Aim and Scope

The objective of the Journal of Residuals Science & Technology (JRS&T) is to provide a forum for technical research on the management and disposal of residuals from pollution control activities. The Journal publishes papers that examine the characteristics, effects, and management principles of various residuals from such sources as wastewater treatment, water treatment, air pollution control, hazardous waste treatment, solid waste, industrial waste treatment, and other pollution control activities. Papers on health and the environmental effects of residuals production, management, and disposal are also welcome.

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aarne.vesilind@gmail.com

Doug Williams  
California Polytechnic State University, USA  
wmsengr@thegrid.net

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Recycling Oily Sludge Pyrolysis Residues as Nano-adsorbents

BING HOU1,*, SHUIXING XIE2, MIAN CHEN1, CHUAN LIANG1, HAO DENG2, RONGSHA WANG2, and GUANGQUAN LIU2

1College of Petroleum Engineering, China University of Petroleum (Beijing), China, 102249
2CNPC Research institute of Safety & Environment Technology, Beijing, China, 102206

ABSTRACT: Oily sludge is a major oily waste originating from the oil refining industry production process. It is very difficult to handle and may harm portions (i.e., ecosystems and human health) of the environment. Oil and gas may be separated from oily sludge and economically recovered by pyrolysis technology. However, the by-product residue of pyrolysis would likely contribute to secondary pollution if a disposal method was not competent. A novel nano-adsorbent, NMA-12, was developed by synthesisization between a supermolecule compound and an oily sludge pyrolysis residue with participation from chemically modified nanometer materials. Static adsorption and desorption kinetic characteristics of the adsorbent (NMA-12) were studied with Congo Red as the test adsorbate. Results suggest adsorption equilibrium time was approximately 150 minutes and that the apparent adsorption rate constant of Congo Red was \( k_{298} = 0.02 \text{ s}^{-1} \). Desorption volume of Congo Red at the same time was greater in stripping liquid where it reached 80.7% versus in pure water. This research was devoted to finding a feasible technology for treatment of oily sludge pyrolysis residues as a means of resource recycling.

INTRODUCTION

The refining industry generates more than \(100 \times 10^7\) Kg of oily sludge in China per year posing a daunting environmental challenge. Also, there is most likely more waste generated than this. Depending on source and composition characteristics, oily sludge can be classified according to four major categories [1,5,6]. The first type of oily sludge comes from cleaning tanks from the production stream for the oil gathering and processing system. It is mainly composed of sand, clay, water, and a high ratio of oil. Sand concentration is decided by lithology within reservoirs. The second type of oily sludge comes from cleaning storage tanks and is mainly composed of fine clay, water, and a high ratio of oil with serious emulsification. The third type of sludge is an oily residue from water treatment disposal systems and is mainly composed of fine clay, oil, water, macromolecular flocculating agents, and microbial slime. This sludge’s characteristics are low oil content and severe emulsification. The last type of oily sludge is soil contaminated with oil and mainly consists of sand, oil, and water.

Today, reduction, recycling, and neutralization are guiding oily sludge treatment around the world [2,3,4,7,8,9,10,11]. Oily sludge is commonly treated by such methods as solvent extraction, incineration, biological processes, carbonization, and comprehensive utilization of oily sludge based on factors such as oily sludge profile. These technologies play a key role in the treatment process but they do have limitations.

Oily sludge pyrolysis residues are wastes mainly composed of coke, ash, and other inorganic matter and require further treatment. Secondary pollution is inevitable if these residues are treated inappropriately. This paper explores the possibility of utilizing oily sludge pyrolysis residues as a nanometer-scale adsorbent by exploiting characteristics of residues. This process may provide an example of innovative resource utilization.

OILY SLUDGE PYROLYSIS TECHNOLOGY

Developed from an understanding of sludge source and composition characteristics emerging from refinery waste water, the proposed pyrolysis flowchart for the treatment process is displayed in Figure 1. After dehydration, three sludges were separated into oil, water, wastes, and non-condensable gas by pyrolysis treatment whereby each component of the mixture un-
underwent a different process. Pyrolysis oil was directly recycled. Water was disposed of via a wastewater treatment system once more. Non-condensable gas was used for pyrolysis fuel without further treatment. Wastes were used as an adsorbent and became a novel nano-scale adsorbent after further treatment.

EXPERIMENTS

Experimental Materials and Equipment

Reagents for this experiment were tetraethylorthosilicate (TEOS, industrial grade), Ammonium persulfate (APS, industrial grade), ammonia and water solution (25%) (chemically pure), N,N-Dimethylformamide, Dehydrated (N-DMF, analytical grade), anhydrous alcohol (analytical grade), acetonitrile (analytical grade), P-toluenesulfonyl chloride (PTSC, chemically pure), and Human integrin β2 ELISA Kit (β-CD, chemically pure) which was recrystallized twice with distilled water and vacuum dried before use. Oily sludge pyrolysis residues were sourced by pyrolyzing oily sludge from China’s Xinjiang Kelamayi petrochemical factory.

Instruments used included a Tensor27 Fourier Transform Infrared Spectrophotometer (Bruker, Germany), a UV-2550 UV-Vis Spectrophotometer (Shimadzu, Japan), and a TECNAI-12 Transmission Electron Microscope (Philips, Netherlands).

Method of Preparing the Nano-adsorbent

A certain amount of supramolecular compounds TEOS, APS, and oily sludge pyrolysis residues were screened out to react with PTSC and Benzene Acylation Esters (BAE) forming intermediates.

Nanometer material TiO$_2$ was found to generate reactive ions on its surface by chemical modification. Nano-adsorbent NMA-12 may be created by reaction between the active hydroxyl and Benzene Acylation Esters by self-assembly of BAE on the surface of the nanometer material.

An electron microscopy photo of the nano-adsorbent NMA-12 is displayed in Figure 2. Nano-adsorbent NMA-12 is a type of spherical particle with an average diameter of approximately 250 nm.

RESULTS

Static Sorption Kinetics Curve

NMA-12 (0.2 g) samples were placed in 100 ml Erlenmeyer flasks and 50 mL of Congo red solution (phosphate buffer, 120 mg/L, pH 6.85) was added to each flask. Flasks were oscillated at 170 rpm at 25°C. Residual concentration of Congo red in the solution was measured by applying a UV-Vis absorption spectrum for a specific time interval until adsorption equi-
librium was reached (See Figure 3) and converted to adsorbance \( (Q) \). By plotting \( Q \) against adsorption time the adsorption equilibrium time was determined to be approximately 150 minutes as displayed in Figure 4.

From the kinetics of adsorption formula, \(-\ln(1 - \frac{Q}{Q_\infty}) = kt\), the adsorption reaction rate constant \( k \) may be obtained from the slope of a straight line of \( \ln(1 - \frac{Q}{Q_\infty}) \) vs. \( t \). \( Q \) and \( Q_\infty \) in the formula indicate reaction time and amount of Congo red adsorbed by each g of adsorbent at equilibrium, respectively. The apparent rate constant of the adsorbent NMA-12 adsorbing Congo red is \( k_{298} = 0.02 \, \text{s}^{-1} \) from the slope of a straight line as displayed in Figure 5.

**Adsorption Isotherms**

Samples of adsorbent NMA-12 (0.1 g) were weighed and placed in 10 conical flasks with a volume of 100 mL per flask. Then, 50 mL of Congo red solution (phosphate buffer, pH = 6.85) at varying concentrations was placed within flasks. Samples were kept at 25°C and oscillated for 5 hours to reach adsorption equilibrium.

---

**Figure 2.** Nano-adsorbent NMA-12 photos taken by transmission electron microscopy.

**Figure 3.** UV-Vis absorption spectrum of Congo red solution with a certain amount of adsorbent NMA-12 at different adsorption times at 25°C (Adsorption time, \( t \) (curve 1–13): 0, 2, 5, 8, 15, 30, 50, 75, 100, 130, 150, 165, and 180 min).

**Figure 4.** Relationship between adsorbance and time (\( t \)).
Concentration of Congo red in the solution was measured by UV-Vis absorption spectroscopy at intervals until equilibrium was reached as seen in Figure 6.

Adsorbance, Q, was calculated and a plot relating Q and adsorbance time was created (See Figure 7). Maximum adsorbance of Congo red to adsorbent NMA-12 is 69.7 mg/g at 25°C.

When concentration of Congo red is lower than 5 mg/L the adsorbed quantity rises rapidly as concentration increases (See Figure 7). There is a different tendency when concentration of Congo red is higher than 5 mg/L. Adsorbed quantity approaches saturation value, 69.7 mg/g, asymptotically. Seen in Figure 6, it can be concluded that adsorption of Congo red to adsorbent NMA-12 follows a Langmuir adsorption model described by the following equation:

\[ \frac{C^*}{q} = \frac{C^*}{q_m} + \frac{1}{Kq_m} \]  

(1)

In this equation, \( C^* \) indicates concentration of Congo red (mg/L) in the solution at the adsorption equilibrium point and \( q \) and \( q_m \) are equilibrium adsorbance and maximum adsorbance (mg/g), respectively. Adsorption equilibrium constant is \( K \). A plot of \( \frac{C^*}{q} \) against \( C^* \) yields the curve displayed in Figure 7. The linear relationship suggests that the adsorption processes conform well to the Langmuir adsorption model. Based on slope and intercept, maximum adsorption quantity \( q_m \) is 70.1 mg/g which is approximately equal to the experimentally derived value of 69.7 mg/g. The adsorption equilibrium constant, \( K \), is 2.2 mg·L·g\(^{-2}\).

Static Desorption Kinetics Characteristics Research

Samples of adsorbent NMA-12 (1.5 g) were exposed to varying quantities of Congo red solution at 25°C under oscillation for 5 hours. Samples were filtered and dried at room temperature. Samples of the adsorbent NMA-12 (0.1 g) were weighed and put into 150 ml conical flasks with 50 mL of water and Congo red solution which contained Congo red at a concentration of 1 × 10\(^{-2}\) mol·L\(^{-1}\). Flasks were oscillated at 25°C and Congo red residual concentration in solution was measured at fixed intervals until adsorption equilibrium was reached. Plotting the desorption concentration, \( c \), of Congo red versus desorption time, \( t \), results in a Congo red static desorption curve as seen in Figure 8. Initial desorption speed was slow while the quantity of Congo red desorbed from adsorbent increased significantly in either pure water or analytical liquid.
Solution reached maximum amount desorbed after 11 hours. Maximum desorption rate in pure water was approximately 30% and increased to 80.7% in analytical liquid. Amount of Congo red desorbing from the analytical agent would increase if concentration of analytical agent in the analytical liquid were increased.

