The Impact of TiO$_2$ Nanoparticles on Aerobic Decomposition of Municipal Solid Waste

Mehmet Sinan Bilgili, Senem Yazıcı Guvenc, and Burcu Alan

Abstract—Titanium dioxide nanoparticles (TiO$_2$NPs) have been used in industrial and commercial products over the last decade. It is likely that these products will last in aerobic or anaerobic municipal solid waste (MSW) landfill at the end of their useful life. Therefore, the study evaluated the impact of TiO$_2$NPs on aerobic decomposition of MSW to investigate the effect of TiO$_2$NPs on leachate characterization and aerobic degradation of solid waste. Six-lab scale reactors including the different amounts of TiO$_2$ nanoparticles (0, 10, 50, 100, 500 and 1000 mg TiO$_2$NPs/kg MSW) were operated over about 106 days. The results indicated that TiO$_2$NPs have not shown a negative impact on the aerobic decomposition of municipal solid waste.

Keywords—municipal solid waste, aerobic degradation, leachate, TiO$_2$ nanoparticles.

I. INTRODUCTION

Due to the increase in the number of the nanoproducts in the market, it is expected that these products will be directly placed in landfills at the end of their useful life. Nanomaterials (NMs) are incorporated into numerous commercial products ranging from pharmaceuticals and cosmetics to alternative energy, electronic devices [1], food items, paints, energy storage devices, coatings, medical technologies and new environmental clean-up technologies [2].

The development of nanotechnology has the potential to lead to remarkable advances in technology sectors, and contribute to substantial economic growth. It is estimated that nanotechnology products will achieve a $3 trillion market with six million workers by 2020 [3]. Despite the mechanistic understanding for the many benefits to using the nanomaterials, their environmental behaviors are not completely understood. Therefore it requires novel approaches to access the likelihood of the predicted concentrations of exposure over time [4]. TiO$_2$ is one of the most used nanoparticle among all other engineered nanomaterials with up to 10,000 t/year of worldwide production [5]. It is mainly used for cosmetics industry in sunscreens and hand creams, coatings and cleaning agents, paints because of its properties as photo-catalytic activity and UV protection [6].

There are currently no regulations regarding the disposal of nanomaterials; moreover, little is known about their behaviors in municipal solid waste (MSW) landfills, the predominant global MSW disposal option. The disposal of nanowastes into landfills raises concern about the effects of the added nanoparticles on aerobic (waste degradation and leachate treatment) processes associated with landfills in addition to the potential release of these nanoparticles to the environment during the interaction with landfill leachate [7].

During aerobic degradation of municipal solid waste (MSW), biodegradable materials are converted mostly to carbon dioxide and water. Aerobic stabilization of Municipal Solid Waste (MSW) landfills has become increasingly popular in the last decade worldwide. Based on the motivation for the use of landfill aeration, the reported cases can be grouped into two main factories; acceleration of the biological stabilization of waste and reduce biogas and leachate generation [8]. Studies of aerobic landfill have indicated that the organic parts of the refuse can be degraded in a relatively short time compared with anaerobic degradation [9]. Also, it has already been successfully applied to several landfills in Europe [10] and all over the world [8, 11, 12]. There has been increasing interest in managing municipal landfills as aerobic bioreactors during recent years, and many pilot-scale and field-scale studies have been recently undertaken [13-24].

Solid waste containing nanomaterials may not be identified as such, and currently waste is not managed separately but is rather collected and treated together with ‘regular’ waste. Nanomaterials release into the environment may take place during all steps in a waste management system (e.g. collection, recycling, incineration and landfilling). Today, landfilling is the most widely applied waste management option [25]. While more than 50% of NMs produced worldwide may be landfilled [26, 27], their long-term behaviour in landfills is still largely unknown [28]. NM mobility in landfills is, therefore, affected by a range of variables, and the final release into the environment is poorly described. Existing waste regulations do not contain specific references to ENMs, although ENMs have been addressed explicitly in other recently adopted regulations (e.g. the European Cosmetics Regulation and Biocidal Products Regulation). As end-of-life (EOL) nanoproducts may not be readily identifiable as nanoproducts, it can be assumed that nanoproducts and waste containing nanomaterials are not managed as a specific waste stream [29].

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The main goal of this research was to investigate the effects of TiO$_2$ NPs on aerobic biodegradation of solid waste and behaviour of these nanoparticles on the amount of generated leachate and the changes of organic and inorganic pollutant parameters in leachate samples. For this purpose, six lab-scale aerobic landfill bioreactors, one of which was used as a control reactor and the others include different amounts of TiO$_2$ nanoparticles, were used. In this study of about 106 days, we evaluated the impacts of TiO$_2$ NPs on aerobic degradation of MSW by determining the changes in leachate pH, alkalinity, conductivity, chloride, nitrogen and organic content and the amount of generated leachate. We also determined the changes in composition of solid waste during aerobic degradation.

