Reduction in Chemical Oxygen Demand of TNT Red Water Using Layered Double Hydroxide Prepared from Red Mud and Brucite

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Abstract
A low-cost organolayered double hydroxide adsorbent prepared under alkali conditions with red mud (waste tailings from alumina production) and brucite is modified by anionic surfactant, sodium dodecyl benzene sulfonate (SDBS), by ion exchange to produce a layered double hydroxide adsorbent (LDH-SDBS). LDH-SDBS was used to treat 2,4,6-trinitrotoluene (TNT) red water that had high toxicity, contained persistent compounds, and had a high chemical oxygen demand (COD). Removal efficiency reached 46% at 20-fold dilution (COD, 4024 mg/L) and kinetics showed that adsorption processes followed a pseudo-second-order model. Negative ΔG and positive ΔH indicated adsorption was spontaneous and endothermic and Gas Chromatography-Mass Spectrometer (GC/MS) revealed that amounts of organic compounds in TNT red water were reduced significantly.

Keywords: adsorption; brucite; layered double hydroxides; red mud; TNT red water

Introduction
The 2,4,6-trinitrotoluene (TNT) explosive, a nitroaromatic compound, is one of the most important products in military and civilian industrial production. According to the conventional production process, which is typically based on complete nitration of toluene, crude TNT is purified by water and sodium sulfite baths leading to two types of products in military and civilian industrial production. Activated carbon, anion exchange resins, and other sorbents have been used to treat TNT red water, for instance, active carbon (Wei et al., 2011), active coke (Zhang et al., 2011; Hu et al., 2014, 2015), bamboo charcoal (Fu et al., 2012), and macroporous polystyrene (Meng et al., 2012, 2013; Zhao et al., 2013). However, to our knowledge, removal of organic materials in TNT red water by adsorption to layered double hydroxides (LDHs) has not been reported to date.

Several methods have been proposed to remove TNT and other organic species from wastewater, for example, adsorption (Zhang et al., 2014), vacuum distillation (Zhao et al., 2010), degradation utilizing microorganisms (Park et al., 2003; Zhang et al., 2015), oxidation by UV/H2O2 (Hwang et al., 2004), Fenton reagent oxidation (Matta et al., 2008), and photolytic oxidation (Zhu et al., 2011; Shen et al., 2014; Ludwichk et al., 2015; Jo et al., 2014). It has been suggested that adsorption is the most effective and practical method of TNT red water removal and many adsorbents have been used to treat TNT red water, for instance, active carbon (Wei et al., 2011), active coke (Zhang et al., 2011; Hu et al., 2014, 2015), bamboo charcoal (Fu et al., 2012), and macroporous polystyrene (Meng et al., 2012, 2013; Zhao et al., 2013). However, to our knowledge, removal of organic materials in TNT red water by adsorption to layered double hydroxides (LDHs) has not been reported to date. The structural formula of LDH is shown as the general formula \( [\text{M}^{m+}\text{A}^{-}\text{m}^{-}\text{o}^{2-}]_{n}^{m-}\text{H}_{2}\text{O}^{+} \), where \( \text{M}^{m+} = \text{Zn}, \text{Mg}, \text{Co}, \text{Ni}, \text{etc.}, \text{M}^{m+} = \text{Al}, \text{Fe}, \text{Cr}, \text{Ga}, \text{etc.}, \text{A}^{-} = \text{CO}_{3}^{2-}, \text{NO}_{3}^{-}, \text{Cl}^{-}, \text{SO}_{4}^{2-}, \text{etc.} \) This is a layered substance containing positively charged metal hydroxide sheets compensated by a large number of exchangeable charge-balancing anions and water molecules in the interlayer space (Bratterman et al., 2004). Owing to the presence of large interlayer spaces and a huge number of exchangeable anions, LDHs are good ion exchangers/adsorbents for the removal of toxic anions from waste water. Therefore, LDHs can be used to absorb the organics in TNT red water.

