



Extraction of organic materials from red water by metal-impregnated lignite activated carbon

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ABSTRACT

Extraction of organic materials from 2,4,6-trinitrotoluene (TNT) red water by lignite activated carbon (LAC) impregnated with Cu^{2+} , Ba^{2+} , Sn^{2+} , Fe^{3+} , Ca^{2+} and Ag^+ was investigated. The affinity to organic materials in red water was found to follow the order: $\text{Cu/LAC} > \text{Sn/LAC} > \text{Ag/LAC} > \text{Ba/LAC} > \text{Fe/LAC} > \text{Ca/LAC}$, which was explained by the hard and soft acid base (HSAB) theory. Cu^{2+} showed the best performance and several parameters were further studied. X-ray photoelectron spectroscopy (XPS) verified effective loading of Cu^{2+} on the LAC surface. The water quality before and after treated by Cu/LAC was evaluated using high performance liquid chromatograph, Gas Chromatography/Mass Spectroscopy (GC/MS), UV-vis spectroscopy and other analyses. The extraction performances and mechanism of organic materials on Cu/LAC were investigated through static methods. The experimental results showed that Cu/LAC possessed stronger extraction ability for the sulfonated nitrotoluenes than the non-sulfonated nitrotoluenes, the kinetic data fitted the pseudo-second-order kinetic model well. In addition, the leaching out of Cu^{2+} from Cu/LAC was found much lower in the 100 times diluted red water (0.074%) than in the raw water (10.201%). Column adsorptions with more concentrated red water were also studied. Finally, Cu/LAC was observed to possess excellent reusability as well.

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1. Introduction

Because of the low manufacturing cost, low melting point, chemical and thermal stability, as well as high explosion power [1], TNT (2,4,6-trinitrotoluene) has been widely used as an explosive in military and other applications. However, the large amount of waste water generated during the manufacturing of TNT harms living organisms and leads to environmental hazards due to its toxic and mutagenic effects [2–5]. According to the characteristic color of the pollutants, TNT waste water can be categorized as yellow water, red water, pink water, and condensates [6]. Red water, which is produced during purification of crude TNT by sodium sulfite, is dark red and hazardous containing dissolved dinitrotoluene sulfonates (mainly 2,4-dinitrotoluene-3-sulfonate and 2,

4-dinitrotoluene-5-sulfonate), trinitrotoluene, nitrotoluene, dinitrotoluene, as well as other by-products [7].

Several methods have been proposed to treat the TNT containing waste water and examples are activated carbon adsorption [8,9], incineration, degradation utilizing microorganisms [10], catalytic destruction such as fenton oxidation [11] and photocatalytic oxidation [12], advanced oxidation employing UV and hydrogen peroxide/ozone [13], as well as supercritical water oxidation [14]. Each method has merits and limitations. In particular, activated carbon is commonly due to its large absorption capacity rendered by the developed pore structures which attract organic molecules [15,16]. Although activated carbon can extract organic materials from TNT waste water, it is not very practical industrially due to the small absorption capacity and high cost [17–19].

Incorporation of metal ions into activated carbon is one of the means to improve the efficiency. Although absorption of sulfur compounds [20–22] and other organic materials [23–25] by activated carbon loaded with metal ions has been reported, that from TNT red water has hitherto been seldom studied. In the work reported in this paper, six metal ions, namely Cu^{2+} , Ba^{2+} , Sn^{2+} , Fe^{3+} , Ca^{2+} and Ag^+ are incorporated individually into lignite activated carbon (LAC) which is one of the cheaper forms of activated carbon

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Table 1
Properties of red water diluted 100 times.

pH	COD (mg L ⁻¹)	Solid content (mg L ⁻¹)	2,4-DNT-3-SO ₃ ⁻ (mg L ⁻¹)	2,4-DNT-5-SO ₃ ⁻ (mg L ⁻¹)	TNT (mg L ⁻¹)	Turbidity	Chromaticity
6	860 ± 20	1980	197	310	50.7	59.8	Reddish brown 1 × 10 ³ times

to improve the extraction efficiency of organic materials from TNT red water. The effects of different metal ions are discussed.

2. Experimental details

2.1. Materials

LAC with a particle size range of 0–97 μm was purchased from Datang Co. Ltd. (Henan Province, China). The Cu(NO₃)₂·3H₂O, BaCl₂·2H₂O, SnCl₂·2H₂O, FeCl₃·6H₂O, CaCl₂ and AgNO₃ were analytical reagents. The TNT and DNT were industrial-grade with a purity of >99% (Number 375 ammunition plant, China), DNTS (2,4-dinitrotoluene-3-sulfonate, SYNCHEM-OHG, Germany), hydroxypropyl-β-cyclodextrin (Yiming Chemical Reagents Factory, China) and dichloromethane (Beijing Chemical Reagent Factory, China) were also analytical reagents. The TNT red water supplied by Dongfang Chemical Corporation (Hubei Province, China) was reddish brown and opaque with high concentrations of TNT and COD. The waste water used in the experiments was diluted 100 times and Table 1 shows the physical and chemical properties.

2.2. Adsorbent preparation

The Cu/LAC, Sn/LAC, Ag/LAC, Ba/LAC, Fe/LAC, Ca/LAC sorbents were prepared by impregnating LACs with the corresponding metal salts, respectively. Portions (10 g) of LACs were weighed and added separately to 0.05 mol L⁻¹ of the metal salt [Cu(NO₃)₂·3H₂O, BaCl₂·2H₂O, SnCl₂·2H₂O, FeCl₃·6H₂O, CaCl₂ and AgNO₃] in 100 mL of the aqueous solution. It was then agitated in a SHA-BA water bath at 150 rpm and 60 °C. After 24 h, the samples were filtered and dried at 393 K for 8 h and then solidified for 12 h at 573 K to obtain the Cu/LAC, Sn/LAC, Ag/LAC, Ba/LAC, Fe/LAC and Ca/LAC adsorbents. These adsorbents were used separately in the equilibrium isotherm experiments.

