have a much stronger affinity for humic acid than montmorillonite by Parazak and colleagues (Parazak et al., 1988). The interaction was expressed through the involvement of polyvalent metals at the clay surface, and since kaolinite had a much higher aluminum content than montmorillonite, it adsorbed humic acid more strongly. In addition, montmorillonite had a high negative charge, largely invariant with pH, while that of kaolinite was much lower at about one tenth the level and dependent on pH. Hence, a strong electrostatic repulsion between montmorillonite and humic acid was expected. From a general perspective, the adsorption of humic acid onto clays was generally accepted as a ligand exchange between the carboxylate groups on the organic molecules and the OH groups bound to a metal on the surface of the solid (Kaiser and Zech, 1998). Moreover, an insignificant role of hydrogen bonding was also presented (Schulthess and Huang, 1991).

Both Freundlich and Langmuir adsorption model parameters (Table 4.31- 4.36) could well visualize the significant role of Ca^{2+} ions in adsorption of humic fractions on the expressed surfaces of the adsorbents. The presence of Ca^{2+} caused shrinkage in the molecular size of the humic acid possibly through screening out the negatively charged moieties by strong electrostatic attractions. Therefore, Ca bound humic structure played the major role in attractions towards the adsorbent surfaces. Moreover, the presence of Ca^{2+} ions exerted an ionic strength effect by changing the charge distribution in the vicinity of the adsorbent surfaces.

Adsorption of humic acid onto sole TiO_2 and TiO_2 in the presence of either montmorillonite or kaolinite could well be characterized by both UV-vis parameters and DOC contents. In case of sole systems, the most significant improvement in adsorption

capacity of humic acid was attained in the presence of $\text{TiO}_2 > \text{kaolinite} > \text{montmorillonite}$. However, the presence of montmorillonite improved significantly the adsorption capacity of humic acid with respect to kaolinite in binary systems composed of TiO_2 and either of the specified clay minerals.

5. CONCLUSION

In this study, the influence of clay minerals i.e. montmorillonite and kaolinite as representative clay minerals on the TiO₂ photocatalytic degradation of humic acid as a model compound of natural organic matter was investigated. The interactions prevailing between humic acid, montmorillonite, kaolinite and TiO₂ surface were assessed prior to the application of photocatalysis in order to address the adsorptive and photolytic behavior of humic acids. Oxidative removal of humic acid was expressed by pseudo first order kinetic modeling of dissolved organic carbon (DOC) and specified UV-vis parameters (Color₄₃₆, UV₃₆₅, UV₂₈₀ and UV₂₅₄). The effect of Ca²⁺ ions was also assessed through baseline experiments performed on binary and ternary systems covering dark interactions as well as by photocatalytic degradation efficiencies. Considering the prevailing molecular size fractionation (100 kDa, 30 kDa and 3 kDa) fractions upon interaction of humic components onto TiO₂ surface and clay minerals prior to photocatalysis, the resultant humic acid sub-fractions attained upon photocatalytic oxidative treatment were also presented by using the specified humic parameters (i.e. SCoA, SUVA₃₆₅, SUVA₂₈₀, and SUVA₂₅₄). Scanning electron microscopic (SEM) images accompanying with energy dispersive X-ray analysis were also examined for the elucidation of the surface morphologies of the binary and ternary systems composed of HA, TiO₂ and Mt or Kt both prior to and following photocatalysis. Excitation emission matrix (EEM) fluorescence spectral features were also evaluated for the elucidation of the photocatalytic degradation of sole humic acid and humic acid in the presence of clay minerals either as montmorillonite or kaolinite. Adsorption properties of humic acid onto sole TiO₂ and TiO₂ in the presence of clay minerals either as montmorillonite or kaolinite were also evaluated in terms of the specified UV-vis parameters as well as DOC.

Based on the prevailing interactions under dark conditions, scanning electron microscopic images accompanying with energy dispersive X-ray analysis were examined for the elucidation of the surface morphologies of the binary and ternary systems composed of HA, TiO₂ and Mt or Kt. The allocation of humic fractions in between TiO₂, Mt or Kt particles expressing efficient surface adsorption satisfied the prerequisite condition of photocatalysis. Scanning electron micrographs accompanied by the Energy

Dispersive X-ray analysis of the adsorbate-adsorbent systems were evaluated. SEM images of the sole TiO_2 particles displayed quite similar particles in size and shape as expected. The SEM image obtained for “humic acid and TiO_2 ” displayed a structure composed of comparatively large embedded humic regions surrounded by TiO_2 particles. Regarding the distinctly different surface morphologies of Mt and Kt, the corresponding EDX-analysis showed the presence of both clay particles as well as TiO_2 . Furthermore, in ternary systems where humic adsorption onto TiO_2 in the presence of clay minerals was investigated, SEM images displayed the presence of humic aggregates located in between the surfaces of TiO_2 , Mt or Kt.

UV-vis spectral features of sole humic acid and humic acid in the presence of either montmorillonite or kaolinite were also elucidated both under non-oxidative and photocatalytic oxidation conditions. The investigation demonstrated the use of specific UV-vis and fractional UV-vis parameters (i.e. E_{254}/E_{365} ; E_{254}/E_{436} ; E_{280}/E_{365} ; E_{280}/E_{436} , and E_{365}/E_{436}) of humic acid for the visualization of the photocatalytic oxidation process. The variations attained in SCoA and SUVA_{254} with respect to E_{254}/E_{436} did not reveal any significant discrimination from clay type point of view, hence could well be modeled by a linear relationship irrespective of the clay type. On the other hand, the relationship of E_{365}/E_{436} and SUVA_{365} and SCoA parameters displayed a discriminative behavior with respect to the type of the clay mineral as represented by the correlation equations. In relation to the UV-vis and fluorescence spectroscopic characterization presented under appropriate subheadings for humic acid both the presence and absence of clay minerals i.e. Mt and Kt, photocatalytic degradation data were also processed using pseudo first order kinetic model. First order kinetic model parameters displayed a slight enhancement effect for humic UV-vis parameters and DOC in the presence of varying doses of either Mt or Kt. On the other hand, photocatalytic mineralization rates could be regarded as insignificantly different from each other. A slight enhancement in the photocatalytic removal of HA could be indicated due to the presence of Ca^{2+} ions in the specified concentration range. Besides the effective removal of higher molecular size fractions (100 kDa and 30 kDa fractions), transformation to lower molecular size fractions ($< 3\text{kDa}$) was more pronounced for sole HA rather than HA in the presence of either Mt or Kt.