Several methods can be used to prepare LDHs. The most common method is coprecipitation at constant pH followed by aging at a certain temperature (Basile et al., 1998). Urea is usually used as the base source to produce large LDH-CO$_3$
crystallites, which form hexagonal platy sheets by homogeneous precipitation (Evans and Slade, 2006). Reconstruction from MgAl oxide generated by calcining MgAl-CO3 LDH at a mild temperature (e.g., 500°C) takes advantage of LDH “memory” effect in preparation of LDHs intercalated with desirable anions, including various inorganic, organic, and biomedical anions (Bontchev et al., 2003; Nakayama et al., 2004). Zhiping Xu et al. have prepared LDH from mixed MgO and Al2O3 (Zhi and Guo 2005). Stanimirova and Balek (2008) have characterized LDH Mg-Al-CO3 prepared by rehydration of Mg-Al mixed oxide. In addition, mixed oxide derived from LDHs has been studied (Stanimirova and Balek 2008).

In this study, LDH is prepared with red mud and brucite that are industrial solid wastes residue and less expensive than laboratory reagents. Red mud, a solid waste with high pH (10–13) from the aluminum industry, contains fine particles mainly including gibbsite (Al(OH)3), sodalite (Na4Al3Si3O12Cl), Muscovite (KAl2(AlSi3O10)(OH)2), hematite (Fe2O3) and goethite (α-FeOOH). For every ton of alumina produced, approximately one to two tons (dry weight) of bauxite residues are generated. The corrosive nature and enormous quantities (90 million tons yearly worldwide) of the red mud cause significant ecological problems and negative environmental impacts. Brucite selected in the study is industrial grade containing Mg(OH)2, serpentine (Mg6[Si4O5](OH)8), magnesite (MgCO3), and dolomite (CaMg(CO3)2). The calcined red mud and brucite contain abundant MgO, Al2O3 serving as the raw materials of LDH. LDH is used to treat the TNT red water, not only to reduce the chemical oxygen demand (COD) of TNT red water but also to realize recycling of solid waste.

Materials and Methods

Materials

Red mud was provided by Shandong Weiqiao Aluminum and Electricity Co. Ltd. (Shandong, China) and brucite was supplied by Kuandian brucite factory (Liaoning, China). The primary mineral components are shown in Table 1. TNT red water was supplied by Dongfang Chemical Corporation (Hubei, China). Sodium dodecyl benzene sulfonate (SDBS, Beijing Chemical Reagent Co.) and the other reagents used in this study were analytical grade and distilled water was used to prepare the solutions.

Adsorbent preparation

Red mud and brucite (1:2 mass ratio) were mixed with distilled water in a beaker and mixed thoroughly. The mixture was dried at 120°C, calcined at 600°C for 3 h, and air cooled to produce LDH dry powder.

The NaOH solution (1 M, 150 mL) and 150 mL of 2 M Na2CO3 solution were mixed with 60 g of LDH dry powder and the reaction proceeded at 30°C for 6 h. After aging for 24 h, the sample was filtrated and washed until the pH of filtrate reached 7. Then, it was dried at 80°C and milled to produce the LDH powder.

LDH powder (10 g) and 90 mL of distilled water were added to a beaker and stirred for 30 min. SDBS (3.6445 g) was dissolved in 40 mL of distilled water. It was added slowly to the mentioned suspension and stirred at room temperature for 24 h. The mixtures were filtrated and washed until the filtrate was
neutral and no bubble was observed. The product was vacuum dried at 80°C for 12 h and milled to produce LDH-SDBS.

