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

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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 programmable 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-dinitrophenol, 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.

**Table 1. Properties of Red Water Diluted 100 Times.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>Solid Content (mg/L)</th>
<th>TNT (mg/L)</th>
<th>Turbidity</th>
<th>Chromaticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red water</td>
<td>6.20</td>
<td>1100 ± 20</td>
<td>1980</td>
<td>50.7</td>
<td>59.8</td>
<td>reddish brown 1×10³ times</td>
</tr>
</tbody>
</table>
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 4. Boehm Analysis Results of LAC.

<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>

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]:

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

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 region 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)]:

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

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_f) \times 10^{-3} (min^{-1})</td>
<td>(q_e^{(exp)}) (mg/g)</td>
<td>(q_e^{(cal)}) (mg/g)</td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>7.37</td>
<td>163.79</td>
<td>44.19</td>
</tr>
</tbody>
</table>
The adsorption 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.
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.

![Figure 8. Effects of temperature on adsorption.](image)

![Figure 9. Scanning electron micrographs: (a) LAC (4000×), (b) LAC with adsorbents (1000×).](image)
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>[30]</td>
</tr>
<tr>
<td>polyvinylbenzyl acid/SiO₂</td>
<td>26.84</td>
<td>[31]</td>
</tr>
<tr>
<td>PEI/SiO₂</td>
<td>14.47</td>
<td>[32]</td>
</tr>
<tr>
<td>PAM/SiO₂</td>
<td>0.873</td>
<td>[33]</td>
</tr>
</tbody>
</table>

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