II. MATERIAL AND METHODS

A. The Setup and Operation of Lab Scale Bioreactors

The operating conditions of six identical laboratory-scale reactors used in this study are given in Table I. The six-lab scale bioreactors were built from 0.5 cm polypropylene material with 30 cm inner diameter and 80 cm height. The bottom part of the bioreactors consisted of 15 cm gravel and a perforated pipe (1 cm diameter) inserted to collect and discharge the generated leachate. The schematic view of these reactors is shown in Fig 1.

<table>
<thead>
<tr>
<th>Reactors</th>
<th>Amounts of TiO$_2$ NPs/MSW (mg/kg)</th>
<th>Waste (kg, wet basis)</th>
<th>TiO$_2$ nanoparticles (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACB (aerobic control bioreactor)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AT10 (aerobic bioreactor with 10 mg/kg TiO$_2$ addition)</td>
<td>10</td>
<td>43,650</td>
<td>0.429</td>
</tr>
<tr>
<td>AT50 (aerobic bioreactor with 50 mg/kg TiO$_2$ addition)</td>
<td>50</td>
<td>43,830</td>
<td>2.147</td>
</tr>
<tr>
<td>AT100 (aerobic bioreactor with 100 mg/kg TiO$_2$ addition)</td>
<td>100</td>
<td>42,250</td>
<td>4.294</td>
</tr>
<tr>
<td>AT500 (aerobic bioreactor with 500 mg/kg TiO$_2$ addition)</td>
<td>500</td>
<td>43,880</td>
<td>21.470</td>
</tr>
<tr>
<td>AT1000 (aerobic bioreactor with 1000 mg/kg TiO$_2$ addition)</td>
<td>1000</td>
<td>43,510</td>
<td>42.940</td>
</tr>
</tbody>
</table>

Leachate samples were collected while discharging leachate from the landfill reactors and kept at 4 °C in plastic bottles. Leachate samples were taken weekly during the study. The quantity of discharged leachate for each reactor was measured and then stored in a refrigerator to use for recirculation and analysis.

The municipal solid waste used in the aerobic bioreactors was obtained from Odayeri Sanitary Landfill (Istanbul, Turkey). The general composition of the municipal solid waste disposed at Odayeri Sanitary Landfill is 44% organic, 8% paper, 6% glass, 6% metals, 5% plastic, 5% textile, 9% nylon, 8% diaper, and 9% ash and others [30]. All aerobic reactors were filled with fresh solid waste, respectively, with the waste representing the bulk composition of MSW determined by waste composition analysis. During operation time, solid mass in reactors were stirred up 3 times a week and solid samples including end products were taken from the reactors and solid quality was determined by analysis.

The aeration was achieved by a compressor that was connected to the aeration pipes replaced at the bottom of the aerobic bioreactors. The aeration was started with the depletion of the available oxygen in the operated reactors. Also, temperature probes were located at 40 cm depth from the top of the waste to measure temperature variations in each aerobic bioreactor.

B. TiO$_2$ Nanoparticles

The TiO$_2$ nanoparticles were added by weight ratio (10; 50; 100; 500 and 1000 mg/kg) to each reactor except for the control reactor in order to determine the effects of titanium dioxide nanoparticles on decomposition processes in aerobic bioreactor landfill. The amount of solid waste and nanoparticles used in the reactors are given in Table I. TiO$_2$ nanoparticles were purchased from Sigma-Aldrich (product code 637254) at anatase form and <25 nm particle size. TiO$_2$ nanoparticles were added proportionally to five reactors. Adequate amount of TiO$_2$ nanoparticles were mixed with every 10 kg of solid waste before loading to the reactors in order to obtain a homogenous distribution of nanoparticles.

C. Analytical Methods

Leachate samples collected from bioreactors were analyzed according to the Standard Methods of APHA [31] and the amount of CO$_2$, CH$_4$, and O$_2$ gases of the reactors were measured by GeoTech GA2000 Plus model device. Also, pH, organic content and moisture content of solid samples were analyzed according to Standard Methods of APHA in order to determine the quality of solid waste samples during degradation. Due to the fact that solids analysis requires finely

![Schematic view of aerobic landfill bioreactor](image-url)
ground homogeneous samples, the samples were ground in a grinder to pass a 1.5 mm screen after drying at 105 °C. On the other hand, the particle size and surface area of TiO$_2$ NPs were determined by Zetasizer and BET (The Brunauer–Emmet–Teller) analysis. Prior to measurements, nanoparticles were dispersed about 20 minutes by sonification.