**Adsorption experiments**

Adsorption experiments were conducted using 4 g of LDH or LDH-SDBS as the adsorbent in a 100 mL flask containing 50 mL of TNT red water. The bottles were shaken in a digital water bath oscillator at 150 rpm. Then samples were filtered and dried under vacuum at 70°C for 8 h. The filtrate was analyzed by a COD rapid detector (5B-6, Lian-Hua Tech. Co., China) with a precision of ±5% to determine the adsorption efficiency. The relative removal of COD (%) of the organic compounds and \( q_e \) (mg/g) in the TNT red water adsorbed by LDH or LDH-SDBS were calculated based on Equations (1) and (2):

\[
\text{Relative removal of COD (\%) } = \frac{\text{COD}_1 - \text{COD}_2}{\text{COD}_1} \times 100%,
\]

\[
q_e = \frac{\left(\text{COD}_1 - \text{COD}_2\right) V}{W},
\]

where COD\(_1\) (mg/L) and COD\(_2\) are the COD of the initial TNT red water and treated red water after reaching equilibrium, respectively. V (L) is the volume of TNT red water and W (g) is the adsorbent weight. At any time, the amount of COD and the adsorbed \( q_e \) (mg/g) were calculated using a similar relationship based on Equation (2).

To determine the optimal contact time, the initial concentration of TNT red water, and temperature, adsorption experiments were performed systematically. TNT red water was diluted 0, 10, 20, 40, and 100 times, and the COD concentrations were 68,510, 9,454, 4,024, 2,964, and 660 mg/L, respectively.

**Characterization**

X-ray diffraction (XRD, Rigaku D/max-rA), scanning electron microscope (SEM, JSM-6301F), energy dispersive X-ray spectroscopy (EDS), thermogravimetric-differential thermal analysis (TG-DTA, Netzsch TG-209C), N\(_2\) adsorption isotherm obtained a micrometric instrument (ASIQM0002-4), and Fourier transform infrared spectra (FT-IR, PerkinElmer Spectrum 100) were performed to characterize the structure, morphologies, and components of LDH or LDH-SDBS before and after adsorption.

**Determination of compounds in TNT red water**

A 6890N/5973 Gas Chromatography-Mass Spectrometer (GC/MS) system (Agilent Corporation) was used to determine the changes in the organic compounds in TNT red water before and after adsorption. The TNT red water samples were treated by liquid–liquid extraction using CH\(_2\)Cl\(_2\) as the extractant (Li et al., 2003). A sample with a volume of 1.0 mL was injected, operated from 40°C to 280°C at a programming rate of 2.0°C/min with the DB-35 MS capillary column (30 m x 0.25 mm x 0.25 μm). Pure helium gas was used as the carrier gas at a flow rate of 1.0 mL/min.

![Scheme for LDH preparation from red mud and brucite. LDH, layered double hydroxide.](image-url)
FIG. 2. (A) XRD patterns of (a) LDH dry powder, (b) LDH, (c) LDH-SDBS, and (d) LDH-SDBS after adsorption. (B) the low angle XRD patterns of (a) LDH dry powder, (b) LDH, (c) LDH-SDBS, and (d) LDH-SDBS after adsorption. LDH SDBS, layered double hydroxide-sodium dodecyl benzene sulfonate; XRD, X-ray diffraction.

FIG. 3. SEM micrographs of (a, b) LDH dry powder, (c, d) LDH, (e, f) LDH-SDBS, and (h, g) LDH-SDBS after adsorption, the selected area EDS are inserted in (d), (f), and (h). EDS, energy dispersive X-ray spectroscopy; SEM, scanning electron microscope.
thermodynamic parameters: changes of free energy (\( \Delta G \)) of organic compounds by LDH-SDBS provides clues to determine the kinetic model is expressed by Equation (3): (Lagergren, 1989). The linear form of the pseudo-first-order kinetic model is expressed by Equation (3):

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

where \( K_f \) (L/min) is the rate constant of pseudo-first-order adsorption and \( q_e \) (mg/g) and \( q_t \) (mg/g) are the amounts of COD adsorbed at equilibrium and at any time \( t \) (min), respectively. The values of \( K_f \) and \( q_e \) for adsorbate adsorption by LDH-SDBS can be determined from the plot of \( \log (q_e - q_t) \) versus \( t \). The pseudo-second-order equation is expressed as Equation (4) (Ho and McKay 1999):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t,
\]

where \( k_2 \) (g/(mg min)) is the pseudo-second-order constant and \( q_e \) and \( k_2 \) can be determined experimentally from the slope and intercept of the plot \( t/q_e \) versus \( t \).