EEM fluorescence spectral structures were assessed for the illumination of the photocatalytic degradation of sole humic acid and humic acid in the presence of Mt or Kt. The role of Ca^{2+} ions was also visualized through EEM under the specified conditions. EEM features reflected the irradiation time dependent transformation of the humic like fluorophores to fulvic like fluorophores in accordance with the photocatalytic removal of humic acid. Upon photocatalytic treatment, the role of Mt was more pronounced with respect to the effects observed in the presence of Kt in comparison to the results achieved for sole humic acid. Upon prolonged irradiation conditions (180 min) almost complete removal of fluorophoric groups were detected in relation to a substantial degree of mineralization (> 75% removal of DOC). As a quantification approach, Fluorescence-derived index defined as Fluorescence Intensity (FI) as represented by the ratio of the emission intensity at λ_{emis} 450 nm to that at λ_{emis} 500 nm, following excitation at λ_{exc} 370 nm was successfully correlated to UV_{254} and UV_{280} revealing an inverse relationship. Moreover, through normalization of the specified UV parameters to DOC contents, SUVA_{254} and SUVA_{280} could also be successfully correlated to FI.

In relation to the individual adsorption properties of humic acid onto TiO_2 , Mt and Kt, adsorption of humic fractions onto TiO_2 in the presence of either Mt or Kt were also elucidated. Regarding the adsorption isotherms, an S type isotherm shape could be indicated for all of the specified UV-vis parameters. However, DOC isotherm data displayed quite different shapes with respect to the characteristics of the studied matrix expressing an L type isotherm shape. Therefore, DOC adsorption data were further modeled by Langmuir adsorption model and the calculated model parameters. Humic acid adsorption onto clay minerals either Mt (2:1 type) or Kt (1:1 type) revealed completely different trends with respect to the clay type characteristics. Although Mt exhibited comparatively larger surface area with respect to the other adsorbents i.e. TiO_2 and Kt, Freundlich adsorption isotherm model parameters reflected a nonsignificant adsorption capacity for all of the specified humic parameters. The reason could be attributed to the presence of the significantly less charged surface sites located on Mt in relation to the diverse surface morphologies of the adsorbent specimens. Adsorption of humic acid onto sole TiO_2 and TiO_2 in the presence of either Mt or Kt could well be characterized both by UV-vis parameters (Color_{436} , UV_{365} , UV_{280} and UV_{254}) and DOC contents. In case of sole systems, the most significant improvement in adsorption capacity of humic acid was

attained in the presence of $\text{TiO}_2 > \text{Kt} > \text{Mt}$. However, the presence of Mt improved significantly the adsorption capacity of humic acid with respect to Kt in binary systems composed of TiO_2 and either of the specified clay minerals.

To examination of the effect of Ca^{2+} ion on adsorption behavior of humic acid, batch adsorption experiments were also carried out using humic acid with varying doses of TiO_2 in the presence of montmorillonite/kaolinite and Ca^{2+} ion. Although the presence of Ca^{2+} ions significantly altered the adsorption properties of humic acid onto the specified adsorbents, Langmuir model could also be successfully applied ($r^2 > 0.90$). The highest surface coverage condition was attained in the presence of sole TiO_2 ($q_{\text{max}} = 2500$). A decreasing order of q_{max} could be assessed for humic acid adsorption onto TiO_2 in the presence of montmorillonite $>$ TiO_2 in the presence of kaolinite. These results were in good accordance with the K_F attained by Freundlich adsorption isotherm model. However, the variations attained in K_L could be explained by different conformational orientations of humic fractions prevailing during surface interactions. The significant role of Ca^{2+} ions in adsorption of humic fractions on the expressed surfaces of the adsorbents could well be visualized by both Freundlich and Langmuir adsorption model parameters.

It could be concluded that, the presence of clay particles i.e. montmorillonite and kaolinite would not significantly alter the photocatalytic degradation efficiency of humic acid. This result signifies that photocatalysis could be an alternative treatment option for the successful removal of natural organic matter in water treatment systems. As shown by the results attained through the application of the UV-vis and fluorescence spectroscopic techniques, the chemical composition of the resultant organic matter would be the indicative parameter for the assessment of the drinking water quality. Since chlorination and/or ozonation is widely applied as the final disinfection step, from public health point of view, it is highly recommended that further research should be directed to the evaluation of the possible side effects related to the formation of the disinfection by-products.

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APPENDIX A: ADSORPTION ISOTHERM OF HUMIC ACID
ADSORPTION ONTO TiO_2 IN THE PRESENCE OF CLAY
MINERALS FOR UV_{280} AND UV_{365} PARAMETERS

