LEACHING BEHAVIOUR OF NANO-TITANIUM DIOXIDE IN MUNICIPAL SOLID WASTE

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BS. in Environmental Engineering, Istanbul University, 2011

Submitted to the Institute of Environmental Sciences in partial fulfillment of
the requirements for the degree of
Master of Science
in
Environmental Sciences

Boğaziçi University
2014

ACKNOWLEDGEMENTS

I am thankful to my thesis supervisor Prof. Dr. Turgut T. Onay for endless support and continuous encouragement. I also want to thank him for his understanding and kindly attitude in every aspect.

I am very grateful to Prof. Dr. Nadim K. Copty, Assoc. Prof. Dr. Burak Demirel, Dr. Ceyda S. Uyguner Demirel and Dr. Tanju Karanfil their opinion, guidance, friendly approach throughout this study and beyond. I am also grateful to my thesis committee member, Assoc. Prof. Bülent Mertoğlu, sparing his valuable time for reading and commenting on my thesis.

The financial support for this study provided by Boğazici University Research Fund with project number 13Y00P5 and TÜBİTAK through Project No 112Y322 is greatly acknowledged. Also, I am thankful to İZAYDAŞ İzmit Plant for providing the samples.

I wish to express my special thanks to Selin Erkişi, D. Hazal Akçalı, Filiz Ayılmaz and E. Tuğçe Sakallıoğlu for their friendship, help, and contributions during my laboratory studies.

I warmly thank to my dear friend Çiğdem Ekmen for her friendship. She made me believe in myself when I lost my motivation. I would like to thank F. Koray Sakarya, Nazire Mercan, İlknur Temizel, Ece Özön, Merve Şahan, Gökçin Gül, S. Mehdi Emedian, İbrahim Şimşek, and Deniz Doğan for their endless support, help, and unique friendship.

I am also giving my special thanks to Hilmi Kurt for his tireless encouragement and emotional support. He put me up with my complaints and frustrations with patience.

The most special thanks go to my dear parents Hamdi and Hamdiye Dülger and my brother Erol for their endless love, support, patience and understanding. Without your support, this study would have been much more difficult. Finally, I wish to dedicate this thesis to my beloved parents and husband.

ABSTRACT

Over the past few decades, the use of nanomaterials (NMs) in consumer and industrial products has showed a rapid growth. Titanium dioxide (TiO_2) is among the most commonly reported engineered nanomaterial (ENM) employed in numerous applications ranging from cosmetics, paints, food products to environmental remediation. Due to the widespread synthesis of TiO_2 and its broad use in many commercial products, nano-TiO_2 will eventually end up in landfills after the disposal of these products. The aim of this study is to assess the leaching potential of nano-TiO_2 from real and synthetically prepared solid waste environments under different environmental conditions (*e.g.,* pH, ionic strength, different concentrations of nano-TiO_2). Batch experiments were conducted by using fresh real solid waste samples from a major landfill located in Kocaeli, Turkey and synthetic solid waste which was prepared according to the waste composition of the landfill site. The waste samples were treated by using nano-TiO_2 stock solutions ranging in concentration between 0 and 100 mg/L. Acidic and basic pH conditions were considered as 5-6 and 8-9, respectively. High ionic strength on the leaching of nano-TiO_2 was also adjusted. Leachate samples were regularly saved over a three-day period and analyzed for pH, electrical conductivity, and Ti content. Preliminary results represent that the leaching behavior of the nano-TiO_2 indicates a complex transient. The majority of the nano-TiO_2 in the batch reactors tends to adsorb on the waste media given the all environmental conditions, followed by a gradual release into the leachate.

ÖZET

Geçtiğimiz son on yılda, nanomateryallerin kullanımı hem tüketici hem de sanayi ürünlerinde hızlı bir artış göstermiştir. Mühendislik çalışmaları sonucunda elde edilmiş nanopartüküllerin arasında en yaygın olarak kullanılan $TiO_{2,}$ boyadan, kozmetiğe, gıda ürünlerinden, çevre iyileştirmeye kadar birçok alanda yer almaktadır. TiO_2 nanomateryalinin geniş çaplı sentezi ve birçok ticari ürünlerdeki kullanımından dolayı, kullanım ömrü dolduktan sonra nihai olarak düzenli depolama alanlarına gidecektir. Bu çalışmanın amacı farklı çevre koşullarında (pH, iyon gücü ve farklı TiO_2 konsantrasyonları) TiO_2 nanomateryalinin gerçek ve sentetik olarak hazırlanan katı atık çevrelerinden sızma potansiyelini değerlendirmektir. Yığma deneyleri, Kocaeli de bulunan düzenli depolama sahasından alınmış taze evsel katı atık ve bu katı atığın kompozisyonuna bağlı olarak elde edilmiş sentetik atık ile yürütülmüştür. Atık örnekleri 0 ile 100 mg/L arasında değişen 4 farklı TiO_2 stok çözeltisi ile işlem görmüştür. Deney setlerinde asidik ve bazik pH olarak iki farklı pH ortamı düşünülmüş ve yüksek iyon gücü ayarlaması yapılmıştır. pH, elektriksel iletkenlik ve Ti içeriğini ölçmek için üç gün boyunca belirli aralıklarda reaktörlerden numuneler alınmıştır. Bulunan sonuçlara göre TiO_2 nanomateryalinin sızma davranışı karmaşık bir geçiş sergilemiştir. TiO_2 nanomateryalinin büyük bir miktarı katı atık matrisi üzerinde tutulma eğilimdedir ve daha sonraki zamanlarda bu eğilim yavaşlamaktadır.

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LIST OF SYMBOLS/ ABBREVIATION

Symbol	**Explanation**	**Units**
TiO_2	Titanium Dioxide	mg/L
CI^-	Chloride	mg/L
NO^-_3	Nitrate	mg/L
SO^{2-}_4	Sulfate	mg/L
PO^{3-}_4	Phosphate	mg/L
MSW	Municipal Solid Waste	
NMs	Nanomaterials	
CNTs	Carbon Nanotubes	
WWTPs	Wastewater Treatment Plants	
PCPs	Personal Care Products	
NOM	Natural Organic Matter	
SPM	Suspended Particulate Matter	
SMPS	Scanning Mobility Particle Sizer	
PEC	Predicted Environmental Concentration	
PNEC	Predicted No Effect Concentration	
DOM	Dissolved Organic Matter	
TOC	Total Organic Carbon	mg/L
TS	Total Solid	%
VS	Volatile Solid	%
MC	Moisture Content	%
COD	Chemical Oxygen Demand	mg/L

1. INTRODUCTION

As a result of rapid development in nanotechnology in recent years, the number of commercially available nanotechnology products has increased significantly. It is predicted that by 2014, the commercial goods of nanotechnology will occupy about one sixth of globally available commercial products. About half of the nanomaterials that anticipate in everyday-use-products as cosmetics, health products, electronic equipments, and fabrics end up in landfills for disposal. The knowledge on nanomaterials (NMs) is very limited. On the other hand, exotoxicity of NMs have been researched over two decades. The fate of nanomaterials during waste stabilization in landfills, which play a very crucial role in integrated waste management systems, is a whole new area of research.

The use of engineered nanomaterials (ENMs) is now becoming a significant fraction of the material in consumer products and industrial processes. As their application spreads, 'engineered nanomaterials' impact on the global economy increases rapidly. Hence, the amount of 'nanowaste' ought to enhance, mirroring the utilization of nanomaterials by industries and it is getting more important to understand their impact on environmental issues. Eventually, after been discharged, NMs enter wastewater streams and landfills. Particularly, wastewater effluent and sewage sludge are predicted to be important release pathways for nanomaterials. There have already been significant advances over the last decade to prove that the engineered nanomaterials (ENMs) can and will enter wastewater treatment plants due to their release form consumer products such as sunscreens, daily care products, clothing, and so on.

Numerous ecotoxicological studies have been done to understand the public health effects of widely used nanomaterials. However, it has not been determined how these materials exhibit a leaching behavior during waste processing and disposal processes. In particular, the potential risks arising from these nanomaterials emissions in waste storage areas are still unknown. It is determined that 50% of the produced nanomaterials were sent to landfills with life cycle assessment studies. There is a significant gap about how these materials behave in an integrated waste management system with changing environmental conditions. The transport behavior of nanomaterials from the solid waste to leachate may differ depending on the characteristics of landfill leachate and environmental factors. Therefore, it is very important to investigate the leaching properties of nanomaterials under various environmental conditions in order to understand the potential environmental impacts that may occur. In this study, the main objective of this is to understand the leaching properties of nano-TiO_2 from real and synthetically prepared solid wastes under different environmental conditions such as pH, ionic strength, and concentration of nano-TiO_2.

2. LITERATURE REVIEW

Together with the rapid progress in the field of nanotechnology, nanotechnological products constitute approximately 15% of all manufactured products and commercial value of the market is expected to reach 2.6 trillion U.S. dollars in 2014 (Nanotech-Project, 2007). The use of nanomaterials (NMs) in consumer products has exponentially increased over the last decade. Number of products has risen from 212 to 1317 within 5 years (Nanotech-Project, 2010). Among these NMs, Silver (Ag), Titanium (Ti), and Zinc (Zn) are the major metallic elements commercially used (Yang et al., 2013). These NMs have been used in cosmetics and clothing products (e.g. nano-silver embedded in the fabric, nano-TiO_2 in sunscreens, and nano-ZnO as a UV-absorber in care products). Titanium dioxide (TiO_2) is among the most frequently reported engineered nanoparticle employed in nanotechnology-based consumer products (Kiser et al., 2009).

2.1. Definition of Nanomaterials (NMs)

While the diameter of nanomaterials (NMs) is less than 100 nm, they are defined as three-dimensional particles, nanomaterials (NMs) between the 1 and 100 nm, are described as one-dimensional materials (British Standards 2007; Roco, 2003). NMs have high surface areas and differ from other commercial materials which exhibit superior properties. The forthcoming properties of NMs are the quantum size effect, the size dependence of the electronic structure, the unique character of the surface atoms, and the high surface / volume ratio. In 1985, new carbon structures which were composed 60 atoms were explored by Buckminster Fuller; therefore, new carbon structures were named fullerenes or buckyballs. In 1991 carbon nanotubes that were synthesized and discovered to be 100 times stronger than steel (Keiper, 2003). Nowadays, fullerenes and other nanomaterials are being produced in bulk amounts (Mraz, 2005). Moreover, they are used in bulk materials in order to improve their physical properties. To strengthen and monitor concrete, carbon nanotubes are added. Silica particle packing in concrete can become better by usage of nanosilica. This cause to densifying of the micro and nanostructure causing in improved mechanical properties (Mann, 2006). Properties of are summarized in Table 2.1.

Table 2.1. Properties of nanomaterials (Luther, 2004).

Catalytic	Surface / volume ratio, catalyst effect
Electrical	Electrical conductivity of ceramics and magnetic nano-composites, dielectric strength of metals
Magnetic	Magnetic behavior
Mechanical	Increased rigidity or softness of metals, elasticity on ceramics
Optical	Increasing optical absorption and increasing quantum effect on semiconductor crystals
Chemical and physical changes	Increasing selectivity on drug distribution into global spaces, controlled release
Biological changes	Increasing permeability

Physical properties, bonding pattern, and material strength of a nano-structure vary substantially on its size and shape. Chemical and physical attitudes of nano-structure depend on core atomic structure and type of the foreigner atom those bonds to the system externally. This special behavior of such materials made preparation of materials of specific technology, such as superconductors, anti-wear additives, surfactants, drug carriers, and specialized diagnostic tools, possible. Classification of nanomaterials (NMs) according to their chemical and physical properties is shown in Table 2.2.

Table 2.2. Classification of NMs according to their chemical and physical properties (J.R. Peralta-Videa *et al.*, 2011).

Nanomaterials	**Types**	
Organic	Carbon allotropes (C_{60}, C_{70})	Carbon nanotubes (CNTs) (Multi and single wall)
Inorganic	Metal Oxides (ZnO_2, CeO_2)	Metals (Au, Ag)

2.1.1. Utilization of Nanomaterials

Along with rapid improvement in nanotechnology, NMs have begun to get more involved in consumer products. Thus, worldwide production of NMs has increased clearly (Li *et al.*, 2007; Nanowerk Nanomaterial Database Inventory, 2009). The areas of use for NMs in various industries were summarized in Table 2.3. NMs are frequently used in the sectors of nanoelectronics, tissue engineering, biomedical and nano-composites (Biswas and Wu, 2005; Aitken *et al.*, 2006; Woodrow Wilson International Centre for Scholars, 2008; Nanowerk Nanomaterial Database Inventory, 2009). Among most frequently used NMs in commercial products are silver (Ag, antibacterial), and zinc oxide (ZnO) (Reinhart *et al.*, 2010). A recent research argues that sunscreen consumption contributes to high rates of titanium oxide (TiO_2) emission to environment (Arvidsson *et al.*, 2012). Despite their frequent use in consumary products, effects of Ag, TiO_2, and ZnO NMs on human health and environment are not still fully known.

Table 2.3. Areas of use for commercially available NMs by different industries (Luther, 2004).

Automotive	Chemical Industry	Engineering
Dyes, catalysts, rubbers, sensors, low weight light weight materials	Nanocomposite bound coating systems, adhesives, magnetic liquid fluids, paint systems	Anti-wear equipment and machines, water and wastewater treatment
Electronics	**Building Materials**	**Medicine**
Memory of data (MRAM, GMR-HD), laser diodes, glass strings, optical buttons, substances which inhibit the accumulation of static electricity	Thermal isolations, flame retardant, cladding, mortar materials, functional building materials (stone, roof, ground and surface coatings)	Medical analyzes, the product used in the treatment of cancer, antimicrobial agents, active agents, drugs
Textile	**Energy**	**Cosmetics**
Surface treated textiles and smart products	Fuel cells, solar panels	Sunscreens, lip balms, creams, toothpaste, deodorants
Food and Beverages	**Home Appliances and Cleaning Products**	**Sports equipment**
Product packaging and additives determining the expiration date	Ceramic coating (ironing), deodorizers, surface and floor cleaners	Reinforced tennis rackets and balls, anti-fouling coating materials (marine vessels), anti-vapor goggles

Even though many of the elements in the periodic table have been included into nanoscale materials, approximately a dozen of these elements, titanium, silver, gold, iron, cadmium, silicon, cerium, and various forms of carbon, are used across a range of different product lines. There are at least four different product lines of ENMs that could potentially cause different release scenarios as shown in Figure 2.1. Firstly, in order to improve texture, preservation, and nutrition, dispersed ENMs are incorporated into food products (Abbas *et al*., 2009; Bouwmeester *et al*., 2009; Arora and Padua, 2010; Magnuson *et al*., 2011; Weir *et al*., 2012). Second, ENMs, attached to surfaces, are utilized in fabrics and food packaging in an attempt in order to diminish bacterial growth or provide self-cleaning capabilities. The third product line, NMs embedded in polymers or other composites are added to materials to develop structural or other performance-enhancing behavior of macro scale products. Industrial processing ENMs such as catalysts or polishing agents, the fourth product line, are used during the manufacturing of products. Even though these different products lines have various loading and temporal rates, they have the potential of releasing of ENMs into sewage during product manufacturing, usage, or disposal. To predict ENMs life cycles, these product lines have been implicit in some articles and they mainly demonstrate release of ENMs to wastewater treatment plants (WWTPs) as a major route to disposal ENM and a potential route into the environment for dispersed and some NMs, attached to surfaces, (Roco, 2005; Aitken *et al*., 2006; Nowack and Bucheli, 2007; Mueller and Nowack, 2008; Nowack, 2009; Nowack *et al*., 2009,2012; Som *et al*., 2010, 2011; Klaine *et al.,* 2012), whereas embedded ENMs can exist in landfills (Westerhoff *et al*., 2012).

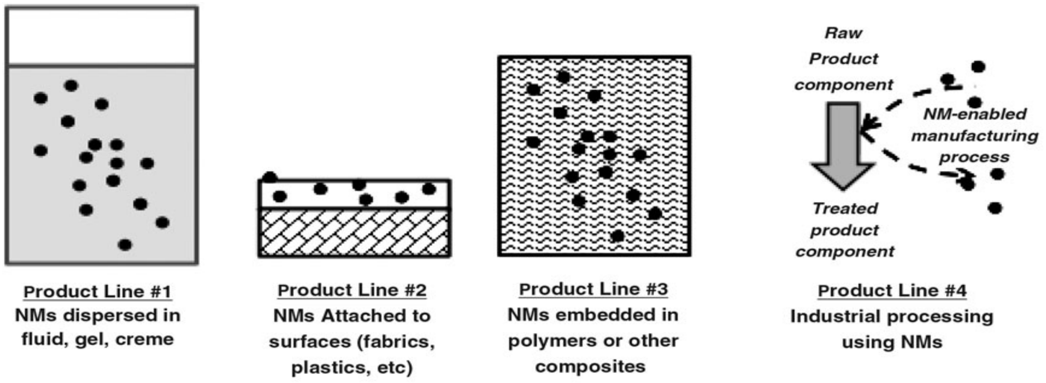

Figure 2.1. Schematic of four generic product lines containing nanomaterials (Westerhoff *et al*., 2012).

Additional to what mentioned above NMs are used in environmental engineering for wastewater treatment (Zhang, 2003; Yantasee *et al.*, 2007; Savage and Diallo, 2005). The exact NMs production of present day is unknown, yet it certainly elevates rapidly in near future (Musee, 2011). Interest in nanotechnology in Turkey has been rising recently in parallel to the developing world. Research centers have been opened for this particular area and studies on nanotechnology have been conducted. There is still no report in the literature about the quantity of NMs produced and/or used in Turkey.

Titanium dioxide nanomaterials, as a bulk material, are mainly used as a pigment due to its brightness, high refractive index, and resistance to discoloration. 4 million metric tons of nano-TiO_2 for all uses is globally produced per year (Robichaud *et al.,* 2009). Almost 70 % of all TiO_2 produced is utilized as a pigment in paints; however, it is also used as a pigment in glazes, enamels, plastics, foods, paper, fibers pharmaceuticals, cosmetics, and toothpastes (ICIS Titanium Dioxide Uses and Market, 2007). Another usage of nano-TiO_2 involves anti microbial applications, catalysts for air and water purification, medical applications, and energy storage. Also, nano-TiO_2 has used to degrade pollutants and as a disinfectant (Serpone and Khairutdinov, 1997; Kuhn *et al.*, 2003; Rincon and Pulgarin, 2003). Currently, the use of nano-TiO_2 as a nanomaterial has been increasing. The global production of TiO_2 nanomaterial, in 2005, was predicted to be 2000 tons worth $70 million (EPA, 2009); about 1300 tons was used for personal care products (PCPs) such as cosmetics and topical sunscreens. The production of nanoscale TiO_2 had risen to 5000 tons, and it is estimated to maintain until at least 2025 (Landsiedel, 2010).

2.2. Behavior of Nano-TiO_2 in the Environment

Because of the fast spreading of nanoproducts in the market, nanotoxicology has started to be a new area that should be investigated and developed in the forthcoming years. Weir et al. (2012) investigated that the amount of titanium in common food products and also discussed the impact of the nanoscale fraction of nano-TiO_2 entering the environment. Candies, sweets, and chewing gums contain highest content of nano-TiO_2. Personal care products such as select sunscreens and toothpastes include 1% to >10% titanium by weight. According to Weir et al. (2012), the fraction of smaller sized nano-

TiO_2 in pigments should be used for environmental ecotoxicology and fate studies because exposure to these materials is probable to be much greater and more representative.

Even though the release of nano-TiO_2 to environment has been demonstrated qualitatively, it is difficult to measure or determine all sources as well as its quantification of how much is released (Semmler- Behnke, 2008). The assessment of human exposure is another difficulty because estimated uptake rates of different types of nanomaterials vary from 0 to 8.5% depending on type, size, and shape of the nanomaterials (Ma-Hock *et al.*, 2009; Neal *et al.*, 2011).

Kaegi et al. (2008) have demonstrated that nano-TiO_2 is leached out of house facades to which nano-TiO_2 including paint has been performed. Nano-TiO_2 was found in a small stream in μg/l level when the particles in wastewater were traced from the house facades into receiving waters. The concentration found is within range of an exposure modeling of engineered nanomaterials for the water compartment (Mueller and Nowack, 2008). The model is based on production and use of nanomaterials in various products, and the knowledge of products' life cycle; and it is for representation of nanoparticle concentrations in air, water, or soil. This study definitely shows that there are some nanomaterials leaching to environment; and give the first insight for the expected concentrations.

To find the effect of pH on nanoparticle aggregation and transport in porous media, Dunphy Guzman et al. (2006) measured nanoparticle transport in two dimensional structures. The effects of surface potential on particle mobility in the subsurface were explored by using titania as a model compound. The results showed that pH, and therefore, surface potential and aggregate size, had control over nanoparticle interactions with each other and surfaces. Distributions of nanoparticle aggregate size were bimodal or trimodal, and aggregate sizes raised as the pH approached the pH of the point of zero charge (pH_{zpc}) in each solution. Over 80% of suspended particles and aggregates were active over the pH range of 1-12, apart from close to the pH_{zpc} of the surfaces, where the particles are greatly aggregated. However, pH was not relevant to transport speed of nanoparticle aggregates.

Another work about nano-TiO_2 was conducted by Romanello and Cortalezzi (2012). A complete characterization of the aggregation dynamics of nano-TiO_2 under environmentally relevant conditions and kinetics and morphology of the aggregates were investigated by them. This study showed that these materials will be subject to transformations after reaching natural waters. Also, the aqueous matrixes will encounter and their fate and transport in environment will be determined. In different electrolyte solution, when nano-TiO_2 is under stable conditions, it creates aggregates of about 200 nm - 300 nm in size. However, when it is unstable, it aggregates at around neutral pHs because of the location of point of zero charge (pzc) of the material. Divalent cations may lead to aggregation at a wider range of pH values because of specific adsorption. Natural organic matter (NOM) has a stabilizing effect on the nanoparticles owing to adsorption of the mostly negatively charged compounds. However, they tend to lose their stabilizing effects under highly acidic conditions; therefore, particles may aggregate. Moreover, at lower cation concentration (0.3 mM), the stabilizing influence of NOM outweighs the divalent ions effect towards aggregation.