Adsorption thermodynamics

The effect of temperature on adsorption of organic compounds by LDH-SDBS provides clues to determine the thermodynamic parameters: changes of free energy (\( \Delta G \)), enthalpy (\( \Delta H \)), and entropy (\( \Delta S \)) using the Van’t Hoff Equations (5)–(7) (Kumar et al., 2008; Eloussaief et al., 2009; Eloussaief and Benzaia, 2010; Kannamba et al., 2010; Zhang et al., 2010).

\[
K_c = \frac{c_0 - c_e}{c_e} \times \frac{\rho V}{m},
\]

\[
\Delta G = -RT \ln K_c,
\]

\[
\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT},
\]

where \( K_c \) is the distribution coefficient, \( \rho = 1 \text{ g/L} \) is the density of the solution mixture, \( c_e \) (mg/L) is the COD of the TNT red water treated by LDH-SDBS until equilibrium, \( q_e \) is the COD amount of adsorption at equilibrium (mg/g), \( T \) is the solution temperature (K), and \( R \) is the gas constant and equal to 8.314 J mol/K. \( \Delta H \) and \( \Delta S \) are calculated from the slope and intercept of the linear plot of \( I/T \) versus \( \ln K_c \).

Results and Discussion

Formation of LDH with red mud and brucite

The preparation mechanism of LDH using red mud and brucite is discussed hereunder. LDH is prepared with MgO and Al\(_2\)O\(_3\) taken from brucite and red mud (Xu and Lu, 2005). Before and during the LDH formation, hydrolysis of MgO and Al\(_2\)O\(_3\) in mixed oxides hydrated and dissociation of Mg(OH)\(_2\) and Al(OH)\(_3\) occurred on the surface of the solid particles as given in the following Equations (8)–(10):

\[
\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- \quad (8)
\]

\[
\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \rightleftharpoons 2\text{Al(OH)}_3 \rightleftharpoons 2\text{Al}^{3+} + 4\text{OH}^- \quad (9)
\]

\[
\text{Al(OH)}_3 + \text{OH}^- \rightleftharpoons \text{Al(OH)}_4^- \quad (10)
\]

Thin layers of Mg(OH)\(_2\) and Al(OH)\(_3\) form on the oxide particle surfaces as shown in the first step in Fig. 1 and prevent the inner oxide phase from further hydrolysis. The inside oxide could be further hydrolyzed when the hydroxide layer is dissolved. Therefore, the possible reactions contributing to the LDH formation are shown as given in the following Equations (11)–(13). Formation of LDH by mixed oxides composed of MgO and Al\(_2\)O\(_3\) is illustrated as shown in Fig. 1.

\[
\text{aMg}^{2+} + \text{Al(OH)}_4^- + 2(2a - 2)\text{OH}^- + x\text{H}_2\text{O} + x^- \rightleftharpoons M_{2a}\text{Al}(\text{OH})_{2a,2a}x \cdot x\text{H}_2\text{O} \quad (11)
\]

Table 2. BET of Layered Double Hydroxide and Layered Double Hydroxide–Sodium Dodecyl Benzene Sulfonate Before and After Adsorption

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size (( \mu ))</th>
<th>BET (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDH</td>
<td>100–650</td>
<td>90.3</td>
<td>0.164</td>
<td>3.412</td>
</tr>
<tr>
<td>LDH-SDBS</td>
<td>120–560</td>
<td>78.5</td>
<td>0.113</td>
<td>3.832</td>
</tr>
<tr>
<td>LDH-SDBS after adsorption</td>
<td>400–1200</td>
<td>21.7</td>
<td>0.099</td>
<td>2.345</td>
</tr>
</tbody>
</table>

BET, Brunauer-Emmett-Teller; LDH, layered double hydroxide; LDH-SDBS, layered double hydroxide-sodium dodecyl benzene sulfonate.