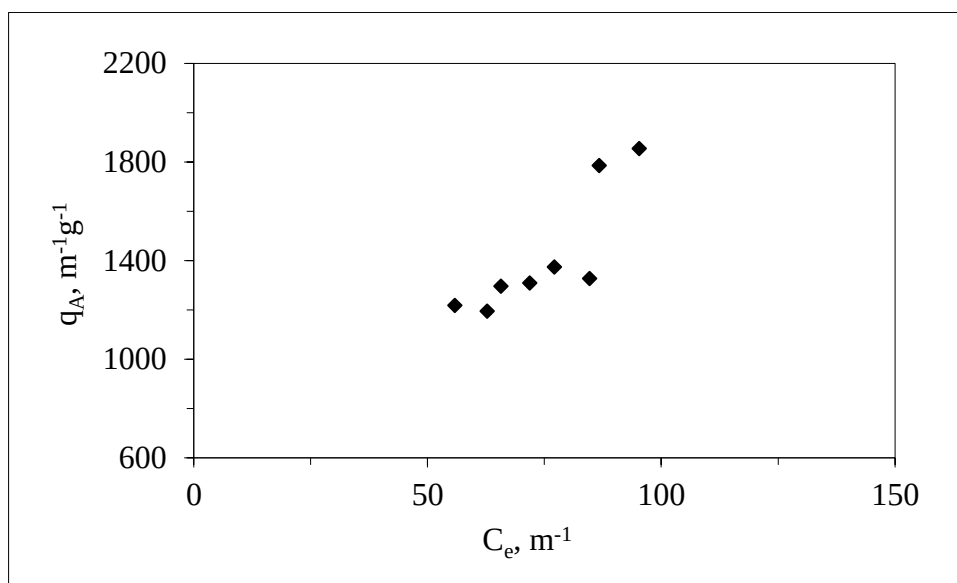


Figure A.1. UV_{280} adsorption isotherm of humic acid adsorption onto TiO_2

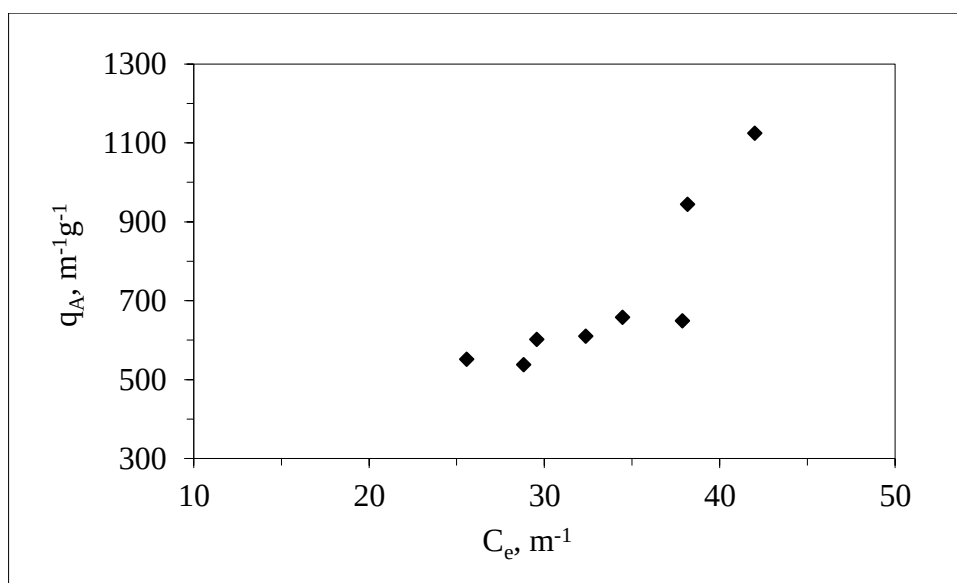


Figure A.2. UV_{365} adsorption isotherm of humic acid adsorption onto TiO_2

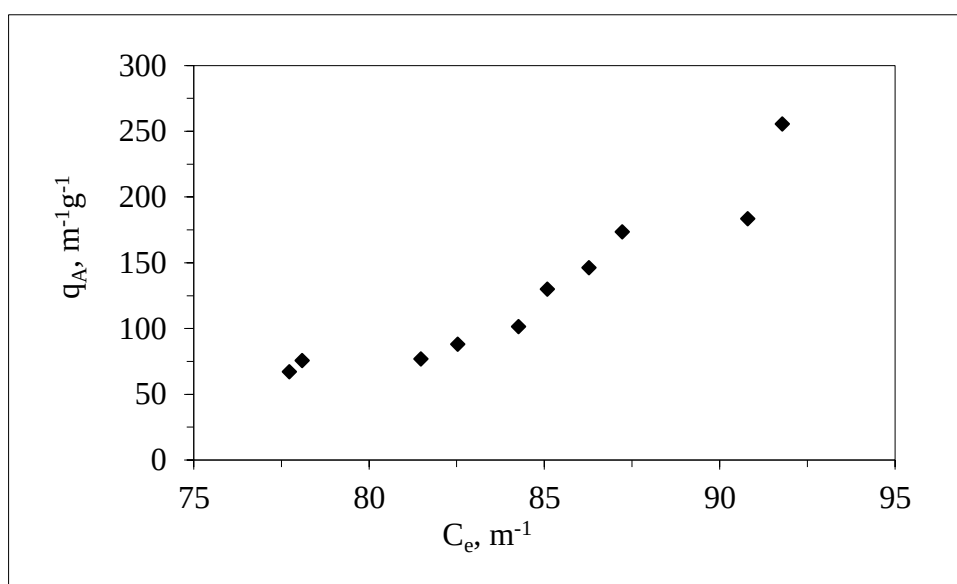


Figure A.3. UV₂₈₀ adsorption isotherm of humic acid adsorption onto montmorillonite

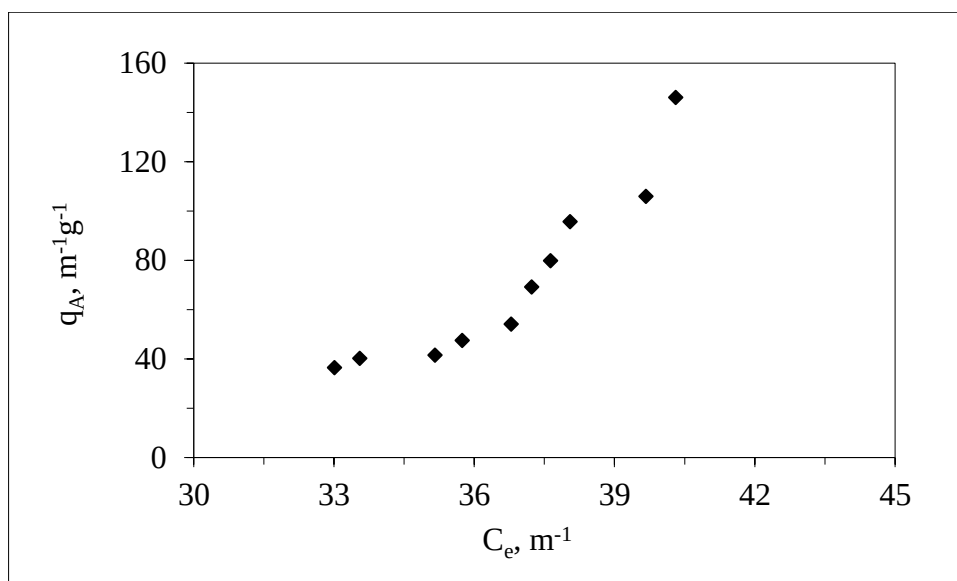


Figure A.4. UV₃₆₅ adsorption isotherm of humic acid adsorption onto montmorillonite