A case study of nano-TiO_2 in the Rhine River was done by Praetorius et al. (2012). Their fate modeling framework is greatly flexible and can be adapted for other ENMs and different environmental settings. The model was based on well-established multimedia box models for organic pollutants. The researchers showed that analogies and crucial differences in environmental fate modeling between ENPs and low-molecular-weight organic pollutants in a two-compartment freshwater-sediment system. Also, they found that an important downstream transport of ENPs is feasible. The heteroaggregation between TiO_2 NMs and suspended particulate matter (SPM) is determined in more detail. Their modeling outcomes indicated the significance of both the SPM properties (concentration, size, density) as well as the affinity of nano-TiO_2 and SPM, represented by the attachment effectiveness, αhet‑agg, on the transport potential of ENPs in a surface water system.

Hsu and Chein (2007), studied emissions of nano-TiO_2 from coating on polymer, wood, and tile by using scanning mobility particle sizer (SMPS). Among these wood, polymer, and tile substrates, tile coated with TiO_2 nano-powder indicated the highest particle emission. They also investigated the influence of sunlight, wind and human contact on the release. The release of particles below 200 nm from coated TiO_2 nanomaterials was increased trough the UV light treatment. In addition, the experiments indicated that a rubber knife scraping motion can decrease sharply the binding force between the TiO_2 nano-powder and the substrate.

Kaegi et al. (2008) showed that TiO_2 would be released in nanoparticulate form into facade runoff from new and aged facade paints by natural weather conditions. Electron microscopy of the released particles revealed that some TiO_2 nanomaterials were still embedded in the organic binder; however, that also many single particles were discharged from aged facades. The particles found in the runoff of the new facade indicated a size range from a few tens to a few hundreds of nanometers. This study was the first evidence to reveal that single NMs were actually released to the environment.

Aggregation of TiO_2 NMs in solution would significantly impact their activity and toxicity (Li and Kaner, 2007). According to Teeguarden et al. (2007) and Zhang et al. (2011), these aggregated nanomaterials with an increased size would decrease their ion delivery rate, the potential to be released to cell surface, and thereby lower their antimicrobial activities.

Fang et al (2012) studied to explore the mechanisms governing the transport and retention kinetics of TiO_2 nanomaterial aggregates in flow- through columns of packed sand, especially under unsaturated conditions. Nano-TiO_2 aggregates were greatly mobile in both saturated and unsaturated porous media under most of the experimental conditions. Both ionic strength and pH were attained to have significant effects on the transport and retention of nano-TiO_2 aggregates.

2.2.1. Behavior of Nano-TiO_2 in Landfills

The fate of NMs will probably be a function of the products matrix and also the surface characteristics of NMs. The use of landfills is supposed to carry on well into the future. Due to the growing demand for NMs, it is mostly that products including NMs will take place of landfills at the end of their useful life (Reinhard *et al.,* 2010). Further, the fate of NMs was based on the condition of landfill and these conditions changes greatly over time by MSW stabilization. Early in the landfill life, if pH tends to be low and small, organic molecules reign and if pH increases, organic matter is mostly dominant on humic substances. Additionally, the age of landfill was important to evaluate of the behavior of NMs. For instance, NMs that attend to aggregate and precipitate in young landfills and may be came the presence of humic and fulvic acids in older landfills (Handy *et al*., 2008).

NMs exactly do not behave in the similar way as a normal waste. Therefore, in order to predict the fate of NMs disposed in landfills, standard experimental tests would not be suitable (Breggin and Pendergrass, 2007).

There has been a few works evaluating the fate of nanomaterials in solid waste environments. Therefore, Khan et al. (2013) studied that evaluating the influence of concentration and organic matter type in landfill. They investigated landfill- relevant condition on single-walled carbon nanotubes (SWNT) transport over a packed-bed of mixed municipal solid waste collectors. They used both young and old leachate to evaluate the influence of individual waste materials on SWNT deposition. They found that if NMs were mobile in landfills, then the potential for release to the surrounding environment advanced. Additionally, they noticed that the presence of preferential flow (e.g., cracks, fissures) in landfills was probable and would be significantly affect nanomaterial mobility, potentially increasing mobility.

Most scientific studies have been conducted to assess the presence of NMs in waste. However, they are mainly applied to a single category of substance or one particular waste treatment. Therefore, Marcoux et al. (2013) focused on a comprehensive review, which was associated with the effect of the presence of NMs on waste treatment schemes such as recycling, composting, digestion, incineration, landfilling, and wastewater treatment. They evaluated that all waste treatment schemes were affected by NMs and they were almost never originally designed to take account of NMs.

In recent years, with the increase in the amount of solid waste in the world as well as in Turkey, nano-TiO_2 containing wastes have begun to be disposed in landfill sites. However, little work has been conducted about the fate of nano-TiO_2 during waste processing and disposal. Also, little is known about assessing the fate of the nano-TiO_2

once it is released into the leachate. Understanding the leaching behavior of land filled nano-TiO_2 is critical in evaluating potential particle releases from landfills. For instance, how the materials will interact with solid waste materials is unknown, whether they will aggregate in leachate, or if the NMs will spread out through bottom liner.

Mueller and Nowack (2008) modeled utilization process of engineered NMs in nature. The most commonly used NMs, nano-TiO_2 was chosen as the subjects of this study. Their model was based on estimated worldwide production volume, allocation of the production, particle delivery from products, and flow coefficients within the environmental components. The results demonstrated that a significant portion of nano-TiO_2 would end up in landfills. They found predicted environmental concentration (PEC) and predicted no effect concentration (PNEC) for nano-TiO_2. These results were found as 0.7-16 and < 1 µm/L, respectively. The modeling advocated that may reveal a risk to aquatic life with a PEC/PNEC between > 0.73 and 16. In contrast, the PEC/PNEC air was poorer than one thousandth. Disposal of nano-TiO_2 to landfills will undoubtedly increase within the next years along with increasing consumption. Hence, there is a lack of information in the literature about fate of nano-Ti after disposal to landfills (Reinhart *et al.*, 2010, Musee, 2011).

De Castro et al. (2012) investigated the mechanism of nano-TiO_2 absorption/desorption by soil landfills. The authors modeled a long term simulation of the nanoparticles motion and contamination plume in the Volta Redonda Municipal Waste landfill for a period of 5 years. Their model evaluated the concentration of nano-TiO_2 in suspension on the leachate of municipal solid waste landfills and the rate of particles dynamically attached into the soil particles. They found that nano-Ti adsorbed into the soil within the protection barriers and given the considered simulation time, the soil was not saturated by nano-Ti. Additionally, the calculated results showed that the barriers had high capacity to absorb the nano-TiO_2.

Bolyard et al. (2013) studied behavior of engineered nanomaterials in landfill leachate. They investigated the effects of Ag, ZnO and TiO_2 nanomaterials as commonly found commercial products on biological landfills as well as the chemical speciation of Ag, Zn, and Ti in landfill leachate. Six different landfill leachates were used as different stages of waste degradation in this study. Both hydrophilic and hydrophobic NMs increased the stability by the presence of dissolved organic matter (DOM) and age differences in leachates did not impact the behavior of NMs. Also, according to the first order rate constants between test reactors and controls and differences in BOD_5, they reported that the addition of NMs to leachate did not change the ability of microorganisms to breakdown organic matter. Therefore, either aerobic or anaerobic processes were not hindered by Ag, ZnO, and TiO_2 NMs, added to leachate. According to chemical speciation modeling, dissolved Zn in leachate was mainly related to DOM, Ti with hydroxide, and Ag with hydrogen sulfide and ammonia.

Due to the lack of information of the behavior of NMs at the interface from the technosphere to the ecosphere, Mueller et al. (2012) studied model the flows of ENM during waste incineration and landfilling in greater depth by including a more detailed description of the different processes and considering ENM-specific transformation reactions. In their nano-TiO_2 model, no ENM loss was estimated during incineration, acid washing or other processes. Therefore, almost all materials enter the landfills. Accordingly, the most crucial flow in the nano-TiO_2-model was the bottom ash flow from the waste incinerator to the bioactive landfill. However, which form of TiO_2 was known in the bottom ash. Other relevant flows defined the input of ENM into the waste incineration plant from products and from the WWTP.

Recently, Boldrin et al. (2014) investigated nanowaste as collectable waste materials which are or include ENMs and also showed a five-step framework for the systematic assessment of ENM exposure during nanowaste management. Their proposed framework was utilized to three selected nanoproducts: nanosilver polyester textile, nano-TiO_2 sunscreen lotion and carbon nanotube tennis racquets. They found that these three products was estimated between 0,5 and 143 mg/year to evaluate the potential global environmental exposure of ENMs. Additionally, the framework showed that noticeable amounts of these nanoproducts entered the waste management system in 2011; for instance, polyester textiles, sunscreen lotion and tennis racquets was globally measured as 23.7-103, 715-1.430, and 313-825 mg, respectively. Especially, nano-TiO_2 was released annually as 14-143 mg into the environment on a global scale.

2.2.2. Behavior of Nano-TiO_2 in Wastewater Treatment

Titanium dioxide nanomaterials are mainly found in many food, personal care, and other consumer products which after use may enter the sewage system and, afterwards, enter the environment as treated effluent discharged to surface waters as well as biosolids applied to agricultural land, incinerated wastes and landfill solids. About a decade ago, the titanium content in some UK food products was determined (Lomer *et al.,* 2000). Many of the same food classes such as candies, salad dressing, creamers, icing, and marshmallows were demonstrated to contain higher levels of nano-TiO_2 in the study of Weir et al. (2012).

Titanium nanomaterial removal and release from wastewater treatments plants (WWTPs) were studied by Kiser et al. (2009). They tried to find out concentration of nano-Ti in a full-scale municipal WWTP and characterize the morphology and composition of nano-Ti based solids in consumer products plus wastewater effluents and biosolids. Also, they investigated to quantify nano-Ti concentration in lab-scale treatment reactors and sorption capacity of wastewater biomass for nano-TiO_2. According to the study, nano-TiO_2 had an affinity for solids, and the majority of nano-TiO_2 in water would be removed by wastewater biomass concentrations of around 2000-3000 mg/L TSS. Even though the majority of nano-Ti sorbed to biomass, 10- 100 μg/l Ti remained in effluents; therefore, the study described environmentally relevant concentrations for studying the toxicity of nano-TiO_2 to organisms. They suggested that nano-TiO_2 were a prime candidate to serve as a sentinel for other nanomaterials by representing the possible fate of nanomaterials in a WWTP. Nano-TiO_2 was possibly distributed in the environment such as rivers, landfills, and agricultural lands; therefore, by monitoring the presence of nano-TiO_2 in the environment, where other ENMs would be located and accumulated in the future. In similar experiments using nano-TiO_2, Wang et al. (2011) indicated that biological WWTPs operated using activated sludge have the potential to disposal of nano-TiO_2 from wastewater. Both small, negatively charged NMs such as *fn*-Ag and larger aggregate of *n*-TiO_2 were taken out by interaction with biomass in systems operated with TSS alike to that of full- scale WWTPs. Electrostatic attraction and size dependent is based on the mechanisms of these interactions between nano-TiO_2 and bacteria (Kalive *et al.*, 2011; Zhang *et al.*, 2011).

2.2.3. Toxicity of Nano-TiO_2

Even if some nanomaterials have been demonstrated to be toxic (Mraz, 2005; Oberdörster *et al.,* 2005), little is known of the mechanisms. The scientific literature on nanotoxicology papers allude to the uptake and accumulation of nanomaterials in human body (Liu, 2006; Marshall *et al*., 2007; Porter *et al*., 2007; Verma *et al*., 2008). For instance, Lin and Xing (2007) and Doshi et al. (2008) recently indicated that exogenous nanomaterials, including zinc and aluminum, apply toxic impacts on germination and growth of roots in the seedlings of six agriculturally appropriate plant species. Ryegrass biomass was considerably diminished, root tip shrank, and root epidermal and cortical cells were greatly collapsed as an impact of adherence of ZnO nanomaterials onto surface of root. Baun et al. (2008) showed the toxicity of $C_{60,}$ carbon nanotubes and titanium dioxide to an aquatic invertebrate, *Daphnia magna*.

The assessment of biocompatibility of nanomaterials is one crucial issue considered in nanotoxicology. Kirchner et al. (2005) discriminate three principal causes of nanoparticle toxicity following contact with live cells:

I. Because of their shape: *e.g.* carbon nanotubes may simply pierce cell membrane.
II. Because of chemical toxicity of materials: Partial release of ions from nanomaterials is very probable due to high area- to- volume ratio of nanomaterials.
III. Because of their small size: nanomaterials can attach to cellular membranes and enter into the cells.

Due to their shape, surface modification of nanomaterials may have an effect on the uptake and nanomaterials toxicity (Kostarelos *et al*., 2007; Verma *et al*., 2008). Aggregation and agglomeration of nanomaterials may be affected by surface modification, which will also impact their toxicity and behavior in the environment (Buzea *et al*., 2007; Kostarelos *et al*., 2007).

Recent reports argue that NMs are not as harmless for humans and other organisms as known before (Colvin, 2003; Hoet *et al.*, 2004; Oberdörster *et al.*, 2005; Moore, 2006; Helland *et al.*, 2007; Kahru and Dubourguier, 2010). As a result of ecotoxicology studies conducted with NMs, it is reported that these materials may become hazardous for human health and pose variable levels of environmental risk (Dick *et al.*, 2003; Donaldson and Golyasnya, 2004; Lam *et al.*, 2004; Maynard and Kuempel, 2005; Oberdörster *et al.*, 2005; Lam *et al.*, 2006; Nel *et al.*, 2006; Lovern and Klapper, 2006; Oberdörster *et al.*, 2006; Roberts *et al.*, 2007; Blaise *et al.*, 2008; Handy *et al.*, 2008; Bystrzejewska-Piotrowska *et al.*, 2009). The main purpose of these published ecotoxicity studies was to investigate the potential risk of NMs. Particularly, Bystrzejewska-Piotrowska et al.(2009) stated that risks on environment resulted from nanomaterials need to be evaluated and accordingly precautions pertaining to these risks should be taken.

Earlier, primary particle size was mainly admitted as a large factor in toxicity because it was thought that smaller particles tended to be more toxic. However, recent studies have indicated that particle size is a minor factor influencing the toxicity of nanomaterials (Warheit *et al*., 2008). Nowadays, it is not easy to assess the risk of certain nanomaterial in environment because there is no good enough reliable information about the physicochemical characteristics of the nanomaterials tasted (Menard *et al*., 2011; Krug and Wich, 2011).

Toxicity studies primarily inform risk from nanoparticular TiO_2 because of inhalation; however, titania has been linked to Crohn's disease from gastrointestinal intake which has been described as a possibly carcinogen (Hussain *et al*., 2011). Once, even though nano-TiO_2 has been indicated to inhibit growth of algae and bioaccumulate in *Daphnia magna,* how nano-TiO_2 influences organisms is less known in the environment (Warheit *et al*., 2008). However, some studies have shown that nano-TiO_2 tends to be less hazardous to organisms than other nanomaterials such as cerium oxide, zinc oxide, and multiwall carbon nanotubes (Suh *et al*., 2009, Landsiedel *et al*., 2010).

3. STATEMENT OF THE PROBLEM

There are many studies in the literature about the fate of NMs in wastewater treatment plants and sewage sludge. However, due to increase in NMs production in the manufacturing sector, there is a need to investigate the fate and leaching behavior of NMs from municipal solid waste in final disposal sites such as landfill. Therefore, in this study, the aim is to understand and compare the leaching properties of various amounts of nano-TiO_2 from real and synthetically prepared solid wastes under different environmental conditions such as pH and ionic strength.

4. MATERIALS AND METHODS

Laboratory scale batch reactor system was set up to simulate and understand the leaching behavior of nano-TiO_2 from real solid waste sample taken from a conventional landfill and synthetically prepared solid waste with similar composition. Leaching potential of nano-TiO_2 from real and synthetically prepared solid was determined via a series of laboratory scale leaching experiments.

4.1. Preparation and Characterization of the Solid Waste

4.1.1. Real Solid Waste

In order to understand the leaching behavior of nano-TiO_2 in landfill, fresh municipal solid wastes were taken from a real landfill site in İZAYDAŞ in Izmit. The average composition of the MSW from the site is given in Figure 4.1.

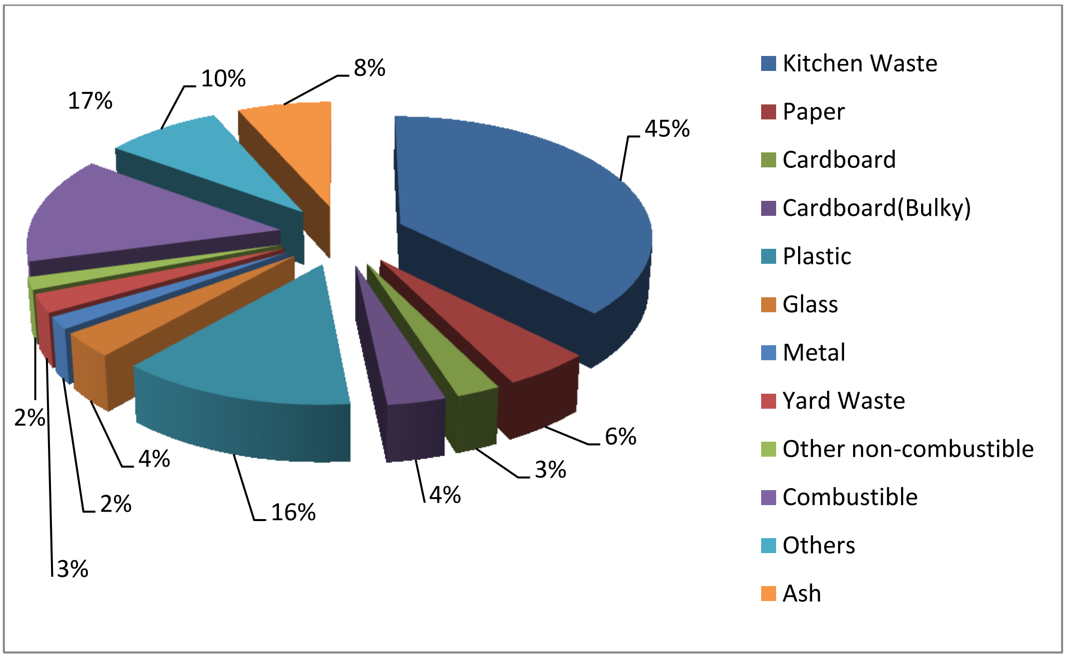

Figure 4.1. The average waste composition of the real solid waste (İZAYDAŞ, Personal Communication).

İZAYDAŞ is the first waste disposal plant in Turkey, which is located 15 km northeast of the center of Izmit established in 1997 on an area of 363,007 m² with a total capacity of 3,163,000 m^3. The main units of the facility are interim storage area, incineration, steam and power generation system, waste gas treatment and emission measurement system, wastewater treatment system, and ash and clinker collection systems. The landfill has the capacity of 4,250,000 tons of domestic and household waste, 969,919 tons of hazardous waste (İZAYDAŞ, Technical Overview, 2013).

The MSW samples used in this study from İZAYDAŞ are taken from a newly-arrived truck. Prior to laboratory simulations, municipal solid waste was loaded in a shredder machine in order to attain the most homogenized form of waste sample and to represent the real waste compositions.

Before the leachate analysis of the shredded real solid waste, total solid (TS), volatile solid (VS), and moisture content (MC) were measured. 30 g fresh solid waste was dried in oven at 105˚ C in three days. Dried solid waste was later digested with proper digestion method. Moreover, metal content, pH, conductivity, and COD of the real solid waste were characterized.

4.1.2. Synthetic Solid Waste

The synthetic solid waste was prepared according to the solid waste composition as given in Figure 4.1. Table 4.1 summarizes the waste composition of synthetically prepared SW. Each component was shredded with scissors (in Figure 4.2.) and homogenously mixed. Homogenized synthetically prepared solid waste was characterized for MC, TS, VS, metal content (Ti, Si, Ag, Zn, Fe, Cu, Mn, Hg, Pb, Co, Al, Mo, Na, K, Ca, and Mg), pH, conductivity and COD of the eluate.

Table 4.1. Synthetic solid waste properties.

SYNTHETIC SOLID WASTE	**%**
Organic Waste	45
Paper	15
Plastic	17
Glass	6
Metal	3
Yard waste	5
Ash- Sand	4
Textile	5
Total	**100**

Figure 4.2. Synthetically prepared solid waste.

4.2. Preparation of (TiO_2) Stock Solution

To add nano-TiO_2 stock solution in each experimental set, a new, fresh stock solution was prepared for each round of experiments. 100 mg/L stock solution was prepared for each set just before the experiments. In this study, the preparation of nano-TiO_2 stock solution was performed from the method in the study of Weir et al (2012). Deionized (DI) water was used and the stock solution was prepared by adding nano-TiO_2 to the DI water followed by 30 minutes of sonication. This step was repeated several times; till no stain of chemical remains on the surfaces of the beaker. After completing the ultrasonication, the stock solution was utilized. The sample was taken immediately before solution settles.