\[
\begin{align*}
\text{aMg}^{2+} + \text{Al(OH)}_3 + (2a - 1)\text{OH}^- + x\text{H}_2\text{O} + X^- & \rightleftharpoons \text{Mg}_a\text{Al(OH)}_{2 + 2a}X \cdot x\text{H}_2\text{O} & (12) \\
\text{aMg(OH)}_2 + \text{Al(OH)}_3^- + x\text{H}_2\text{O} + X^- & \rightleftharpoons \text{Mg}_a\text{Al(OH)}_{2 + 2a}X \cdot x\text{H}_2\text{O} + 2\text{OH}^- & (13)
\end{align*}
\]

where \( X^- \) denotes \( \text{OH}^- \), \( \text{Cl}^- \), or \( 1/2 \text{CO}_3^{2-} \).

Characterization of samples

XRD, SEM, EDS, TG, N2 adsorption, and FT-IR were performed to characterize the structure, morphologies, and components of LDH and LDH-SDBS before and after adsorption. Figure 2 shows the XRD patterns of (a) LDH dry powder, (b) LDH, (c) LDH-SDBS, and (d) LDH-SDBS after adsorption. Figure 2A shows that LDH dry powder contains MgO, quartz, calcite, sodalite, and hematite. The XRD peaks at 11.2°, 22.8°, and 34.2° confirm the formation of LDH (Liao et al., 2012). The quartz diffraction peaks are very weak because quartz is dissolved by alkaline solution. The LDH-SDBS peaks shift to smaller angles because of the intercalation of SDBS. After adsorption in TNT red water, the diffraction peaks of LDH-SDBS shift further to smaller angles (Fig. 2B), indicating that the part of organic compounds in TNT red water has been extracted by LDH-SDBS.

SEM shows that the calcined and mixed powders are particles (Fig. 3a, b). The lamellar particles may be the residue of \( \text{Mg(OH)}_2 \). The lamellar structures of LDH (Fig. 3c, d) and LDH-SDBS (Fig. 3e, f) indicate that the LDH is prepared with red mud and brucite. Compared with LDH (Fig. 3c, d), LDH-SDBS has irregular shape. After adsorption, a thin layer covers the adsorbent (Fig. 3g, h). EDS (Fig. 3h) shows 1.2% N in LDH-SDBS after adsorption, further proving that the organic compounds in TNT red water have been extracted.

The TG plots of LDH (Fig. 4a) show that the first stage \((50^\circ C–198^\circ C)\) is mainly attributed to elimination of physically adsorbed and interlayer water molecules. The second stage \((198^\circ C–442^\circ C)\) stems from loss of hydroxyl groups from the brucite-like layer along with interlayer carbonate ions followed by destruction of the layered structure. The overall behavior of LDH is in agreement with that reported for MgAl-LDH samples. Figure 4b shows the TG plots of LDH-SDBS, revealing two-step decomposition in SDBS-modified samples in the range \(145^\circ C–412^\circ C\). However, the weight loss (18.2%) of LDH-SDBS is larger than that of LDH (10.7%). Decomposition of SDBS also takes place during this process and probably interferes with the decomposition of the host materials, especially decomposition of benzene rings and hydrocarbon chains in the absence of free oxygen, which can delay the overall thermal decomposition of the host materials. After adsorption, the TG plots of LDH-SDBS are shown in Fig. 4c. The weight loss of 22.6% of LDH-SDBS after adsorption is larger than those of LDH-SDBS (18.2%) and LDH (6.3%). The larger weight loss is because of adsorption of organic compounds from the TNT red water.

![Graph A](image)

**FIG. 6.** (A) The relative removal of COD at different contact time and initial COD of TNT red water; (B) \( q_t \) at different contact time and initial COD of TNT red water (adsorbent mass = 4.0 g/50 mL; agitation speed = 150 rpm; \( T = 298 \text{K} \)). COD, chemical oxygen demand; TNT, 2,4,6-trinitrotoluene.
When the temperature goes up, the organic species break down, leading to higher weight loss (Zhao et al., 2002).