In order to determine the optimal conditions for the Cu/LAC adsorbent preparation, different concentrations of Cu(NO₃)₂ aqueous solutions (0.01, 0.025, 0.050, 0.100, 0.200, 0.500, and 1.00 mol L⁻¹), different pH values (1, 2, 3, 5, 10, 14, adjusted by 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NaOH), time (1, 2, 4, 6, 8, 10, 12, and 24 h), and temperature (20, 30, 40, 50, 60, 70, 80, and 90 °C) were investigated.

2.3. Adsorption experiments

The batch experiments were carried out in 100 mL conical flasks to which 1 g of the adsorbent was introduced into 50 mL of TNT red water at 1 g/50 mL. The bottles were shaken in a SHA-BA water bath at a speed of 200 rpm and temperature of 25 °C for 6 h.

After equilibrium had been reached, the suspension was filtered rapidly and 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 of adsorbents, The uptake ability, relative removal of COD (%), of the organic materials in the TNT red water absorbed by the metal incorporated LACs was calculated by:

$$\text{Relative removal of COD (\%)} = \frac{\text{COD}_0 - \text{COD}_e}{\text{COD}_0} \times 100\% \quad (1)$$

where COD₀ and COD_e are the original and final COD values of the TNT red water, respectively.

2.4. Column adsorption tests

An organic-glass column with 500 mm length and 15 mm diameter filled with 40 g of Cu/LACs was fed with red water that diluted various times (30, 20, 10 times). The flow rates were controlled at about 8 mL min⁻¹ using a peristaltic pump (HL-2B, Shanghai, China). The effluent solutions were intermittently collected at time intervals, and every 8 mL was selected as a sample to determine the COD values of the effluent solutions. The flow to the column was continued until the effluent COD value (*c_t*) approached the influent COD value (*c₀*), *c_t*/*c₀* = 0.99. TNT red water was diluted by distilled water. All experiments were carried out at room temperature (25 ± 2 °C) without pH adjustment.

The column sorption capacity (*q_{ed}*) was calculated by the equation expressed as:

$$q_{ed} = \frac{c_0vt - v \sum c_n t_n}{1000m} \quad (2)$$

where *q_{ed}* is the amount of organic materials sorption per gram Cu/LAC at saturation (mg g⁻¹), *c₀* is the original COD value of the influent (mg L⁻¹), *v* is the flow rates (8 mL min⁻¹), *t* is the saturated time (min), *c_n* is the COD value of sample *n* (mg L⁻¹), and *t_n* is the adsorption time of sample *n* (min), *m* is the amount of Cu/LAC (g).

2.5. Repeated use experiment

In order to investigate the repeated usability of the adsorbent, the desorption of the adsorbed organic materials from the Cu/LAC was also studied by static experiment. The adsorbed organic materials were desorbed using the solution of hydroxypropyl-β-cyclodextrin as eluting agent. The Cu/LAC that adsorbed organic materials were placed in the eluent and stirred continuously at room temperature for 12 h. After washed with distilled water and dried, the regenerated adsorbent was used again in the subsequent experiments. The uptake ability of the regenerated adsorbent was determined and calculated by relative removal of COD (%). In order to test the reusability of Cu/LAC, the adsorption–desorption procedure was repeated 8 times using the same material. Red water used in the repeated use experiment was 100 times diluted water.

2.6. Characterization

2.6.1. High performance liquid chromatography (HPLC) analysis

The concentrations of 2,4-dinitro-toluene-3-sulfonate (2,4-DNT-3-SO₃⁻) and 2,4-dinitrotoluene-5-sulfonate (2,4-DNT-5-SO₃⁻) in TNT red water before and after treated by LAC and Cu/LAC were determined by HPLC [26]. A Shimadzu LC-20A liquid chromatograph (Shimadzu Corporation, Japan) was used with the detection wavelength of 230 nm. The separation was carried out at 40 °C on a Shimpack VP-ODS column (250 mm × 4.6 mm) from Shimadzu. 20 μL of the sample was injected and the flow rate was 1.0 mL min⁻¹. Data processing was carried out with the LC solution software.

2.6.2. Gas chromatograph/mass spectrometer analysis

A 300 mL water sample was extracted by 5 mL dichloromethane three times under acidic, neutral and basic conditions, respectively. The three extract layers were combined and dried by using

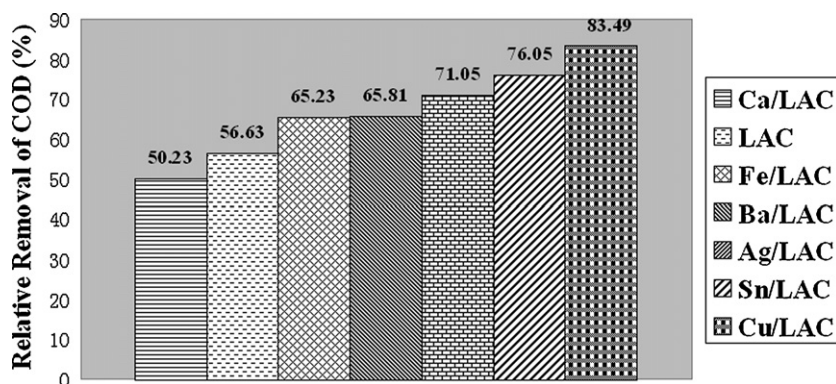


Fig. 1. Effects of different metal ions on the removal of COD from TNT red water.

nitrogen, and then the residue was dissolved in dichloromethane to 1 mL.