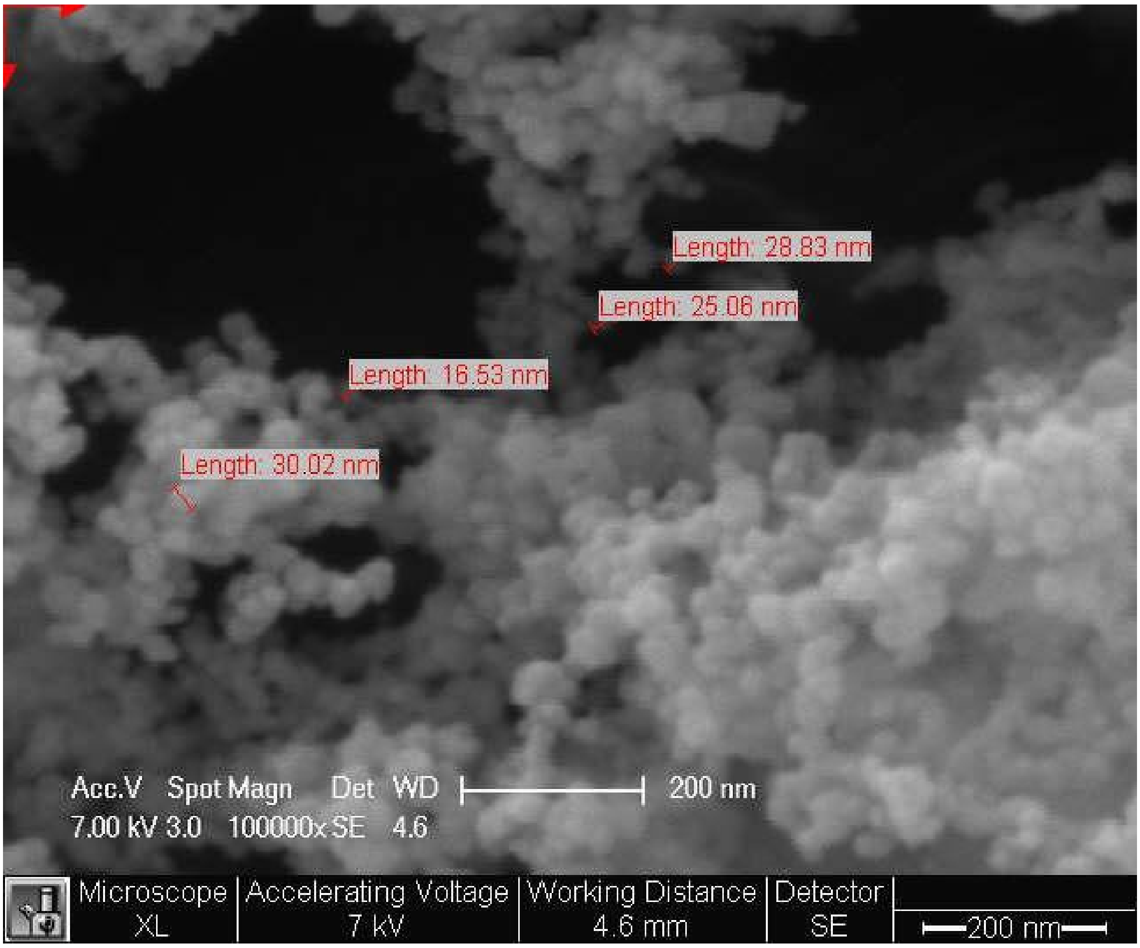

Figure 4.3. Average particle size of nano-TiO_2 by SEM analysis.

Table 4.2. Nano-TiO_2 properties.

NP	TiO_2 (non-coated)
Name	Titanium (IV) oxide
Brand	Sigma Aldrich
Form	Nanopowder
Average Particle Size	21 nm

In this study, nano-TiO_2 was commercially purchased from Sigma Aldrich and its properties as indicated from the manufacturer are listed in Table 4.2. Additionally, purchased nano-TiO_2 was water soluble according to its MSDS and its particle size was obtained by using Scanning Electron Microscopy (SEM) (Figure 4.3).

4.3. Digestion Method

As the first step of project, in order to achieve the highest recovery rate with microwave assisted digestion, the most suitable digestion method was selected from the literature. Nitric acid and hydrofluoric acid (HNO_3/HF) combination is often used to reduce of organic matter during metal analysis (Stephanie *et al.*, 2013); however, HF was not used during these experiments, because it is a health and safety hazard under the current laboratory conditions (Dunphy *et al.*, 2006; Sun *et al.*, 2007). In the literature, there are various digestion methods and they are carried out with different combination such as nitric acid (HNO_3), nitric acid and hydrochloric acid (HNO_3 + HCl), nitric acid, hydrochloric acid and hydrofluoric acid (HNO_3 + HCl + HF), and nitric acid and perchloric acid (HNO_3 + $HClO_4$) (Szymczycha- Madcja and Mulka, 2009; Larrea et al., 1997). Instead, HNO_3/H_2SO_4 or HNO_3/HCI (1:1) combination were preferred which were another successful combination for nano-TiO_2 digestion as a result of the literature search. For instance, Bolyard et al., (2013) used the combination of HNO_3 and HCI (1:1) for coated NMs in their study and the recovery rate was about 71 %.

Microwave assisted digestion according to Standard Methods (1998) was used to digest samples by using MARS 6 Microwave Accelerated Reaction System Instrument (CEM), USA. 5 mL nano- TiO_2 stock solution sample, 8 mL of nitric acid and 2 mL of hydrochloric acid combination was used for digestion since it gives the highest recovery rate in the preliminary trial experiments conducted before the initial start up as given in Table 4.3. After microwave assisted digestion step, samples were diluted to 50 mL and filtered with 0, 45 µm Syringe Filter. The operational conditions for microwave digestion are summarized in Table 4.4.

Table 4.3. Recovery rates obtained from the digestion method.

5 mL nano-TiO_2 stock solution sample + 8 mL HNO_3 + 2 mL HCI (1:1)		
Nano-TiO_2 conc. in mg/L	Average recovery rate	Standard deviation
1	87	0,29
10	86	0,36
100	84	0,16

Table 4.4. The operational conditions for microwave digestion.

Selected Program			
Section	**T in ˚C**	**Time in min.**	**Slope in min.**
step 1	160	2	5
step 2	180	5	5
step 3	200	25	5
step 4	100	1	1
step 5	100	1	1

4.4. Design and Operation of Batch Reactors

The volume of glass batch reactors that were used in leaching experiments was 1 liter. For each experimental set, bottles of 1 liter were used and 250 gram fresh and synthetically prepared solid wastes were loaded into the batch rector. 300 ml of nano-TiO_2 stock solution with required concentration to the solid waste was added in each batch reactor. Batch reactors were agitated by WiseShake SHR-2D (Wise Laboratory Instruments) for three days (72 hours) as shown in Figure 4.4.

Figure 4.4. Batch reactors in shaker.

In order to understand the leaching behavior of nano-TiO_2 in different stages of landfill stabilization, various environmental conditions (pH change and increase in ionic strength) were applied. As shown in Table 4.5, four different concentrations of TiO_2 were used in each set and two pH ranges were considered to simulated acid forming and methanogenic phases. The first pH range was acidic: 5-6, the second was basic: 8-9. Based on the initial pH of the sample, the pH was adjusted by using 1N NaOH or 6N H_2SO_4. In addition, for adjustment of ionic strength, 0,6 gram NaCI was added to 300 mL DI water. For each sets of experiment four (4) reactors were used.

Table 4.5. Experimental sets used in leaching tests.

<table>
<tr><th colspan="8">For Real MSW</th></tr>
<tr><th rowspan="2">Set</th><th colspan="4">Concentration of TiO_2 (mg/L)</th><th rowspan="2">Ionic Strength</th><th rowspan="2">pH</th><th rowspan="2">Duration</th></tr>
<tr><th>Control Reactor</th><th>Reactor 2</th><th>Reactor 3</th><th>Reactor 4</th></tr>
<tr><td>1</td><td>0</td><td>10</td><td>25</td><td>100</td><td>Unadjusted</td><td>Unadjusted[*]</td><td>3 days</td></tr>
<tr><td>2</td><td>0</td><td>10</td><td>25</td><td>100</td><td>Unadjusted</td><td>Basic</td><td>3 days</td></tr>
<tr><td>3</td><td>0</td><td>10</td><td>25</td><td>100</td><td>Increased Ionic Strength</td><td>Unadjusted</td><td>3 days</td></tr>
<tr><td>4</td><td colspan="4">Control Experiment
(250 g solid waste+ 300 mL Distilled water+ no TiO_2 addition)</td><td>Unadjusted</td><td>Unadjusted</td><td>3 days</td></tr>
<tr><th colspan="8">For Synthetically Prepared Solid Waste</th></tr>
<tr><th rowspan="2">Set</th><th colspan="4">Concentration of TiO_2 (mg/L)</th><th rowspan="2">Ionic Strength</th><th rowspan="2">pH</th><th rowspan="2">Duration</th></tr>
<tr><th>Control Reactor</th><th>Reactor 2</th><th>Reactor 3</th><th>Reactor 4</th></tr>
<tr><td>1</td><td>0</td><td>10</td><td>25</td><td>100</td><td>Unadjusted</td><td>Acidic</td><td>3 days</td></tr>
<tr><td>2</td><td>0</td><td>10</td><td>25</td><td>100</td><td>Unadjusted</td><td>Basic</td><td>3 days</td></tr>
<tr><td>3</td><td>0</td><td>10</td><td>25</td><td>100</td><td>Increased Ionic Strength</td><td>Unadjusted</td><td>3 days</td></tr>
<tr><td>4</td><td colspan="4">Control Experiment
(250 g solid waste+ 300 mL Distilled water+ no TiO_2 addition)</td><td>Unadjusted</td><td>Unadjusted</td><td>3 days</td></tr>
</table>

[*] It was already acidic.

4.5. Analytical Methods

Conductivity and pH sensor were embedded in reactors continuously measure the pH and conductivity values and these data was stored. Conductivity was measured in order to investigate the ionic strength of the solid waste in the batch reactors. Moreover, the leachate samples taken from the solid waste in reactors were analysed for heavy and trace Metal (Ti, Zn, Si, Ag) by using ICP-OES instrument (Perkin Elmer, Inductively Coupled Plasma - Optical Emission Spectroscopy). C, N, and H were executed with a Costec Elementary Analysis device. The characteristics of the waste material were determined before the reactors were loaded. In this context, the Carbon (C), Nitrogen (N), Hydrogen (H), Contents, pH, COD, and heavy metals were measured. All experimental analyzes were carried out according to Standard Methods (APHA, AWWA, WPCF, 1998). The equipment and infrastructure of Institute of Environmental Sciences, Environmental Technology Laboratory of Boğaziçi University were used to conduct these experiments. Use of the equipment list for analysis and methodology is given in Table 4.6.

Preliminarily, the experiments lasted about 3 days and sampling frequency was hourly for the first 6 hours, then once every 12 hours until the end of the test. To minimize the change in solid: liquid ratio in the reactor, the sample volume was kept as 5 mL. The sample was taken from the bottom of the reactor by using a pipette for analysis.

In this work, in order to obtain a high recovery rate to digest nano-TiO_2, the most suitable digestion combination was selected from the literature. In this context, 5 ml sample and 8 ml HNO_3 and 2 ml HCl/distilled water (1:1) were mixed and digested by using CEM, MARS 6 Microwave Accelerated Reaction System instrument. After the digestion, leachate samples were completed with 50 mL distilled water and filtered with 0,45 μm filters and their nano-TiO_2 concentrations measured by using Inductively Coupled Plasma (ICP) Instrument Perkin Elmer OES Optima 2100 DV.

Additionally, in this study, the conductivity of a leachate was measured to evaluate and determine the ionic strength condition of the leachate; especially in third set experiment because the conductivity of a leachate reflects the total concentration of ionic solutes. Also, it is a measure of the ability to convey an electric current. This ability depends on the presence of ions, their relative concentration, total concentrations and on the temperature of measurement (EPA, 2014).Therefore, leachate conductivity found as a function of ionic strength. When conductivity decreases, the ionic strength will decrease and in this study, ionic strength was assessed on the basis of the following empirical linear approximation (Snoeyink and Jenkins, 1980).

$$M = \text{Ionic Strength} = 1{,}6\text{x}10^{-5} \text{ x Conductivity in } \mu\text{mho} \qquad (4.1)$$

Table 4.6. The equipment list for analyses and methodology.

Name/Model	**Aim**	**Method**
COD reactor	COD	5220 D Method Closed Reflux, Colorimetric (APHA, AWWA, WPCF, 1998)
Perkin Elmer AAS	Determination of Alkali and Heavy Metal	ASTM 3010
ICP-OES	Determination of Heavy and Trace Metal (Ti, Zn, Si, Ag)	ASTM 3010
Nuve Oven and Oven	Determination of Solid Waste TS, VS and MC	2540 Method (APHA, AWWA, WPCF, 1998)
Sartorius Precision Balance	Determination of Solid Waste TS and MC	2540 Method (APHA, AWWA, WPCF, 1998)
WTW pH meter	pH	Standard Method
WTW Conductivity Meter	Conductivity	Standard Method
IC	Determination of Ions	ASTM 3010

5. RESULTS AND DISCUSSION

All experimental results including real and synthetically prepared solid wastes, initial and final leachate analysis were assessed in this section.

5.1. Initial Solid Waste Analysis

5.1.1. Real Solid Waste

Municipal solid waste samples were collected from İZAYDAŞ in İzmit. TS, VS, MC, and COD analysis were done following Standard Methods for the Examination of Water and Wastewater. MSW samples were also examined for their metal content after microwave assisted digestion process. The results are displayed in Tables 5.1 and 5.2.

Table 5.1. The results of MSW characterization.

Parameter	**Unit**	**İZAYDAŞ MSW**
TS	%	44
VS	%	52
MC	%	56
COD	mg/L	10480

Table 5.2. Heavy metal content of MSW.

Heavy Metals	Results in mg/kg
Ti	124,00
Ag	0,00
Si	656,25
Zn	292,00
Al	4240,00
Cd	2,25
Co	3,25
Cr	212,75
Cu	48,75
Fe	9530,00
Mn	179,50
Mo	0,75
Ni	25,25
Pb	76,50

5.1.2. Synthetic Solid Waste

Synthetically prepared solid waste was analyzed to determine TS, MC, COD and metal content at the beginning of the experiments. The COD value of the synthetically prepared solid waste was measured as 1903 mg/L. TS, MC and metal content of the synthetically prepared solid waste are given in Tables 5.3 and 5.4.

Table 5.3. TS and MC of synthetically prepared solid waste.

Parameter	**Results in**	**Unit**
TS	65	%
MC	35	%
COD	1903	mg/L

Table 5.4. Initial heavy metal content of synthetically prepared solid waste.

Heavy Metals	**Results in mg/kg**
Ti	43,60
Cr	28,57
Mn	55,40
Ni	22,30
Cu	8,03
Pb	2,53
Co	1,37
Mo	2,90
Cd	ND
Fe	15475,00
Zn	680,83
Al	18275,00
Si	437,33
Ag	ND

5.2. Control Experiments

In this study, control experiment was done to observe the changes in pH and conductivity values of the batch reactors during leaching test; without, nano-TiO_2 addition. 250 g solid waste and 300 ml deionized (DI) water were used also in the control batch reactors without any ionic strength and pH adjustment. In addition, leachate samples were taken from the batch reactors once every 24 hours until the end of the experiment to measure concentration of ions and TOC values.

Control experiment was performed for both types of the solid waste (real and synthetically prepared solid wastes). The results are given in the following sections.

5.2.1. Control Experiments for Real Municipal Solid Waste

Interactions between volatile organic acids, alkalinity, and partial pressure of the produced carbon dioxide affect the pH of the solution (Pohland et al., 1995; Onay, 1995). According to the age of landfills, leachate pH values may change. For young landfills, the range of pH is 4.5 - 7.5, for mature landfills, it is measured between 6.6 and 7.5 (Tchobanoglous et al., 1993). Initial pH value was found as 7.34 and an unchanged trend was observed in this experiment as shown in Figure 5.1.

Leachate conductivity value was 2.03 mS/cm at the beginning of the experiment which increased to 3.38 mS/cm rapidly in six hours and then it showed a more stable trend. In a study, it was measured that conductivity for old landfill was detected to range between 6.2 and 34.0 mS/cm while for fresh landfill it was ranged from 23.0 to 35.5 mS/cm (Tatsi and Zouboulis, 2002). In addition, Chu et al. (1994) found similar results which the conductivity for 3.5 year landfill leachate was found to range between 8.5 and 12.0 mS/cm and for 11 year landfill ranged from 2.5 to 8.4 mS/cm. According to the outcomes of the studies in the literature, conductivity of leachate diminishes as landfill ages. Since, fresh municipal solid waste used in this study, lower conductivity values was obtained which are not similar to those given in the literature.

In this study, the measured conductivity values were converted to ionic strength (M) by using equation 4.1 and the values of leachate ionic strength as a function of time are plotted in Figure 5.2. According to the results, leachate ionic strength values showed an increasing trend until the end of the study.

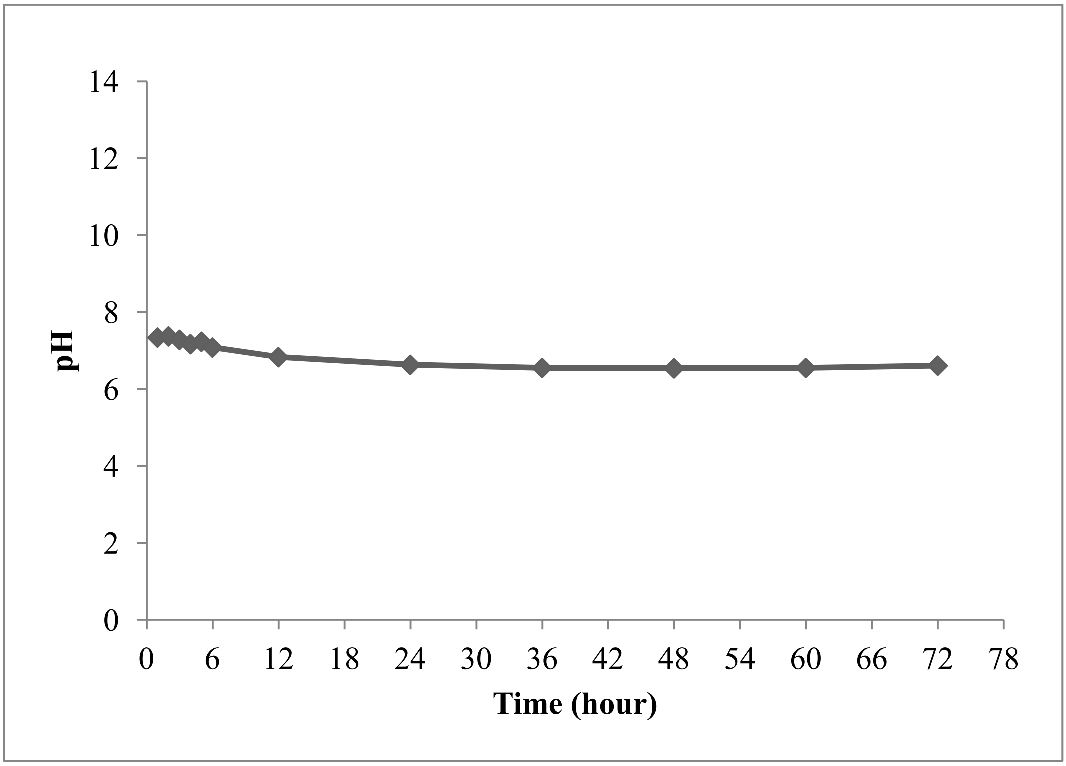

Figure 5.1. Leachate pH values in the control experiment (real solid waste).

TOC starts to appear as a result of the microbial solubilization of the organics. Leachate TOC concentrations as a function of time in the control reactors are presented in Figure 5.3. Initial TOC value was measured as 152 mg/L and then the concentration showed an upward trend due to the release of organics by time during the experiment. Real leachate composition is more complex than simulated experiments and organic matter and salt concentrations are mainly high in landfill leachate. For instance, leachate TOC values range from 30 to 29000 mg/L and also salt concentration such as chloride ranges from 150 to 4500 mg/L (Khan *et al.*, 2013). The results of leachate TOC and chloride were similar with the values to given in the literature.

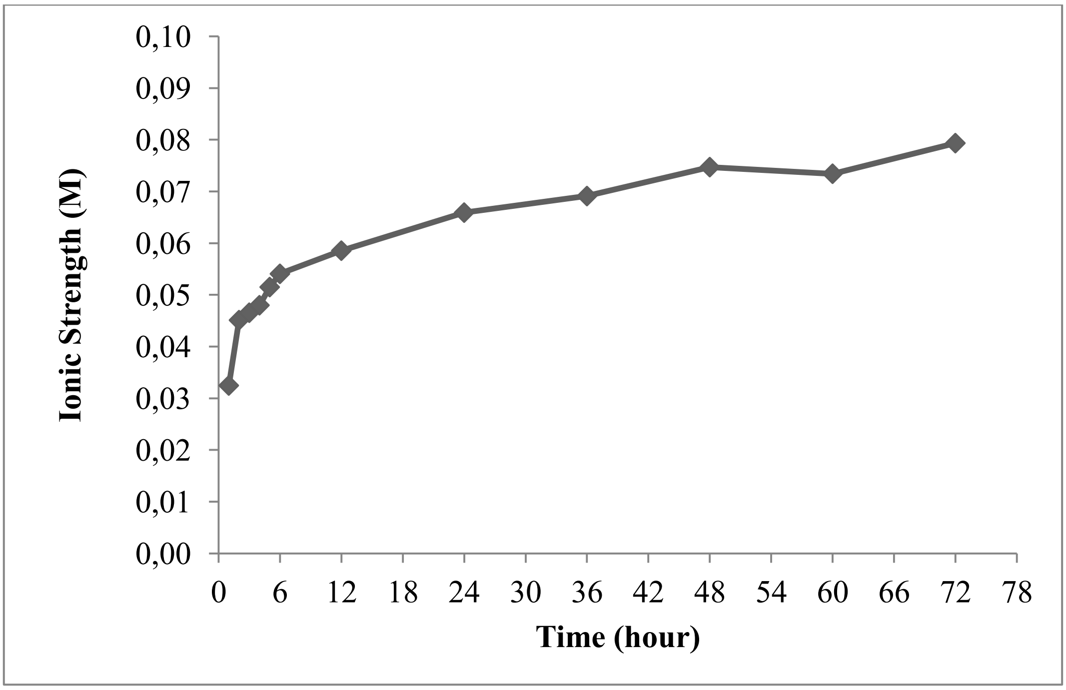

Figure 5.2. Leachate ionic strength values in the control experiment (real solid waste).