III. RESULTS AND DISCUSSION

A. Characterization of TiO$_2$ NPs

The particle size measurement of TiO$_2$ NPs was given in Fig 2 and the average particle size of TiO$_2$ NPs was determined to be 92 nm. BET surface area of TiO$_2$ NPs was 38,813 m$^2$/g. The other studies in literature were reported that the surface area of TiO$_2$ NPs were 21.53 m$^2$/g [32], 50 m$^2$/g [33] and 140 m$^2$/g [34].

![Fig 2. The surface area of TiO$_2$ NPs (BET analysis)](image)

B. Leachate Quality

The amount of leachate generated and cumulative leachate generation in the bioreactors are shown in Fig. 3. The lowest leachate amounts were measured at AT10 and AT50 bioreactors. After 40 days of operation, 1 liter of distilled water was added to these two bioreactors due to the not occurrence of leachate. The decrease in leachate quantity in all reactors caused by the evaporative effects of the waste temperature and the effects of air-drying of the waste [13].

The variations of pH values in all bioreactors are shown in Fig. 4. The initial pH values were about 7 in all bioreactors excluding AT10. Approximately the first 20-day period in the AT10, leachate generation was not observed. After 20 days of storage, the pH values of the bioreactors increased to 8-10 range and were changed in this range during 80 days, possibly because high-degree aerobic degradation which results in less acidification [35]. Indeed, it is common to encounter initial acidic conditions (pH=4-6) associated with the formation and dissolution of organic acids, whereas higher pH values (7-9) dominate at later stages due to the degradation of these acids and the generation of ammonium (NH$_4^+$) and CO$_2$ [25, 36]. The pH values in all bioreactors were decreased to 7.5-8 range in 90th day and there were no significant changes until the end of operation. According to the results, the presence of TiO$_2$ nanoparticles with different amounts in aerobic landfill sites did not affect the pH change over time, during aerobic degradation.

The alkalinity of water is a parameter of acid neutralization capacity and is due primarily to the salts of weak acids. The change of alkalinity in the leachate generated from bioreactors were given in Fig. 4. The initial alkalinity values were in 20,000 - 40,000 mg CaCO$_3$/L ranges in all bioreactors. Alkalinity of leachate samples decreased to 5,000 – 7,000 mg CaCO$_3$/L ranges in the first 20 days of operation in all reactors except AT10 and remained in this range during 80 days. At the end of 106 days of operation, the alkalinity was measured around 3,000 mg CaCO$_3$/L. Due to the differences in the amount and rate of leachate generation in AT10 reactor, the variations of alkalinity was varied. The initial and the final alkalinity values were 22,000 and 5,000 mg CaCO$_3$/L, respectively in AT10 reactor. According to these results, TiO$_2$ has no effect on the variations of alkalinity in leachate during aerobic degradation.

![Fig. 3 Daily and cumulative leachate generation in aerobic bioreactors](image)

The variations of the conductivity of the leachate samples from the bioreactors is shown in Fig. 5. During the aerobic degradation in all bioreactors, the conductivity of leachate varied between 10 and 25 mS/cm. Depending on the distilled water addition at 40th day, the conductivity concentrations were increased to 28 and 24 mS/cm in AT10 and AT50 reactors, respectively. However, it is not possible to say that the TiO$_2$ nanoparticles in aerobic landfill sites affects the variations of the conductivity during aerobic degradation of solid waste.
Chloride is a non-degradable parameter and the change of its concentration is commonly used to assess the variation of leachate dilution. Ehrig and Scheelhaase [37] suggested that there is no observable difference in chloride concentration between acidogenic and methanogenic phases. Similarly, Andreottola and Cannas [38] admitted that in non-recirculation landfills, chloride concentration is expected to decrease very slowly with landfill age due to washout by infiltrating water.

In Fig. 6, the initial Cl\textsuperscript{-} concentrations of leachate samples of all bioreactors were between 8,000 to 13,000 mg/L. The chloride concentrations in each reactor decreased with time to around 5,000 mg/L. The Cl\textsuperscript{-} concentrations of AT10 and AT50 bioreactors were decreased to around 5,000 mg/L at the end of the study.

The change of COD concentrations in the leachate from bioreactors is shown in Figure 7. The initial COD concentrations were between 20,000 – 75,000 mg/L range except for AT10 and AT50 bioreactors. The initial COD concentrations of these two bioreactors were measured around 10,000 mg/L in the first leachate samples generated after 25 days of operation. The maximum COD concentrations of leachate of these two reactors was not determined due to aerobic degradation conditions occurred (hydrolysis of the biodegradable organic matter) during the first 20 days operation. An increase in COD concentrations in leachate of AT10 and AT50 bioreactors was determined on 40th day. Furthermore, COD concentrations were rapidly decreased to 10,000 mg/L in the rest of the bioreactors after 20 days of operation. The final COD concentrations in leachate from ACB, AT10, AT50, AT100, AT500 and AT1000 were 3542, 5951, 4781, 4681, 3324, 3202 mg/L after 106 days, respectively.