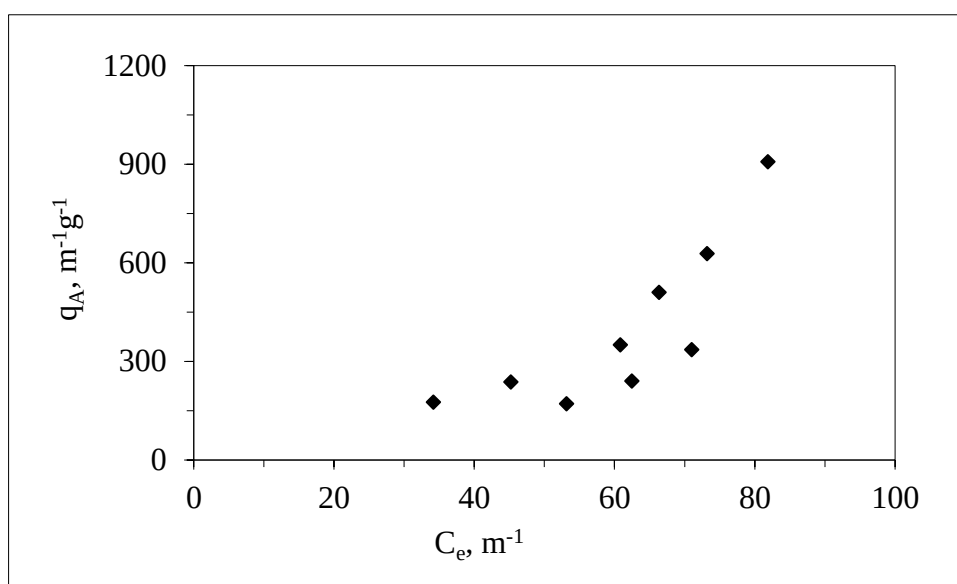


Figure A.5. UV₂₈₀ adsorption isotherm of humic acid adsorption onto kaolinite

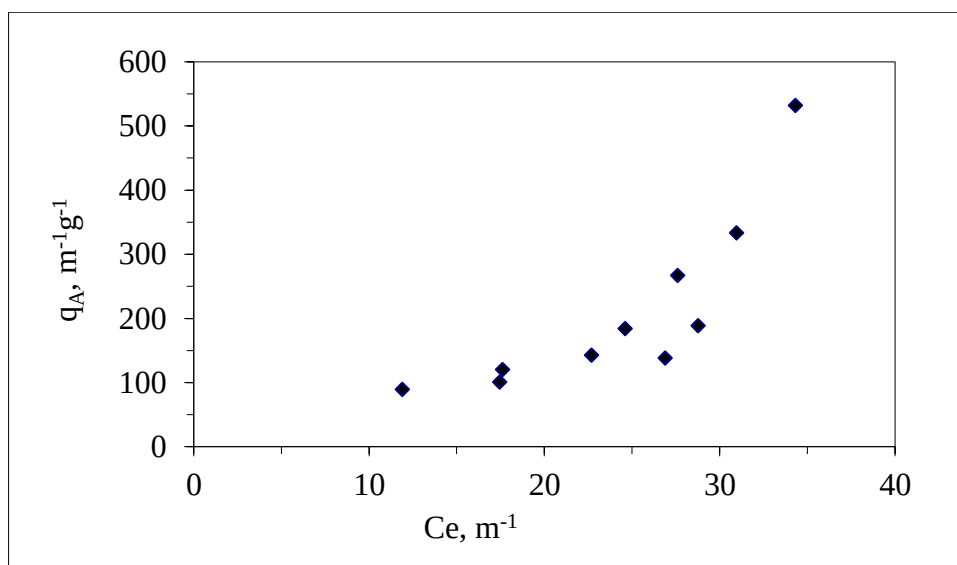


Figure A.6. UV₃₆₅ adsorption isotherm of humic acid adsorption onto kaolinite

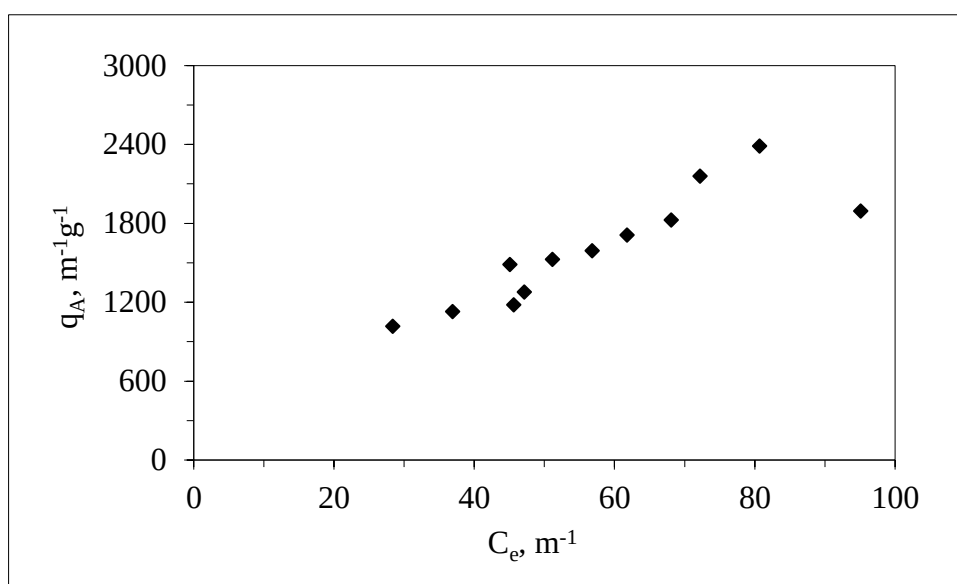


Figure A.7. UV₂₈₀ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of montmorillonite