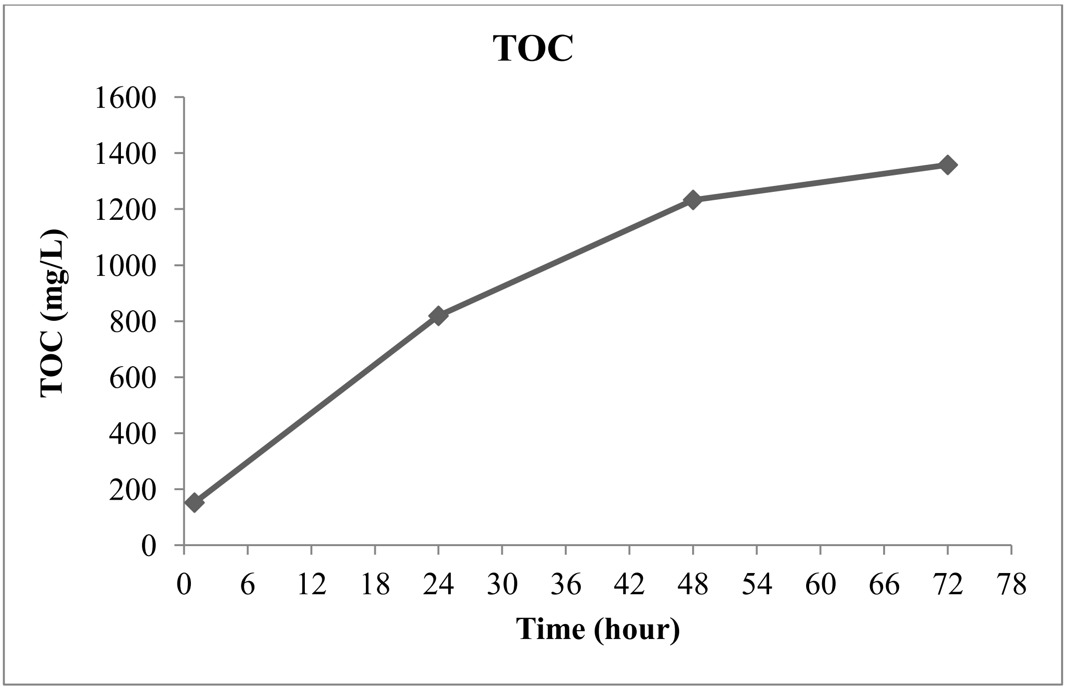

Figure 5.3. Leachate TOC values in the control experiment (real solid waste).

The leachate samples taken from the reactors at particular times were measured to determine the concentration of chloride and the values are shown in Figure 5.4. Leachate chloride concentration was recorded as 210.4 mg/L at the beginning of the experiment, which then increased rapidly to 662.4 mg/L on Day 1. After that day, a slight increasing trend occurred.

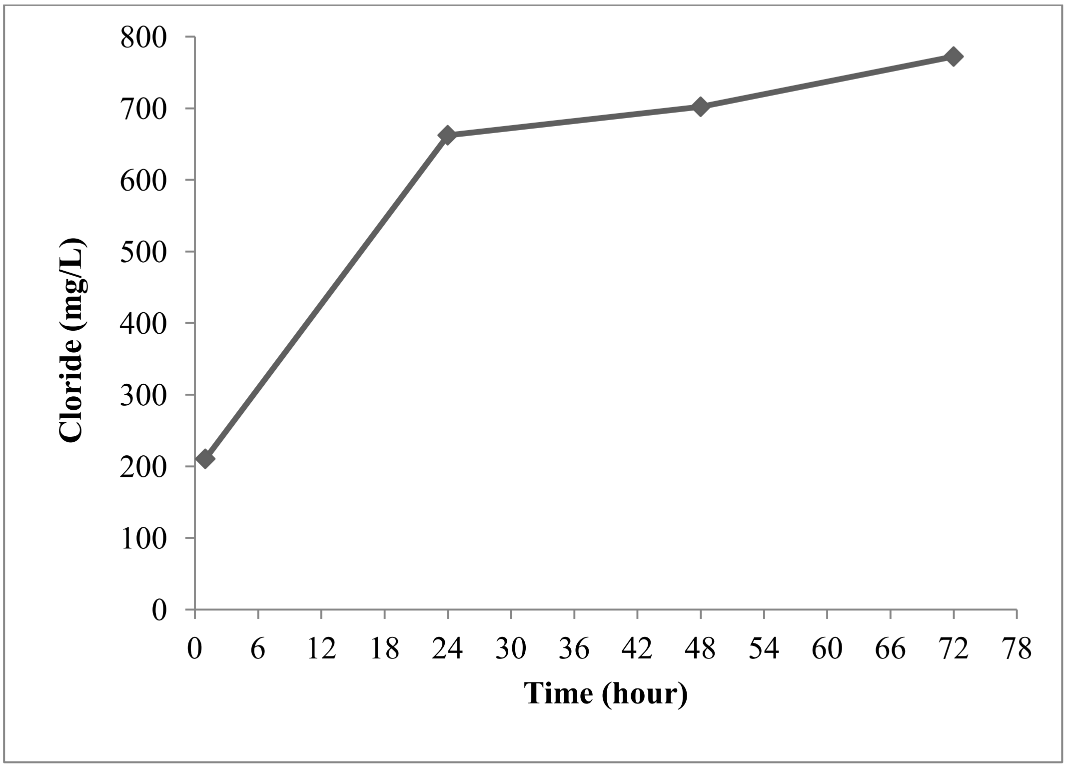

Figure 5.4. Leachate Cl^- concentrations in the control experiment (real solid waste).

As can be seen from the figures, in most of the analyzed parameters a substance release into leachate mechanism was observed.

5.2.2. Control Experiments For Synthetically Prepared Solid Waste

Similar to the control experiments carried out for real MSW, batch control experiments for synthetically prepared waste samples were also run to understand the release of substances during the leaching tests in the absence of nano-TiO_2. The results of leachate pH and ionic strength based on the conductivity values are shown in Figures 5.5

and 5.6. Initial pH value was measured as 6.66 and then it showed a very slight decreasing trend in the reactor.

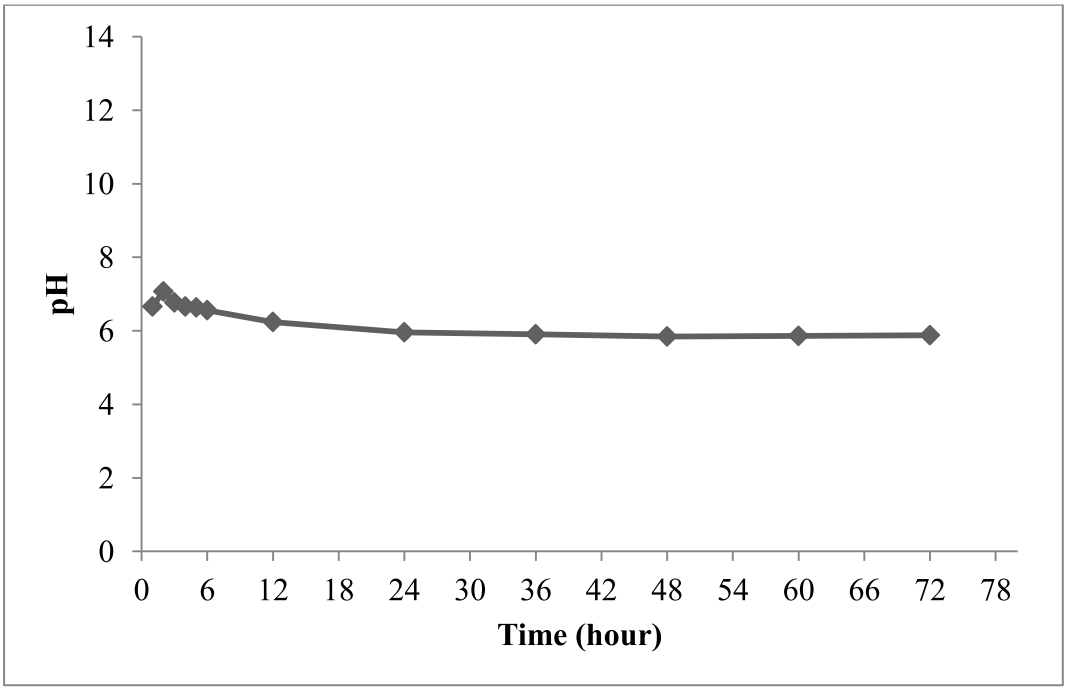

Figure 5.5. Leachate pH values in the control experiment (synthetic solid waste).

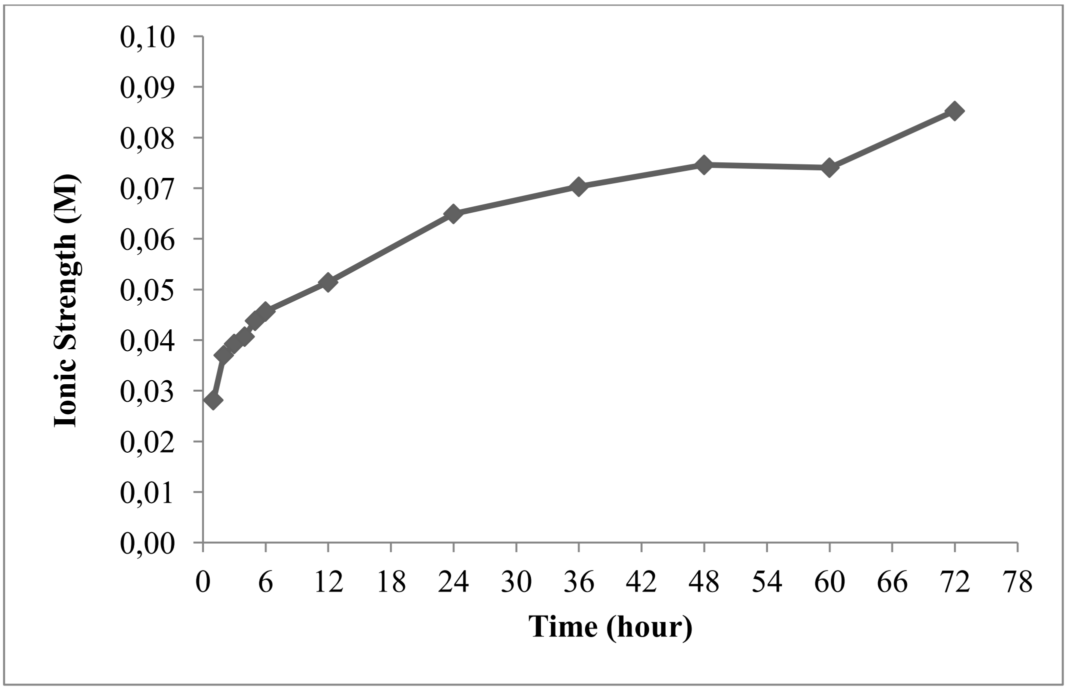

Figure 5.6. Leachate IS values in the control experiment (synthetic solid waste).

Conductivity of leachate samples was measured and then converted to IS. The initial ionic strength value was 0.03 M and after three days, final ionic strength value reached to 0.09 M. In this experiment, increasing ionic strength trend was observed during the three days as shown in Figure 5.6.

Initial TOC concentration was measured as 1009 mg/L on Day 1 as shown. The final TOC concentration of leachate was recorded as 4403 mg/L at the end of the study. As seen in Figure 5.7, TOC concentration of leachate increased precisely by time.

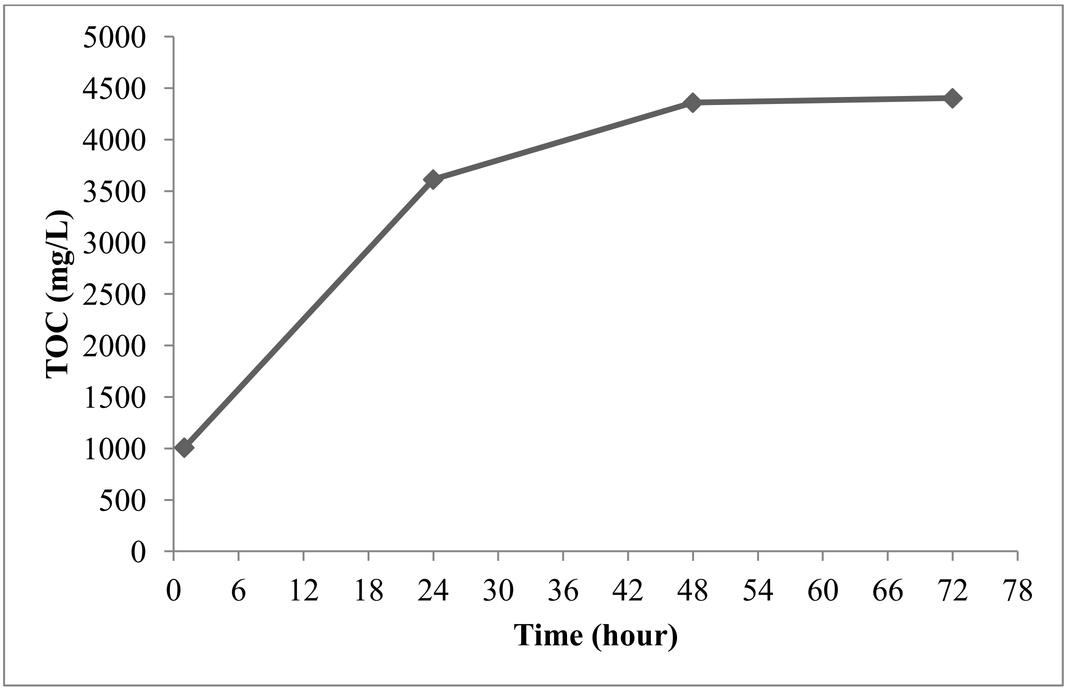

Figure 5.7. Leachate TOC values in the control experiment (synthetic solid waste).

Once every 24 hours, samples were taken to measure chloride of the leachate for three days. Cl^{-} was measured by using Ion Chromatography (IC) instruments. Initial Cl^{-} concentration of the leachate was found as 248 mg/L and the concentration showed an increasing trend which reached to 549 mg/L at the end of the experiment (Table 5.8).

As can be seen from the results retrieved from both real and synthetic waste batch control experiments, most of the parameters showed a similar release pattern from the solid samples. However, leachate TOC concentration values in the synthetically prepared solid waste were higher than the real MSW. Given the relationship between COD and TOC, the real waste COD value was recorded 5 times higher than the synthetic COD value. Therefore, according to the results, the real solid waste TOC values would be much more than the synthetic TOC values.

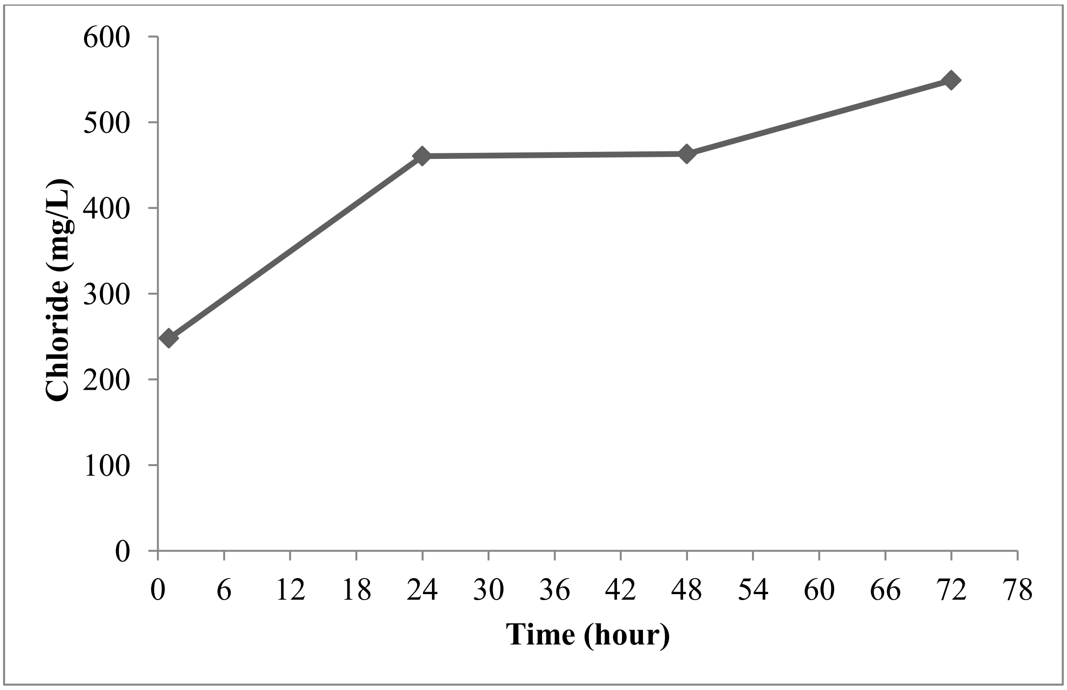

Figure 5.8. Leachate Cl^- concentrations in the control experiment (synthetic solid waste).

5.3. Leachate Analysis

In this research, leaching experiments from both and synthetic solid wastes were conducted to understand the fate of nano-TiO_2 in landfills. Therefore, operating parameters such as pH, conductivity and concentrations of Ti were measured and interpreted in order to understand the interactions and the extent of nano-TiO_2 release in leachate. Except the control experiment, three different experimental batch sets were run (Table 4.5) with three (10, 25, and 100 mg/L) nano-TiO_2 concentrations. The results of these experiments are given and discussed in the following sections.

Additionally, the change in initial pH values in the real solid waste batch reactors for the control, first, and third experimental set can be explained by utilization of new solid waste taken from İZAYDAŞ landfill site.

5.3.1. First Set Experiments

In the first set, the conditions were: unadjusted ionic strength, and acidic adjusted pH for nano-TiO_2 concentrations of 0, 10, 25, and 100 mg/L, respectively. Firstly, initial leachate pH valued from the batch reactors were measured to decide the amount of H_2SO_4 to be added. Therefore, 13 ml of 6N H_2SO_4 was added in each synthetically prepared solid waste batch reactors to reduce pH levels. However, there was no pH adjustment for the real solid waste batch reactors, since the initial pH in the leachate sample from the real MSW batch reactors were already acidic. The change in leachate pH for the first set is given in Figures 5.9 and 5.10.

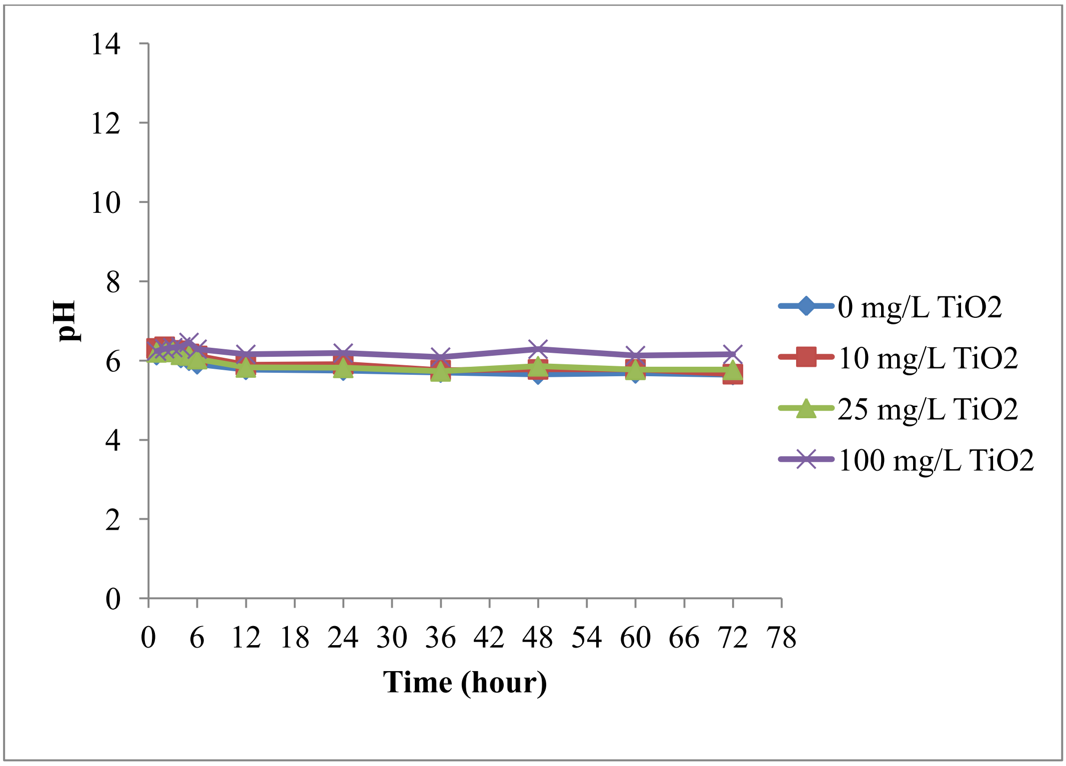

Figure 5.9. Leachate pH values in the first set experiments (real solid waste).

Leachate pH values from the real MSW reactors ranged between 5.64 and 6.35; however, for synthetically prepared solid waste reactors, the original pH value before the sulfuric acid addition was about 7.4- 8.1. After the acid addition, the pH dropped to 2.33 and increased back to 5.97 during the first six hours of the experiments. After that, for both types of the wastes, pH values were almost stable at approximately 6.0 and remained unchanged and unaffected from the applied nano-TiO_2 concentrations in the batch reactors.

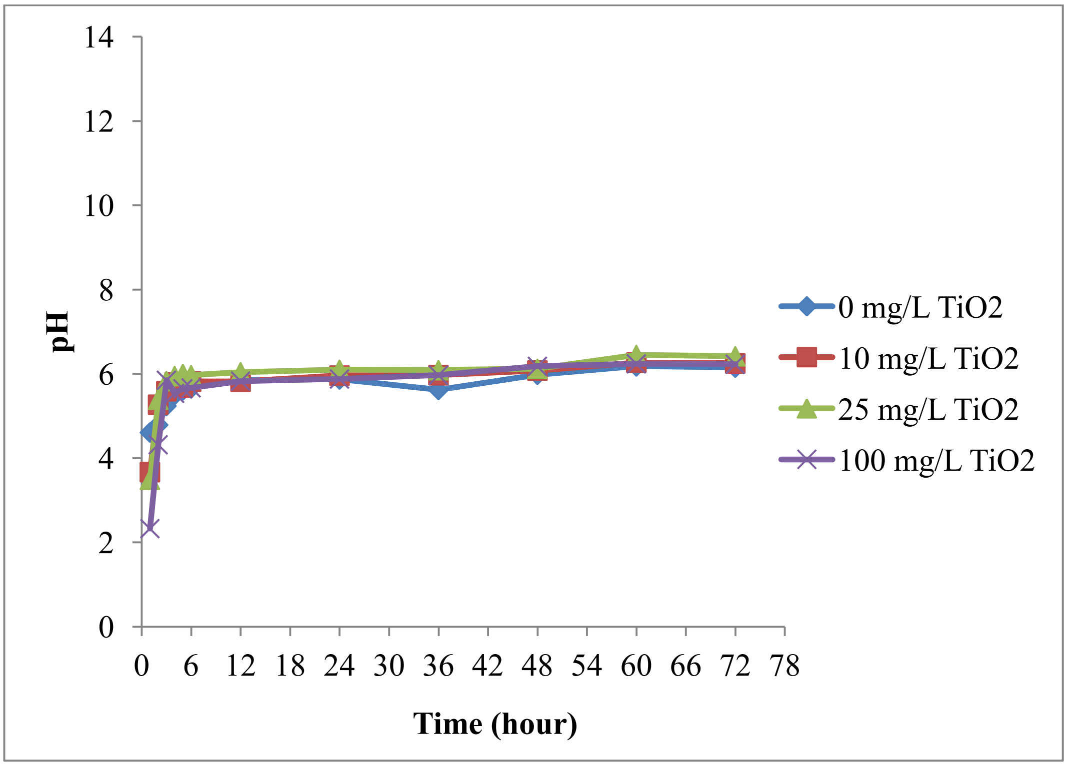

Figure 5.10. Leachate pH values in the first set experiments (synthetic solid waste).

