PHOTODEGRADATION OF NON-BIODEGRADABLE ORGANIC COMPOUNDS IN LANDFILL LEACHATE BY Mn-TiO$_2$-BENTONITE

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ABSTRACT

The photocatalytic process helps to enhance biodegradability of landfill leachate. TiO$_2$-bentonite nanocrystalline powders with various Mn-doping levels were synthesized by the sol–gel process using TiCl$_4$ and manganese nitrate as precursors. The synthesized nanomaterials were characterized by X-ray diffraction analysis (XRD), Scanning electron microscopy (SEM) and Energy dispersive X-ray analysis (EDX). The experimental results indicated that the removal of chemical oxygen demand (COD), biological oxygen demand (BOD$_5$), total organic carbon (TOC) and color by 2%Mn-TiO$_2$-bentonite photocatalyst could be reached more than 81%, 83%, 65% and 96%, respectively. Under optimal conditions, the BOD$_5$/COD ratio was elevated from 0.08 to 0.40. The organic compounds in landfill leachate before and after treatment using Mn-TiO$_2$-bentonite photocatalyst were analyzed by means of high performance liquid chromatography (HPLC). The analysis result of HPLC diagrams revealed phenol, p-nitrophenol, p-crezol and some kinds of organic pollutants in the landfill leachate were totally decomposed after 12 h of treatment. Moreover, the re-usability of Mn-TiO$_2$-bentonite catalysts was also studied with good efficiency. It was concluded that the Mn-TiO$_2$-bentonite photocatalyst could be a cost-effective method for the pre-treatment of non-biodegradable organic pollutants in the landfill leachate.

Keywords: treatment of landfill leachate, Mn-TiO$_2$-bentonite, Mn doping nano TiO$_2$, photocatalyst.

1. INTRODUCTION

The leachate containing many toxic contaminates from the landfills has great threat to groundwater and surrounding soil [1]. The leachate mainly derives from percolating rainwater, containing water of the wastes piles and the degradation of organic fraction [2]. Thus, characteristics of leachate predominantly depend on ingredients of solid garbage and the biological and chemical reaction processing in the landfill as well as the climate, hydrogeology,
ages and landfill size [3–5]. In addition, the leachate has complex ingredients with high concentrations of organic compounds and ammonia, at the top strengths of 5000–20,000 mg/l and 3000–5000 mg/l, respectively [3, 4]. If the leachate is not treated appropriately and discharged directly into groundwater, it will cause serious consequences such as hypoxia, eutrophication and deterioration of the water [2–4]. In recent years, biological techniques, with advantages of reliability, simplicity and low cost, can show reasonable performance when treating young leachate (landfill age <5 years). However, when treating aging leachate (landfill age ≥5 years), physicochemical treatments can effectively remove refractory substances while biological techniques are not able to do this [6]. Recently, several studies have used advanced oxidation processes (AOP) to convert organic compounds persistent to biodegradation into the intermediate compounds which are easily biodegradable. Among these AOPs, method of heterogeneous photocatalysis oxidation using TiO₂ nanoparticles is considered as the most promising because TiO₂ is an environmentally friendly photocatalyst with high photocatalysis activity. There has been a number of studies using TiO₂ as catalyst for treatment of organic compounds with low biodegradability in leachate. However, the treatments using UV/TiO₂ grains are not economically feasible and the recovering efficiency is still low [4]. The main objective of this study is to produce the nanomaterial of Mn-TiO₂-bentonite that can be used under visible light with high photocatalytic efficiency and considerable ability to be recovered for their reuse. This study also assesses the impact of some parameters such as pH, reaction time, concentration of the catalyst on the decomposition of the organic compounds in landfill leachate.

2. MATERIALS AND METHODS

2.1. Materials

TiCl₄ 99 %, Mn(NO₃)₂, citric acid, NH₃, NH₄NO₃, methanol. All chemicals used in this research are pure. The bentonite was collected from Co Dinh, Thanh Hoa was also refined. These samples are old leachate, are collected from Kieu Ky landfill (Gia Lam district, Hanoi), which has a total area of approximately 6 hectares. This landfill has been designed for treatment of domestic wastes and operated since 1999.