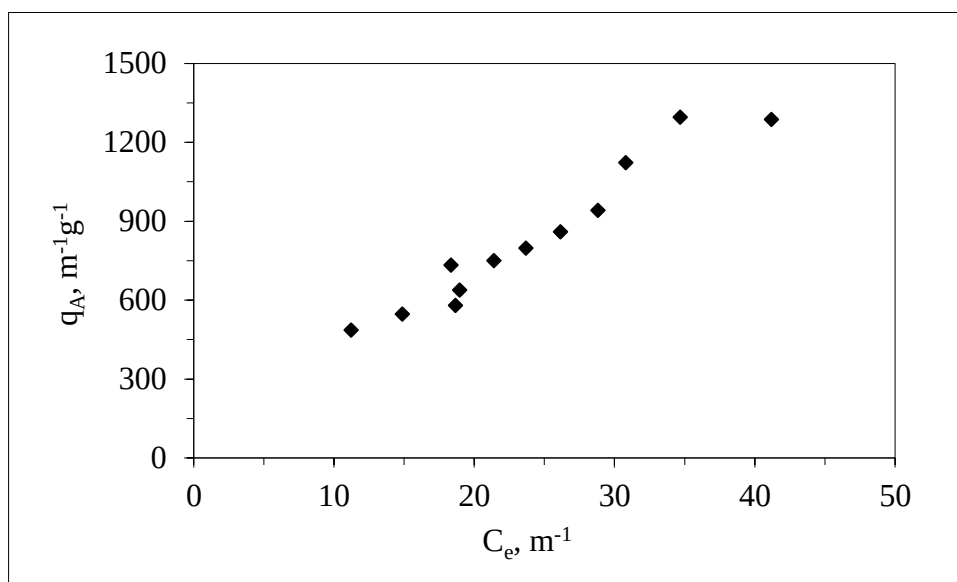


Figure A.8. UV₃₆₅ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of montmorillonite

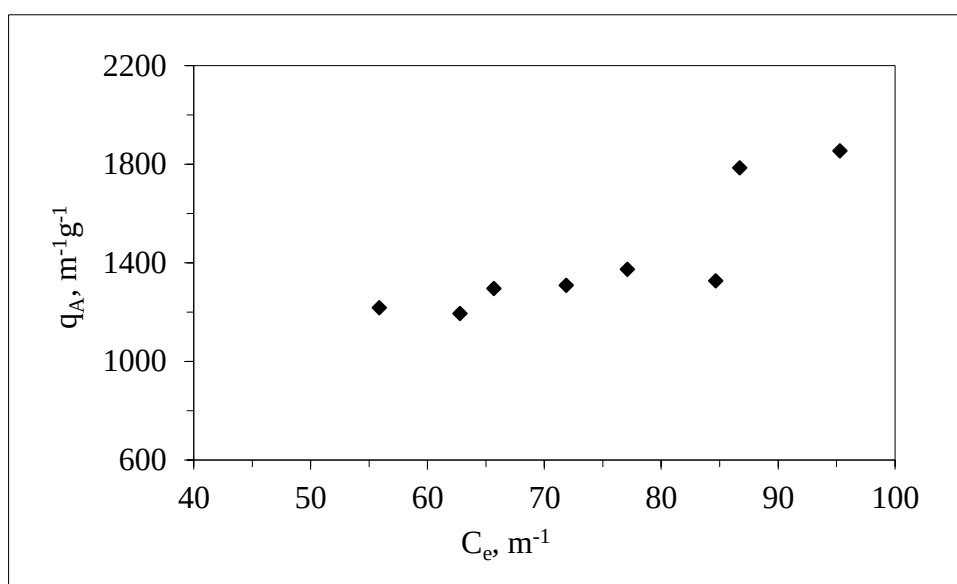


Figure A.9. UV₂₈₀ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of kaolinite

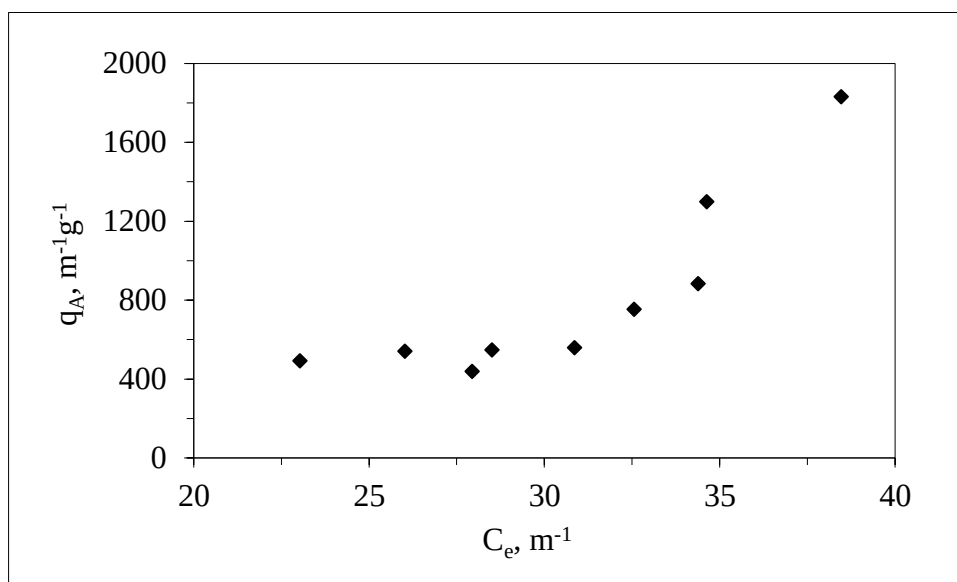


Figure A.10. UV₃₆₅ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of kaolinite.