The proportionate amount (1.0 μ L) of water sample was injected into a Gas Chromatography/Mass Spectroscopy (GC/MS) (GC6890N/MSD5973, Agilent Technologies, USA) equipped with a DB-35 MS capillary column (60 m \times 0.25 mm), operated from 40 to 280 $^{\circ}$ C at a programming rate of 2.0 $^{\circ}$ C min $^{-1}$. Pure helium gas was employed as carrier gas at a flow rate of 1.0 mL min $^{-1}$ [7]. The mass spectra obtained were used to analyze the organic compositions of red water before and after treated by LAC and Cu/LAC.

2.6.3. UV-vis analysis

The UV-vis absorption of TNT red water and that adsorbed by LAC, Cu/LAC, respectively, was determined by using a Perkin Elmer LAMBDA 900 dual beam UV-vis spectrophotometer. The scanning range was 200–800 nm, with an accuracy of ± 1 nm, and the scanning rate was 0.2 nm/s. A 1-cm quartz cell was also used.

2.6.4. Inductively coupled plasma-atomic emission spectrometer (ICP) analysis

The concentration of Cu $^{2+}$ in the red water after treatment by Cu/LAC was determined using a Perkin-Elmer 2400 element analyzer. The inductively coupled plasma (ICP) analyses were carried out on a Perkin-Elmer Optima 3300DV ICP instrument with RSD less than 0.5%.

2.6.5. X-ray photoelectron spectroscopy (XPS) analysis

XPS was conducted on the LAC and Cu/LAC samples specifically to determine the chemical composition. The samples were ground with a mortar and pestle to expose fresh surfaces and were dusted onto adhesive tape. The XPS data were acquired on the Kratos AXIS and Physical Electronics PHI 5600. The X-ray was generated from an Al anode at a power of 150 W and the data were calibrated with respect to the Au (4f7/2), Ag (3d5/2), and Cu (2p3/2) lines at 83.98, 368.26, and 932.67 eV, respectively. The survey and narrow scans were acquired at pass energies of 58.7 eV and 23.5 eV, respectively. The minimum energy resolution of the instrument was 0.48 eV (Ag 3d5/2) with an accuracy of 0.2 eV.

3. Results and discussion

3.1. Effects of ions on extraction efficiency

Fig. 1 compares the absorption capacity of the seven different types of activated carbons, LAC, Cu/LAC, Sn/LAC, Ag/LAC, Ba/LAC, Fe/LAC, and Ca/LAC, at 293 K and reveals differing capacities. The relative removal of COD (%) of organic materials by Cu/LAC is the highest whereas that by Ca/LAC is the lowest. In comparison with

the original LAC, the absorption capacity of Cu/LAC, Sn/LAC, Ag/LAC, Ba/LAC, and Fe/LAC is enhance but that Ca/LAC is worse.

The phenomenon may be ascribed to the variation of the local hardness of the activated carbon surfaces and explained by the hard and soft acid and base (HSAB) principle proposed by Pearson [27]. Generally speaking, the adsorption properties of an adsorbent are not only determined by its porous microtexture but also strongly influenced by the chemical property of their surface [28]. When metal ions with different hardness were separately loaded onto the adsorbent, the local hardness of the adsorbent surfaces would vary and thus affected the interaction of the adsorbent surfaces with an adsorbate. In this case, the HSAB principle was locally applied as “hard regions of a system prefer to interact with hard reagents, whereas soft regions prefer soft species”. In order to determine the hardness quantitatively, the density functional theory (DFT) is adopted [29]. The absolute hardness and electronegativity of a metal can be estimated using the following formula [29,30]:

$$\eta = \frac{1}{2}(I - A) \quad (3)$$

where η , the absolute hardness (always positive), is half the difference between I , the ionization energy, and A , the electron affinity.

Based on Pearson's classification, Ag $^{+}$ and Sn $^{2+}$ belong to the soft acid category, Cu $^{2+}$ is a borderline acid, and Ca $^{2+}$, Fe $^{3+}$, and Ba $^{2+}$ are hard acids [29,31]. The absolute hardness values of these metal ions are listed in Table 2. When different metal ions are incorporated, the local surface hardness of the adsorbent is altered. According to the HSAB principle that hard acids prefer to bond to hard bases and soft acids prefer to bond to soft bases [27,30,31], incorporation of hard acids M $^{2+}$ can enhance the interactions between hard bases and M/LAC. On the other hand, a soft acid M $^{2+}$ will most likely weaken the interactions between hard bases and the M'/LAC surface. The removal ability of organic materials from red water by the metal-incorporated LAC has an inverse relationship with absolute hardness of the metals (Fe $^{3+}$ > Ba $^{2+}$ > Ag $^{+}$ > Sn $^{2+}$ > Cu $^{2+}$). However, Ca $^{2+}$ with the largest absolute hardness of the six metal ions weakens the absorption ability of LAC, as shown in Fig. 1. Our results suggest that most of the organic materials in the red water are soft bases although there is a small amount of hard base, thereby

Table 2
Pearson's classification and absolute hardness of metal ions.