Surface area, pore size, and pore volume of LDH and LDH-SDBS before and after adsorption are measured by N2 adsorption. The Brunauer-Emmett-Teller (BET) of LDH is 90.3 m2/g, pore volume is 0.164 cm3/g, and average pore size is 3.412 nm as shown in Table 2. After LDH is modified by SDBS, the BET and pore volume of LDH-SDBS decline slightly because of the adsorption of SDBS on the surface of LDH. After adsorption, the BET, pore volume, and average pore size of LDH-SDBS decrease further because of the attachment of organic pollutants from TNT red water. The smaller pore size and volume show that organic species are adsorbed effectively by LDH-SDBS.

FT-IR spectra (Fig. 5) show the functional groups of (a) LDH, (b) LDH-SDBS, and (c) LDH-SDBS after adsorption. The broad and strong absorption band at 3438 cm⁻¹ is attributed to stretching vibrations of physically adsorbed water, structural OH group, and/or hydrogen-bonded hydroxyl group (OH-OH). The band at 1,622 cm⁻¹ corresponds to bending mode of interlayer water molecules. The sharp intense band at 1,356 cm⁻¹ is assigned to O-C-O stretching vibrations of monodentate carbonate species (Iglesias et al., 2005). The FT-IR spectrum of LDH-SDBS shows new peaks at 2,962, 2,926, and 2,854 cm⁻¹ assigned to C-H stretching vibrations of SDBS. Moreover, the characteristic peaks of C=C and C-C at 1,462 cm⁻¹ and 1,408 cm⁻¹ are observed (He et al., 2004), indicating that LDH is modified by SDBS. After adsorption, the C-H stretching vibrations peaks of SDBS at 2,962, 2,926, and 2,854 cm⁻¹ still exist except the peaks of N=O at 1,429 cm⁻¹, indicating that the organic materials are adsorbed by LDH-SDBS.

Adsorption kinetics of organic components on LDH-SDBS

Adsorption of organic components of TNT red water occurs very quickly at the beginning of the experiments (Fig. 6) and slows gradually after 60 min. The adsorption processes reach equilibrium at 240 min. LDH-SDBS possesses higher adsorption ability than LDH (Fig. 6A). At the same initial concentration of TNT red water (4,024 mg/L), the COD removal efficiency increases from 26% to 46% and final COD of TNT red water decreases from 4,024 to 2,253 mg/L. Figure 6B shows that $q_t$ of LDH-SDBS at equilibrium increases from 3.2 to 52 mg/g with increasing initial COD, whereas COD removal efficiency decreases from 46% to 6%. The initial COD of TNT red water plays an important role in adsorption on LDH-SDBS. It can be explained by that rapid adsorption during initial exposure arises from the availability of physisorbed molecules of SDBS on the LDH-SDBS. The slow rate of organic components adsorption later is probably because of gradual penetration through the pores in the interior surfaces and interlayer of LDH-SDBS as the exterior became saturated (Pavan et al., 2000; Eloussaief et al., 2011; Eloussaief et al., 2013).

Both kinetic models fit the experimental data well (Table 3), but the pseudo-second-order model provides the best overall fit.
fit and the calculated $q_{e, cal}$ with this model is consistent with the experimental value $q_{e, exp}$. It suggests that pseudo-second-order adsorption is predominant (Mandal et al., 2014).