CONCLUSIONS

There are three major items to conclude:

1. Benzene acylation ester was synthesized by reaction of the main synthetic monomers such as supermolecular compounds and oily sludge pyrolysis residues with PTSC. Benzene acylation ester was modified by nanometer materials and self-assembled on the surface of nanometer material. Nano-adsorbent NMA-12 was the product.

2. Using Congo red as the test adsorbate, static adsorption kinetics characteristics of adsorbent NMA-12 were studied and adsorption equilibrium time was approximately 150 minutes. The apparent rate constant of adsorption was $k_{298} = 0.02 \text{ s}^{-1}$.

3. Static desorption kinetic characteristics of adsorbent NMA-12 were also investigated. Experimental results suggest initial desorption speed was slower while the desorbed quantity of Congo red increased significantly over time regardless of pure water or analytical liquid as the reaction medium. The solution achieved maximum desorbed amount in 11 hours. Maximum desorption rate was approximately 30% in pure water and 80.7% in analytical liquid.

ACKNOWLEDGEMENTS

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Photocatalytic Degradation of Phenol-Containing Wastewater over Cu-Bi$_2$WO$_6$ Composite under Visible Light Irradiation

JING WANG, XIAOMING GAO, FENG FU*, LIPING ZHANG and YUFEI WU

Department of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Reaction Engineering, Yan’an University, Yan’an 716000, China

ABSTRACT: A semiconductor-based Cu-doped Bi$_2$WO$_6$ photocatalyst was synthesized successfully via the hydrothermal method. As-prepared samples were characterized by XRD, UV-vis DRS, SEM, and specific surface area. Results revealed that Cu-Bi$_2$WO$_6$ presented a structure of porous microspheres and a nanosheet as well as a crystal structure of orthorhombic phase. Photocatalytic properties were evaluated by degrading phenol-containing wastewater under visible light irradiation. Results showed that Cu-Bi$_2$WO$_6$ can display a more improved photocatalytic oxidative ability than pure Bi$_2$WO$_6$. Furthermore, the possible mechanism of photocatalysis has been addressed.

INTRODUCTION

The problem that an aromatic fraction is not effectively degraded and is more poisonous in wastewater treatment has a serious influence on water quality. It had been confirmed that after it was induced by a light semiconductor, TiO$_2$ could be efficient in decomposing organic compounds [1]. Since then many studies about TiO$_2$ have been done in hopes of opening a new method for wastewater purification. However, the large band gap of TiO$_2$ makes it necessary for excitation only by UV light which limits usage efficiency of solar energy (max. 5%) and commercialization of this technology. Therefore, in order to eliminate the drawback the development of a new visible-light-driven photocatalyst has attracted greater attention.

Bismuth-oxide-based visible photocatalysts such as BiVO$_4$ [2–5], Bi$_2$WO$_6$ [6–8], and Bi$_2$MoO$_6$ [9–11] have recently drawn much interest because of their unique physical and chemical properties useful to photocatalytic oxidation. Understanding, Bi$_2$WO$_6$ a typical Aurivillius oxide structurally, related oxides with layer structure is a new hotspot for further study. It has been found to be effective to decompose organic dyes and contaminations under visible light radiation [12]. Much work has been carried out in order to enhance photocatalytic properties such as acid treatment [7], calcining [8], ionic liquid-assisted hydrothermal method [13], and the hydrothermal method [14]. These methods could improve photocatalytic properties to some extent but cannot efficiently decrease photogenerated $e^-/h^+$ recombination rate. Recently, some reports have demonstrated that doping metal or nonmetal is a feasible method for eliminating the recombination rate of photogenerated $e^-/h^+$ and improving photocatalytic activity for instance for Ag-Bi$_2$WO$_6$ [15], C-Bi$_2$WO$_6$ [16], and AgBr-Ag-Bi$_2$WO$_6$ [17].

Considering synergetic effect between metal and semiconductor components in this study, Cu was loaded on Bi$_2$WO$_6$ to promote separation of the photogenerated electron-hole and to improve the photocatalysis. Cu-Bi$_2$WO$_6$ sample was prepared by hydrothermal method. Optical properties were characterized and photocatalytic activity of the Cu-Bi$_2$WO$_6$ sample was evaluated via photodegradation of phenol-containing wastewater under visible light irradiation. As an environment-friendly and economical oxidant, air was added into the photocatalytic reaction system with which the photocatalytic reaction effect can be promoted. A possible mechanism for phenol photocatalytic degradation over Cu-Bi$_2$WO$_6$ catalyst was also discussed.

EXPERIMENTAL

Preparation of Photocatalysts

All reagents were analytically “pure” and were...
employed without any further purification. 10 mmol Bi(NO₃)₃·5H₂O was dissolved in 6 mL 15% nitric acid, 5 mmol Na₂WO₄·2H₂O was dissolved in 6 mL 15% Sodium hydroxide solution and then 0.002 g SDBS (sodium dodecyl benzene sulfonate) was added, respectively. After being stirred magnetically for 30 min the two solutions were mixed and mixture pH was adjusted by the acid/base solution above. Then, with an appropriate amount added (0.5%) Cu(NO₃)₂ the resulting solution was stirred for another 30 min. The yellowish precursor was sealed in a 25 mL Teflon liner stainless vessel which was heated to 140°C for 24 h. After the temperature slow-cooled from 140°C to 20°C the sample was filtered and washed using distilled water and absolute ethanol several times. Therefore, the yellow powder Cu-Bi₂WO₆ sample was obtained via drying at 80°C for 4 h.

**Characterization of the Photocatalyst**

Cu-Bi₂WO₆ was characterized with an X-ray diffractometer (XRD) by using monochromatized Cu Kα radiation under 40 kV (λ = 0.15418 nm) and 100 mA with the 20 altering from 20° to 80° (Shimadzu 7000, Japan). Optical diffuse reflectance spectra of Cu-Bi₂WO₆ were obtained using a UV-vis spectrophotometer (Shimadzu UV-2550, Japan) with BaSO₄ as a reference and spectral range conversion from 200 to 800 nm. Morphologies and microstructures for samples were analyzed using a scanning electron microscope (SEM) (Hitachi TM3000, Japan). Specific surface area was analyzed by N₂ adsorption-desorption measurement (V-Sorb 2800P, China).

**Photocatalytic Oxidative Degradation**

Photocatalytic properties of Cu-Bi₂WO₆ samples were evaluated by degrading phenol-containing wastewater (concentration of phenol is 5 mg/L) at ambient temperature. A reaction solution of a suitable amount (0–2.0 g/L) of photocatalyst and phenol-containing wastewater were irradiated under a visible light source (i.e., metal halogen lamp, 400 w) and stirred magnetically. Meanwhile, a specific volume (10–35 mL/min) of dry air was blown into the reaction system. The reaction solution was centrifuged at a given time interval and phenol concentration was calculated by detecting absorbance using a UV-vis spectrophotometer. Degradation rate was calculated from percentage of phenol in wastewater before (c₀) and after (cᵢ) the photocatalytic oxidation reaction according to: \( x = \frac{(c_0 - c_i)}{c_0} \times 100\% \).

**RESULTS AND DISCUSSION**

**XRD Patterns of Cu-Bi₂WO₆**

XRD patterns for samples are provided in Figure 1. Sharp and obvious diffraction peaks show that samples are well crystallized and can be readily indexed to the orthorhombic phase of Bi₂WO₆ (JCPDS No.73-1126) which has characteristic diffraction peaks at 2θ = 28.24°, 32.77°, 47.04°, and 55.90°. Because of the small amount of Cu species content (0.5%) and high dispersion in samples no obvious diffraction peaks of the Cu species may be clearly detected in samples. However, a weak peak detected at 2θ = 35.5° maybe a CuO diffraction peak so it is deduced that for these tests CuO is present in the Cu-Bi₂WO₆ system [18]. Seen in Figure 1 with a variation of pH value from 1 to 7 intensity of diffraction peaks gradually strengthens. When pH value is altered to 9 diffraction peaks quickly weakened. This indicated an improperly synthesized environment.

**UV-vis Spectra of Cu-Bi₂WO₆**

The optical absorption property of a semiconductor material is determined by electronic structure and is relative to its photocatalytic activity [19]. UV-vis spectra samples are displayed in Figure 2. According to Figure 2, both Bi₂WO₆ and Cu-Bi₂WO₆ have absorption properties from the UV light region to visible light region. Fundamental absorption edge of Bi₂WO₆ was observed in a visible light region at about 440 nm indicating visible light absorption was due to intrinsic
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Band-gap transition [20]. Considerable visible light absorption of Bi$_2$WO$_6$ is attributed to transition from the hybrid orbital of O 2p and Bi 6s to the W 5d orbital [21]. After Cu species doping, Cu-Bi$_2$WO$_6$ samples display a broader absorption edge than pure Bi$_2$WO$_6$. Absorption commences to enhance along with an increase of pH (1–7). These observed redshifts occurring after Cu species doping may be ascribed to a charge-transfer between metal ions and Bi$_2$WO$_6$ conduction band or valance band [18].

**SEM Images of Cu-Bi$_2$WO$_6$**

Light absorption and photochemical reaction take place on solid surfaces of photocatalysts. Thus, surface microstructure plays a key role in the photocatalytic process. Sample morphology and microstructure are displayed in Figure 3. Figure 3(a) shows SEM images of Cu-Bi$_2$WO$_6$ samples prepared at pH = 1 which appear as a homogeneous microspheres structure with average diameters of 3–4 µm. The high-magnification SEM image shows a rough surface and a porous structure for microspheres. Homogeneous nanosheet structure with an average size of 300 nm emerges when pH value was adjusted to 7 [See Figure 3(b)]. After pH value was adjusted to 9 as seen in Figure 3(c), the nanosheet became irregular and particle size increased to 1 µm. The aforementioned demonstrate that pH value plays a powerful role in crystal structure and microstructure.