Metal ions	Pearson classification	Absolute hardness
Ca $^{2+}$	Hard acid	19.7
Fe $^{3+}$	Hard acid	13.1
Ba $^{2+}$	Hard acid	12.8
Ag $^{+}$	Soft acid	6.9
Sn $^{2+}$	Soft acid	3.05
Cu $^{2+}$	Borderline	8.3

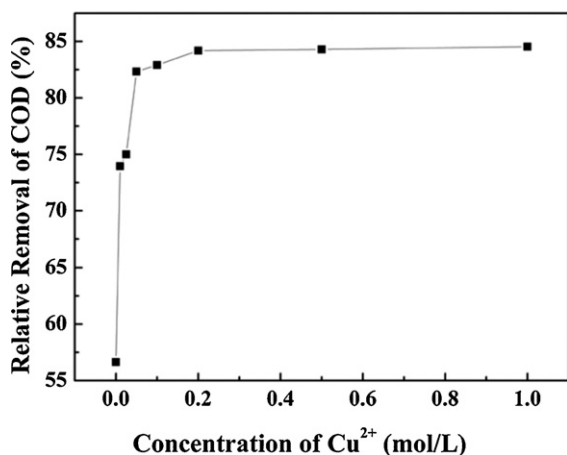


Fig. 2. Effects of different concentrations of Cu²⁺ on the removal of COD from TNT red water.

making the absorption ability of Cu/LAC the highest for Cu²⁺ is a borderline acid. In addition, Cu is cheaper than Ag and Sn and so Cu is chosen for further investigation in this work.

3.2. Optimal conditions for Cu/LAC preparation

3.2.1. Effects of Cu²⁺ concentration

The effects of the Cu²⁺ concentration are significant. As shown in Fig. 2, the relative removal of COD (%) increases from 56.63% to 84.19% as the concentration of Cu²⁺ increases from 0 to 0.200 mol L⁻¹. The results indicate that the COD removal efficiency is enhanced by a higher amount of impregnated Cu²⁺. However, the rate is not affected significantly when the concentration increases from 0.2 to 1.00 mol L⁻¹. This is because although a higher Cu²⁺ concentration can increase the loading capacity, the total active sites on the LAC are limited, and the number of active sites on the LAC for Cu²⁺ depends on mainly the number of metal particles and partially acid functional groups that exist on the LAC, for the loading of Cu²⁺ onto LAC is believed mainly through ion exchange. Based on our experimental results, a Cu²⁺ concentration of 0.2 mol L⁻¹ is used in our study.

3.2.2. Effects of pH

Fig. 3 shows the experimental results obtained at different pH values. The absorption ability of Cu/LAC is higher under acidic conditions than alkaline conditions. The absorption capacity increases as the pH goes up from 1 to 3 and it can be attributed to that the

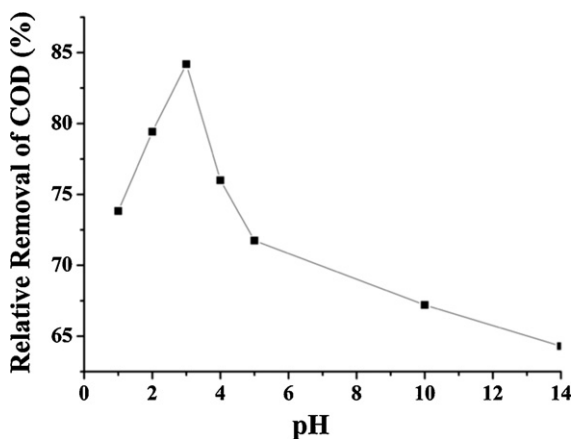


Fig. 3. Effects of different loading pH on the removal of COD from TNT red water by Cu/LAC.

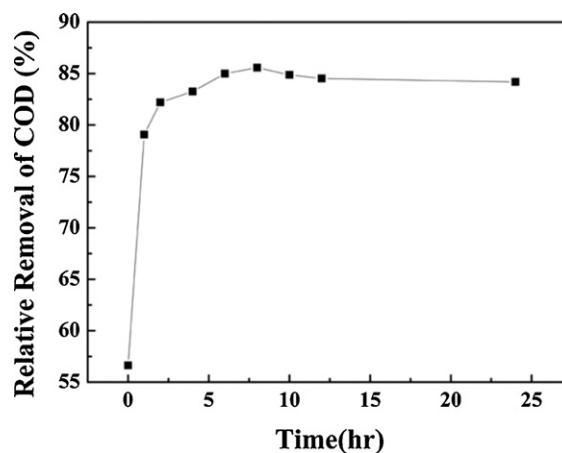


Fig. 4. Effects of different loading time on the removal of COD from TNT red water by Cu/LAC.

higher concentration and higher mobility of H⁺ in the solution favor absorption of hydrogen ions to the surface over Cu²⁺. However, as the pH increases from 3 to 14 the absorption efficiency diminishes markedly because of precipitation of Cu(OH)₂ [32]. As a result, a pH of 3 is used as the optimum pH for further study.

3.2.3. Effects of loading time

Fig. 4 shows the experimental results obtained from the Cu/LAC samples prepared using different loading time. The relative removal of COD (%) of the TNT red water increases rapidly in the initial 8 h, suggesting that the amount of Cu²⁺ incorporated onto the LAC increases rapidly with loading time up to 8 h. The relative removal of COD (%) is 85.58%, which is 28.25% compared to the case without Cu²⁺ incorporation of 56.63%. This is because there are enough adsorption sites on the LAC. After 8 h, the loaded amount does not increase with time while desorption begin to occur, albeit not obviously. The loaded amount of Cu²⁺ reaches an equilibrium as the absorption sites are gradually saturated. The equilibrium loading time is thus experimentally determined to be about 8.