2.2. Preparation of Mn-TiO₂-bentonite

The following materials were used to synthesize the material samples: pure TiO₂ particles, Mn-doped TiO₂ [5], TiO₂-bentonite [6], and Mn-TiO₂-bentonite prepared according to sol-gel citrate method. First, Citric acid and NH₄NO₃ were mixed with Mn(NO₃)₂ 0.1M solution in beaker A. Then, TiCl₄ was gradually added to this solution while mixing in 1 hour. Thirdly, the mixture of bentonite and water in beaker B was stirred in 1 h. Fourthly, the solution in beaker A was then transferred into beaker B. The pH was adjusted using NH₃ solution, pH value is 7.0. The mixture was then stirred continuously using a magnetic stirrer at 80 °C in 4 h until the gel forms. The gel was then dried, burned and heated in the oven at 500 °C in 3h to obtain the nanocomposite.

2.3. Characterization

The structure of the resulting nanocomposite was determined using X-ray diffraction (XRD), scanning electron microscope (SEM) and Energy-Dispersive X-ray spectroscopy (EDX) at the Faculty of Physics, VNU University of Science (HUS).
2.4. Experiment

Photocatalytic experiments were carried out in a 600 mL beaker, using an 85 W fluorescent lamp, located at the center of the reactor. In all experiments, the reactor was continuously aerated to provide oxygen for the photocatalytic oxidation and to enhance the contact between the contaminants and the catalysts. In all the experiments, the pH of landfill leachate samples was adjusted using NaOH 2M or H2SO4 2M. In order for powder TiO2 in leachate samples to be uniformly distributed, the suspensions were vibrated ultrasonically for at least 30 min in the dark so that adsorption equilibrium of the system prior to irradiation can occur. Then, the samples were irradiated and aerated continuously during 12 h. After reaction time of 1; 2; 3; 4; 6; 8; 10 and 12 hours, the treated leachate samples were taken from the reactor, after that the samples were centrifuged and then filtered. The nanocomposite of Mn-TiO2-bentonite was recovered after reaction. The treated samples were analyzed in HPLC and their COD, BOD5, TOC values were determined. For references, similar experiments were carried out at similar conditions but without Mn-TiO2-bentonite catalysts. Similar experiments were performed in the dark to evaluate the ability of removing organic compounds due to the absorption by Mn-TiO2-bentonite.

2.5. Analytical method

The landfill leachate samples were taken at Kieu Ky landfill (Gia Lam, Ha Noi) and stored at 5 °C. The basic physicochemical property of the landfill leachate including conductivity, pH, COD, BOD5, TOC, TSS, NH4+ were determined at the Analytical Chemical Laboratory at HaNoi National University of Education (HNUE) and Vietnam Academy of Science and Technology (VAST). The phenols compounds in the leachate were analyzed using HPLC, UV-Vis spectrophotometer, ODS C18 column. The wavelength used is 275 nm, the ratio of the solvent is: 40 % Methanol: 60 % H3PO4 (pH=2), and the column temperature is 30 °C [8].

3. RESULTS AND DISCUSSION

3.1. Characterization of material

To determine the size of synthesized TiO2, XRD patterns were measured and the size of particles was calculated using Sherrer’s formular [6]. The result is shown in Figs 1 and 2.

![Figure 1. X-Ray patterns of 2.0 % Mn-TiO2.](image1)

![Figure 2. X-Ray patterns of 2.0 % Mn-TiO2-ben.](image2)

![Figure 3. SEM images of the 2.0 % Mn – TiO2.](image3)

![Figure 4. SEM images of the 2.0 %Mn-TiO2-bentonite.](image4)

The analysis of X-ray diffraction patterns of the samples shows that the synthesized TiO2 particles occur only in antase phase, the crystal sizes calculated according to the Scherrer formular are about 15 nm for pure TiO2 and 25 nm for TiO2 doped with 2.0 % Mn. For Mn-doped TiO2 samples, there appear no strange peaks other than the ones belonging to pure TiO2, suggesting that the doping metal replaces Ti in the anatase lattice without forming a separate phase [5, 6, 9]. As shown in Fig 3, Fig 4, the SEM images indicated the uniform distribution of nanoparticles with sizes ranging from 20 nm to 30 nm. For uniformly distributed particles, the decrease in the particle sizes would increase the specific surface area and thus improve the
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Photocatalytic efficiency of TiO₂ nanoparticles. The SEM images also showed that the bentonites impregnated with Mn-doped TiO₂ have much larger sizes [5]. In this case, the Mn-doped TiO₂ is attached on the surface of bentonite to form catalytic center, the particles were uniformly distributed and the adhesion of the material on the carrier is relatively effective, increasing the yield of recovering and reusing the catalyst [5, 6]. The SEM studies of Ruby Chauhan showed that the size of Mn- TiO₂ is in the range from 10 to 20 nm [5]. In Fig. 6, the EDX diagram indicates that the percent of Mn in the lattice of TiO₂ is 1.7 %, while the theoretical value is about 2.0%. This shows that the doping by Mn is going into the crystal structure of TiO₂. The percent yield of the process is 85 %. The results are consistent with the report by by Ruby Chauhan [5].