**Specific Surface Area Cu-Bi$_2$WO$_6$**

Specific surface area is one of the key factors which
effect catalyst abilities. Surface area values for the samples are displayed in Table 1. It is clear that specific surface area for all Cu-Bi\(_2\)WO\(_6\) samples is larger than pure Bi\(_2\)WO\(_6\) sample synthesized using the same method. BET surface area increases at first and then decreases with pH value for precursors changed from 1 to 9. The largest value is 47.114 m\(^2\)/g for a sample prepared at pH = 7.

**PHOTOCATALYTIC OXIDATION PROPERTIES OF Cu-Bi\(_2\)WO\(_6\)**

**Influence of Different Prepared pH Value on Phenol Degradation**

Figure 4 displays influence of different pH values for precursors on photocatalytic activity under visible light irradiation. It can be observed that with an irradiation time increase all samples exhibit increased degradation rate. During the beginning of the reaction O\(_2\) was easily adsorbed on the catalyst surface and captured photoinduced electrons. Then, the phenol was oxidized by O\(_2\) and photoinduced holes. Until 150 min the degradation rate tends to be stable. Maybe this is because a little polymeride was produced by some by-product degradation and polymeride blocked light transmission. In addition, Cu-Bi\(_2\)WO\(_6\) demonstrates a higher degradation effect than pure Bi\(_2\)WO\(_6\). Photodegradation of Cu-Bi\(_2\)WO\(_6\) is weakened as precursors’ pH is increased. This is mainly because Cu-Bi\(_2\)WO\(_6\) crystallinity increases gradually while specific surface area quickly decreases. The latter led to a lower absorptive capacity of phenol on the surface of Cu-Bi\(_2\)WO\(_6\) particles.

**Effect of the Catalyst Amount on Phenol Degradation**

Catalyst amount is an important factor in the application of a catalyst. Figure 5 displays the result of degradation rate variation with time in the presence of different catalyst amounts. According to Figure 5, with an increase of catalyst amount from 0 g/L to 1.5 g/L degradation rate exhibits a marked increase. There are two reasons. One is an increase of catalyst amount can promote absorptive performance between active centers of a catalyst surface to phenol and movement of electron-hole pairs of Cu-Bi\(_2\)WO\(_6\). The other is an increase of catalyst amount may accelerate ·OH and O\(_2\)\(^-\) formation rate. However, when catalyst amounts are added to 2.0 g/L photodegradation is weakened. A reasonable explanation is that the catalytic particle may effect light transmittance of a solution causing higher light scattering and subsequently blocking light absorption by the catalyst.

**Affect of Air Flow on Phenol Degradation**

Appropriate addition of another oxidizing substance such as hydrogen peroxide (H\(_2\)O\(_2\)) into a photocatalytic oxidative system is a common means used to accelerate reaction. Figure 6 displays the result of degradation

### Table 1. Specific Surface Area of Samples.

<table>
<thead>
<tr>
<th>pH Value</th>
<th>Bi(_2)WO(_6)</th>
<th>Cu-Bi(_2)WO(_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>30.895</td>
<td>31.624</td>
</tr>
<tr>
<td>1</td>
<td>31.624</td>
<td>37.733</td>
</tr>
<tr>
<td>4</td>
<td>37.733</td>
<td>43.473</td>
</tr>
<tr>
<td>6</td>
<td>43.473</td>
<td>47.114</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>34.733</td>
</tr>
<tr>
<td>9</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>BET Value (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.895</td>
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<tr>
<td>31.624</td>
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<tr>
<td>43.473</td>
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<tr>
<td>47.114</td>
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<tr>
<td>34.733</td>
</tr>
</tbody>
</table>

![Figure 4. Influence of different prepared pH value on phenol degradation.](image)

![Figure 5. Effect of catalyst amount on phenol degradation.](image)
rate variation with time under different air flow rates. Two sets of information may be observed. First, one is with irradiation time lasting until 150 min and tends to be stable. Degradation rate increases quickly. The other is with an increase of air flow from 10 mL/min to 35 mL/min. Degradation rate increases first and then decreases. The largest one is obtained under 25 mL/min. A possible explanation is that oxygen absorption on the photocatalyst surface is excited by visible light generating the superoxide ion \(\text{O}_2^–\) [22] and meanwhile decreasing \(e^-/h^+\) recombination rate. The reaction was accelerated as a consequence of synergy between Cu-Bi\(_2\)W\(_6\) and O\(_2\).

**Mechanism Analysis of Photocatalytic Oxidation of Phenol**

Photochemical oxidation and photocatalytic oxidation co-exist in the Cu-Bi\(_2\)W\(_6\) photocatalytic oxidative degradation process. Under visible light irradiation, Cu-Bi\(_2\)W\(_6\) absorbs photons of specific wavelength resulting in electrons in the valence band being excited to the conduction band meanwhile leaving charged holes in the valence band [Equation (1)] which is known as light-generated electrons \((e^-)\) and hole \((h^+)\):

\[
\text{Cu-Bi}_2\text{W}_6 + h\nu \rightarrow \text{Cu-Bi}_2\text{W}_6 (h^+) + \text{Cu-Bi}_2\text{W}_6 (e^-) \tag{1}
\]

However, light-generated electrons \((e^-)\) and hole \((h^+)\) can easily recombine in bulk or on the surface of the semiconductor in the migration process leading to a marked decrease of photocatalytic reaction. A light-generated hole \((h^+)\) may migrate to the surface to directly take part in oxidation reactions with phenol [Equation (2)] and also to react with H\(_2\)O molecules to form \(\cdot\text{OH}\) free radicals [Equation (3)] that may further oxidize phenol [Equation (4)].

\[
\text{Cu-Bi}_2\text{W}_6 (h^+) + \text{Phenol} \rightarrow \text{Cu-Bi}_2\text{W}_6 + \text{Phenol Oxidation Products} \tag{2}
\]

\[
\text{Cu-Bi}_2\text{W}_6 (h^+) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \cdot\text{OH} + \text{H}^+ \tag{3}
\]

\[
\cdot\text{OH} + \text{Phenol} \rightarrow \text{Phenol Oxidation Products} \tag{4}
\]

O\(_2\) can capture light-generated electrons \((e^-)\) and thus restrain recombination of electron-hole pairs effectively [23] and produce O\(_2^–\) [Equation (5)] non-selective strong oxidizing agents that react directly with the phenol molecule causing its degradation. [Equation (6)].

\[
\text{O}_2 + \text{Cu-Bi}_2\text{W}_6 (e^-) \rightarrow \text{Cu-Bi}_2\text{W}_6 + \text{O}_2^- \tag{5}
\]

\[
\text{O}_2^- + \text{Phenol} \rightarrow \text{Oxidation products of Phenol} \tag{6}
\]

The degradation reaction was effectively enhanced regarding combined action of photochemical oxidation and photocatalytic oxidation.

**CONCLUSIONS**

A visible-light-driven photocatalyst, Cu-Bi\(_2\)W\(_6\), was successfully synthesized using a hydrothermal
method and characterized by conventional techniques. A photocatalytic property was evaluated to better understand photodegradation of phenol-containing wastewater. Results suggest the Cu-Bi$_2$WO$_6$ photocatalyst exhibited much higher photocatalytic oxidative ability than pure Bi$_2$WO$_6$. It is the desire of the authors this study may be helpful in the area of wastewater treatment.

**ACKNOWLEDGEMENT**

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Effect of Different Aeration Rates on the Composting Process and Its Enzymatic Activities

Z. XU\textsuperscript{1}, L. L. ZHANG\textsuperscript{2} and J. LF\textsuperscript{*}

\textsuperscript{1}College of Resources and Environmental Science, Yunnan Agricultural University, Kunming 650201, China.
\textsuperscript{2}College of Resources and Environmental Science, China Agricultural University, Beijing 100193, China

ABSTRACT: A pilot experiment was carried out to investigate effects of different aeration rates (A: 0.01, B: 0.02, C: 0.03, and D: 0.04 m\textsuperscript{3}·min\textsuperscript{-1}) on decomposition of organic waste and enzymatic activities during the composting process in a 100L bioreactor. Compared with lower aeration rates (A and B), higher aeration rates (C and D) could effectively improve the composting process in terms of promoting temperature and oxygen consumption, lowering C/N ratio, and significantly increasing all enzyme activities including those for protease, urease, dehydrogenase, β-glucosidase, and cellulase during the composting period.

INTRODUCTION

CHINA is a large agricultural country with large quantities of organic solid wastes generated every year. Annual production of animal manure, municipal solid waste, and sewage sludge were around 2,400, 160, and 14 million tons. Most organic solid wastes were discarded without any treatment and wastes had been considered a main non-point source form of pollution on farmland and in water bodies [29].

Composting was an important method regarding conversion of organic solid wastes into organic fertilizer which may increase concentration of organic matter in the soil. Enzymes released by microorganisms during composting break down complex organic compounds into simple water soluble material [5]. Numerous studies have shown major active enzymes involved in the composting process include: cellulases, β-glucosidases, proteases, urease, and dehydrogenase [4,6,19]. There were significant correlations between those enzymatic activities [6] and the composting process such as that of Castaldi et al. (2008) who found that hydrolase (protease, urease, cellulase, and b-glucosidase) and dehydrogenase activities were an increase of easily decomposable organic compounds in maturaition phase [6]. Enzymatic activities tended to gently decrease suggesting stabilization of organic matter. A high correlation among all enzyme activities and between each activity and water-soluble carbon (WSC) led to a conclusion that both hydrolytic and dehydrogenase activities could be feasible indicators of state and evolution of organic matter [5]. Quantifying and characterizing enzymatic activities during composting may reflect the dynamics of the composting process in terms of decomposition of organic matter and nitrogen transformations. It may also provide information about maturity of composted products [25]. Enzymatic activity determination in contrast to most analytical techniques used for compost stability evaluation was easy, fast, and relatively expensive [19].