3.2.4. Effects of temperature

In order to fathom the influence of the temperature, loading experiments were conducted at different temperatures and the results are shown in Fig. 5. The relative removal of COD (%) increases with temperature suggesting that the loading process is endothermic. This can be explained by several reasons. On the one hand, at higher temperature, the kinetic energy of Cu²⁺ ions is high; therefore, contact between Cu²⁺ ions and the active sites of LAC is sufficient, leading to an increase in loading efficiency. Similar trends were also observed by other researchers for aqueous phase adsorption [33]. On the other hand, as shown in Table 3, Cu²⁺ ions are incorporated onto the LAC in a way that other metal ions (e.g. Al³⁺, Mg²⁺, Ca²⁺) are partially replaced, which denoting that some kind of chemical interactions take place during adsorption process, and hence a large amount of heat is consumed to transfer the Cu²⁺ cations from aqueous onto LAC and the metal ions (e.g. Al³⁺, Mg²⁺, Ca²⁺) from the solid phase to the aqueous. What's more, since the ion exchange may also occur between the Cu²⁺ ions and the functional groups, such as carboxylic and phenolic, on the surface of LAC, the loading of the Cu²⁺ ions increases with higher temperature may due to the increase in the negative surface charge of the LAC [34]. Additionally, an increase in loading capacities of the adsorbents at higher temperature may also be attributed to the enlargement of pore size [35]. However, until a certain temperature limit, the increase of the temperature encourages the process of agglomeration in a very determined sense, beyond which the desorption begin

Table 3
XPS surface composition (as % of all elements present) in the original LAC and Cu/LAC.

Sample	Sample composition (%)								
	C(1s)	O(1s)	N(1s)	S(2p)	Si(2p)	Al(2p)	Mg(2p)	Ca(2p)	Cu(2p)
LAC	70.55	21.11	0.43	0.76	2.00	2.49	1.45	0.75	0
Cu/LAC	61.21	28.98	0.67	1.69	2.26	0	0.94	0.22	4.03

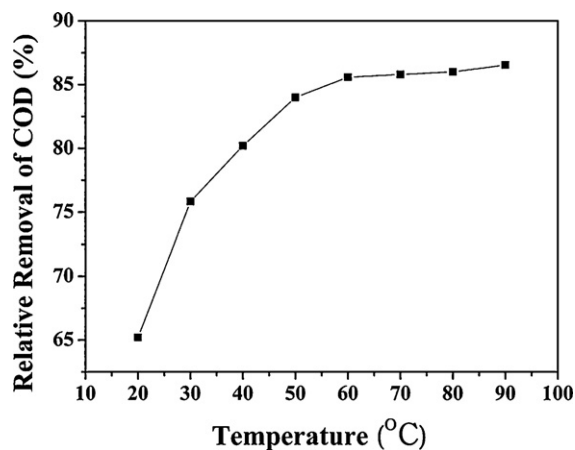


Fig. 5. Effects of different loading temperature on the removal of COD of TNT red water by Cu/LAC.

with the adsorption [36]. This may explain why when the loading temperature reaches 60 °C, the increase in loading efficiency of LAC is no longer apparent. Consequently, a temperature of 60 °C is chosen in the experiments.

3.3. Characterization of Cu/LAC

XPS was conducted to obtain information about the elemental composition and oxidation state. Fig. 6 shows the XPS spectra of the original LAC and Cu²⁺ incorporated LAC. According to the surface compositions shown in Table 3, Cu²⁺ ions are incorporated into the LAC in a way that other metal ions are partially replaced. Fig. 6 clearly shows that there is shakeup satellite peak at 935.25 eV that is indicative of Cu(II) species. The results verify successful incorporation of Cu²⁺ ions into the carbon surface.

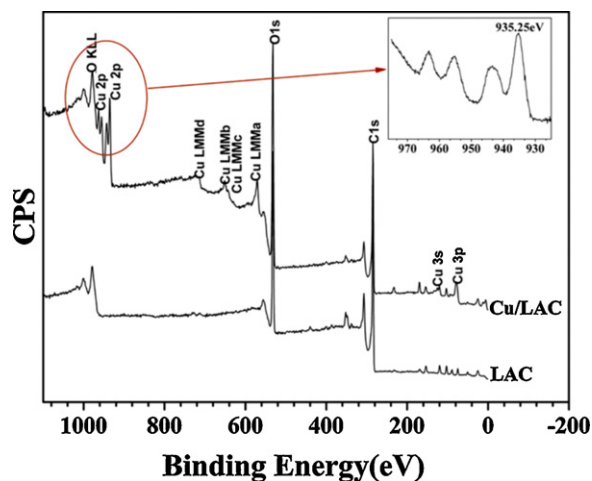


Fig. 6. XPS spectra of the original LAC and Cu/LAC.

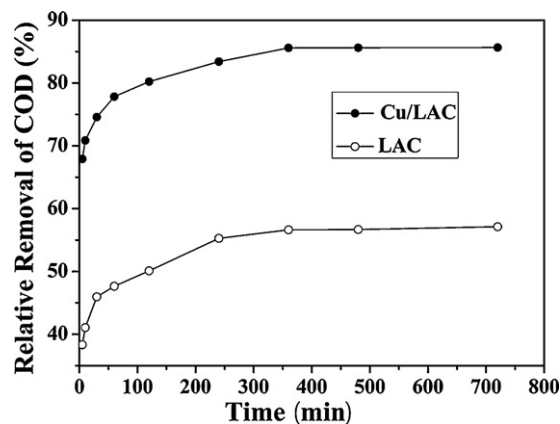


Fig. 7. Kinetic adsorption of TNT red water on LAC and Cu/LAC. Conditions: 100 times diluted red water; temperature: 298.15 K; adsorbent dose, 1 g.

3.4. Kinetic adsorption curve of organic materials on Cu/LAC

Fig. 7 shows influence of contact time on organic materials of red water sorption on LAC and Cu/LAC. It can be seen that the adsorption of organic materials on LAC and Cu/LAC reaches to equilibrium both in 6 h, and the adsorption rate of Cu/LAC is much faster than that of LAC. The relative removal of COD (%) of the TNT red water on Cu/LAC can reach to 85.58%, which is much higher than that on LAC (56.63%). It is implied that Cu/LAC possesses strong adsorption ability and affinity for the organic materials in red water.