Table 1. Characteristics of landfill leachate from Kieu Ky.

<table>
<thead>
<tr>
<th>Properites</th>
<th>Units</th>
<th>Concentration</th>
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<tbody>
<tr>
<td>COD</td>
<td>mg O₂/l</td>
<td>1208±1400</td>
</tr>
<tr>
<td>BOD₅</td>
<td>mg O₂/l</td>
<td>106±132</td>
</tr>
<tr>
<td>TOC</td>
<td>mg/l</td>
<td>125.6±155.4</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>mg/l</td>
<td>150±200</td>
</tr>
<tr>
<td>TSS</td>
<td>mg/l</td>
<td>320±345</td>
</tr>
<tr>
<td>Turbidity</td>
<td>FTU</td>
<td>20.61±21.72</td>
</tr>
<tr>
<td>Color</td>
<td>Pt–Co</td>
<td>3505±3630</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.8±8.5</td>
</tr>
<tr>
<td>Phenol</td>
<td>mg/l</td>
<td>0.05±17.02</td>
</tr>
<tr>
<td>p-nitrophenol</td>
<td>mg/l</td>
<td>0.01±2.50</td>
</tr>
<tr>
<td>p-cresol</td>
<td>mg/l</td>
<td>0.02±5.75</td>
</tr>
</tbody>
</table>

(*) non-biodegradation organic compound

3.2. Characteristics of the Raw Landfill Leachate

The landfill leachate samples were collected at Kieu Ky landfill - Gia Lam, Ha Noi. The composition was initially measured using HPLC method and the other parameters such as pH, COD, BOD5, TOC were also determined. Using high performance liquid chromatography, several organic compounds were analyzed. Based on retention time and the standard UV spectrum of the compounds, it is found that the leachate composition contains phenol (5.3 minutes), p-nitrophenol (7.1 minutes) and p-cresol (7.5 minute). The concentrations of these compounds were determined based on standard curves of phenol and p-nitrophenol, p-cresol. The analysis of COD, BOD5 showed that the COD and BOD5 concentrations of the landfill leachate are 4.5 and 3 times higher than the concentration allowed, respectively; according to national standard code 25:2009 of the Ministry of natural resources and environment of the Socialist Republic of Vietnam (QCVN:25-2009). The ratio BOD5/COD = 0.08 at pH greater than 7.8 (the results were shown in Table 1).

3.3. Optimization of photocatalytic processes

3.3.1. Effect of 2.0% Mn-TiO₂-bentonite concentration on photocatalysis of landfill leachate

The leachate was treated with 2.0 % Mn- TiO₂-bentonite sample. The amounts of catalyst used in different times were 0.0 g; 0.2 g; 0.4 g; 0.6 g; 0.8 g; in 200 ml leachate whose pH was maintained at pH = 4, and the processing time was 12 hours. The results are shown in Figure 7.
The results showed that the largest changes in COD, TOC, BOD5 occur when the catalytic 2.0 % Mn- TiO2-bentonite concentration is 2 g/l. For this concentration, COD decreases by 81 %, but BOD5 decreases by 85 %, TOC decreases by 65 % and color decreases by 96 % as compared to the case of no catalyst used (Fig. 9). After 12 hours of treatment by catalytic 2.0 %Mn- TiO2-bentonite, 24 in 26 organic compounds were completely removed (Fig. 11, Fig. 13). With the presence of above catalytic, the BOD5/COD ratio was elevated from 0.08 to 0.40. For catalytic 2.0% Mn- TiO2-bentonite concentration of 3 g/l and 4 g/l, the values of COD, BOD5 decrease but not as much as it does at catalytic concentration of 2 g/l (Fig. 7). This can be due to the fact that too much catalyst can make the solution cloudy, preventing the light refraction. Additionally, it can form precipitate that obstructs the photocatalytic reactions. The optimized amount of the catalyst obtained as 2 g catalyst per liter of leachate. Chenzhong Jia et al. [4] have studied the leachate treatment of landfills in China by P25 photocatalyst (commercial TiO2 produced in Germany), which showed that the yield of treatment is above 60 % for COD, and above 70 % for BOD5. Besides, after 72 hours of treatment by catalytic P25, 37 out of 72 organic compounds were completely removed.