Aeration rate is considered to be the most important factor influencing successful composting [10]. Insufficient aeration (i.e., low aeration rate) may facilitate anaerobic conditions due to lack of oxygen. Pagans et al. (2006) reported that limiting oxygen decreased biodegradability [20] while excessive aeration may increase costs and slow down the composting process via heat, water, and ammonia losses [12]. Time-continuous or intermittent ventilation were chosen. Studies have shown that different ventilation modes, composting of raw materials, and rate of aeration is not the same (e.g., 0.25 L·min\textsuperscript{-1}·kg\textsuperscript{-1} volatile solids [ventilation method is continuous aeration and raw material is dairy manure with rice straw] [15], 0.1 m\textsuperscript{3}·min\textsuperscript{-1}·m\textsuperscript{-3} [ventilation method is intermittent aeration of 30 min on/30 min off and raw material is chicken manure with straw and dry grasses] [24], and 0.4 L·min\textsuperscript{-1}·kg\textsuperscript{-1} organic matter [ventilation method is intermittent aeration of 15 min on/45 min off and raw material is grass, tomato, pepper

*Author to whom correspondence should be addressed. E-mail: ceup_si@163.com
Adequate and appropriate aeration is an important factor affecting compost temperature variation, improvement of aerobic microbial activities and enzymatic activities [21,27], and further decomposition of organic wastes [8,23]. Changes of temperature, oxygen concentration, and enzyme activities under four different aeration rates during composting were investigated. The aim was to explain a relationship between various indicators and optimal aeration mode. Furthermore, this provides a basic parameter of forced aeration for rapid composting.

**MATERIALS AND METHODS**

**Experimental Materials**

Mixtures of air-dried chicken manure, fresh furfural residue, and dry bagasse in the ratio of 4:4:1 (w.w./w.w.) were used. Chicken manure was from a farm owned by the China Agriculture University in Beijing, China. Furfural residue and bagasse were purchased from a sugar factory in Gaocheng, Hebei province, China. C/N ratio and moisture content of the mixtures were adjusted to 30% and 55%, respectively. Properties for raw materials are displayed in Table 1.

**Experimental Design**

**Basic Aeration Rate Determination**

Total weight of materials was 50 kg and about 50% of materials were assumed to be degradable. 25% was degraded after the first phase. Meanwhile, moisture was reduced by 45%. It had been calculated that total aeration was 108.34 kg of which biochemical aeration was 12.93 kg and moisture elimination aeration was 95.41 kg [7]. The time of the first fermentation phase was 15 days and the air blower switching time was in a proportion of 1:5 (opening/closing). According to these aforementioned assumptions, basic aeration rate was set as 0.02 m³·min⁻¹ (4.82 kg air·kg⁻¹ dry matter).

**Composting Set-up**

A mixture (50 kg) was thoroughly mixed as a homogenous feedstock into a horizontal and cylindrical reactor of 48 cm inner diameter and 56 cm length. Figure 1 provides a display of the structure of the experimental reactor. An “S” shaped pipeline was welded at the bottom of the fermentation tank and along the pipeline gas was pumped through a series of holes (1 mm diameter) located at 80 mm intervals.

According to the basic aeration rate of 0.02 m³·min⁻¹ (4.82 kg air·kg⁻¹ dry matter), the experiment contained 4 treatments as follows: 0.01 m³·min⁻¹ (A, 2.41 kg air·kg⁻¹ dry matter), 0.02 m³·min⁻¹ (B, CK, 4.82 kg air·kg⁻¹ dry matter), 0.03 m³·min⁻¹ (C, 7.23 kg air·kg⁻¹ dry matter) and 0.04 m³·min⁻¹ (D, 9.64 kg air·kg⁻¹ dry matter). Aeration frequency was at half-hour intervals after six minutes of aeration. The experiment was continually operated for 15 days from January 21 to February 6, 2008. Composting material was turned over once every 7 days. Samples were taken every 3 days and five sub-samples of composting material (about 500 g each) were taken from each reactor on days 0, 3, 6, 9, 12, and 15 and thoroughly mixed. Each sample was divided up into two samples, an air-dry and a fresh. The air-dried sample was prepared for chemical analysis and the fresh sample was stored at 4°C in a refrigerator for enzyme activities analysis.

**Analytical Methods**

**Physico-chemical Analysis**

Temperature and oxygen concentration were measured using thermal probes (PT100 sensor, Beijing Sailing Tech. Co., Ltd., China) and an oxygen sen-

<table>
<thead>
<tr>
<th>Materials</th>
<th>Moisture Content (%)</th>
<th>TOC (g/kg)</th>
<th>TN (g/kg)</th>
<th>C/N (–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-dried chicken manure</td>
<td>17.2</td>
<td>180</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>Furfural residue</td>
<td>46.1</td>
<td>350</td>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td>Bagasse</td>
<td>41.7</td>
<td>468</td>
<td>12</td>
<td>39</td>
</tr>
</tbody>
</table>

**Figure 1.** Schematic of the experimental reactor. (1) Fermentation vessel, (2) Electromotor, (3) Reducer, (4) Churn-dasher, (5) Probes, (6) Exhausted gas, (7) Flow meter, (8) Ventilator, and (9) Computer monitoring.
Effect of Different Aeration Rates on the Composting Process and Its Enzymatic Activities

Enzymatic Activity Assays

Samples of enzymatic activity assays were fresh and sieved (< 2 mm). Activities of protease, urease, and dehydrogenase were measured according to Alef and Nannipieri (1995) [2]. Procedures for evaluating cellulase activity was taken from Li et al. (2008) [15].

Statistical Analysis

Statistical analysis of data was carried out using SPSS 11.5 for windows. One-way analysis of variance (ANOVA) was used to compare mean values from different treatments (LSD, P < 0.05). Bivariate correlation was used to analyze relationships among various indicators.

RESULTS AND DISCUSSION

Temperature and Oxygen Concentration Changes

Effect of different aeration rates on composting temperature is displayed in Figure 2(a). The experiment was conducted in spring with an ambient extra ventricular temperature below 5°C and room temperature at about 10°C. Temperatures of treatment C and D were increased above 50°C after four days of composting and average growth rates of temperature were 0.76°C·h⁻¹ and 0.8°C·h⁻¹, respectively. On other hand, 6 days and 5 days were needed for treatment A and B to get temperatures above 50°C. Average growth rates of temperature were only 0.53°C·h⁻¹ and 0.66°C·h⁻¹, respectively. The thermophilic phase (> 50°C) of treatment A, B, C, and D were 5.0, 5.2, 5.9, and 6.2 days, respectively. The highest temperature of treatment A, B, C, and D were 58.5, 57.5, 60.5, and 64.5°C, respectively. Results suggest that a higher aeration rate (C and D) could effectively improve the composting process compared with the lower aeration rates of A and B.

Changes of oxygen concentration during composting are displayed in Figure 2(b). Oxygen concentrations for all treatments had no differences for the first two days. Oxygen consumption started to increase and oxygen concentration of the pile reduced markedly within 4–9 days of thermophilic phase. Oxygen concentrations in the pile were increased at the later stages of 10–15 days. During the entire process of composting, oxygen concentration in the piles was maintained from 8 to 20%. However, treatments with a higher aeration rate (C and D) could maintain a higher degree of oxygen concentration than that of lower aeration rates (A and B) during periods of high temperature.

Aeration rate effected rate of raising temperature during composting. Conversely, the temperature of composting effected oxygen concentration in piles and there was a very significant negative correlation observed between temperature and oxygen concentration ($r = -0.918, p < 0.01$).
C/N Ratio and Water-Soluble Carbon (WSC)

C/N ratio is a proper index used to evaluate compost maturity. Changes in C/N ratios were a result of changes in nitrogen contents and organic matter. As seen in Figure 3(a), C/N ratio for all treatments gradually declined from 29 to around 20 at the end of 15 days of composting. Especially, C/N was reduced more rapidly in higher aeration rate treatments for C (20) and D (18.9). This decline was due to the formation and loss of CO$_2$ [13]. Raut et al. (2008) also suggested a C/N ratio below 20 is indicative of acceptable compost maturity that during efficient composting is obtained due to degradation of organic matter [21]. However, treatment C and D were not significantly different (p < 0.05) for day 15.

Water-soluble carbon (WSC) was one of the readily biologically active parameters effecting compost stability [6,17]. WSC concentrations decreased gradually during the composting process for all treatments of A, B, C, and D. Figure 3(b) also displays degradation of soluble organic carbon for all treatments during 6–12 days of composting. Therefore, it showed that a higher aeration rate promoted decomposition of organic matter and benefited the process of composting.

Enzyme Activities

Protease activity was closely related to the nitrogen cycle and catalyzes the hydrolysis of proteins to ammonia while acting on short-chain polypeptide substrates. Liu et al. (2011) also reported protease is an important enzyme and considered as an appropriate indicator of organic matter decomposition during composting [17].

During the beginning days of the in-vessel composting process protease activity was increased for all treatments [See Figure 4(a)]. Enzymes were decreased gradually up to 15 days of treatment after three days of composting. Initial increase of protease may be due to availability of polypeptides in the initial mixture. It was interesting that a higher aeration ratio benefited protease activity during an earlier stage of composting (0–3 days) with a peak order of D > C > B > A. Aira et al. (2007) suggested protease activity is highly dependent on substrate availability. Here, the decline of protease at end of the composting process is demonstrated [1].

Changes of urease activity were similar to those of protease [See Figure 4(b)]. Among the different aeration treatments urease activity was higher for treatment D and C than for B and A. Urease activity increased at the beginning of composting most likely due to a high degree of substrate availability [11]. Also, urease activity was closely related to the nitrogen cycle since it is related to hydrolysis of urea to ammonium and carbon dioxide.