**Thermodynamics adsorption of organic components on LDH-SDBS**

The thermodynamic parameters are calculated and the slope and the intercept are shown in Table 4. $\Delta G$ is less than 0 (kJ/mol) ($-5.57$, $-6.01$, $-6.93$, $-7.39$, and $-7.67$) under the experimental conditions, indicating that adsorption of organic species is spontaneous. The increasingly negative $\Delta G$ with increasing temperature implies that adsorption becomes more favorable at higher temperatures. The positive $\Delta H$ indicates that adsorption on the LDH-SDBS is endothermic, suggesting that a higher temperature increases the number of adsorption sites on LDH-SDBS. In general, uptake of solutes from an aqueous solution by a solid sorbent has the following mechanisms: physisorption and chemisorption. This classification is based on $\Delta H$ during the mass transfer process. If the interaction between the solute and sorbent is based on chemical bonding, $\Delta H$ is greater than 40 kJ/mol. Here, $\Delta H$ (11.20 kJ/mol) is between 2 and 40 kJ/mol, thus indicating physical adsorption (Eloussaief et al., 2012; Yang et al., 2014). TNT red water has water as a solvent. Adsorption of organic compounds from TNT red water by LDH-SDBS displaces water molecules, and the entropy change $\Delta S$ of water molecules desorption is greater than that of organic compounds, being consistent with an increase in randomness during adsorption (Zheng et al., 2008).

**Compounds in TNT red water**

GC/MS (Fig. 7 and Table 5) shows some organic species such as 4-methyl-2,6-dinitro-phenol, 5-nitro-1H-indazole, and 3,5-dinitro-$p$-toluidine cannot be detected and so they have been removed. In addition, the acute toxicity tests before and after treatment have been conducted by Zhang et al. (2011) and the acute toxicity of TNT red water is greatly reduced compared with that of the unprocessed TNT red water (Zhang et al., 2011).

**Cost analysis**

Sorption cost of COD for activated carbon, activated coke (Zhang et al., 2011), bamboo charcoal (Fu et al.), RS-50B, bentonite (Zhang et al., 2014), and LDH-SDBS to TNT red water is compared in Table 6. Based on this analysis, the sorption capacity of RS-50B is the largest. In addition, the

**Table 6. Costs of Different Adsorbents for TNT Red Water**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Sorption capacity (mg COD/g)</th>
<th>Price (CNY/kg)</th>
<th>Sorption cost (CNY/g COD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>10.4</td>
<td>10</td>
<td>0.96</td>
</tr>
<tr>
<td>Activated coke</td>
<td>60.5</td>
<td>0.5</td>
<td>0.0083</td>
</tr>
<tr>
<td>Bamboo charcoal</td>
<td>31.77</td>
<td>1.3–1.9</td>
<td>0.041–0.06</td>
</tr>
<tr>
<td>RS-50B</td>
<td>136.00</td>
<td>45</td>
<td>0.33</td>
</tr>
<tr>
<td>Bentonite</td>
<td>45.4</td>
<td>1–1.2</td>
<td>0.022–0.026</td>
</tr>
<tr>
<td>LDH-SDBS</td>
<td>52.00</td>
<td>0.6–0.8</td>
<td>0.012–0.015</td>
</tr>
</tbody>
</table>
sorption cost of activated coke was a little higher than that of LDH-SDBS. However, the cost of RS-50B is 45 China Yuan (CNY)/kg, which is much higher than that of LDH-SDBS. The sorption cost for LDH-SDBS is only 0.012–0.015 CNY/g COD, which is much lower than that of RS-50B, activated carbon, bamboo charcoal, and bentonite and slightly higher than that of activated coke. According to the analysis of these adsorbents, it can be concluded that LDH-SDBS is an inexpensive and effective absorbent for the treatment of TNT red water.

Conclusions

LDH-SDBS prepared from brucite and red mud shows large potential pertaining to the removal of organic compounds from TNT red water. The COD of TNT red water is reduced from 4,024 to 2,253 mg/L and removal efficiency reaches 46%. The adsorption kinetics of COD removal from TNT red water fit the pseudo-second-order kinetic model. Thermodynamic analyses indicate that adsorption is endothermic and spontaneous and GC/MS results show that most organic compounds were removed by LDH-SDBS. Compared with that of other adsorbents, the sorption cost of LDH-SDBS is quite low at 0.012–0.015 CNY/g COD.

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Author Disclosure Statement

No competing financial interests exist.

References


Zhao, Q.L., Gao, Y.C., and Ye, Z.F. (2013). Reduction of COD in TNT red water through adsorption on macroporous polystyrene resin RS 50B, Vacuum. 95, 71.