Taking into account that the main components of the red water can be divided into two types: sulfonated and non-sulfonated nitro-toluenes, some of the representative components of red water (such as DNTS, TNT and DNT) were studied as chemical probes. Fig. 8 shows the effect of contact time on the Cu/LAC removal of 100 mg L⁻¹ DNTS, TNT and DNTS simulated wastewater. The removal of DNTS, TNT and DNT increases with time and reaches a maximum after 2 h, 6 h and 8 h of agitation, respectively. The Cu/LAC has the highest removal rate (99.35%) of DNTS, compared

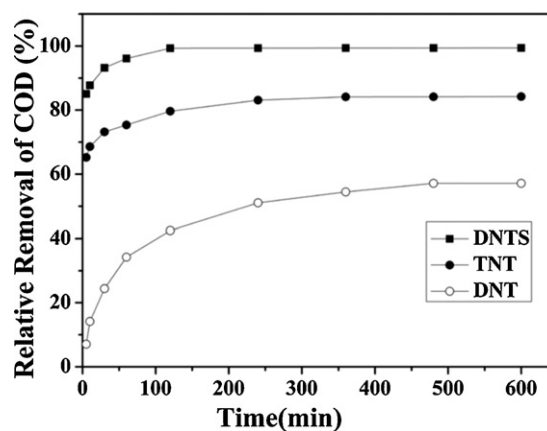


Fig. 8. Kinetic adsorption of DNTS, TNT and DNT on Cu/LAC. Conditions: initial concentration of DNTS, TNT and DNT: 100 mg L⁻¹; temperature: 298.15 K; adsorbent dose, 0.05 g.

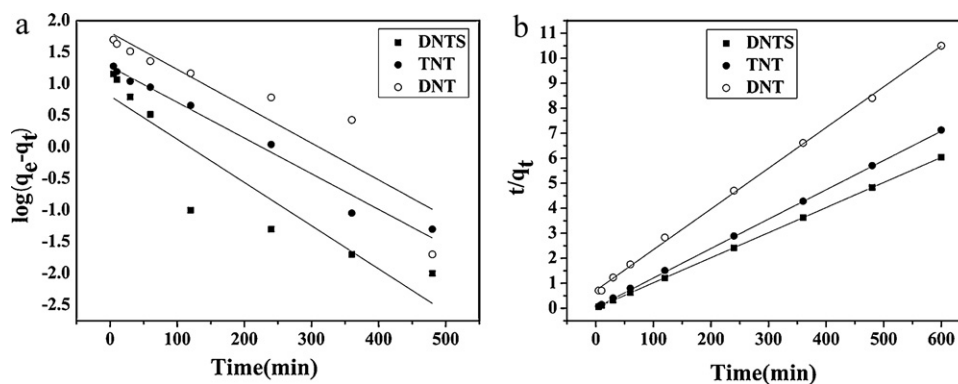


Fig. 9. Kinetics plot: (a) pseudo-first order, (b) pseudo-second order for the adsorption of DNTS, TNT and DNT onto Cu/LAC.

with TNT (84.11%) and DNT (57.12%), indicating that Cu/LAC has stronger affinity to DNTS. This may be associated with complexation reaction which occurs between Cu/LAC and DNTS in the solution. Nevertheless, for TNT and DNT, they are believed to adsorb mainly through hydrogen bonds between the Cu/LAC and TNT and DNT, since there are many oxygen functional groups such as hydroxyl groups, carboxyl groups, phenolic groups, and inner ester on the surface of Cu/LAC.

To analyze the adsorption rates and kinetics of DNTS, TNT and DNT onto Cu/LAC, two kinetic models, namely pseudo-first-order and pseudo-second-order models were tested.

The Lagergren's equation is one of the most widely used rate equations to describe the adsorption of an adsorbate from the liquid phase [37]. The linear form of pseudo-first-order rate expression of Lagergren's equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \quad (4)$$

where k_f ($L \text{ min}^{-1}$) is the rate constant of pseudo-first order adsorption, q_e and q_t (mg g^{-1}) are the amounts of adsorbate (DNTS, TNT, DNT respectively) adsorbed per gram of Cu/LAC at equilibrium and at any time t , respectively. The values of k_f and q_e for adsorbate adsorption by Cu/LAC were determined from the plot of $\log(q_e - q_t)$ versus t (Fig. 9a).

The pseudo-second order kinetics can be expressed in a linear form as [38]:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k_s ($\text{g mg}^{-1} \text{ min}^{-1}$) is rate constant of pseudo-second order adsorption. The plot of t/q_t versus t is shown in Fig. 9b. The values of k_s and q_e can be calculated from the slope and intercept of the plot in Fig. 9b.

The value of h was calculated using the k_s rate constant obtained from pseudo-second-order kinetic data and expressed as:

$$h = k_s q_e^2 \quad (6)$$

h is the initial adsorption rate ($\text{mg g}^{-1} \text{ min}^{-1}$) of the adsorbate [39].

The constants of kinetic models for the adsorption of TNT, DNT and DNTS on Cu/LAC are listed in Table 4. It is observed that

the calculated adsorption capacity ($q_{e,cal}$) values estimated by the pseudo-first-order model differ substantially from those measured experimentally, whereas $q_{e,cal}$ values obtained from the pseudo-second-order kinetic model are very close to experimental data. Moreover, the correlation coefficient values for pseudo-second-order model are much higher than those of pseudo-first-order model, suggesting that the adsorbent systems can be well described by the pseudo-second-order kinetic model.

3.5. Water quality analysis

After treated by Cu/LAC, most of the organic materials in TNT red water were extracted onto Cu/LAC, the COD of the water reduced from 860 to 124 mg L^{-1} . Dinitrotoluene sulfonates are the main organic components in TNT red water. After extracted by Cu/LAC, most of the two dinitrotoluene sulfonates in TNT red water were removed. The concentration of 2,4-DNT-3- SO_3^- decreased from 197 to 20.6 mg L^{-1} , while that of 2,4-DNT-5- SO_3^- decreased from 310 to 23.3 mg L^{-1} .