In the first set, when pH level of the batch reactors was adjusted as acidic, the changes in leachate nano-Ti concentrations in batch reactors with real and synthetic MSW were investigated and results are given in Figures 5.11 and 5.12. The initial concentrations of nano-Ti for real solid waste batch reactors receiving 0, 10, 25, and 100 mg/L of TiO_2 obtained on Day 1 were 0.81, 2.21, 7.98, and 10.04 mg/L, respectively. The final concentrations were measured as 3.42, 2.88, 2.57, and 4.31, respectively on day 3. For each reactor, leachate Ti concentrations decreased in twelve hours and after that hour, they showed an irregular trend.

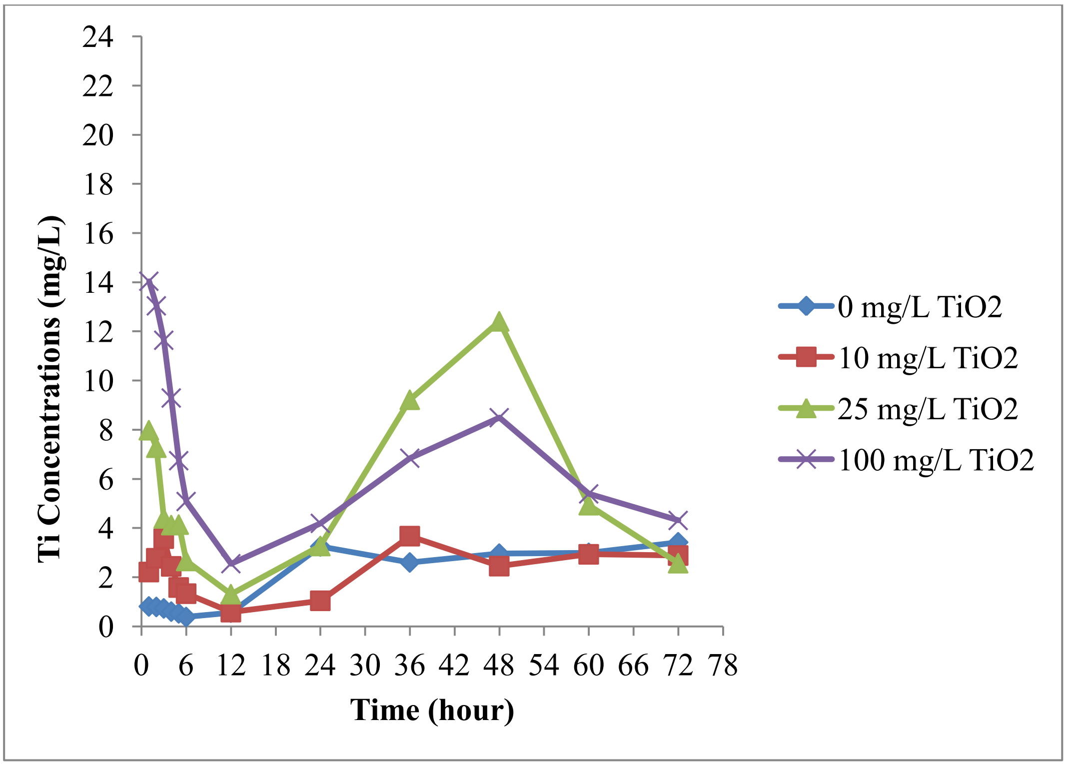

Figure 5.11. Leachate Ti concentrations in the first set experiments (real solid waste).

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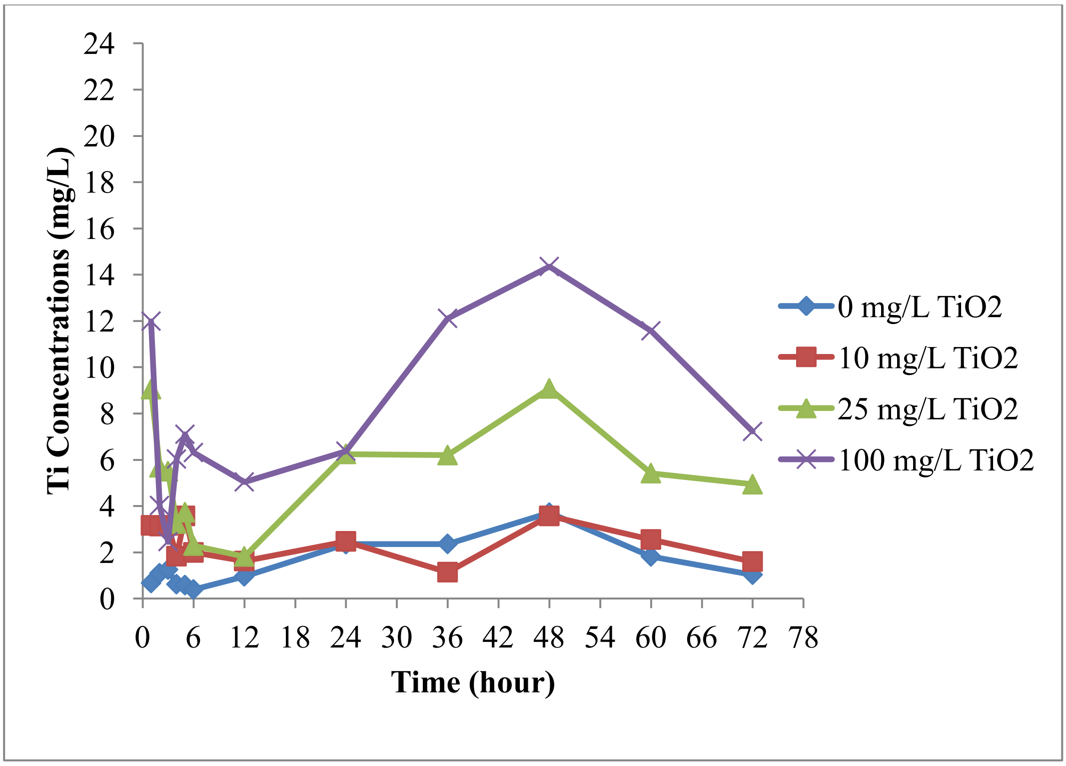

Figure 5.12. Leachate Ti concentrations in the first set experiments (synthetic solid waste).

The background concentration of nano-Ti containing 0 mg/L of TiO_2 was measured about 2 mg/L in the MSW reactors. The concentration of Ti decreased in the first 12 hours and after that hour, it increased in the range between 12 to 48 hours. Leachate Ti concentration containing high amount of nano-TiO_2 decreased between 48 and 72 hours in the batch reactors containing 25 and 100 mg/L of TiO_2. In the reactors containing low nano-TiO_2, the concentration of Ti did not change dramatically.

The initial Ti concentration in the reactor including 0 mg/L of nano-TiO_2 stock solution was recorded as 0.67 mg/L. Initial Ti concentrations of 3.16, 9.03, and 11.99 mg/L were measured for reactors containing 10, 25, and 100 mg/L of nano-TiO_2 stock solution, respectively. It can be said that the maximum leaching of Ti into the leachate took place at 48 hours for both types of the waste.

5.3.2. Second Set Experiments

In the second set, the conditions were: unadjusted ionic strength, and basic adjusted pH for nano-TiO_2 concentrations of 0, 10, 25, and 100 mg/L, respectively. Firstly, initial leachate pH values in the batch reactors were measured to decide the amount of NaOH to be added; 18- 20 ml of 1N NaOH was added in each nano-TiO_2 stock solution. After the adjustment of the pH, the initial pH levels of the synthetic solid waste and real solid waste batch reactors were measured between 12.4-12.6 and 9.3-11.4, respectively.

As shown in Figures 5.13 and 5.14, the leachate pH values from both real and synthetically prepared solid waste reactors showed a similar decreasing trend. Leachate pH values at the end of the study were about 7.00 - 7.77 in the reactors with real solid waste. Likewise, the final leachate pH values were measured between 5.87 and 6.02 for the reactors with synthetically prepared solid waste.

There wasn’t a specific trend based on the concentration of nano-TiO_2 in the reactors in terms of the changes of pH values. For the reactors containing different concentration of nano-TiO_2, leachate pH values indicated similar trend (Figures 5.13 and 5.14). The various amount of nano-TiO_2 in the reactors did not affect the changes in leachate pH values.

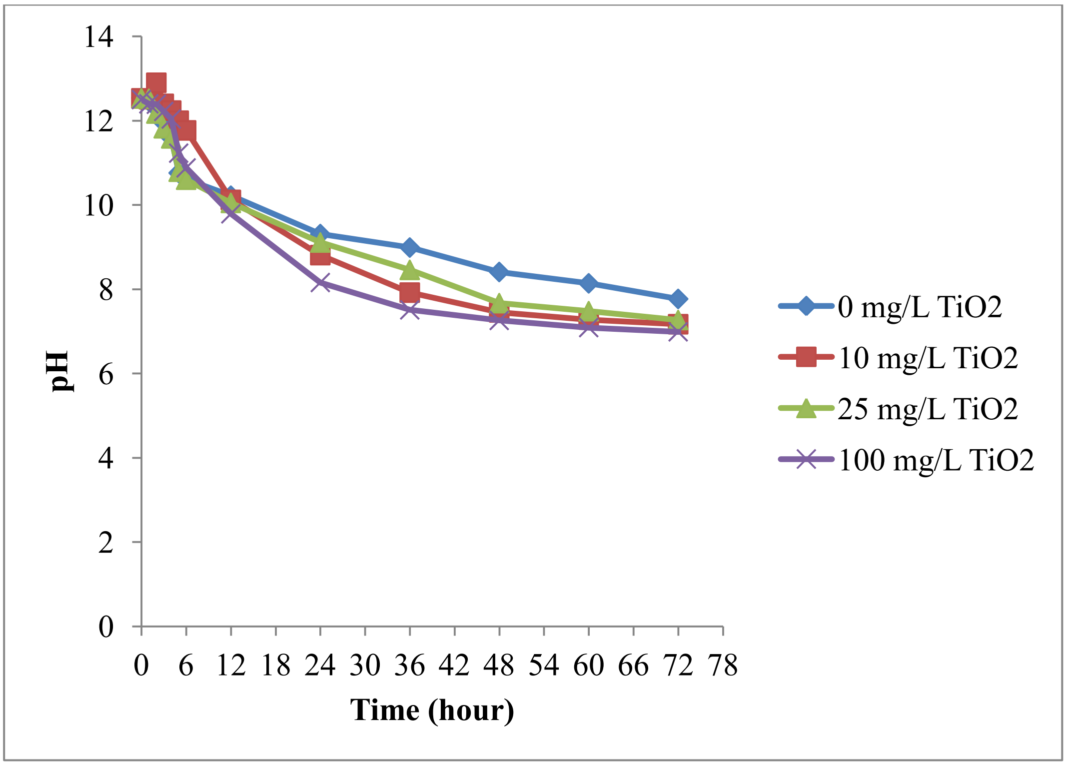

Figure 5.13. Leachate pH values in the second set experiments (real solid waste).

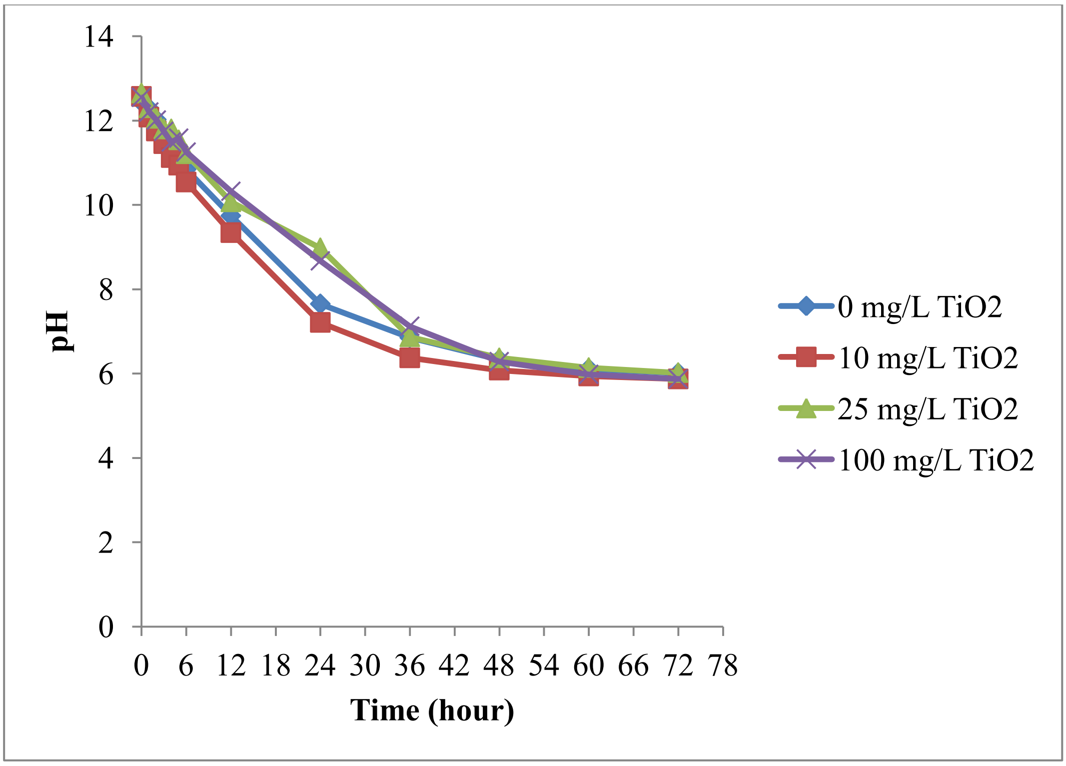

Figure 5.14. Leachate pH values in the second set experiments (synthetic solid waste).

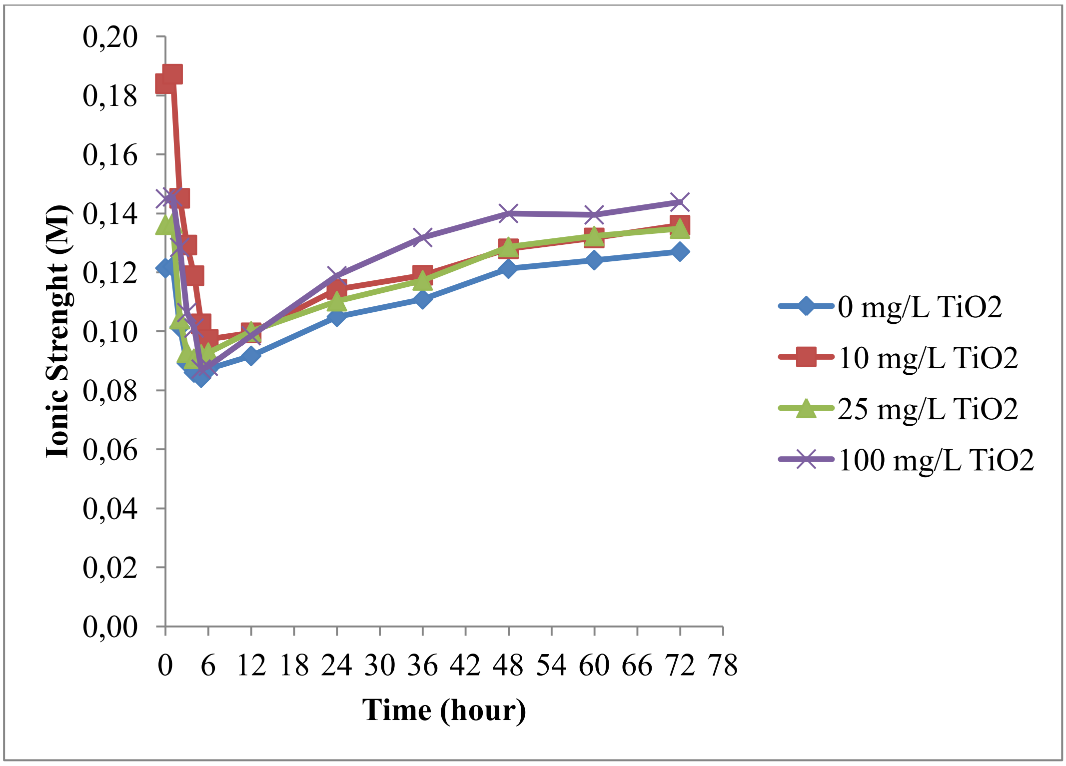

Figure 5.15. Leachate IS values in the second set experiments (real solid waste).

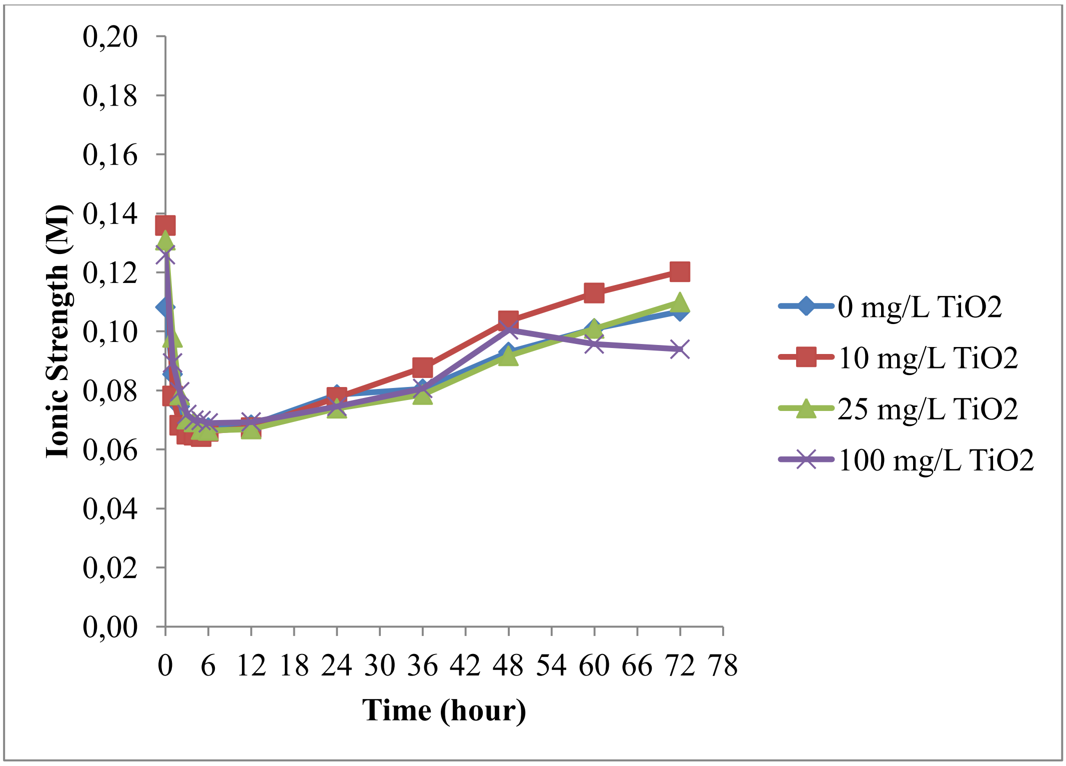

Figure 5.16. Leachate IS values in the second set experiments (synthetic solid waste).

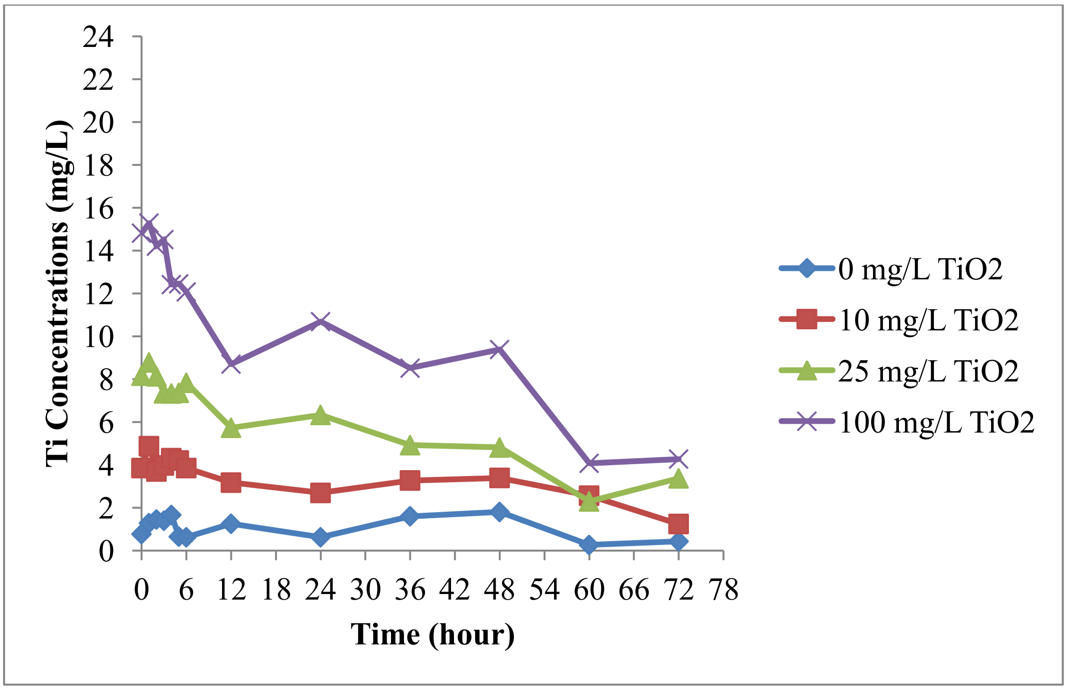

Figure 5.17. Leachate Ti concentrations in the second set experiments (real solid waste).