Figure 4(c) displays changes in dehydrogenase activity during composting. Mokhtari et al. (2011) suggested the dehydrogenase enzyme was produced as a result of microbial activity [18]. Xiao and Zeng (2009) found dehydrogenase enzyme activity increases rapidly from 0.75 to 3.42 mg Triphenylformazan (TPF)/g.day in the early days of composting and then a decreasing trend starts that finally reaches 0.45 mg TPF/g.day at the end of the cooling (mesophilic) phase [29]. It was discovered that dehydrogenase activity increased rapidly up to 6 days and hits the peak at high-temperature stage. Then, it decreased gradually. Xiao and Zeng (2009) also found a similar pattern of initial increases and final decreases of dehydrogenase activity for the
Effect of Different Aeration Rates on the Composting Process and Its Enzymatic Activities

in- vessel composting process [29]. Dehydrogenase activity for treatments D and C were significantly higher than for treatments A and B (p < 0.05). Dehydrogenase activity for treatment B was also higher than for treatment A but there were no significant differences between treatments C and D (p < 0.05). Since dehydrogenase was involved in respiratory chains for all microorganisms its activity was used as a measure of overall microbial activity [22]. Dehydrogenase activity was negatively correlated with oxygen concentration and positively correlated with temperature similar to those of Barrena (2008) [4]. Dehydrogenase activity was correlated with urease activity ($r = 0.892$, p < 0.01) and cellulase activity ($r = 0.695$, p < 0.01).

Figure 4(d) displays cellulase activity for different aeration experiments. Results suggest that cellulose activity increased in the first 9 days and then was followed by a decline in accordance with the findings of Raut et al. (2008) [21]. However, cellulase activity increased again during the cooling phase. During the high-temperature period, cellulase activity for treatment D was significantly higher than that for other treatments (p < 0.05). Cellulase activity for treatment A was the lowest and there were no significant differences between treatments B and C (p < 0.05). Finally, cellulase activity was correlated with temperature ($r = 0.608$, p < 0.01), WSC ($r = 0.507$, p < 0.05).

CONCLUSIONS

Treatment using a basic aeration rate ($0.02 \text{ m}^3\text{min}^{-1}$, $4.82 \text{ kg air} \cdot \text{kg}^{-1} \text{dry matter}$) was able to complete the composting process. It was appropriate to increase aeration (i.e., $0.03$ or $0.04 \text{ m}^3\text{min}^{-1}$, $7.23$ or $9.64 \text{ kg air} \cdot \text{kg}^{-1} \text{dry matter}$). It was more advantageous to raise temperature, maintain concentration of oxygen in the pile, decrease C/N, and promote aerobic activity for the in-vessel composting process.

Regarding treatments with an aeration rate of $0.03–0.04 \text{ m}^3\text{min}^{-1}$ ($7.23–9.64 \text{ kg air} \cdot \text{kg}^{-1} \text{dry matter}$), it was observed that notable enzyme activity increased with protease, urease, dehydrogenase, and cellulase during the earlier stages of composting as compared with those with a rate of $0.02 \text{ m}^3\text{min}^{-1}$ or less. This reflects the fact that appropriately increasing aeration rate could promote the process of aerobic composting.

The aeration rate ($0.02 \text{ m}^3\text{min}^{-1}$, $4.82 \text{ kg air} \cdot \text{kg}^{-1} \text{dry matter}$) was used to meet the basic needs of the composting process. Aeration rates of $0.03–0.04 \text{ m}^3\text{min}^{-1}$ ($7.23–9.64 \text{ kg air} \cdot \text{kg}^{-1} \text{dry matter}$) were more helpful for carrying out the composting process.
ACKNOWLEDGMENTS

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REFERENCES

Trimethylamine Biofiltration and Isolation of a TriMethylamine-Degrading Strain from the Biofilter

JUN YIN¹,²,* and WENFENG XU³

¹School of Environmental Science & Engineering, Zhejiang Gongshang University, Hangzhou 310012, P.R. China
²Department of Environmental Engineering, Zhejiang University, Hangzhou 310029, P.R. China
³Hangzhou Academy of Environmental Science, Hangzhou 310014, P.R. China

ABSTRACT: A bacterium colonized in a laboratory-scale compost biofilter fed with trimethylamine (TMA) was isolated and characterized. The compost biofilter was operated with an influent TMA for 60 days. Results demonstrated that nearly all influent TMA may be removed in the biofilter. A microbial isolate TDB1 was selected based on its efficiency for maximum and faster biodegradation of TMA. It may grow both aerobically as well as anaerobically under nitrate reducing conditions with TMA as a sole carbon and energy source. According to 16S rDNA gene sequencing, strain TDB1 was assigned to the species Paracoccus aminovorans.

INTRODUCTION

TRIMETHYLAMINE (TMA) is potentially toxic and a likely carcinogenic volatile organic compound responsible for strong odor emissions. It is also a threat to public health because of its tissue-corrosive and tissue-penetrative properties. TMA is often released from the fish-meal manufacturing processes [1–3], the wastewater treatment process, waste disposal via a landfill, livestock farming, and hog manure [4–7]. TMA has also been known to inhibit synthesis of macromolecules such as DNA, RNA, and proteins as well as having a teratogenic effect on animal embryos [8]. Thus, microbial degradation would be useful to eliminate TMA from contaminated environments.

Biofiltration is believed to be one of the best technologies in terms of its technical and economical aspects and especially for treatment of low-concentration polluted air streams. Under proper conditions, high removal efficiencies may be achieved and the process is environment friendly [9,10]. Few reports have been made related to bioconversion of TMA as a sole target in biofilters. Chang et al. [7] used an aerobic biofiltration system containing entrapped mixed microbial cells (EMMC) for removal of (CH₃)₃N-dominant waste gases. Various natural or synthetic materials are widely used in biofiltration reactors. Most commonly, peat, bark, compost, and wood pellets are used. Synthetic media include ceramic, plastic, and glass. The choice of filter material is based on many parameters influencing attainable degradation performance but also on the avoidance of channelling and clogging problems. One kind of commercial compost was used which was mainly composed of pig manure and agricultural by-products and was chosen to exploit microflora.

Recently, efforts are also being made to find high-performance biocatalysts. Inoculating bacteria in biofilters or simply favoring their growth seems to represent an interesting option for improving performance of biofilters treating air contaminated with volatile organic compounds. Conventional techniques of isolating bacteria were used to obtain pure bacterial stains. Until now, mainly two species of denitrifying bacteria, Hyphomicrobium sp. [11] and Paracoccus sp. [12,13], have been reported as trimethylamine degraders. High elimination capacity of TMA was established in a biofilter filled with compost. The design was to isolate and identify TMA-degrading bacterial species from a compost biofilter using 16S rDNA gene sequencing. Results are useful for understanding mechanisms related to conversion of a target contaminant and for providing an economical and effective alternative for odor control.

MATERIALS AND METHODS

Biofiltration Experiment

The biofiltration experiment was performed using an
identical biofilter system (15 cm in diameter and 1.0 m in length) as described by Yin et al. [14] The bench-scale biofilter was divided into three equal sections for representative gas sampling from the bottom to the top along the column, Port 1, Port 2, and Port 3, respectively. Sections were flanged and each section could be dismantled to replace and sample filter material and to clean filter columns before and after use. TMA gas was made by injecting a TMA-containing solution into a mixing bottle using a syringe pump and a gas-tight syringe. Inlet air from the air pump was humidified to prevent the biofilter matrix from drying and then it flowed into the biofilters mixed with TMA-containing gas. The gas inlet flow was controlled by a rotameter. TMA concentration by gas flow was kept constant by adjusting the injection rate of the solution and flow rate of the air stream. TMA concentration was initially set at 19.2 mg/m³ and then was gradually increased from 19.2 to 57.2 mg/m³ after 14 days. TMA was provided as sole carbon source and nitrogen source. Compost was used as packing material for the biofilter. Compost was a commercial product and was composed mainly of pig manure and agricultural by-products.

Bacterial Isolation

Compost samples were collected from the bottom layer of the biofilter. Compost (10 g) was placed directly into 90 mL of sterile mineral medium (i.e., 1.0 g of KH₂PO₄, 2.6 g of K₂HPO₄, 0.2 g of MgSO₄·7H₂O, 0.2 g of NH₄Cl 0.2 g, 0.25 g of KCl, 0.01% yeast extraction, 1,000 mL of distilled water, and a pH of 7.2) and was shaken for 15 min. A series of dilutions were made to reduce cells in samples. One mL of diluted sample was spread onto the surface of the mineral medium containing TMA in petri dishes and inoculated at 30°C and allowed to grow for 48–72 h. A single developed colony was picked on the TMA-mineral medium plates and subcultured to purification. Pure bacterial strains were obtained after successive transfer of individual colonies in TMA-mineral medium plates and incubated for 24 h at 30°C. After purity tests microorganisms were subjected to an extensive phenotypic investigation including cell morphology, Gram staining, and carbon and nitrogen source typing.

16S rDNA Sequencing and Data Analysis

DNA isolation and genomic DNA extraction from isolated cultures was performed as described by Ausubel et al. [15]. Universal bacterial 16S rDNA gene primers corresponding to the Escherichia coli position 8f and 1541r were used for polymerase chain reaction (PCR) amplification of the 16S rDNA gene. The forward primer 8f was 5'-AGAGTTTGATCTGCTCAG-3'. The reverse primer sequence R1541 was 5'-AAGGAGGTGTCAGCCTGCA-3'. These 50-µl reactions were performed using Taq polymerase with the following thermocycling program: 1 × (2 min, 94°C), 30 × (1 min, 94°C; 1 min, 56°C; and 2 min, 72°C), 1 × (10 min, 72°C), and 1 × (10 min, 60°C). All reactions were run using an Eppendorf Thermal Cycler (Hybaid, Teddington, Germany). PCR products were purified using a QIAquick PCR purification kit (Qiagen, Valencia, Calif.). Purified PCR products were sequenced by the Shenyou Biotechnology Company (Shanghai, China). Sequence was initially analyzed at the NCBI server (http://www.ncbi.nlm.nih.gov/) using the BLAST (blastn) tool. Corresponding sequences were downloaded.

Performance of the Strain under Aerobic and Anaerobic Conditions

All aerobic batch cultivations were carried out in 500-mL Erlenmeyer flasks containing 100 mL of medium. Flasks were shake-incubated at 30°C at 110 rpm. Strict anaerobic techniques were followed for anaerobic medium preparation, for aseptic handling, and for sampling of denitrifying cultures throughout the study. 100 mL of MSM with 30 mM nitrate was dispensed into a 125 mL serum bottle. Nitrogen gas was passed through an oxygen-trap filter (Chemical Research Supplies, Addison, IL) and was continuously flushed during dispensing of the medium. It was placed into the bottle for 5 min before it was tightly closed with a butyl-rubber stopper and aluminium seal. The redox potential of the medium was reduced by adding an anoxically prepared stock solution of Na₂S (0.2 M) to a final concentration of 0.2 mM. To avoid oxygen contamination during withdrawal of culture samples after sampling, nitrogen gas was additionally supplied. All cultures were incubated in the dark at 30°C and 110 rpm.