In this work, GC/MS analysis was used to detect the organic molecule compositions of red water before and after treated by Cu/LAC. The mass spectra obtained were utilized to identify the components according to NIST05 mass spectral library database. The GC/MS results of the initial and the treated red water are listed in Table 5. It can be seen that after extracted treatment by Cu/LAC, some organics (such as 3-methyl-2-nitrophenol, 5-methyl-2-nitrophenol, 3-methyl-6-nitrobenzoic acid, 2-methyl-3,5-dinitrophenol and 3,5-dinitro-p-toluidine) cannot be detected through GC/MS analysis anymore, indicating that they are extracted onto Cu/LAC. This is may associated with the hydrogen bonds that between the organics and Cu/LAC.

Fig. 10 shows the UV-vis absorption spectra of TNT red water (diluted 100 times) before and after treated by LAC and Cu/LAC. It can be seen that there are still large concentration of aromatic compounds in the 100 times diluted red water since strong absorption take place in visible and ultraviolet region for TNT red water. After TNT red water sample has been treated by LAC, the absorbance of the red water at visible region decreases in a certain degree, while the absorbance of the red water that treated by Cu/LAC at visible region decreases greatly, suggesting that the majority of organic

Table 4

The pseudo first-order and second-order kinetic parameters for the adsorption of DNTS, TNT and DNT onto Cu/LAC.

Adsorbate	$q_{e,exp}$ (mg g^{-1})	Pseudo first-order kinetic			Pseudo second-order kinetic			
		$q_{e,cal}$ (mg g^{-1})	k_f ($L \text{ min}^{-1}$)	r^2	$q_{e,cal}$ (mg g^{-1})	k_s ($\text{g mg}^{-1} \text{ min}^{-1}$)	$h = k_2 q_e^2$ ($\text{mg g}^{-1} \text{ min}^{-1}$)	r^2
DNTS	99.35	6.42	0.01575	0.85849	99.70	0.007553	75.08	0.99999
TNT	84.11	18.76	0.01301	0.98277	84.89	0.002579	18.59	0.99991
DNT	57.12	64.90	0.01343	0.86284	61.39	0.000373	1.40	0.99914

Table 5
GC/MS results of the initial and the treated TNT red water.

The initial red water		The treated red water	
Retention time (min)	Assignments	Retention time (min)	Assignments
30.0	2-Nitrotoluene	29.0	2-Nitrotoluene
33.8	4-Nitrotoluene	32.5	4-Nitrotoluene
34.6	3-Methyl-2-nitrophenol	45.4	2,6-Dinitrotoluene
36.7	5-Methyl-2-nitrophenol	49.5	2,4-dinitrotoluene
50.8	2,6-Dinitrotoluene	52.0	2,5-Dinitrotoluene
53.5	2,4-dinitrotoluene	63.5	1,3,5-Trinitrobenzene
55.0	2,5-Dinitrotoluene		
60.1	3-Methyl-6-nitrobenzoic acid		
60.6	2-Methyl-3,5-dinitrophenol		
67.1	1,3,5-Trinitrobenzene		
67.8	2,4,6-Trinitrotoluene		
79.7	3,5-Dinitro- <i>p</i> -toluidine		

compounds containing chromophore and auxochromous group are extracted onto the Cu²⁺ impregnated LAC. However, there is still strong absorption in ultraviolet region demonstrating that some certain organic compounds remained in water, but the organic compounds remained in the water treated by Cu/LAC is smaller than that in treated by LAC.

3.6. Metal leaching test

Desorption of Cu²⁺ from Cu/LAC after treating different concentrations of TNT red water was examined. The aqueous phase analysis results show that the desorption rate of Cu²⁺ is 0.074%, 0.116%, 2.431% and 10.201% respectively, for treating 100, 50, 10 and 0 times diluted red water. The desorption of copper from Cu/LAC increases with the concentration of red water. When the TNT red water is diluted 100 times, the desorption is not significant, and less than 1% of the copper was desorped from Cu/LAC. While the desorption rates of Cu²⁺ is up to 10.201% when the TNT red water was not diluted. This may be because that when the concentration of red water is high, the amount of Na⁺ that exists in the red water is much bigger, the Cu/LAC ((L-RO)₂Cu²⁺) would shift the ion-exchange equilibrium in the reaction (Eq. (7)) to the right what results in the displacement of divalent ions (Cu²⁺) with monovalent ones (Na⁺) from the functional groups. Similar situations were observed in other ion-exchange systems where the ion-exchange reaction was coupled with a solid phase formation [40]. For this

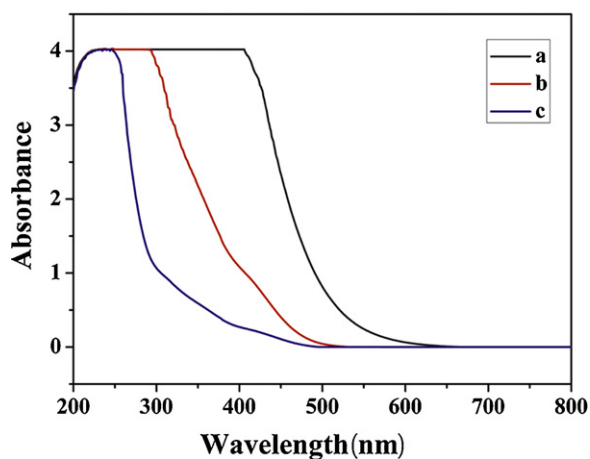


Fig. 10. UV-vis absorption spectra of (a, right curve), TNT red water (diluted 100 times) before and after treated by (b, middle curve), LAC and (c, left curve), Cu/LAC. (For interpretation of the references to color in this text, the reader is referred to the web version of the article.)