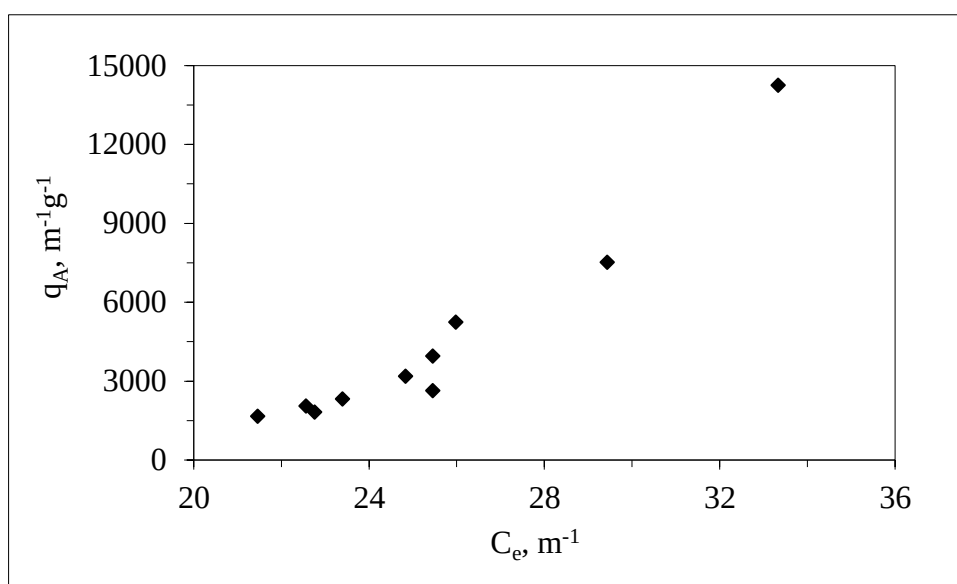


Figure A.11. UV₂₆₅ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of Ca²⁺.

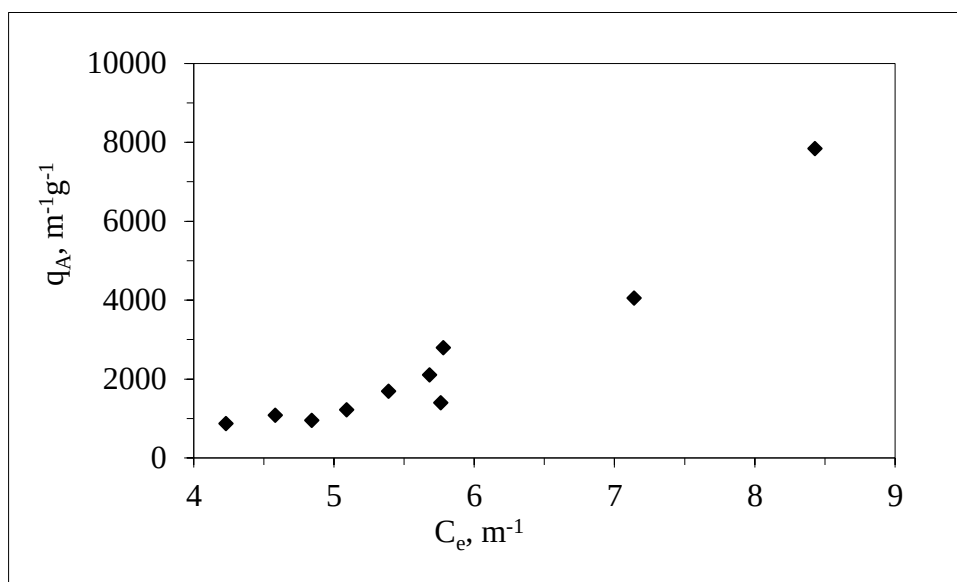


Figure A.12. UV₃₆₅ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of Ca²⁺.

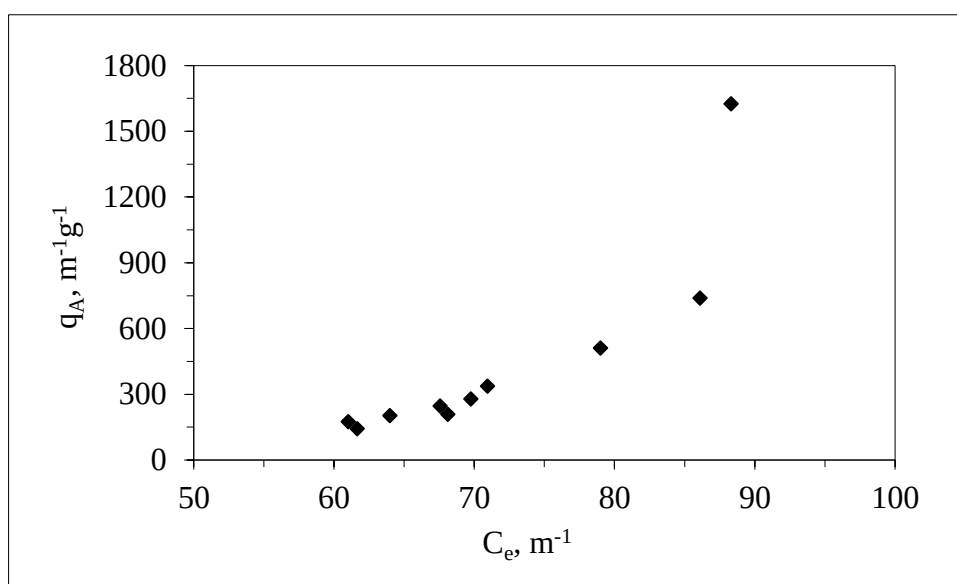


Figure A.13. UV₂₈₀ adsorption isotherm of humic acid adsorption onto montmorillonite in the presence of Ca²⁺.

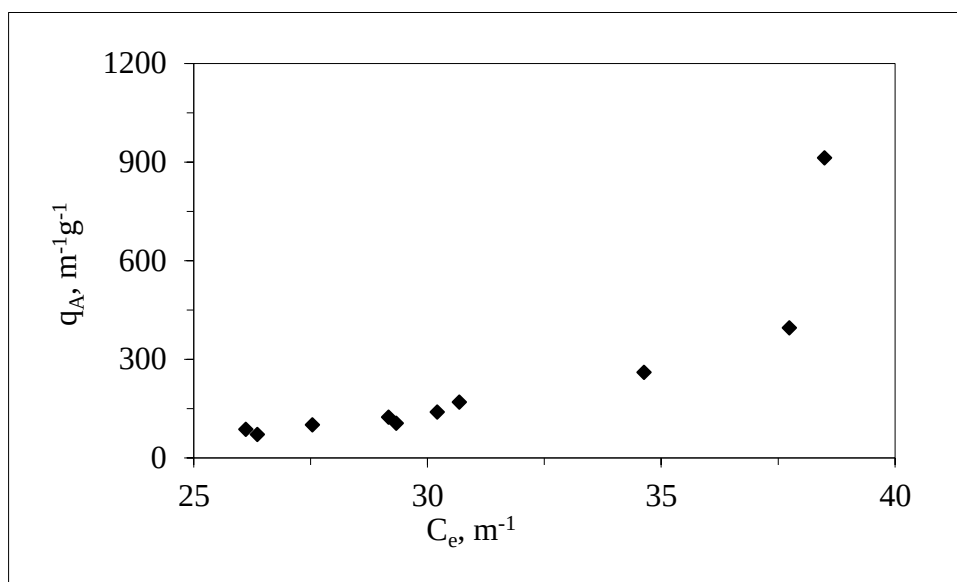


Figure A.14. UV₃₆₅ adsorption isotherm of humic acid adsorption onto montmorillonite in the presence of Ca²⁺.