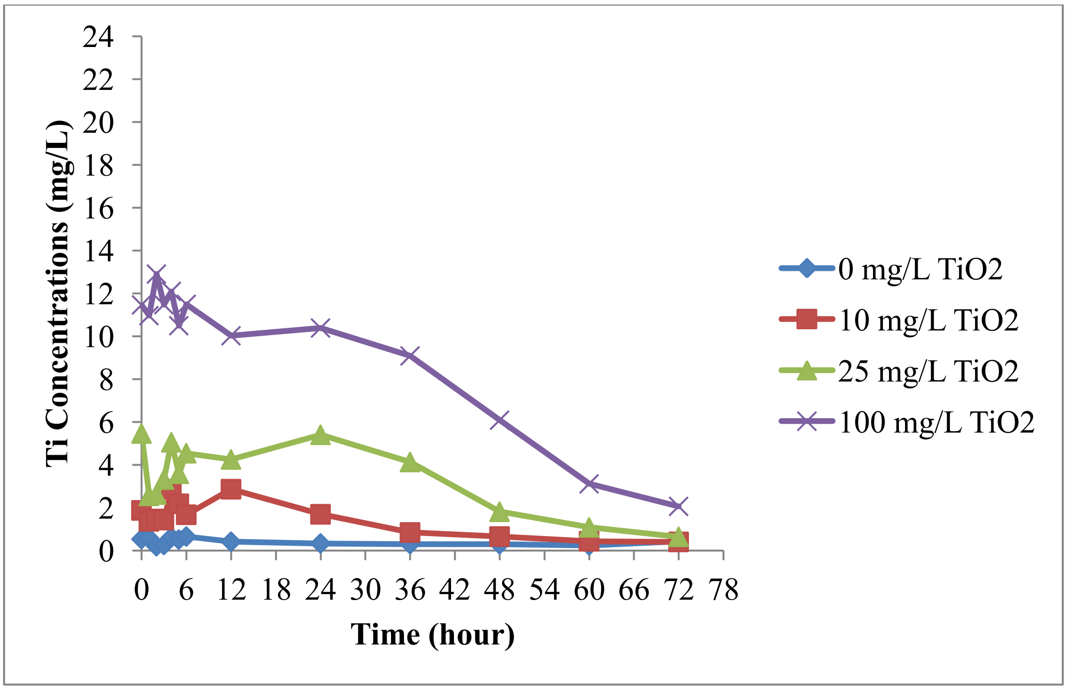

Figure 5.18. Leachate Ti concentrations in the second set experiments (synthetic solid waste).

Additionally, in this experimental set, leachate conductivity values were measured to calculate the ionic strength for each sample. The initial leachate ionic strength values for all nano-TiO_2 concentrations were calculated about 0.12- 0.18 M in the real solid waste reactors and about 0.10-0.13 in the synthetically prepared solid waste reactors. In both real and synthetically prepared solid waste reactors, leachate ionic strength values showed a similar behavior. In the first six hours, the level of leachate ionic strength reduced remarkably and then it started to increase (Figures 5.15 and 5.16).

In the reactors including real solid waste, leachate Ti values showed similar behavior and a decreasing trend versus time as shown in Figure 5.17. In the second hours, the maximum values of Ti were observed to pass into the leachate in the reactors containing 10, 25, and 100 mg/L of TiO_2 stock solution.

Leachate Ti values in the reactors with synthetically prepared solid waste indicated a decreasing trend like in the real solid waste reactors (Figure 5.18). 0, 10, 25, and 100 mg/L of nano-TiO_2 represented virtually the same behavior in the reactors. However 100 mg/L of nano-TiO_2 batch reactor showed a more precisely decreasing trend compared to the other batch reactors.

5.3.3. Third Set Experiments

In the third set, the ionic strength levels of the batch reactors for both real and synthetic solid wastes were increased. In the first step, initial leachate ionic strength valued from the batch reactors were found to decide the amount of NaCI to be added; therefore, 0.6 gram of NaCI added to 300 mL DI water was used in each solid waste batch reactors. However, pH levels of the batch reactors were not changed.

The changes of pH level in the reactors did not show differences between the concentrations of nano-TiO_2. Leachate pH values in the all batch reactors indicated the same trend as shown in Figures 5.19 and 5.20. Initial leachate pH values were measured in the range between 8 and 9 for the real solid waste batch reactors, 6 and 8 for the synthetically prepared solid waste batch reactors. Especially after the first six hours, leachate pH values ranged between 6 and 8 in the both real and synthetically prepared solid waste batch reactors until the end of the study.

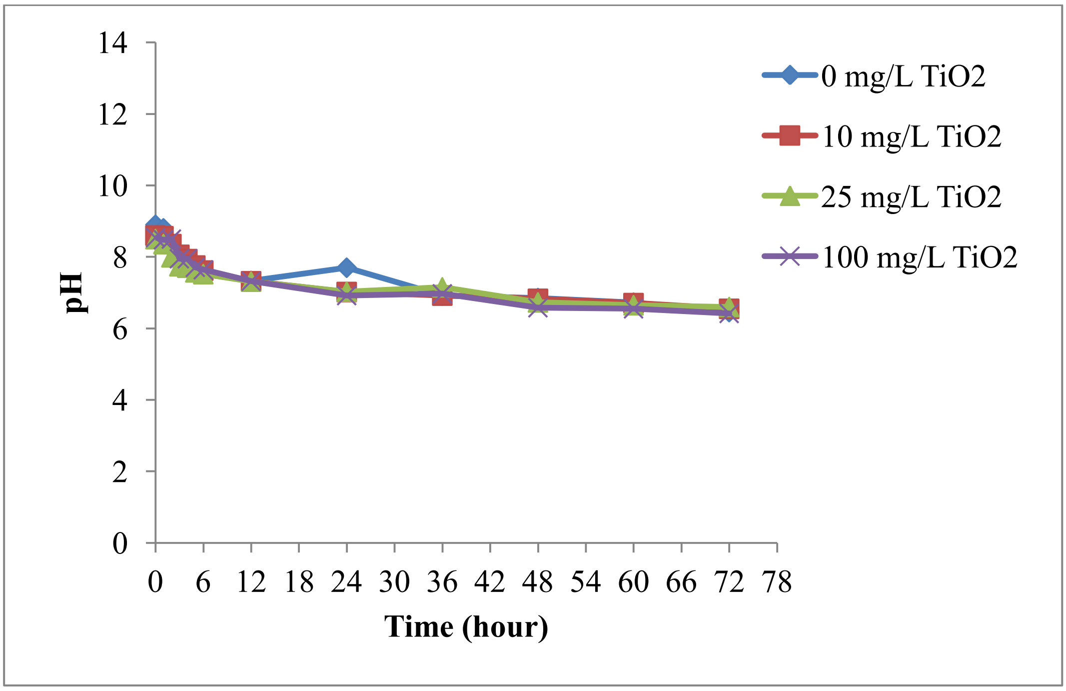

Figure 5.19. Leachate pH values in the third set experiments (real solid waste).

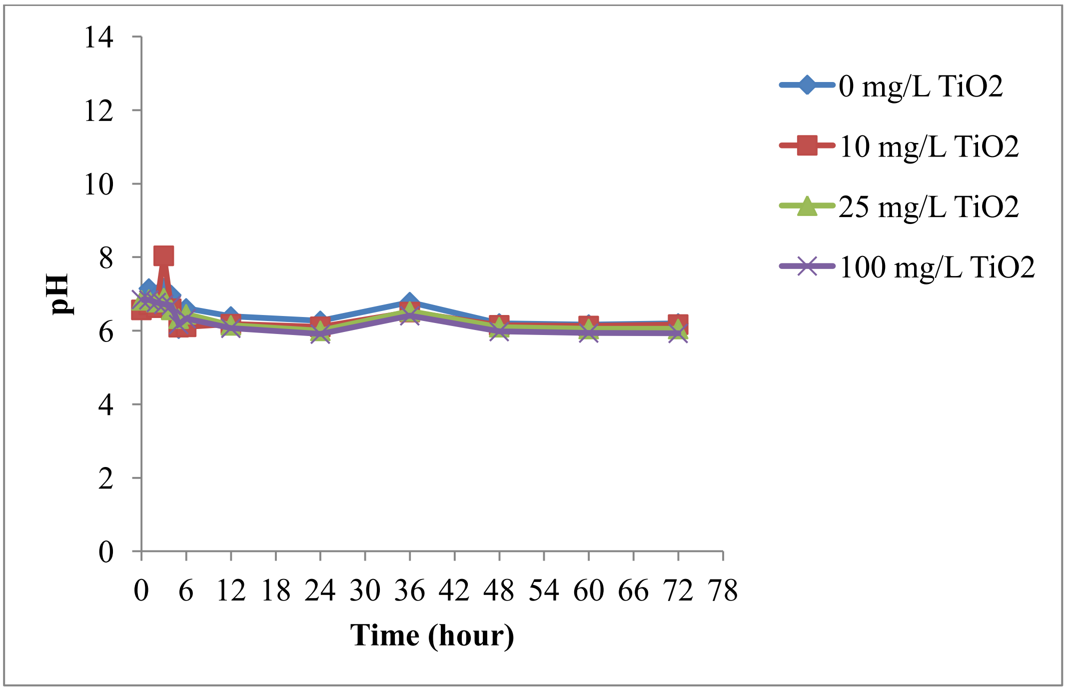

Figure 5.20. Leachate pH values in the third set experiments (synthetic solid waste).

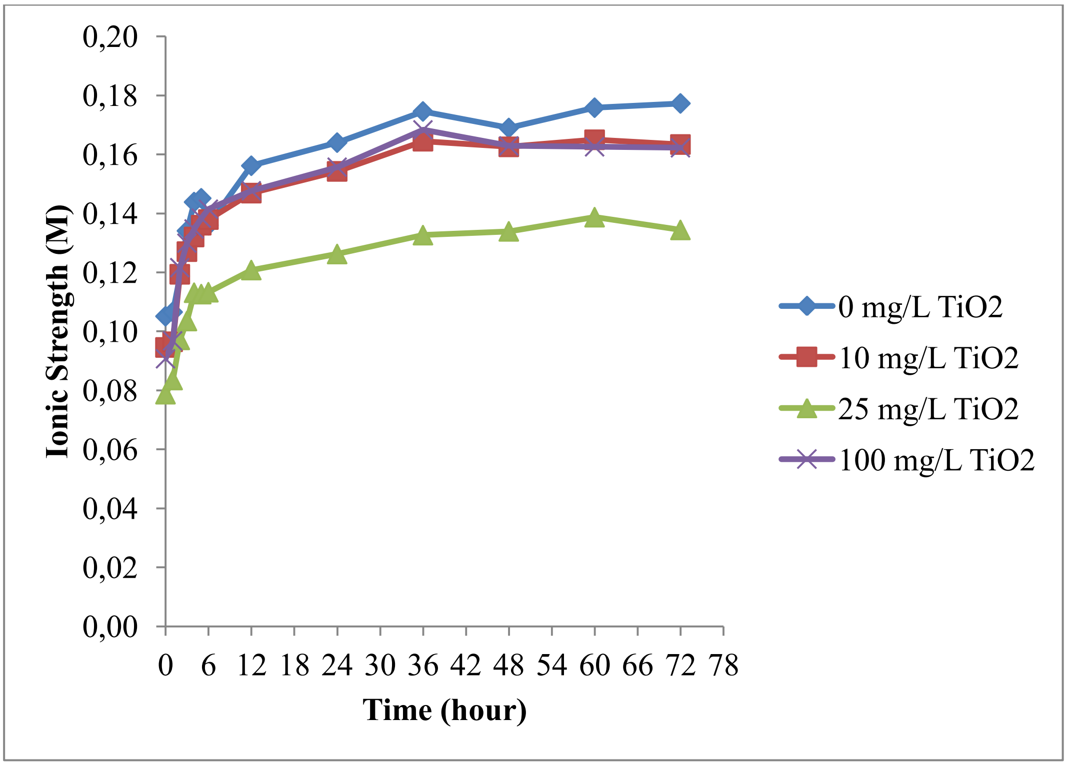

Figure 5.21. Leachate IS values in the third set experiments (real solid waste).

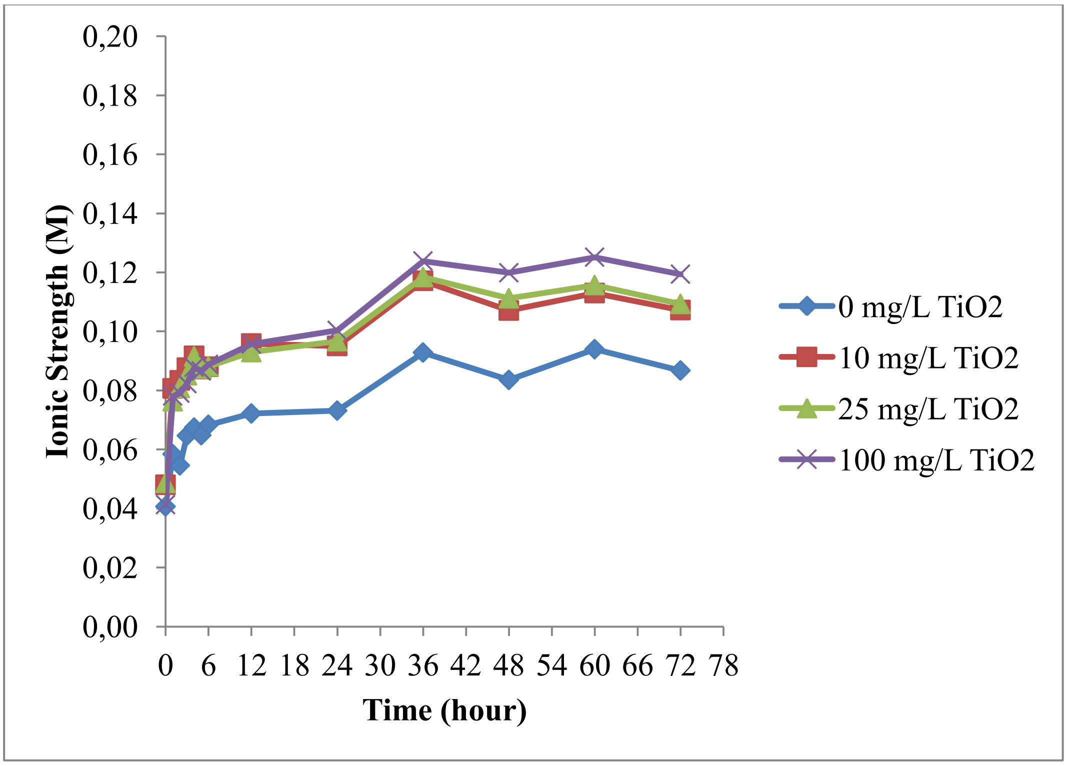

Figure 5.22. Leachate IS values in the third set experiments (synthetic solid waste).

Conductivity, which is related to ionic strength, temperature and the mobility of ions ability of a solution to conduct; therefore, in the third experimental set, leachate conductivity values were measured to have an idea about ionic strength of the samples and the values of the conductivity were converted to ionic strength.

In the reactors of the real solid waste, the ionic strength of leachate samples indicated a sharp increasing trend in six hours and after that hour, the ionic strength showed a slight upward trend at the end of the study. For example, in the last reactor including 100 mg/L of TiO_2 stock solution, the initial leachate ionic strength values was measured as 0.09 M and it reached 0.14 M in six hours and the final value was recorded as 0.16 M as shown in Figure 5.21.

In the same way, leachate ionic strength values in the synthetically prepared solid waste batch reactors showed similar behavior like the reactors including real solid waste. In six hours, the ionic strength values of the leachate samples represented a precise upward trend and then began to increase on a small scale as seen in Figure 5.22.

In this experimental set, the ionic strength of the batch reactors was increased. Also, how much concentration of Ti would be passed into the leachate was investigated. In the first real solid waste batch reactor, initial and final Ti concentrations were measured as 1.01 and 0.24 mg/L, respectively, as shown in Figure 5.23. The maximum leaching of Ti into the leachate occurred in fourth hours as 2.96 mg/L. Then, leachate Ti concentrations were fluctuated at the end of the study.

Initial Ti concentration in the second real solid waste batch reactor was recorded as 4.33 mg/L. The maximum Ti concentration was 6.92 mg/L at four hours. After that hour, a decreasing trend was observed roughly until the 60 hours and the Ti concentration in the leachate was increased to 4.36 mg/L at the end of the experiment.

The Ti concentration in the third real solid waste batch reactor was 6.98 mg/L at the beginning of the study. The Ti concentration reached to its maximum value of 8.10 mg/L at 5 hours and this value decreased to 13.27 mg/L at the end of the experiment.

At the final real solid waste batch reactor, the initial concentration of Ti in the leachate was recorded as 8.49 mg/L. Leachate Ti concentrations fluctuated within 6 hours and then the concentration reached to its maximum value of 18.21 mg/L. The final Ti concentration was measured as 13.27 mg/L.

Likewise, the reactors containing synthetically prepared solid waste showed almost the same behavior like the real solid waste reactors as shown in Figure 5.24. Initial Ti concentrations of the reactors including 0, 10, and 25 mg/L TiO_2 stock solution were measured as 0.92, 3.35, and 3.62 mg/L, respectively. The concentrations of Ti were unstable within six hours, which then decreased to 0.46, 0.94, and 1.41 mg/L. However, the final reactor adding 100 mg/L of TiO_2 was found as 4.32 mg/L at the beginning of the study. The leachate Ti concentration increased rapidly to 13.74 mg/L in the first six hours, which then showed a decreasing trend until the end of the experiment.

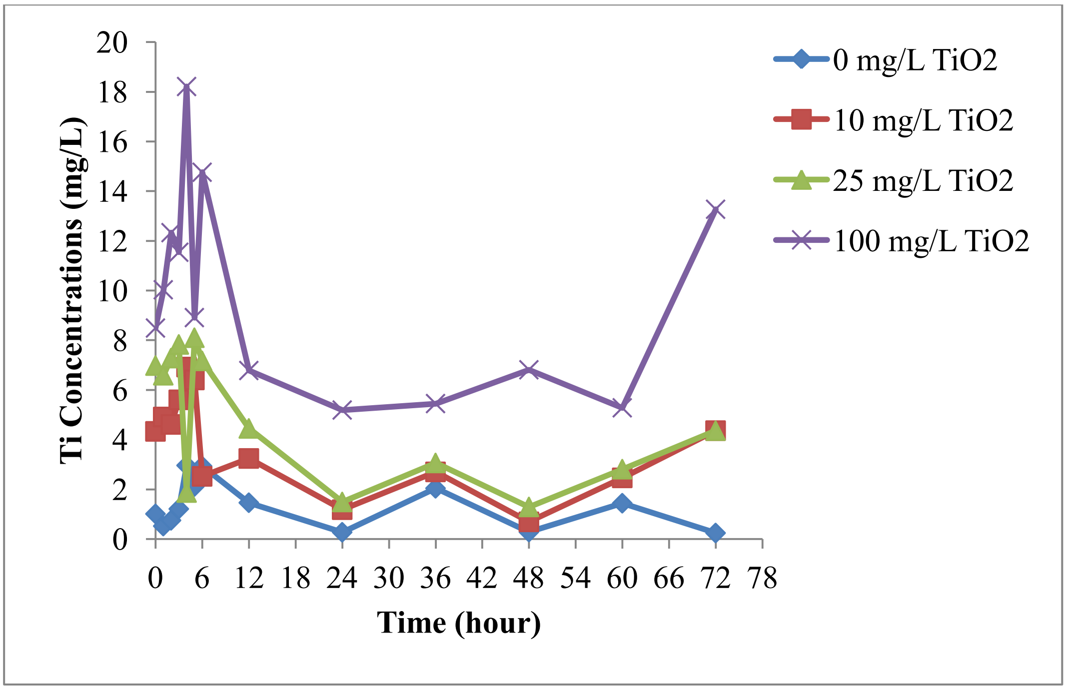

Figure 5.23. Leachate Ti concentrations in the third set experiments (real solid waste).

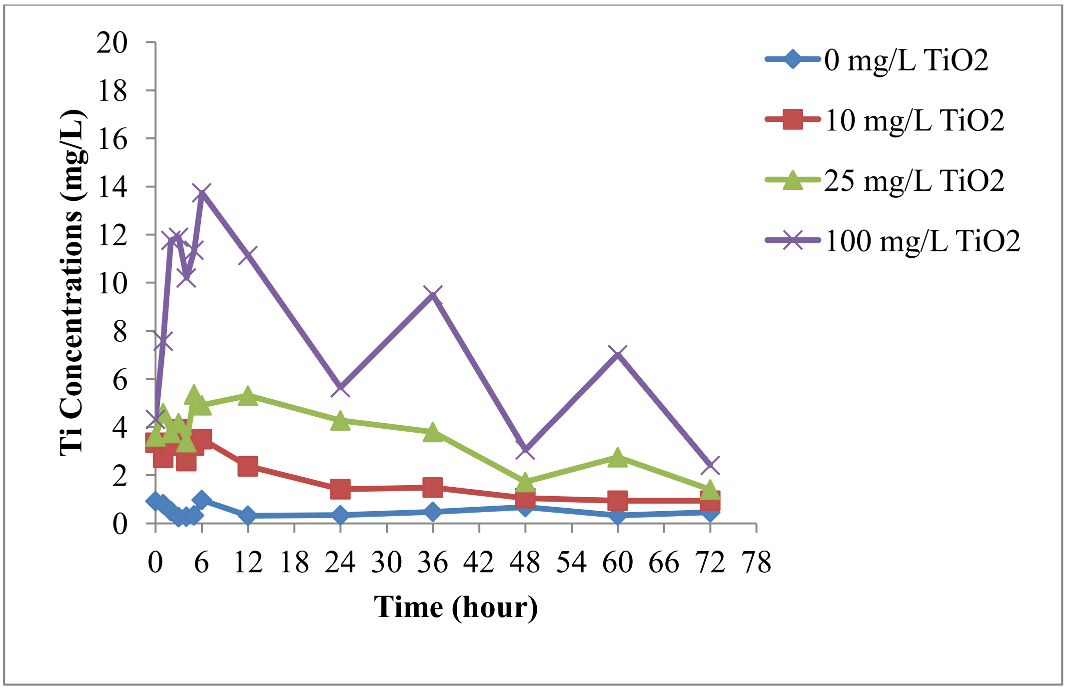

Figure 5.24. Leachate Ti concentrations in the third set experiments (synthetic solid waste).