Analytical Methods

Cell growth was determined by the optical density (OD) of cultures at 650 nm using a spectrophotometer (Beckman, Fullerton, CA). During incubation, 2mL of culture fluid was sampled. Samples were filtered through a PVDF 0.22-µm-pore-size Millipore filter
and stored at −20°C until analyzed. Trimethylamine, dimethylamine, and methylamine were analysed in a gas chromatograph (GC) (SP-2000, Shandong, China) equipped with a glass column packed with GDX-401 coated with 4% PEG-20M + 1% KOH and with a flame-ionization detector. Injector temperature was 180°C, the detector temperature was 110°C, and the oven temperature was 180°C. Nitrogen at 40 mL/min was used as a carrier gas for GC analysis. Ammonia concentration was determined by the spectrophotometric method using Nessler reagent. Nitrite and nitrate were analysed using standard analytical methods (Chinese Standard Methods for the Examination of Water, 2002).

RESULTS AND DISCUSSION

TMA Removal

Compost had lower bulk density and porosity and therefore was easily compressed. Properties of lower bulk density and higher gas resistance for compost indicated that compost had a higher volumetric specific area for microbial growth. Bardke et al. [16] reported that media with a higher volumetric specific area were more efficient than those with a lower specific area for removing VOCs from gas streams. Therefore, the compost biofilter was expected to achieve better effectiveness in terms of TMA removal.

Results from removal of TMA by the biofilter is displayed in Figure 1. During the experiment, removal efficiency (RE) of TMA maintained 100% (i.e., no TMA detected). It was noticed that because the biofilter was operated in an upward-flow regime a majority of TMA was removed in the first section (Section 1). From day 45 TMA in the effluent of Port 1 was detected (See Figure 1), whereas for the other ports no TMA was observed. No NH₃ was detected during the initial period at any port before day 15 indicating complete elimination of TMA through sorption and absorption. However, on day 28 a steadily increasing concentration of NH₃ was observed in Port 1 which indicated the absorbed TMA had been degraded into NH₃ by microorganisms in the packing material. Highest concentration of NH₃ was detected in the effluent of Port 1 but little was detected in Port 2 and 3 (data not shown). It may be estimated that biodegradation of TMA mostly occurred in the first section of the biofilter. Ammonia generated in Section 1 was absorbed and partially nitrified in the upper sections. Due to relatively low NH₃ loading nearly all NH₃ was eliminated from the gas.

These results indicate that the biofilter may remove all potential odor and elimination ability was high.

Metabolic products including pH, ammonia, nitrite, and nitrate in compost were analysed within Section 1. Variations of pH, ammonia-N, nitrite-N, and nitrate-N contents in the biofilter are displayed in Figure 2. Discussed previously, TMA in the medium was biodegraded into NH₃. Content of NO₂⁻-N from day 26 remarkably increased indicating that nitrification had taken place. Ammonia was continuously transformed into NO₃⁻-N by nitrifiers which accumulated in each section and resulted in a pH decline. After day 39, the content of NO₃⁻-N in section 1 suddenly dropped and was probably attributed to the decline of sorption of NH₃ with decreasing moisture from 67.2% to 59.2% (data not shown).
Mechanism of Biodegradation of TMA

According to results, TMA elimination mechanisms by microbial communities in the packing material may properly be proposed with the following reaction equations Equation (1), Equation (2), and Equation (3):

\[ 2(CH)_3N + 9O_2 \rightarrow 6CO_2 + 6H_2O + 2NH_3 \]  

\[ 2NH_3 + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 2H^+ \]  

\[ 2NO_2^- + O_2 \rightarrow 2NO_3^- \]  

It was discovered that there was NH_3 in the effluent gas stream from Section 1 of the biofilter which indicated degradation of TMA carried out by TMA-degrading bacteria and hydrolysis of the influent TMA to NH_3 was evident [See Equation (1)]. NH_3 products could further be successfully converted to NO_2^- [See Equation (2)] and then to NO_3^- [See Equation (3)] and accumulated in the medium. Compost with features of higher volumetric specific area and better water-holding capacity could help maintain an advantageous medium for growth and activity of ammonia-oxidizing bacteria. Also, Bardtke [16] results were confirmed. It needn’t be inoculated with nitrifying bacteria because ammonia-oxidizing bacteria had already existed there [14].

Isolation of Bacterium

Since accurate identification of environmental bacteria is essential in order to achieve a better understanding of the biodegradation process, microbial isolation and identification were performed and evaluated. Using agar plates containing TMA as a sole carbon source colonies are pinhead size, circular, smooth, convex, entire, transparent, and yellowish white after 10 days of incubation. The isolate, strain TDB1, is gram-negative, non-motile, non-spore forming, and a short rod (0.5 × 0.9–1.2 µm). Figure 3 displays gram-staining identifications from the compost biofilter. The culture exhibited good degradation ability in a pH range from 6.5 to 8.0 and in a temperature range from 30 to 37°C. No addition of vitamins is required. Electron acceptors are oxygen and nitrate. Physiological reaction profile of strain TDB1 was characterized by successful growth on the TMA, DMA, and MA. This property was also found for Paracoccus aminovorans. Glucose, mannitol, acetate, and formate may serve as carbon sources. However, glutamate and malate cannot be used. Amino acid, sodium nitrite, ammonium sulphate, and urea may serve as nitrogen sources. Nitrate may not be utilised as a nitrogen source. Yet in contrast, Paracoccus aminovorans could not utilize formate. Strain TDB1 could use urea as nitrogen source and converted nitrate to nitrite under anaerobic conditions.

Bacterial Identification Based on 16S rDNA

Using internal primers the 509 bp sequence of amplified 16S rDNA gene fragment was determined. Sequence analysis results for 16S rDNA are displayed in Figure 3. The BLASTN search indicated that the organism belongs to Proteobacteria, α subdivision, Paracoccus genus. According to the BLASTN analysis, the 16S rDNA nucleotide sequence from the TMA-degrading bacterium was 98.8% identical to a corresponding sequence from Paracoccus aminovorans.
Trimethylamine Biofiltration and Isolation of a Trimethylamine-Degrading Strain from the Biofilter

Kim et al. [17] first reported that a strain T231 had two different pathways for aerobic and anaerobic degradation of trimethylamine. Based on 16S rDNA analysis the strain was identified as a Paracoccus sp.

**Aerobic Degradation of TMA**

Under oxic conditions biodegradation of TMA as a sole carbon and energy source by strain TDB1 is displayed in Figure 4. Cell growth entered into the exponential-growth phase after 10 hours. Within 24 hours the biomass reached a maximum value followed by a decline in biomass concentration. Aerobic degradation of TMA supported cell growth indicates the strain utilized these substrates as a carbon source as well as an energy source. Strain TDB1 completely degraded 8.9 mM TMA in 15 h (See Figure 4). During degradation of TMA dimethylamine (DMA) was accumulated and subsequently degraded suggesting DMA is a metabolic intermediate of TMA. Ammonium concentration followed a similar pattern to biomass growth. It concomitantly increased during degradation of TMA and then experienced an obvious decline. It has been demonstrated that ammonium is an end metabolic product of degradation of methylated amines. The fact that ammonium was released in the culture fluid in each case suggests methylated amines were completely metabolized by this strain.

**Anaerobic Degradation of TMA**

Under denitrifying conditions with 30 mM nitrate, the anaerobic biodegradation of TMA by strain TDB1 is displayed in Figure 5. Cell growth entered into the exponential-growth phase after 12 hours. In the presence of 30 mM nitrate strain TDB1 completely degraded 16 mM trimethylamine in 42 h [See Figure 5(a)]. During anaerobic degradation dimethylamine and methylamine were produced and accumulated. When TMA was degraded completely at 42 h the DMA concentration reached a maximum at 15 mM and subsequently degraded. At 60 h MA accumulated to 1.9 mM. This suggests TMA was metabolized via DMA and MA. During degradation of TMA concomitant nitrate consumption and cell growth were observed [See Figure 5(b)]. Nitrite, an intermediate of nitrate reduction, was detected during this culture period but its concentration was very low suggesting nitrate was an electronic acceptor during degradation of TMA.

![Figure 4. Aerobic degradation of TMA by strain TDB1.](image)

![Figure 5. Anaerobic degradation of TMA by strain TDB1 in the presence of 30 mM nitrate.](image)
Enzymes related to TMA degradation were not assayed. According to the literatures some enzymes have been reported to catalyze methyamine metabolism such as methyamine oxidase [17], methyamine dehydrogenase [18], N-methylglutamate synthase [19], and N-methylalane dehydrogenase [20]. Cell-free extracts of Paracoccus sp. T231 grown on trimethylamine under aerobic conditions created (i.e., detected) the following enzyme activities: trimethylamine mono-oxygenase, dimethylamine mono-oxygenase, methyamine mono-oxygenase, and trimethylamine N-oxide demethylase [3]. Trimethylamine dehydrogenase and dimethylamine dehydrogenase were found in cells grown under denitrifying conditions which suggests the pathway for anaerobic degradation of trimethylamine is different from the pathway for aerobic degradation. Hyphomicrobium X oxidized trimethylamine with trimethylamine dehydrogenase both aerobically and under anaerobic denitrifying conditions.

CONCLUSIONS

A laboratory-scale biofilter was operated with an influent TMA concentration of 19.2–57.2 mg/m³ for 60 days. TMA was successfully removed by the biofilter with an efficiency of 100% and most of which was eliminated in the first section. Evaluating analysis of variations for the properties of the compost packing material it was observed that compost not only treats TMA effectively but also eliminates NH₃ produced completely by the nitrification process. According to above phenomenon, TMA elimination mechanisms by microbial communities in the packing material may properly be proposed. First, TMA was biodegraded to NH₃. NH₃ produced may further be converted to NO₃⁻-N and then to NO₂⁻-N accumulating in the compost.