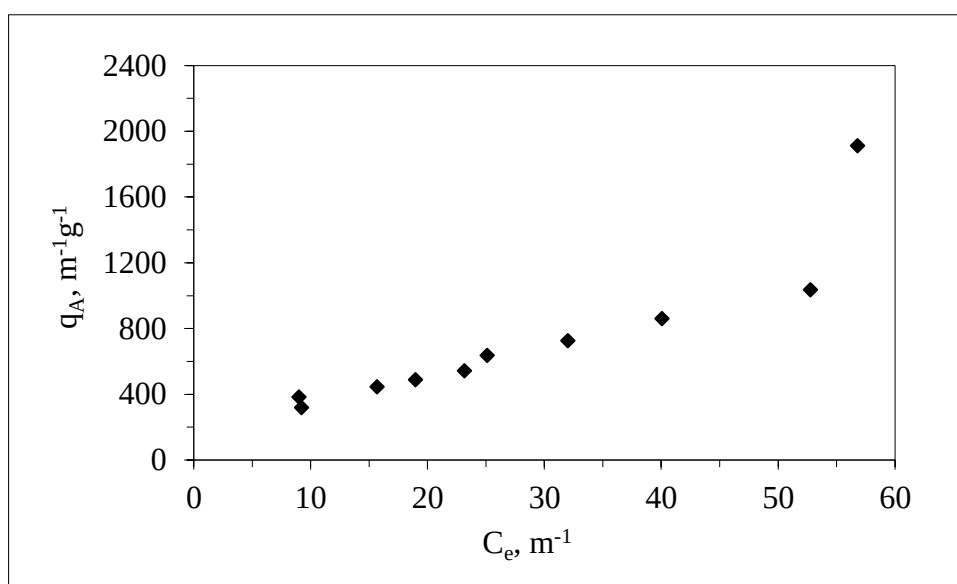


Figure A.15. UV₂₈₀ adsorption isotherm of humic acid adsorption onto kaolinite in the presence of Ca²⁺.

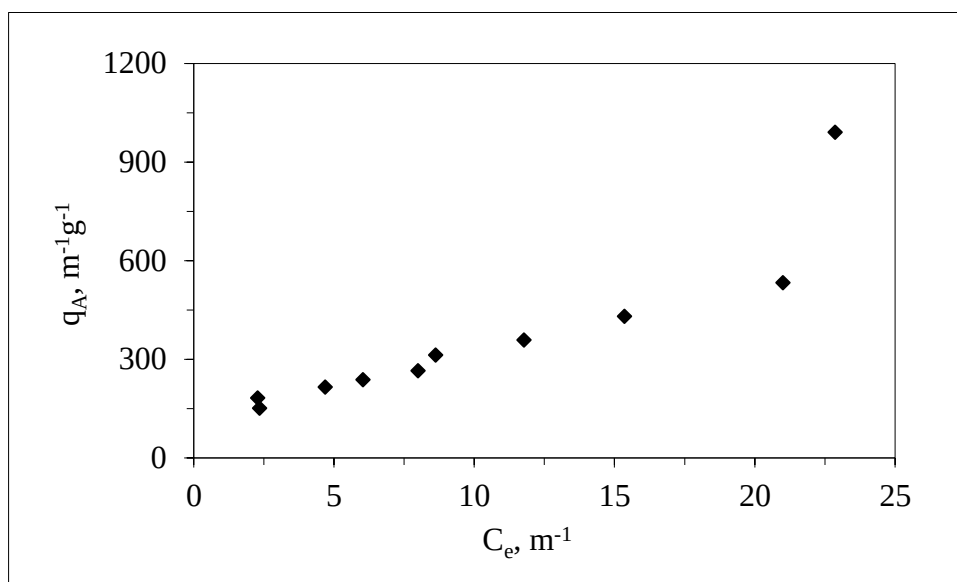


Figure A.16. UV₃₆₅ adsorption isotherm of humic acid adsorption onto kaolinite in the presence of Ca²⁺.

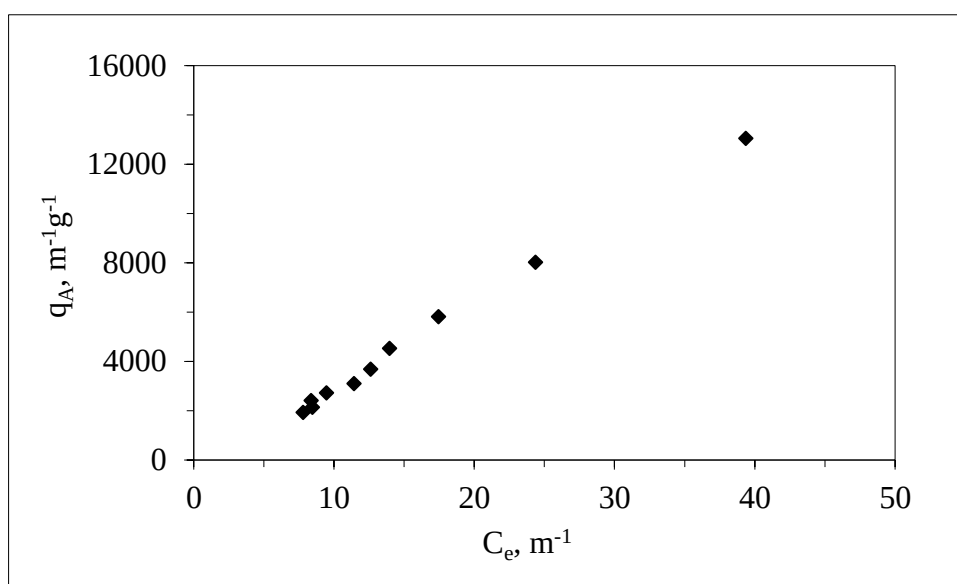


Figure A.17. UV₂₈₀ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of montmorillonite and Ca²⁺.