5.4. Comparison of Real Waste and Synthetic Solid Waste for Each Sets

In this study, three different sets of batch experiments with four different nano-TiO_2 concentrations were conducted for both real and synthetically prepared solid waste samples. The conditions for the sets are given in Tables 4.5. Under these conditions, the leaching behavior of Ti from waste samples was evaluated and results are compared in the following section.

The total mass of Ti within the leachate at the end of each experiment for both real and synthetically prepared solid waste was presented in Figures 5.25 and 5.26. In the real solid waste batch reactors, the maximum leaching was observed under the increased IS condition for the reactors containing 100 mg/L of nano-TiO_2 stock solution and the value was recorded as 0.93. Likewise, 0.73 mg was found as the maximum leaching in the synthetically prepared solid waste batch reactors receiving 100 mg/L of nano-TiO_2 stock solution under the basic condition. These values were calculated by using equation of 5.1. In addition, in this study, initial mass of Ti in MSW and synthetically prepared solid waste was not directly used to calculate of mass Ti leached. However, the mass Ti leached from the waste control experiment (with zero nano-TiO_2) was subtracted from the total leached mass.

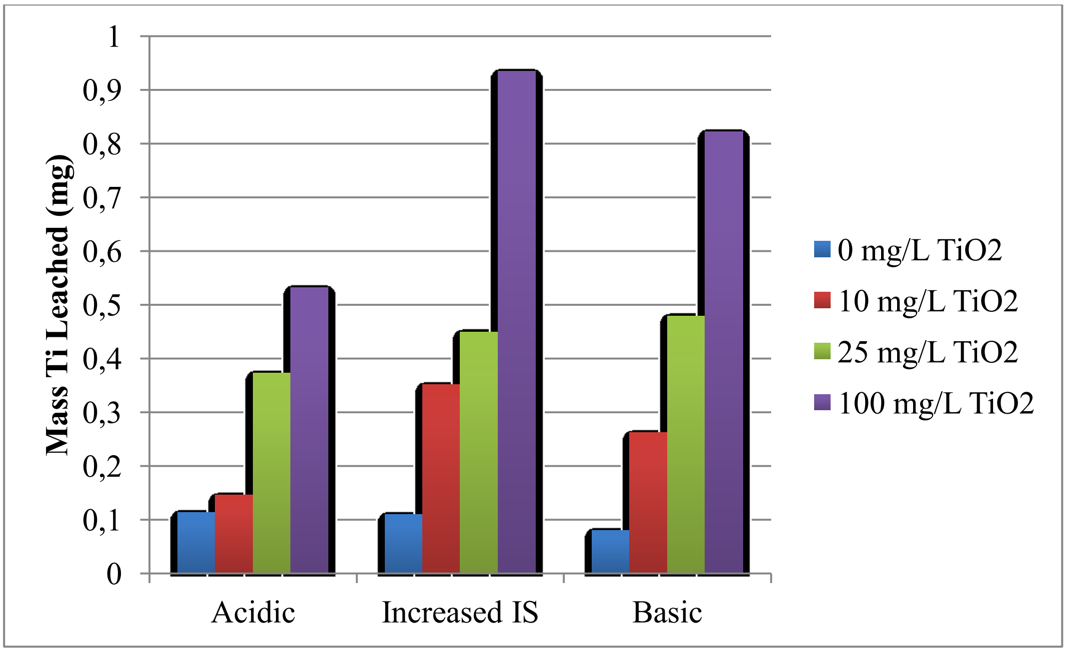

Figure 5.25. Mass Ti leached (mg) (real solid waste).

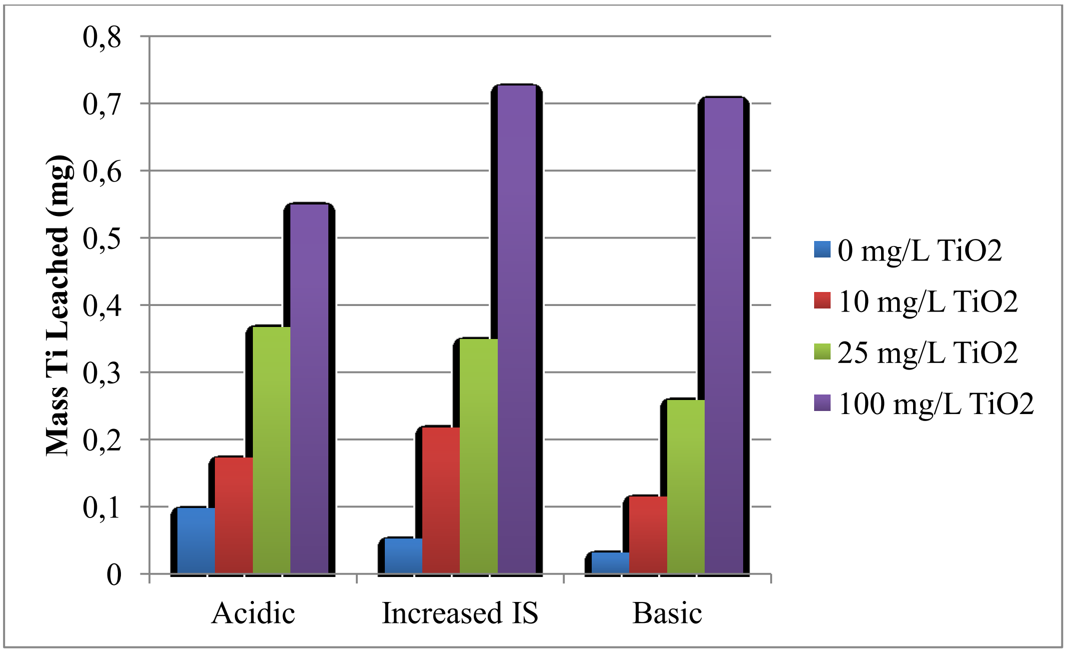

Figure 5.26. Mass Ti leached (mg) (synthetic solid waste).

Mass Ti leached (mg) = $\sum C(t)_{\text{leached}} * V_{\text{sample}} *$ Recovery rate (5.1)

Mass leachate (%) = (mass leached (mg/L) – mass Ti leached from control (mg/L))/ mass Ti added *100 (5.2)

On the other hand, for the reactors receiving lower concentration of nano-TiO_2, the minimum leaching was recorded under the basic condition in the same way. As can be seen from the reactors receiving 25 mg/L of nano-TiO_2, while the maximum leaching of nano-TiO_2 in the real MSW reactors occurred under the basic condition, this maximum values were obtained under the acidic condition for the reactors containing synthetically prepared solid waste. For 10 mg/L nano-TiO_2, with the real MSW the mass of Ti leached under acidic, increase ionic strength and basic conditions, were found as 0.15, 0.35, and 0.26 mg, respectively. On the other hand, for the synthetically prepared solid waste under the same conditions, the mass of Ti in the leachate sample was found as 0.17, 0.22, and 0.12 mg, respectively.

The results of the percent leached mass of Ti (%) are given in Figure 5.27 for the real MSW batch reactors which were calculated by using equation of 5.2. As can be seen from the Figure, under the acidic condition, leached Ti percentage reached to its maximum value at 5.78 % in the reactor receiving 25 mg/L of nano-TiO_2 stock solution. However, under the increased ionic strength and basic conditions, Ti for all examined concentrations of nano-TiO_2 stock solutions showed similar leaching behavior. Percentage leached mass of nano-TiO_2 increased as the concentration of nano-TiO_2 in the stock solution decreased.

Based on these measurements, the Ti leached in the batch reactors with synthetically prepared solid waste ranged between 2.51 and 9.19 % for all adjusted conditions (Figure 5.28). The maximum leached Ti was measured under the increased strength conditions for the reactors receiving 10 mg/L of nano-TiO_2 and the minimum value was recorded in the rectors containing 100 mg/L of nano-TiO_2 under the acidic condition. The percentage leached mass of Ti was found to be slightly higher in the real solid waste than that of the synthetic solid waste.

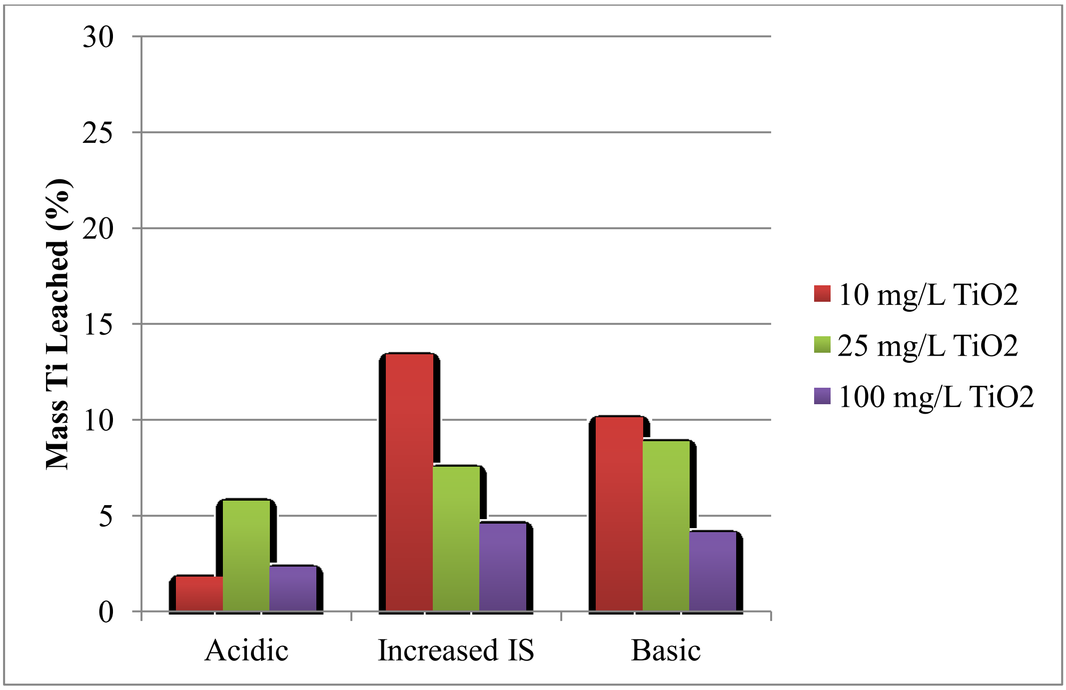

Figure 5.27. Mass Ti leached (%) (real solid waste).

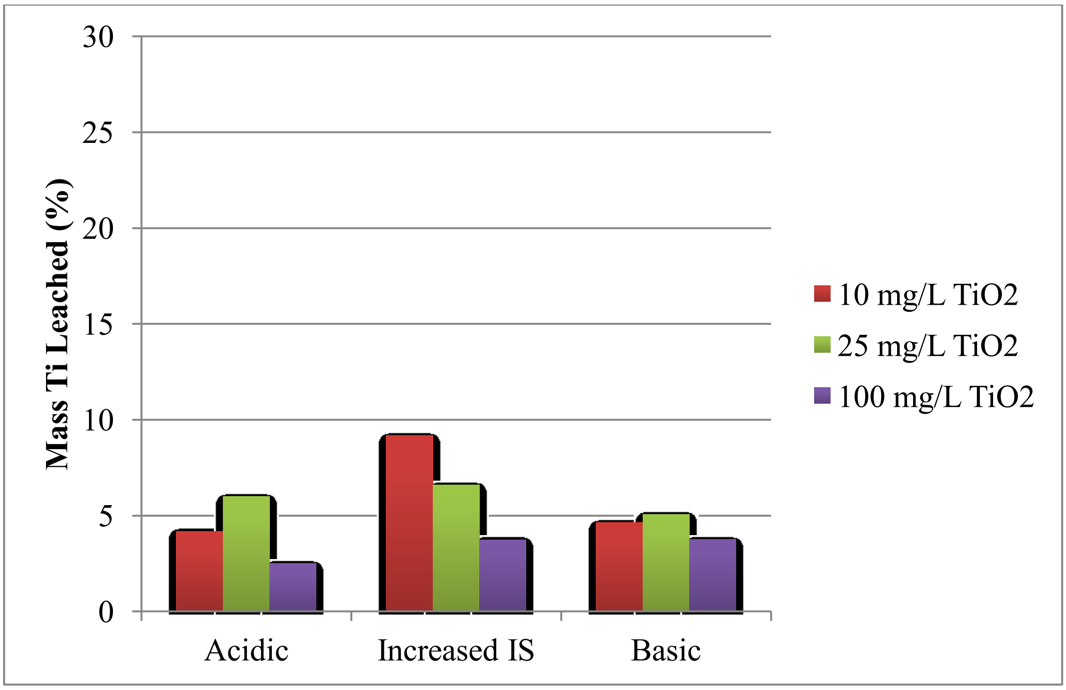

Figure 5.28. Mass Ti leached (%) (synthetic solid waste).

Figures 5.29 and 5.30 show the total mass of Ti retained in the solid waste at the end of each experiment. The mass Ti retained was calculated as shown in the Figures for the reactors containing the nano-TiO_2 stock solutions (10, 25, and 100 mg/L).

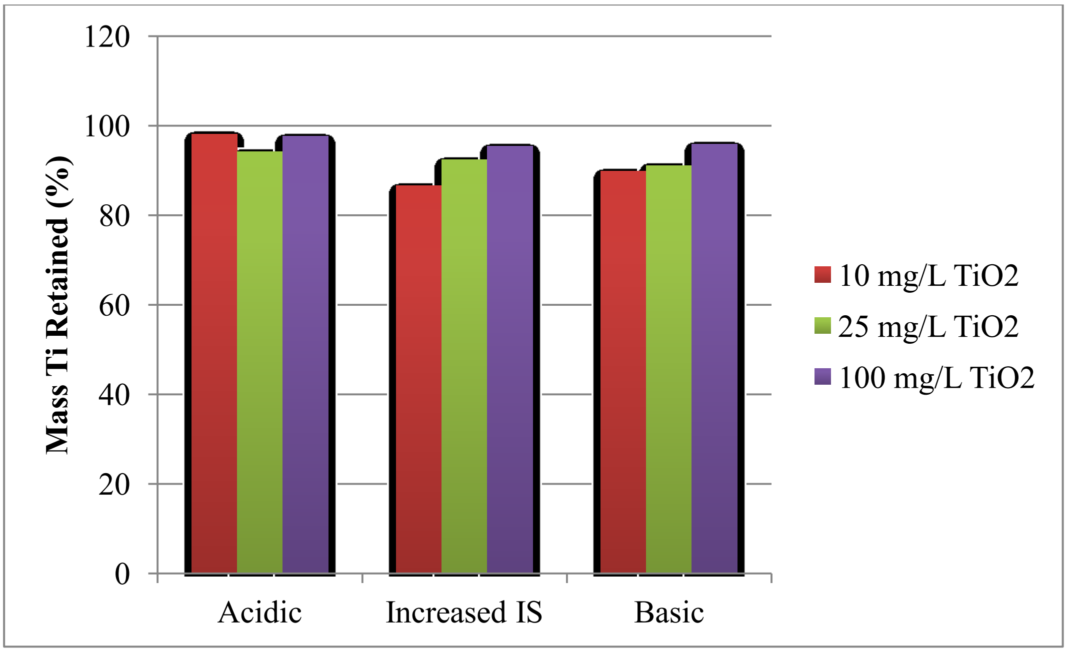

Figure 5.29. Mass of Ti retained (%) (real solid waste).

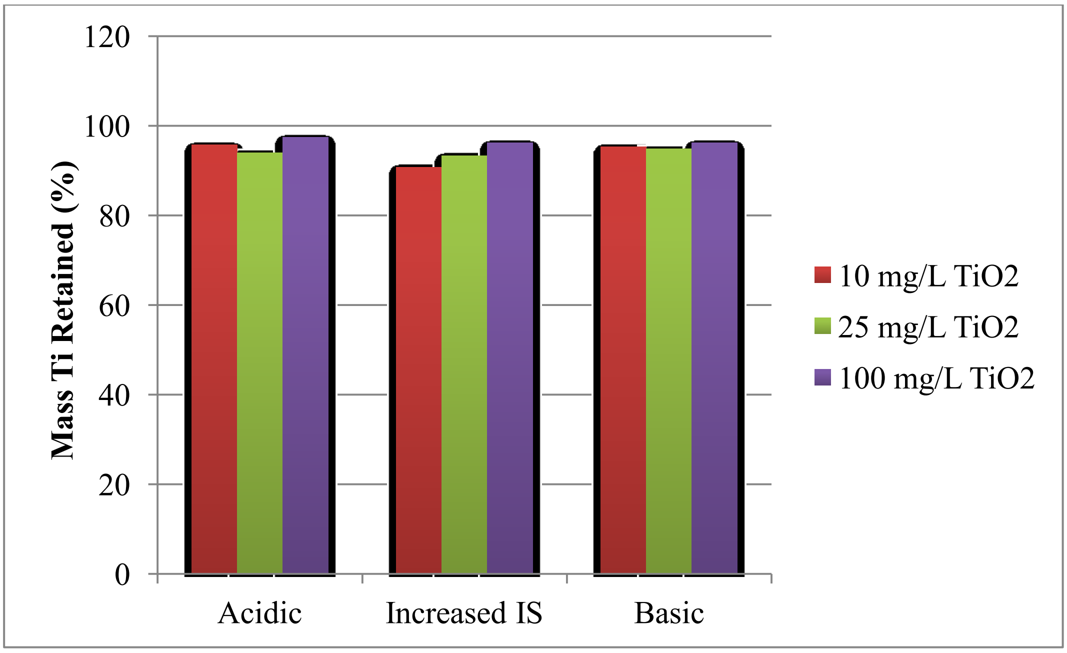

Figure 5.30. Mass of Ti retained (%) (synthetic solid waste).

In the real solid waste batch reactors containing 10 mg/L of nano-TiO_2 stock solution, for all adjusted conditions (acidic, increase ionic strength, and basic conditions), the percentage of retained nano-Ti was calculated as 98.18, 86.59, and 89.89%, respectively. For the reactors receiving 25 mg/L of TiO_2 stock solution, these values were 94.22 % for acidic pH condition, 92.45 % for increase ionic strength condition, and 91.13 % for basic pH condition. Additionally, about 95-97 % of the nano-TiO_2 was retained within the solid waste for all adjusted conditions in the batch reactors with 100 mg/L of nano-TiO_2 stock solution.

In the same way, for the synthetically prepared solid waste batch reactors, the total mass of nano-Ti retained within the solid waste is showed in Figure 5.30, which ranged between 90 to 97 % of nano-TiO_2 for all adjusted conditions.

As can be seen from the figures, for all examined conditions about 86- 98 % of the nano-TiO_2 was retained within the solid waste. Results of the experiments indicated that in both real and synthetically prepared solid waste batch reactors, with various nano-TiO_2 concentrations and under different environmental conditions (acidic or basic pH levels, ranging Ti concentrations, or high ionic strength), nano-TiO_2 tended to be retained on to the solid surface. Therefore, it can be said that the low leaching tendency of nano-Ti into the leachate was observed.

As a result of these experiments, changing pH level, the concentration of nano-TiO_2 or/and increase in ionic strength in the batch reactors showed that there was no effect on the leaching behavior of nano-TiO_2 in the real and synthetically prepared solid waste.

5.5. Nano-Ti Concentration During The First Six Hours

Given the results of all experiments, after the first six hour, pH and ionic strength values were balanced; therefore, the first six hours is an important criterion in order to evaluate the effect of the experimental conditions and the concentration of nano-TiO_2 on the leaching behavior of nano-TiO_2 in the all batch reactors.

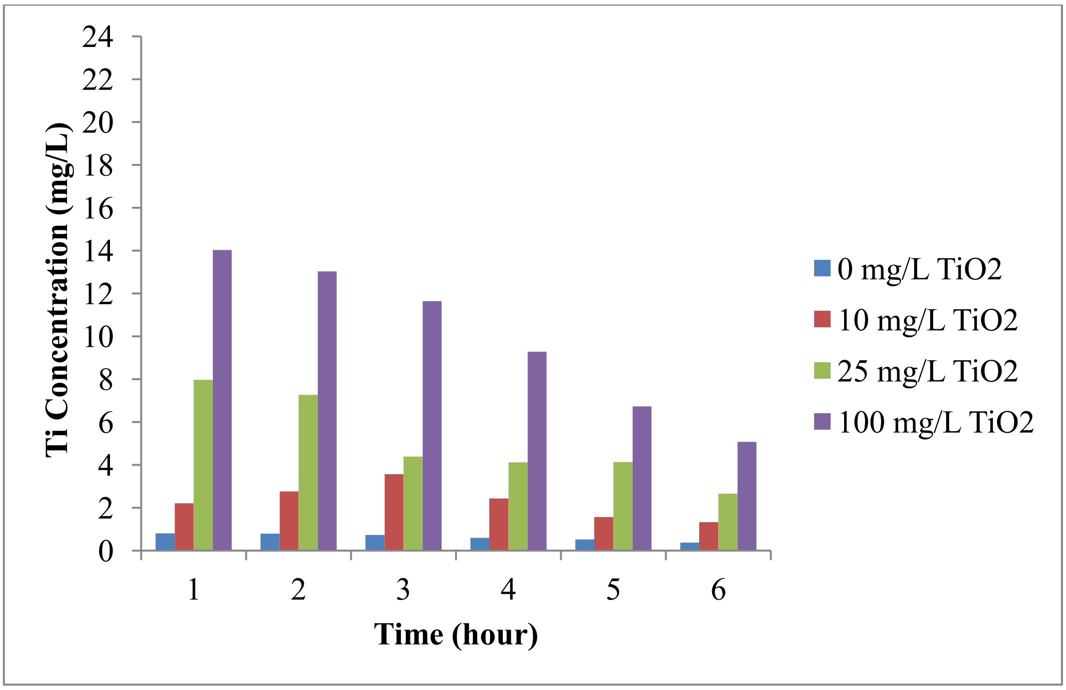

Figure 5.31. Leachate Ti concentration in the first set experiment (real solid waste).