3.3.2. Effect of initial pH on the photocatalysis of landfill leachate

pH of landfill leachate is an important factor to determine the efficiency of photocatalysts because it can change the pathways and the kinetic order of the degradation. The initial pH of the leachate samples was adjusted by H₂SO₄ 2M or NaOH 2M. The experiments were carried out at initial pH ranging from 2.0 to 8.0 and with 2.0 %Mn- TiO2-bentonite concentration of 2.0 g/L. The results are averaged data of three times of analysis and then are treated by statistical method.

As shown in Figure 8, the reduction of COD is more effective in strong acidic environment than that in neutral or basic environments. Specifically, at pH = 4, the reduction rates of COD, TOC, BOD5 and color are much higher than those at pH = 2 and pH > 6 [4].

3.3.3. Results of removing phenol, p-nitrophenol and p-crezol in Kieu Ky landfill leachate

To investigate the ability to remove organic compounds in leachate, acetic acid, phenol, p-nitrophenol and p-crezol were analyzed and their decreases in concentration over time were investigated. The leachate samples were treated with 2 % Mn- TiO2-bentonite photocatalyst and taken out after different treatment times to be analyzed in high performance liquid chromatography at optimized conditions. The results were shown in Figure 10 and Table 1.
The comparison of chromatographs in Figure 11, Figure 12 and Figure 13 indicated that the concentration of phenol, p-nitrophenol, p-crezol and other organic compounds in leachate relatively decreases after being irradiated by the light from an 85 W compact lamp. After 8 h, phenol decreases by 62 %, p-nitrophenol decreases by 67 %, p-crezol decreases by 78 % (Fig 10, Fig. 11, Fig. 12) . In HPLC chromatograph (Fig. 11), there are peaks of initial organic compounds, but in Fig. 13, there is no peak of p-nitrophenol, p-crezol. Peaks belonging to several other organic compounds appear but with extremely low intensity. The results showed that the initial leachate contains around 26 organic compounds. The HPLC analysis revealed that some kinds of organic pollutants in the landfill leachate were totally decomposed after 12 h treatment by 2.0 %Mn-TiO₂-bentonite. This indicates that the poisonous organic compounds in leachate samples were mineralized to form CO₂ và H₂O. This is important in the application of 2.0 % Mn-TiO₂-bentonite as a catalyst to treat landfill leachate as well as wastewater contaminated by toxic organic compounds like p-nitrophenol, p-crezol and phenol derivatives. Remziye Yazıcı and colleagues have studied the degradation of phenol compounds in anaerobic landfills, which showed that after 150 days, the concentration of phenol reduces, but for nitrophenol and the nitro group was converted into amine without being decomposed into more simple and easily biodegraded compounds [7].

4. CONCLUSIONS

In this experiment, the leachate samples at Kieu Ky landfill - Gia Lam – Ha Noi were analyzed. The analysis results showed that the concentration of amoni, SS, TOC, COD, BOD₅, organic compounds like phenol, p-nitrophenol, p-crezol, acetic acid are much higher than the amount allowed according to the QCVN25/BTNMT -2009.

The catalyst material of 2 % Mn-TiO₂-bentonite gained as nanocomposite and was used in the treatment of leachate at Kieu Ki landfill. The research results showed that pH =4 is the optimized value when studying the ability of catalyst material of 2.0 % Mn-TiO₂-bentonite.

The results demonstrated the strong oxidizing property of anatase TiO₂ nanoparticles and that Mn doping would shift the treatment wavelength to visible range region. When coating material with bentonite -based carrier, the ability to recover and reuse the material is enhanced. Therefore, the use of the material in treatment with sunlight would lower the cost considerably. Hopefully, the authors's research could contribute to the advanced methods for treatment of polluted wastewater, especially leachate from landfills in Vietnam at lower cost.
REFERENCES