A bacterium (TDB1) colonized in the compost biofilter was isolated and characterized which is identified as Paracoccus sp. by biochemical methods and 16SrRNA analysis. The strain may grow both aerobically as well as anaerobically under nitrate reducing conditions with TMA providing a sole carbon and energy source. It aerobically degraded trimethylamine via dimethylamine and methyamine and released the ammonium ion into the culture fluid as a metabolic product. The strain also degraded trimethylamine under denitrifying conditions and consumed nitrate. This demonstrates that complete degradation of trimethylamine was coupled with nitrate reduction. According to the 16S rDNA gene sequencing the isolated strain was assigned to the species Paracoccus aminovorans.

ACKNOWLEDGMENTS

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REFERENCES


Adsorption Behavior and Removal of Organic Materials from TNT Red Water by Lignite Activated Carbon

YIHE ZHANG¹,*, FANGFANG WEI¹, JING XING¹, FENGZHU LV¹, XIANGHAI MENG¹ and PAUL K. CHU²

¹National Laboratory of Mineral Materials, School of Materials Sciences and Technology, China University of Geosciences, Beijing, 100083, China
²Department of Physics & Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

ABSTRACT: Red water produced by manufacturing of 2,4,6-trinitrotoluene (TNT) is treated by lignite activated carbon (LAC) which is much cheaper than common activated carbon. Optimized conditions for adsorption were determined and experimental results suggested pH, initial concentration, time, and adsorbent dose effect adsorption. The adsorption process follows a pseudo-second-order kinetics model controlled by pore diffusion and an adsorption isotherm may be fitted using the Langmuir model. Most organic components in red water are adsorbed by hydrogen bonds between the LAC and organic materials. Results suggest LAC is an alternative for treatment of red water.

INTRODUCTION

According to pollutant characteristics, TNT waste water may be categorized as yellow water, red water, pink water, and condensates [1]. TNT red water is an aqueous effluent produced during the purification step of trinitrotoluene (TNT) production. During the purification stage, sodium sulfite is added to react with the asymmetrical nitrotoluenes leading to formation of dinitrotoluene (DNT) sulfonates (2,4-DNT-3-sulfonate and 2,4-DNT-5-sulfonate) [2]. Red water contains products of incomplete nitrate compounds as well as other complex by-products formed during nitration and purification stages in addition to DNT sulfonated compounds. They create concern related to environmental pollution and public health since most of them are toxic and mutagenic to humans and other animals even at low concentrations [3–6]. Dark red and opaque waste water has high concentrations of dissolved organics and tends to be difficult to handle.

Common treatment methods for TNT waste water include activated carbon adsorption [7–8], incineration, biodegradation [9], advanced oxidations such as oxidation with hydrogen peroxide/ozone [10], supercritical water oxidation [11], Fenton reagent oxidation, photocatalytic oxidation [12,13], and so on. Although incineration of TNT is one of the most effective and commonly used processes it is expensive due to high fuel costs [14]. Also, burning emits gaseous pollutants into the environment [15,16]. There have been relatively few studies on biodegradation of TNT in an aqueous medium and most previous studies on TNT biodegradation focused on treatment of TNT contaminated soils [17–19]. There are several challenges such as resistance under aerobic conditions in the presence of electron-withdrawing nitro constituents in explosives that inhibit electrophilic attack through enzymes [20]. Furthermore, biological methods require a longer degradation time. Since the method of advanced oxidations must be carried out under extreme reaction conditions it is difficult for many TNT plants to perform the costly task.

Activated carbon is frequently utilized to clean polluted water and it is feasible to use granular activated carbon (GAC) to treat drinking water contaminated with TNT. Maloney et al. [21] have evaluated an anaerobic fluidized bed reactor (FBR) composed of GAC in the treatment of TNT pink water. It can remove 99% of DNT and is a highly efficient method. Rajagopal and Kapoor [7] have studied adsorption characteristics of nitro-organics such as trinitrotoluene (TNT), dinitrotoluene (DNT), and nitrobenzene (NB) on GAC and obtained optimal conditions. A model has been developed to predict adsorption dynamics and the effects of various parameters on adsorption characteristics. Marinovic et al. [22] have investigated effects of dynamic TNT adsorption on GAC. Effects of temperature, concentration, and flow rate using a chromatographic system were examined and the possibility of desorb-
ing TNT from saturated activated carbon was explored. Vasilyeva et al. [23] have studied the oxidation mechanism of carbon on TNT and found that activated carbon can accelerate TNT oxidation forming unextractable residues. Strong binding may be attributed to catalyzed oxidation of the TNT methyl group, probably via a free radical mechanism involving chemisorption of the oligomers and polymerized products that do not desorb from micropores. Therefore, TNT oxidation and residue formation after adsorption by activated carbon increase effectiveness of activated carbon to decontaminate water.

It is important to find an economical and efficient method to remove TNT in spite of scattered success. LAC which is much cheaper than common activated carbon and seldom used to treat TNT red water was employed. The optimal conditions, thermodynamics, and kinetics of the adsorption process were also studied.

METHODLOGY

Materials

TNT red water was supplied by Dongfang Chemical Corporation, Hubei Province, China. LAC was supplied by Datang Co. Ltd. All other chemicals were analytical reagent grade.

Experimental Procedures

Batch experiments were carried out in a series of 100 mL conical flasks in which a certain quantity of LAC and 50 mL of TNT red water were added. Bottles were shaken in an SHA-BA water bath with a constant temperature oscillator at a speed of 150 rpm and temperature of 25 ± 0.2°C. Effects of pH and reaction temperature on TNT adsorption were investigated under specific conditions. Suspension was filtered rapidly with filter paper and the filtrate was used immediately to determine adsorption efficiency of LAC.

Analyses

TNT concentrations in the solutions were determined by sodium sulfite spectrophotometry using a 722 SP visible spectrophotometer (Shanghai Lengguang Instrument Co., Ltd) at 420 nm (Chinese Standardization, 1993). Organic compositions of TNT red water were determined by gas chromatography/mass spectrometry (GC/MS, GC6890/MSD5973 N, Agilent Corporation, USA). A sample of 1.0 µL was injected into the GC/MS operated from 40 to 280°C at a programable rate of 2.0°C min⁻¹. A DB-35 MS capillary column with an inner diameter of 0.25 mm and length of 60 m was adopted in the separation system. Helium gas was used as the carrier gas and introduced at a flow rate of 1.0 mL min⁻¹. Dried red water samples were characterized by Fourier transform infrared spectroscopy (FTIR, Spectrum 100, Perkin Elmer). Adsorbent surface was examined using scanning electron microscopy (SEM, HITACHI S450) before and after adsorption experiments. Oxygen demand was determined using a COD rapid detector (5B-6, Lian-Hua Tech. Co., China).

RESULTS AND DISCUSSION

Water Quality Analysis

TNT red water is reddish brown and opaque containing high concentrations of TNT and chemical oxygen demand (COD). Waste water used in the experiments was diluted 100 times and important properties may be seen in Table 1. FTIR and GC/MS are used to identify composition of TNT red water and results are displayed in Figure 1 and Table 2. The infrared spectrum seen in Figure 1 displays characteristic bands of nitryl at 1539 and 1365 cm⁻¹ and a characteristic band of heterocyclic nitrogen compounds at 616 cm⁻¹. GC/MS results seen in Table 2 indicate organic components in the TNT red water are complex and 3-methyl-6-nitrobenzoic acid, 2-methyl-3,5-dinitro-phenol, 1,3,5-trinitrobenzene, and 2,4,6-trinitrobenzene are the largest components appearing at 60 and 67 min.

Properties of LAC

Important properties of LAC which effect adsorption characteristics are provided in Table 3. LAC has high microporosity, iodine number, and BET surface area. However, the bulk density value is not very large.
and from the pH values it may be concluded that the LAC has acidic characteristics. Types and amounts of surface functional groups in the LAC samples are determined using Boehm analysis and results are provided in Table 4. Amounts of carboxylic, lactonic, and phenolic groups are determined by neutralizing them with basic solutions of different base strengths such as NaHCO₃, Na₂CO₃, NaOH, and C₂H₅ONa. Basic group content was determined by titration using HCl.

As seen in Table 4, LAC contains mainly oxygen groups with weakly acidic properties and basic groups. Boehm analysis suggests that the amount of carboxylic functional groups is much larger than that of the basic groups. It is believed that acidic functional groups cause adsorption of organic compounds because removal of organic compounds is positively affected by acidic functional groups having hydrogen bonds.

### Adsorption of Organic Materials from TNT Red Water

**Effects of Adsorbent Aose**

Adsorbent dose is an important parameter because it determines the capacity of the adsorbent for a given initial concentration of adsorbate. Effects of the adsorbent dose on TNT degradation are illustrated in Figure 2. Removal rates of TNT increase from 18.0 to 84.7% and those of COD increase from 15.7 to 70.3% as quantities of LAC are increased from 0.05 to 2.0 g. When quantity reaches 5.0 g, removal rates of TNT and COD are 95.8 and 87.6%, respectively. Results indicate that TNT and COD removal efficiency is enhanced by larger adsorbent dose. This is because total specific surface area and active sites on the LAC increase. When adsorbent dose increases degradation of TNT and COD is favored. However, rates are not affected significantly when dose is increased from 2.0 to 5.0 g and accordingly, an LAC dose of 2.0 g/50 ml is considered an optimal dose for TNT removal in our experiments.
Effects of Exposure Time

In order to determine optimal adsorption time for activated carbon used in this study, effects of exposure time are determined at 298 K. Seen in Figure 3, removal rates of TNT and COD increase gradually with time. Initially, TNT adsorption rate is high but diminishes gradually with time. It may be because adsorption area decreases as the surface of LAC is covered by TNT and other organic compounds from red water. Minimum contact time required to reach equilibrium is 6 hours for LAC and in our experiments soaking time was fixed at these values to make sure equilibrium is achieved.