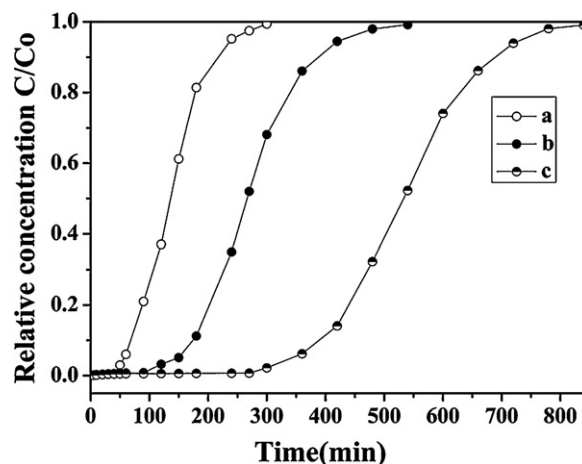


Fig. 11. Effect of influent concentration: (a) 10 times diluted red water; (b) 20 times diluted red water and (c) 30 times diluted red water on the breakthrough curves.

reason, the Cu²⁺ would be partially replaced by the Na⁺, which will inhibit the adsorption ability of Cu/LAC towards the organic materials in the water. Therefore, the adsorbent is suggested to be applied to the treatment of lower concentration of TNT red water.



3.7. Column adsorption

The effect of TNT red water concentrations (diluted 30, 20, 10 times, respectively) on the breakthrough curves at a constant flow rate of 8 mL min⁻¹ is shown in Fig. 11. As seen from Fig. 11, the breakthrough points occur at 420, 180 and 60 min for influent red water concentrations diluted 30, 20, 10 times, respectively. By increasing the feed initial concentration, the volume of solution treated before breakthrough point is considerably reduced. These results demonstrate that the change of influent concentration affects the saturation rate and breakthrough time, in a word, the diffusion process is concentration dependent [41]. As the influent concentration increases, organic materials loading rate increases which results in decrease of driving force for mass transfer for a fixed sorption zone length. However, it is observed that the q_{ed} of Cu/LAC for different initial influent concentrations (diluted 30, 20, 10 times) is about 361, 358, 352 mg g⁻¹, respectively, which indicating that the influent concentration has little effect on the sorption capacity of the adsorbent. This may be attributed to the concentration gradient which will enhance the sorption process at higher influent concentrations [42].

3.8. Reusability

As previous article described that hydroxypropyl- β -cyclodextrin could increase the solubility of nitro-compound in water because of the formation of inclusion compound [43], Cu/LAC absorbed with organic materials from TNT red water was regenerated by hydroxypropyl- β -cyclodextrin, the organic materials were released into the eluent, the active sites of the adsorbent were partly recover. Therefore, the Cu/LAC can be used again to treat another sample. In order to show the reusability of the Cu/LAC, the adsorption-desorption cycle was repeated 8 times using the same material. The adsorption-desorption cycle of Cu/LAC is shown in Fig. 12. The results clearly show that the Cu/LAC can be used repeatedly without significantly losing its adsorption capacity.

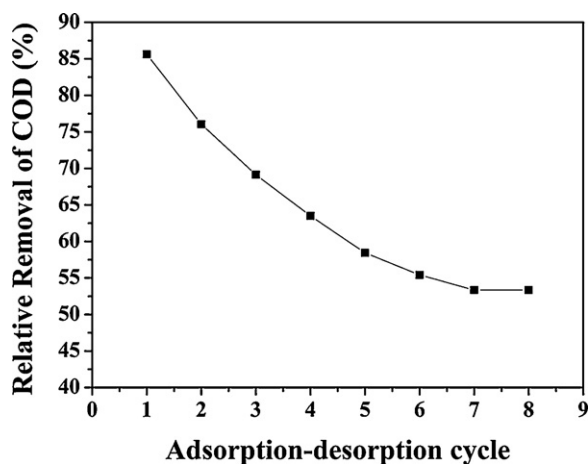


Fig. 12. Adsorption-desorption cycle of Cu/LAC.

4. Conclusions

In this study, the extraction ability of LAC modified with different metal ions towards organic materials in TNT red water was investigated. Introduction of Cu^{2+} , Sn^{2+} , Ag^+ , Ba^{2+} , and Fe^{3+} improves the absorption capacity but Ca^{2+} produces opposite results. Our results suggest that most of the organic materials in the red water can be categorized as soft bases although a small amount of hard bases is present. Cu^{2+} is the most effective in removing organic materials from the TNT red water among the metal ions that studied. The extraction ability of the Cu/LAC depends on the Cu^{2+} concentration, loading time, as well as temperature. The optimal loading conditions determined experimentally are: 8 h, 60°C , and 0.200 mol L^{-1} of Cu^{2+} . Almost 91.34% of dinitrotoluene sulfonates and 85.58% of COD in TNT red water can be removed after treated by Cu/LAC. GC/MS and UV-vis results show that the majority of the organic components in TNT red water can be extracted onto Cu/LAC. Cu/LAC has stronger affinity to sulfonated nitrotoluenes (represented by dinitrotoluene sulfonates) than non-sulfonated nitrotoluenes (represented by TNT and DNT), this is may because that complexation reaction occurs between the sulfonated nitrotoluenes and Cu/LAC, while the non-sulfonated nitrotoluenes are believed to adsorb mainly through hydrogen bonds onto Cu/LAC. Moreover, Column adsorption show that the influent concentration has little effect on the sorption capacity of the adsorbent. Finally, Cu/LAC is found to possess excellent reusability properties in the lower concentration of TNT red water.

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