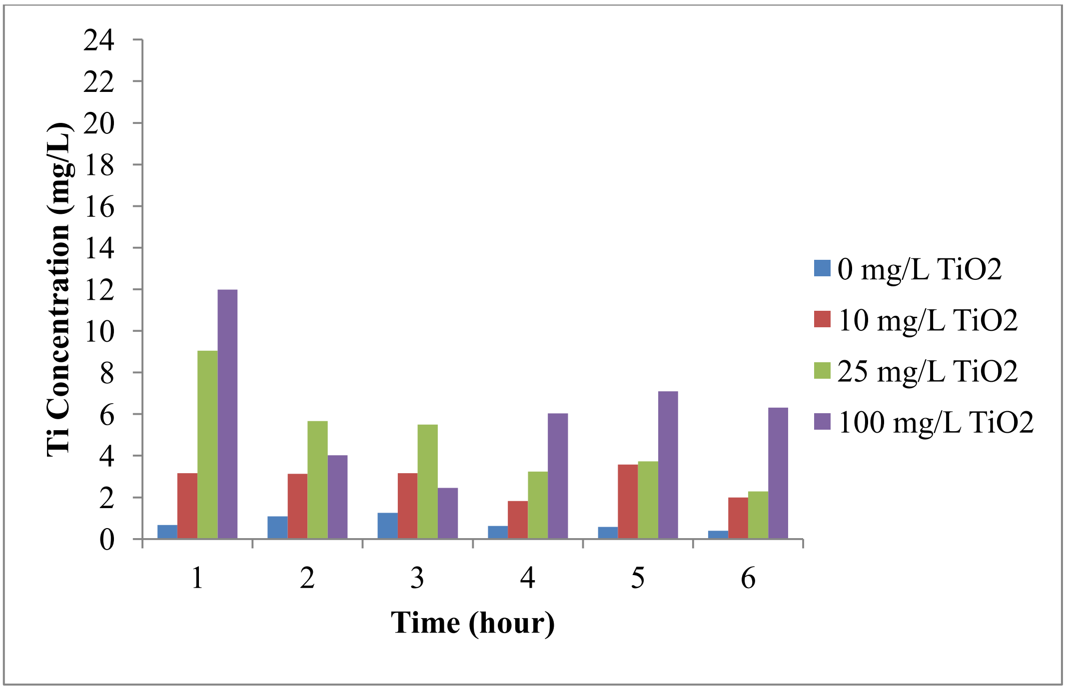

Figure 5.32. Leachate Ti concentration in the first set experiment (synthetic solid waste).

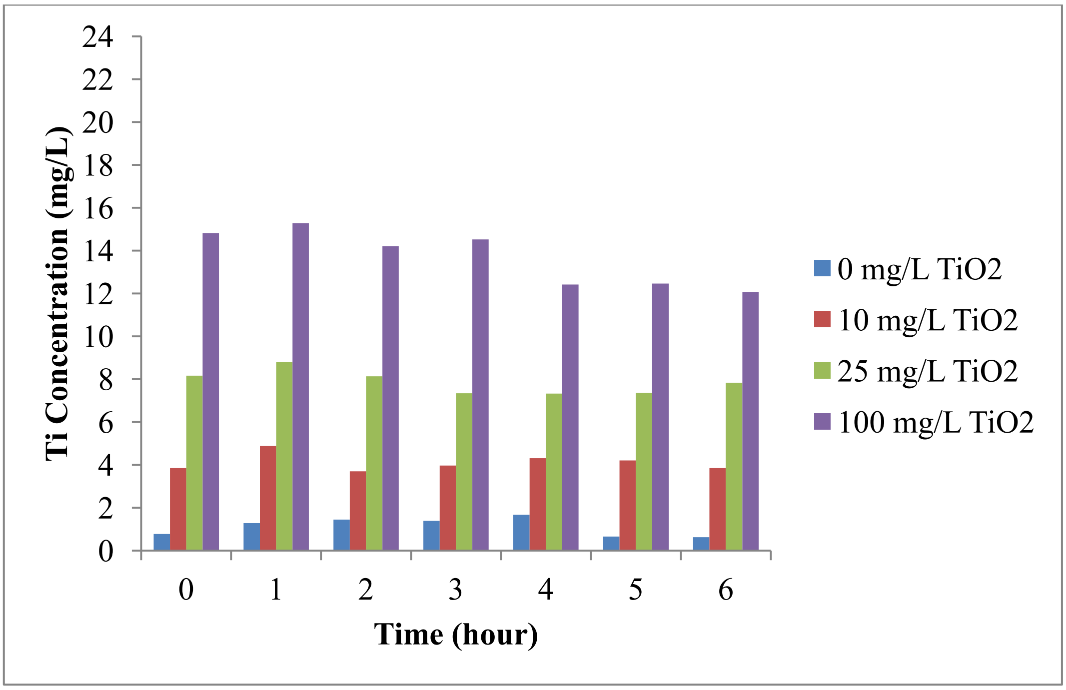

Figure 5.33. Leachate Ti concentration in the second set experiment (real solid waste).

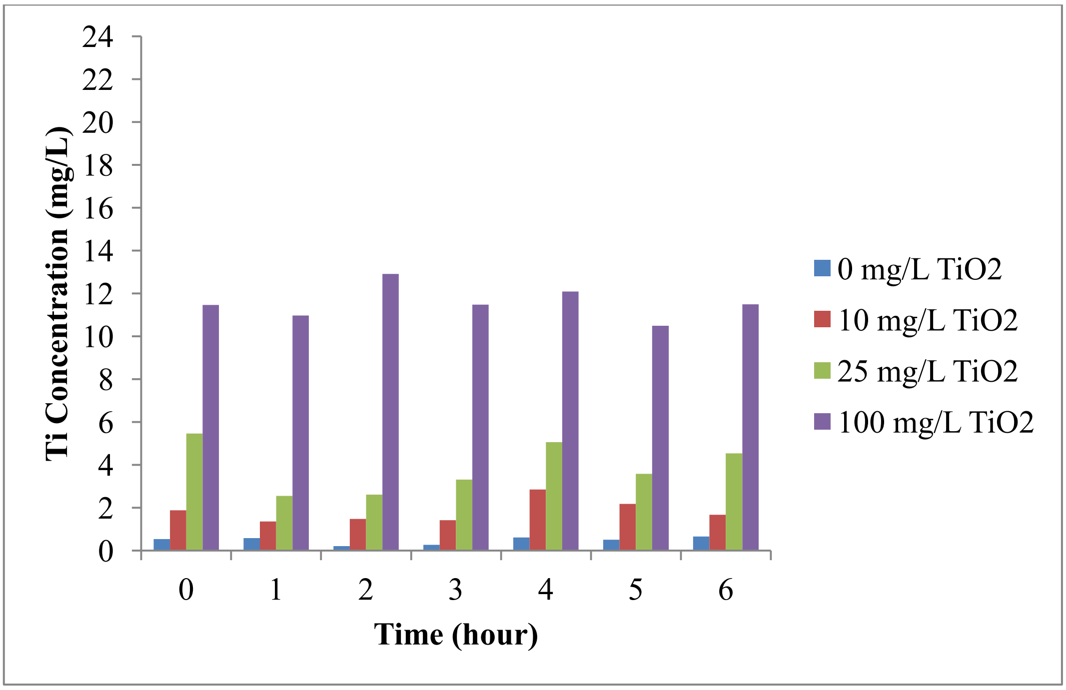

Figure 5.34. Leachate Ti concentration in the second set experiment (synthetic solid waste).

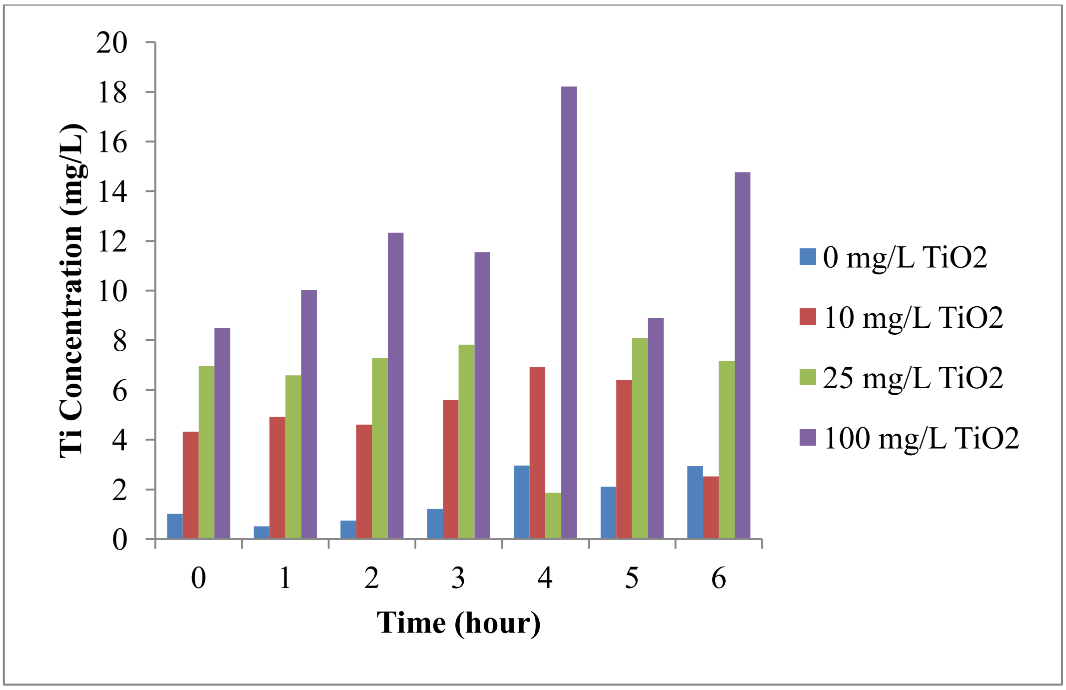

Figure 5.35. Leachate Ti concentration in the third set experiment (real solid waste).

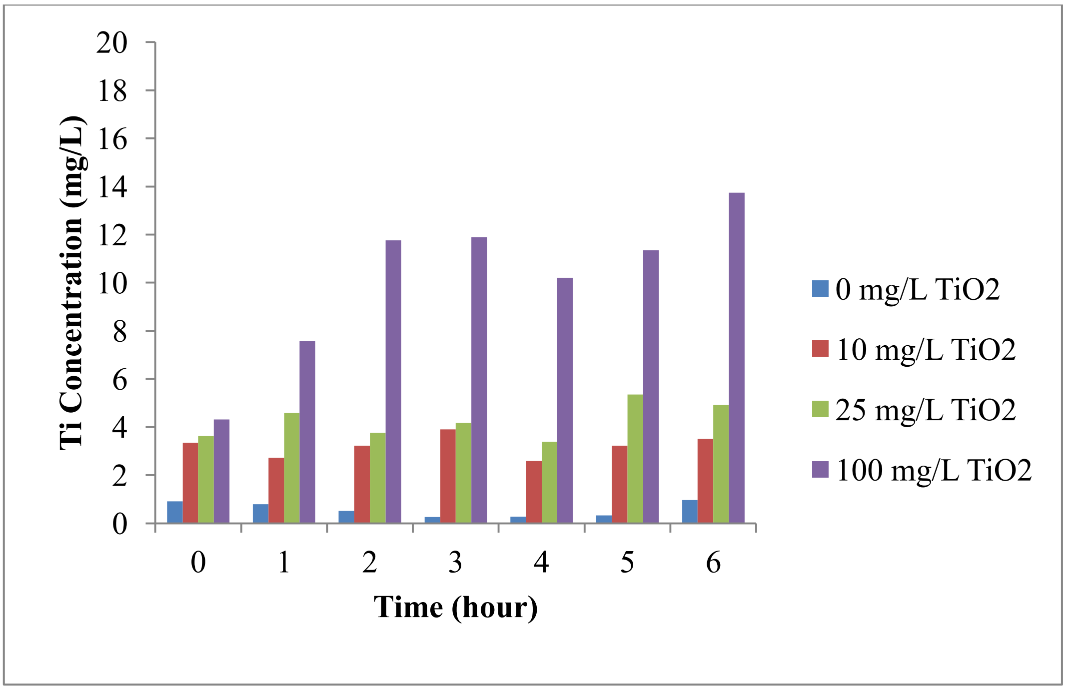

Figure 5.36. Leachate Ti concentration in the third set experiment (synthetic solid waste).

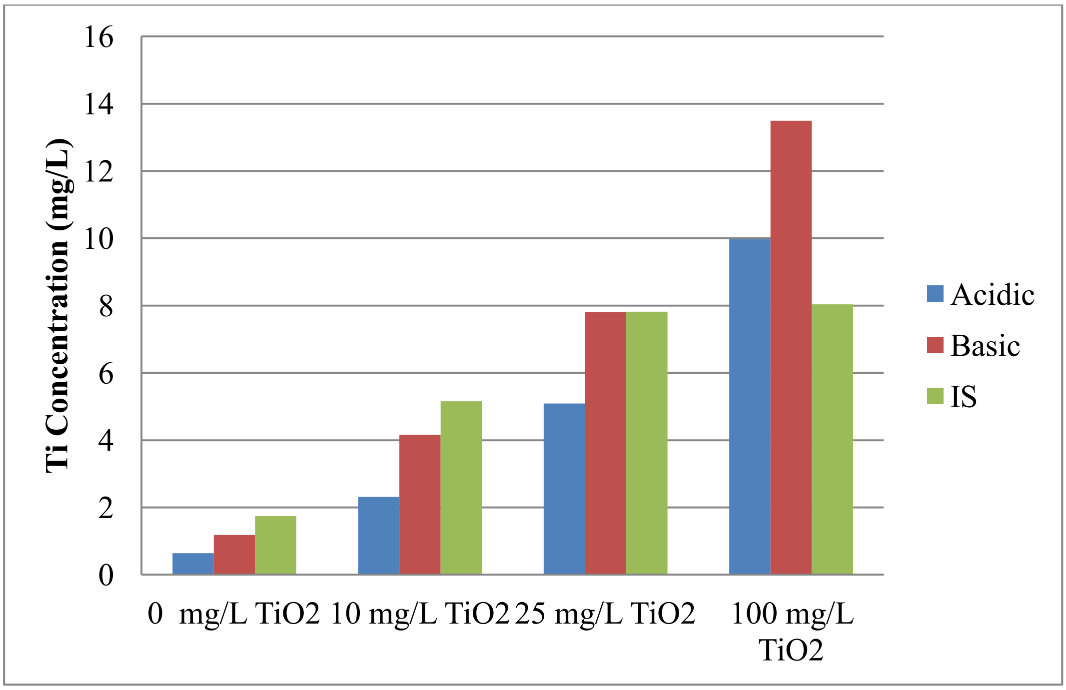

Figure 5.37. Average Ti concentration during the first six hours (real solid waste).

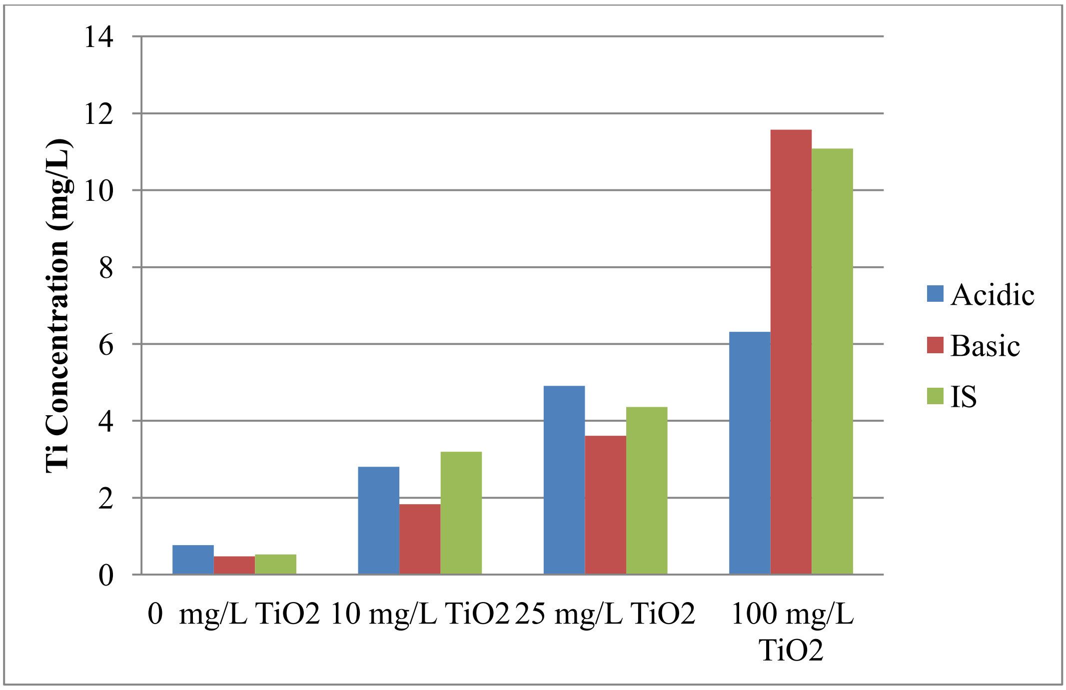

Figure 5.38. Average Ti concentration during the first six hours (synthetic solid waste).

As can be seen from the Figures 5.31 and 5.32, for both real and synthetic solid waste, leachate Ti concentration under the acidic condition showed a similar behavior, which generally was a decreasing trend as a function of time.

Under the basic condition, leachate Ti concentration for all examined concentration of nano-TiO_2 stock solution represented a stable trend over time in the real and synthetic solid waste batch reactors as shown in Figures 5.33 and 5.34. It can be said that basic pH does not have an important impact on the leaching behavior of nano-TiO_2 in this experiment.

Leachate Ti concentration in the all concentrated nano-TiO_2 batch reactors under the increased ionic strength condition increased over time as shown in Figures 5.35 and 5.36.

As can be seen from Figures 5.37 and 5.38, the average leachate Ti concentration under the basic condition in both real and synthetic solid waste batch reactors was found to be the highest; however, the average leachate Ti concentrations under the acidic and increased ionic strength did not represent a consistent behavior given the examined conditions and concentration of nano-TiO_2.

Overall, the results obtained from this work suggest that the investigated environmental condition does not seem to influence the short term leaching behavior of nano-TiO_2 from MSW.

6. SUMMARY AND CONCLUSIONS

Given the rapid development of nanotechnology in recent years, the number of commercially available nanotechnology products has exceeded one thousand. For 2014, it is anticipated that 15% of globally available commercial goods will be nanotechnology products. Among the reported engineered nanomaterials employed in nanotechnology-based consumer products, nano-TiO_2 was the most frequently used nanomaterial. Due to the significant increase in nano-TiO_2 in commercial products, at the end of their life span, they will be ultimately sent to landfills for disposal. However, the leaching behavior of NMs during waste stabilization in landfills, which play a very vital role in integrated waste management systems, is unknown.

In order to evaluate the leaching potential of NMs from municipal solid waste in landfills, nano-TiO_2 was selected because of its widespread utilization in many commercial products. Under different environmental conditions; such as acidic or basic pH, high ionic strength, and with different concentrations of $TiO_{2,}$ batch experiments were conducted by using real and synthetic solid waste. Experiments lasted three (3) days by running three different batch tests with control experiments. The major findings of this study can be summarized as follows. For each experimental set, pH values showed a similar behavior. After the first orientation for the all operational conditions, leachate pH values were varied in the range between 5 and 7. Likewise, conductivity behaved the same way for all experimental sets. After the first adjustment as the behavior of pH, leachate conductivity values represented an increasing trend over time.

The leaching behavior of nano-TiO_2 from fresh municipal solid waste and synthetically prepared solid waste, in a broad perspective, showed approximately the same trend. Given the complexity of the real solid waste, in the reactors with synthetically prepared solid waste, Ti tended to attach to the solid surface whereas, the concentration of Ti in the real leachate was measured slightly more than the synthetic leachate had.

In most cases, calculated results suggest that a complex transient behavior of nano-TiO_2 is observed in the leachate. The majority of the TiO_2 tends to attach on the waste matrix under the all environmental conditions in this study, followed by a gradual release into the leachate.

Based on experimental results obtained during the investigation, the following conclusions are reached;

1. In the control experiment, leachate pH values were measured in the range from 6 to 8 and leachate ionic strength values showed an upward trend for both real and synthetic real waste batch reactors.
2. All concentrated nano-TiO_2 reactors showed similar behavior under the acidic condition. Leachate pH values did not change as a function of time. Moreover, leachate Ti concentrations increased between 12 and 48 hour and after that, it tended to retain to the real and synthetic solid waste surface.
3. After the adjustment of basic pH, leachate pH values reached to 6-8 in twenty-four hours and after that time, it showed a stable trend until the end of the study for both real and synthetically prepared solid waste.
4. In the high pH levels, ionic strength values showed a downward trend. Under the basic condition, leachate IS level decreased in the first six hours and it started to increase when leachate pH level reached to about 6-8.
5. In the real and synthetically prepared solid waste batch reactors, leachate Ti concentration under the basic condition displayed a decreasing trend, especially higher concentrated nano-TiO_2 tended to retain to the solid waste surface than others.
6. Under the increase ionic strength condition, leachate pH levels stayed the same level like the control experiment and when leachate pH values were between 6 and 8, leachate IS values showed an increasing trend for both real and synthetic solid waste batch reactors in the third set experiment.
7. Generally, lower concentrated of nano-TiO_2 in the batch reactors showed more tendency of retaining on the solid surface.
8. For all examined conditions, about 97- 99 % of the nano-TiO_2 was retained within the solid waste. In the both real and synthetically prepared solid waste batch reactors, the experiments performed with nano-TiO_2 showed that nano-TiO_2 tended

to retain to the solid surface under the different test conditions (acidic or basic pH levels, ranging Ti concentrations, or high ionic strength).

9. As a result of these experiments, changing pH level, the concentration of nano-TiO_2 or/and increase in ionic strength in the batch reactors showed that there was no effect on the leaching behavior of nano-TiO_2 in the real and synthetically prepared solid waste.

7. RECOMMENDATION

In this study, short term experiments were done; therefore, in order to understand and determine the leaching potential of nano-TiO_2 in municipal solid waste landfill sites, long term simulated reactor experiments are required.

In the literature, there are a lot of digestion method combinations to gain the highest recovery rate for nanomaterials. Therefore, in order to provide the most suitable digestion method for nano-TiO_2, digestion combinations should be developed.

In this study, different solid waste sample was used for each set experiment. Especially given the experiment with the real solid waste sample, it is difficult to obtain homogenized form; therefore, it may be lead to different consequences for each set experiment. Hence, if the same solid waste sample uses during the study, the results obtained from the study may be more significant and reliable.

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