Cossu et al. [39] determined in their study that the COD values of leachate from aerobic dry and wet reactors were lower than from an anaerobic reactor. They found that the COD value of aerobic dry and wet reactors were 3000 and 800 mg/L, respectively. The results of this study are similar to study of Cossu et al.[39], and clearly show that, the addition of TiO\textsubscript{2} NPs has not affected the rate of solid waste degradation in aerobic landfills.

The changes in the NH\textsubscript{3}-N and TKN (Total Kjeldahl Nitrogen) concentration during aerobic degradation in
bioreactors is shown in Fig. 8. The initial NH$_3$-N and TKN concentrations in leachate from all bioreactors were between 400-1200 mg/L and 500-1750 mg/L range, respectively. At the end of about 50 days of operation, NH$_3$-N concentrations in leachate from all bioreactors decreased rapidly and measured as 50 mg/L. At the end of about 80 days of operation, TKN concentrations of all leachate were decreased to 250 mg/L.

The primary aim of aerobic stabilization of solid waste is to enhance the removal processes, achieve optimum waste stabilization, decrease concentrations of leachate contaminants, reduce methane production and waste mass subsidence. Besides, the aeration of landfill has also been used as an enhancement of ammonia-nitrogen removal during the stabilization of solid waste [40]. The NH$_3$-N concentrations of each reactors were decreased during the aerobic stabilization due to the fact that most of the nitrogen in solid waste is in the form of ammonia and is produced from the degradation of proteins and amino acids [13, 41]. Therefore, the TKN concentrations in all reactors were similarly decreased due to the nitrification and denitrification processes in aerobic conditions.

Fig. 8: The changes in NH$_3$-N and TKN concentrations versus time in bioreactors

C. Solids Quality

The variations of moisture content, organic content and pH in solid samples are given in

Fig. 9: The initial moisture content of solid waste used in each reactor was measured as 62%. During aerobic stabilization, the moisture content of each reactor were decreased and the moisture content of ACB;AT10;AT50;AT100;AT500;AT1000 final products were measured as 51;56;48;57;57; and 44%, respectively. The average pH value of the final product from ACB was 7.91. Similarly, the pH values of AT10, AT50, AT100, AT500 and AT1000 products were 8.5; 8.36; 8.37; 8.1; 8.23, respectively. The amount of volatile solid in reactors was 80%, the removal efficiencies of volatile solid in ACB;AT10;AT50;AT100;AT500;AT1000 reactors were 46.25; 46.25; 40; 45; 50; 50 % at the end of 106 days stabilization, respectively. It is observed that these removal efficiencies are in accordance with the literature data. Erses et al. [42] determined that the amount of volatile solids in aerobic bioreactor was decreased from 84% to 46% (45% removal). Also, Das et al. [43] measured the amount of volatile solids decrease as 58% in their study.
D. Gas Components

Microbial respiration is a commonly used indicator in order to determine the extent of biological activity present in the aerobic degradation process. Thus, potential effects of TiO₂ NPs on aerobic degradation of solid waste could be indirectly evaluated using gas emissions. CO₂ and O₂ percentages of the generated gas samples were measured during the study. Variations of gas components versus time in bioreactors is given in

Fig. 9 Variations of pH, moisture and volatile solid content of solid waste during the experimental study

E. The Changes of Temperature in Solid Mass

As can be seen from Fig. 10, the average O₂ percentage correlated with CO₂ percentage as a result of aerobic respiration in all reactors.

Fig. 10. As expected, the average O₂ percentage correlated with CO₂ percentage as a result of aerobic respiration in all reactors.

Fig. 11, temperatures of solid mass in all reactors were increased in the first stage of aerobic degradation. After 20 days of operation, the temperatures of solid mass in all reactors were around 60 – 70 °C, because of the high-rate microbial activity. The temperatures were decreased to 22-30 °C, after the decomposition of the significant part of organic matter was completed. Thus, the temperatures of solid waste mass in all reactors were not changed during 106 days.
Depending on the obtained results, it is concluded that TiO\(_2\) NPs have not shown a negative impact on the aerobic decomposition of solid waste. Cherchi and Gu [44] and Zhen et al. [45] were explained that TiO\(_2\) NPs in high concentrations inhibited removal of nitrogen. One of the advantages of aerobic landfill is removal of nitrogen. Therefore, it is suggested that studies depending on TiO\(_2\) NPs with high concentrations are also required for the determination of removal of nitrogen in aerobic bioreactors.
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