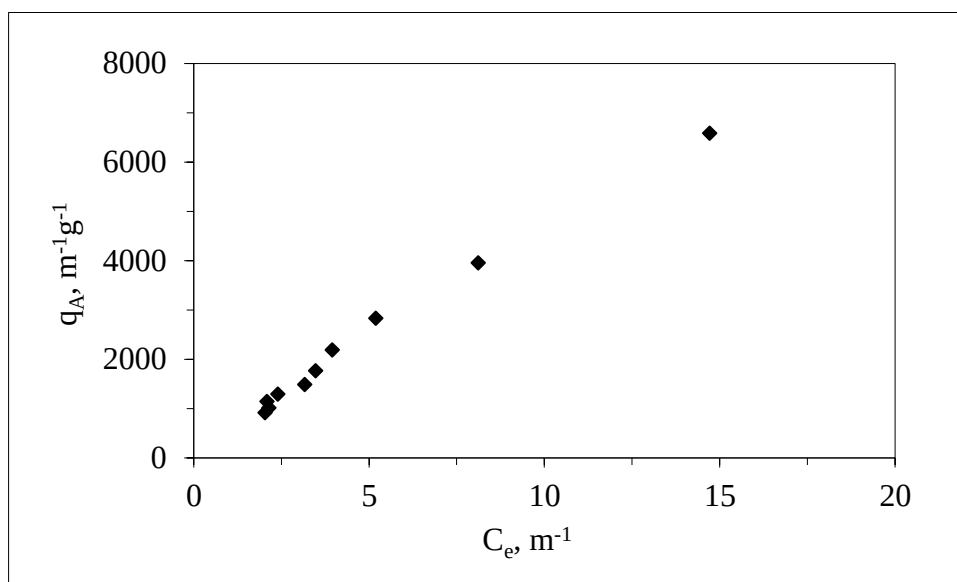


Figure A.18. UV₃₆₅ adsorption isotherm of humic acid adsorption onto TiO₂ in the presence of montmorillonite and Ca²⁺.

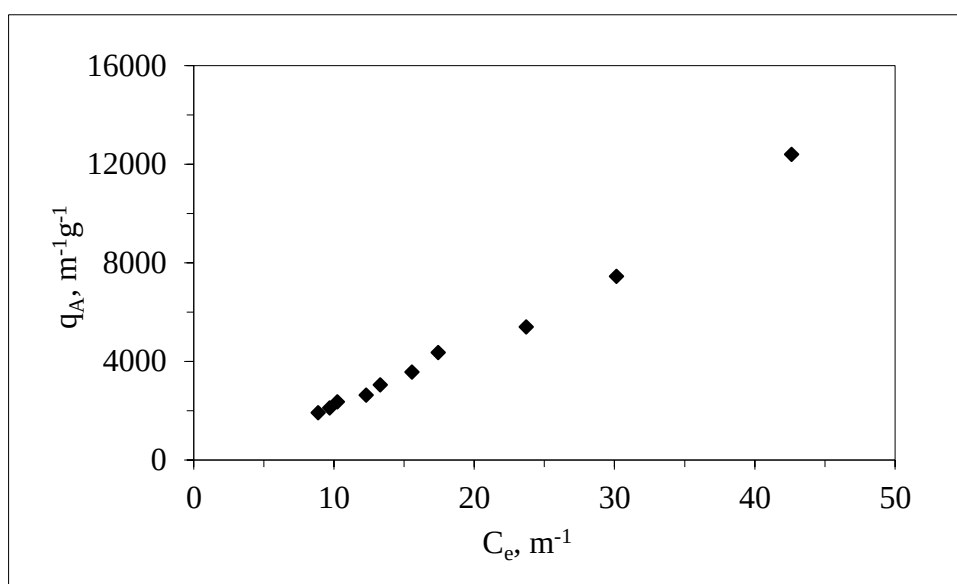


Figure A.19. UV_{280} adsorption isotherm of humic acid adsorption onto TiO_2 in the presence of kaolinite and Ca^{2+} .

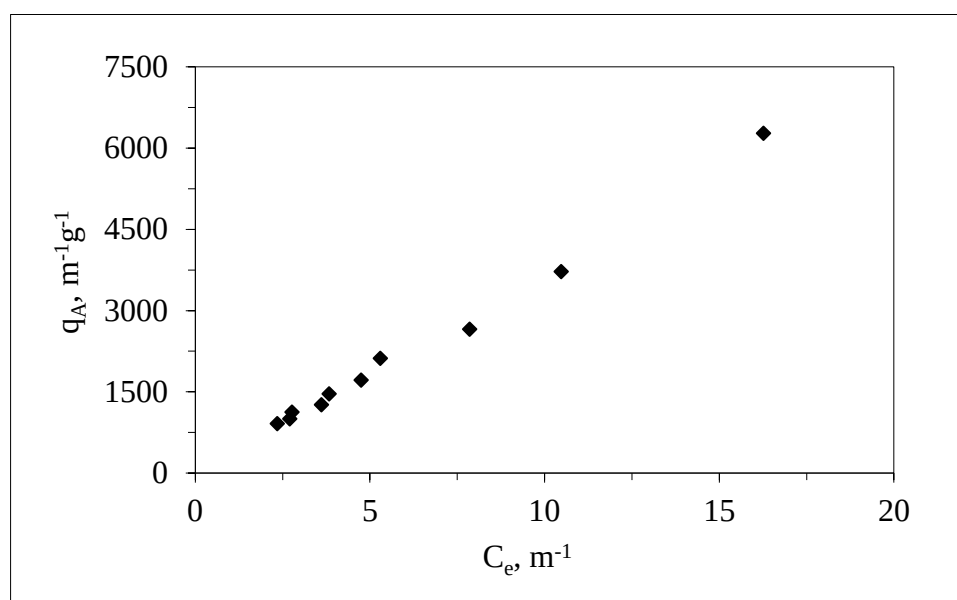


Figure A.20. UV_{365} adsorption isotherm of humic acid adsorption onto TiO_2 in the presence of kaolinite and Ca^{2+} .