To analyze adsorption rates and kinetics of organic materials adsorption from TNT red water by the LAC, three kinetic models, namely pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were evaluated. The Lagergren’s equation is one of the most widely used rate equations to describe adsorption from a liquid phase [24]. The linear form of the pseudo-first-order rate expression of Lagergren’s equation [Equation (1)] is given as:

\[
\log (q_e - q_t) = \log q_e - \frac{k_f}{2.303} t
\]  

where, \( q_e \) and \( q_t \) are amounts of the TNT adsorbed (mg/g) at equilibrium and at time \( t \) (min) and \( k_f \) is the rate constant. Values of \( k_f \) and \( q_e \) for adsorption by LAC are determined from the plot of \( \log (q_e - q_t) \) versus \( t \) [See Figure 4(a)].

<table>
<thead>
<tr>
<th>Material</th>
<th>Basic Groups</th>
<th>Carboxylic Groups</th>
<th>Lactonic Groups</th>
<th>Phenolic Groups</th>
<th>Total Acidic Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAC</td>
<td>0.23</td>
<td>1.30</td>
<td>0.14</td>
<td>0.031</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Table 4. Boehm Analysis Results of LAC.

Figure 3. Effects of exposure times on adsorption.

Figure 4. (a) Pseudo-first-order model, (b) Pseudo-second-order model, and (c) Intra-particle diffusion model pertaining to TNT removal from red water by LAC.
Adsorption kinetics may be described by the following pseudo-second-order process [Equation (2)] [25]:

\[ \frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \]  

where, \( q_e \) and \( q_t \) have the same connotation as mentioned previously and \( k_s \) is the rate constant in the pseudo-second-order kinetics model. The plot of \( t/q_t \) versus \( t \) is displayed in Figure 4(b). Values of \( k_s \) and \( q_e \) may be calculated from the slope and intercept of the plot in Figure 4(b).

Concentration dependence of the adsorption rate is frequently used to analyze the nature of the rate-determining step. Use of the intra-particle diffusion model has been explored in this regard and is represented by Equation (3) [14]:

\[ q_t = k_{ip} t^{1/2} + C \]  

where \( k_{ip} \) is the intraparticle diffusion rate constant and \( C \) is the intercept related to the thickness of the boundary layer. The plot of \( q_t \) versus \( t^{1/2} \) is seen in Figure 4(c).

Constants for kinetic models are provided in Table 5. It may be concluded that adsorption of TNT by LAC does not follow a pseudo-first-order model since calculated adsorption capacity was 44.19 mg/g and very different from an experimental adsorption capacity of 163.79 mg/g. A better correlation coefficient (0.999) in contrast and smaller difference between the calculated saturated adsorption capacity and experimental adsorption capacity are observed using the pseudo-second-order model. Using the intra-particle diffusion model, the fitted curve is divided into two regions, surface diffusion and internal diffusion, due to influence by boundary layer diffusion and internal diffusion, respectively. The rate parameter \( k_{ip1} \) (11.01) calculated from the first region is higher compared to \( k_{ip2} \) (1.99) from the second stage indicating surface diffusion is much faster than internal diffusion.

**Adsorption Isotherms**

Figure 5 displays results obtained from a series of experiments performed using different concentrations of waste water. Removal rates of TNT decrease approximately from 92 to 53% and COD values increase from 51 to 95 mg/l when initial concentrations are changed from 10 to 200 mg/l (See Figure 5). Although higher concentrations of TNT red water can promote adsorption, the number of active sites on the LAC is limited. Superfluous adsorbates cannot be adsorbed when a balance is reached. Hence, the adsorption rate is reduced and results suggest waste water should be diluted before treatment to improve adsorption efficiency.

The equilibrium relationship between adsorbent and adsorbate is described by the adsorption isotherms. Two adsorption isotherm Equations (4) and (5) are used in the present study, namely Langmuir [23] and Freundlich [26]. Applicability of isotherm models was compared by evaluating correlation coefficients. Linear forms of the Langmuir and Freundlich isotherms are represented by the following equations [Equations (4) and (5)]:

\[ \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \]  

where \( q_e \) is the amount (mg/g) adsorbed at equilibrium concentration \( C_e \) (mg/L), and \( q_m \) (mg/g) and \( b \) (L/mg) are the maximum adsorption capacity of the adsorbent and adsorption energy coefficient, respectively.

Table 5. Pseudo First-order, Pseudo Second-order, and Intraparticle Diffusion Kinetic Parameters for TNT in Red Water by LAC.

<table>
<thead>
<tr>
<th>Pseudo First-order</th>
<th>Pseudo Second-order</th>
<th>Intraparticle Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_r \times 10^{-3} ) (min⁻¹)</td>
<td>( q_e^{(exp)} ) (mg/g)</td>
<td>( q_e^{(cal)} ) (mg/g)</td>
</tr>
<tr>
<td>7.37</td>
<td>163.79</td>
<td>44.19</td>
</tr>
</tbody>
</table>
\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where \(K_F\) is Freundlich constant (mg/g) associated with the adsorption capacity and \(1/n\) is the heterogeneity factor related to the adsorption intensity or surface heterogeneity.

Figure 6 displays adsorption isotherms according to the Langmuir and Freundlich models. Theoretical parameters of adsorption isotherms along with regression coefficients are provided in Table 6. The Langmuir isotherm model has the highest values of regression coefficients compared to other isotherm models suggesting the homogeneous nature of the adsorbent. Maximum adsorption capacity and Langmuir constant are calculated from slope and intercept of linear plots \(C_e/q_e\) versus \(C_e\) which gives a straight line of slope \(1/q_m\) corresponding to complete monolayer coverage (mg g\(^{-1}\)) and an intercept of \(1/q_m b\).

The effects of pH on solid/liquid adsorption processes are significant in such reactions. Here, adsorption of TNT by LAC over a broad pH range (2–12) is performed in red water that has been diluted 100 times at a temperature of 298 K and at an agitation speed of 150 rpm. Results are provided in Figure 7. The pH indeed has a large impact on adsorption characteristics. Adsorption efficiency and removal rate of COD decreases with increasing pH. The optimal pH for TNT removal is 2 and adsorption is not easy when the pH is higher than 10. There are large amounts of aromatic compounds with nitro groups and both oxygen and nitrogen are electronegative elements with oxygen having a higher electronegativity [27]. The nitro groups may be bonded easily to hydrogen thereby accelerating extraction of TNT. When pH is higher than 10, there is not enough hydrogen and adsorption is hindered. A pH of 2.0 is optimal and is now used in subsequent experiments.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(q_m) (mg/g)</th>
<th>(b) (L/mg)</th>
<th>(R^2)</th>
<th>(K_F) (mg/g(L/mg)(^{1/n}))</th>
<th>(1/n)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>160.45</td>
<td>0.069</td>
<td>0.9929</td>
<td>0.97</td>
<td>0.56</td>
<td>0.9808</td>
</tr>
</tbody>
</table>
Adsorption Behavior and Removal of Organic Materials from TNT Red Water by Lignite Activated Carbon

Effects of Temperature

In order to better understand temperature effects on adsorption of TNT and removal rate of COD, experiments were conducted at 25, 35, 45, and 55°C and results are displayed in Figure 8. After adsorption, COD and TNT contents increase with temperature denoting that some kind of endothermic chemical interactions may have taken place during adsorption. In addition, increase in adsorption with temperature may enlarge pore size which may also affect carbon adsorption capacity [28]. However, increase in the COD and TNT contents is not obvious. This may be because a higher temperature favors agglomeration up to a certain temperature limit beyond which desorption becomes more important. Hence, adsorption rate is reduced with time [29]. Results reveal that temperature effects on adsorption are not significant on account of the small energy of liquid adsorption. Consequently, room temperature is the desirable temperature in practice.

Morphology of Adsorbent

SEM micrographs of activated carbon are displayed in Figure 9. SEM images are very useful to obtain details before and after adsorption. Aforementioned, physical properties and surface morphology of activated carbons influence adsorption capacity. It is clear from the SEM micrograph in Figure 9 that LAC has a porous surface [See Figure 9(a)]. After adsorption the LAC surface becomes smoother [See Figure 9(b)] implying that components from the red water attach to pores of the LAC.

Adsorption Mechanism

The adsorption performance of LAC is evaluated based on surface groups type, specific surface area, pore size, and so on. There are many oxygen functional groups such as hydroxyl groups, carboxyl groups, phenolic groups, and inner ester on the surface of LAC for efficient adsorption. Most organic components in red water are polar and therefore are believed to adsorb mainly via hydrogen bonds between LAC and organic materials (See Figure 10). According to results, the phenomenon is mainly single molecule layer adsorption.
Comparison with Other Adsorbents

Several studies have been conducted using various types of adsorbents for TNT adsorption. Table 7 compares adsorption capacities and LAC shows a comparable adsorption capacity with respect to other adsorbents revealing that LAC is suitable for removal of TNT from aqueous solutions since it has a relatively high adsorption capacity.

CONCLUSIONS

Feasibility of using LAC as an adsorbent to remove TNT from red water was investigated. Results demonstrate that pH value, initial concentration, time, and dose of adsorbent all affect adsorption, significantly. The lower the pH the higher the adsorption capacity. Optimal adsorption time is 6 hours and room temperature is adequate. The adsorption mechanism follows a pseudo-second-order kinetics model controlled by pore diffusion and the adsorption isotherm may be fitted well by the Langmuir model. Results suggest organic materials in red water adsorb via hydrogen bonds between activated carbon and organic materials.

ACKNOWLEDGEMENTS

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Table 7. Adsorption Capacity of TNT by Various Adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Qe (mg g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAC</td>
<td>163.79</td>
<td>This study</td>
</tr>
<tr>
<td>Aminated lignin</td>
<td>55.7</td>
<td>Zhang et al. [30]</td>
</tr>
<tr>
<td>polyvinylbenzyl acid/SiO₂</td>
<td>26.84</td>
<td>An et al. [31]</td>
</tr>
<tr>
<td>PEI/SiO₂</td>
<td>14.47</td>
<td>An et al. [32]</td>
</tr>
<tr>
<td>PAM/SiO₂</td>
<td>0.873</td>
<td>An et al. [33]</td>
</tr>
</tbody>
</table>

REFERENCES

18. Van Dillewijn, P., Caballero, A., Paz, J.A., Gonzalez-Perez, M.M.,
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