Organic pollutants removal from 2,4,6-trinitrotoluene (TNT) red water using low cost activated coke

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Abstract

We treated 2,4,6-trinitrotoluene (TNT) red water from the Chinese explosive industry with activated coke (AC) from lignite. Since the composition of TNT red water was very complicated, chemical oxygen demand (COD) was used as the index for evaluating treatment efficiency. This study focused on sorption kinetics and equilibrium sorption isotherms of AC for the removal of COD from TNT red water, and the changes of water quality before and after adsorption were evaluated using high performance liquid chromatography, UV-Vis spectra and gas chromatography/mass spectroscopy. The results showed that the sorption kinetics of COD removal from TNT red water onto AC fitted well with the pseudo second-order model. The adsorption process was an exothermic and physical process. The sorption isotherm was in good agreement with Redlich-Peterson isotherm. At the conditions of initial pH = 6.28, 20°C and 3 hr of agitation, under 160 g/L AC, 64.8% of COD was removed. The removal efficiencies of 2,4-dinitrotoluene-3-sulfonate (2,4-DNT-3-SO_3^-) and 2,4-dinitrotoluene-5-sulfonate (2,4-DNT-5-SO_3^-) were 80.5% and 84.3%, respectively. After adsorption, the acute toxicity of TNT red water reduced greatly, compared with that of unprocessed TNT red water.

Key words: TNT red water; activated coke; adsorption; acute toxicity

DOI: 10.1016/S1001-0742(10)60619-5

Introduction

Trinitrotoluene (TNT) is an important and widely used explosive in the world (Clark and Boopathy, 2007; Boparai et al., 2008; Kalderis et al., 2008; Lee and Jeong, 2009; Nyanhongo et al., 2009). During the TNT manufacturing process, unsymmetrical TNTs produced from the nitration of toluene must be removed to meet military specifications (Akhavan, 2004). In the purification stage, sodium sulfite is added to react with unsymmetrical TNT to produce dinitrotoluene sulfonates (DNTS'), such as 2,4-DNT-3-SO_3^- and 2,4-DNT-5-SO_3^-, which are water-soluble and easily separated from symmetrical TNT. The wastewater after phase separation has a dark red color and is commonly called "TNT red water". Dinitrotoluene sulfonates like 2,4-DNT-3-SO_3^- and 2,4-DNT-5-SO_3^- are the main organic components in TNT red water (Xiao et al., 2006; Yinon and Zitrin, 1996). In addition, TNT red water also contains incomplete nitration products, such as 2,4-DNT and 2,6-DNT, and complicated toxic byproducts formed during the nitration and purification stages. Therefore,

TNT red water is a highly hazardous and toxic wastewater, which is classified by the U.S. Environmental Protection Agency as a RCRA-regulated hazardous waste based on its reactivity. Direct discharge of untreated TNT red water into waterways or soils causes severe water and soil pollution.

Many methods for TNT red water treatment have been studied. Hao et al. (1993a, 1994) studied the treatment of TNT red water by wet air oxidation (WAO), which demonstrated WAO to be available for TNT red water treatment. Incineration is the most widely used process, but the cost of fuel is high and this process usually generates secondary pollution during treatment (Lewis et al., 2004). Zhao et al. (2010) have studied the possibility of vacuum distillation to treat TNT red water.

Biological treatment has been widely used in wastewater treatment. As TNT red water is highly toxic to microorganisms and contains high concentrations of many organic and inorganic compounds. One way to solve this would be for the TNT red water to undergo a cost-effective preprocess before biological treatment. Adsorption technique is widely used for wastewater treatment due to its versatility and efficiency in separating a wide range of chemical compounds and its easily operational procedure. Activated

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carbon is one of the main adsorbents, but adsorption by activated carbon for TNT red water demonstrates difficulty of carbon regeneration by chemical means and the hazard of thermal regeneration (Walsh et al., 1973). Activated coke (AC) is an adsorbent material used as a substitute for activated carbon, and is produced from naturally occurring carbonaceous materials like lignite, petroleum coke, wood, and other biomass. Activated coke is usually made from low micropore volume macro- and meso-porous materials, which favor adsorbing contaminants from liquid phase (Kojima et al., 2002; Wieβner et al., 1998). In previous research, AC was proved to be an effective adsorbent of organic pollutants from coking wastewater (Shawwa et al., 2001). However, no studies have reported on the adsorption treatment of TNT red water by using AC.

The aim of this study was to investigate the adsorption properties of AC for the treatment of TNT red water. Sorption kinetics and equilibrium isotherms were studied. The changes in the chemical constitution of TNT red water before and after adsorption onto AC were evaluated by gas chromatography/mass spectroscopy (GC/MS), HPLC high performance liquid chromatography (HPLC), and UV-Vis spectra. The acute toxicities before and after adsorption were investigated by bacterium bioluminescence assays.

1 Materials and methods

1.1 Materials

The TNT red water was obtained from the Dongfang Chemical Corporation (Hubei Province, China). It had a dark red color with complicated compositions and high chemical oxygen demand (COD) (9.66×10^3 mg/L). The water samples used in the experiments were diluted ten times with distilled water. The initial pH was 6.28.

AC made by lignite was obtained from the Datang Yima Coke Plant (Henan Province, China). The particle range was 0.45–0.90 mm, surface area was 408 m^2/g, total pore volume was 0.266 cm^3/g, and average pore diameter was 2.61 nm, which were measured by N$_2$ adsorption isotherm using an ASAP 2010 Micromeritics instrument.

The AC was washed several times with distilled water, and then dried in an oven at 105°C for 48 hr and stored in an air-tight glass bottle for later use.

The luminescent bacterium *Vibrio qinghaiensis* sp. Nov. was provided by Beijing Hamatsu Photon Techniques Inc., China.

1.2 Adsorption experiments

The batch adsorption experiments were performed using 50 mL of TNT red water and 1.0 g of AC in 250 mL triangular flasks with a stopper. The experiments were carried out at 20, 25, 30 and 40°C in an air-bath shaker without pH adjustment. The COD was determined at different contact time. The initial concentrations of TNT red water samples ranged from 3.22×10^3 to 1.60×10^4 mg/L for equilibrium isotherms determination. Effects of AC dosage on COD removal were also determined.

1.3 Cost analysis

A 50-mL TNT red water sample was added to a 250-mL triangular flask with stopper, into which 0.5 g of four kinds of adsorbents were added. The experiments were carried out in an air-bath shaker bath at pH 6.28, 25°C and agitated for 3 hr. The water samples were centrifuged at 8000 r/min for 10 min, and the supernate was then analyzed.

1.4 Water quality detection

Since the composition of TNT red water is very complicated, COD was used to evaluate the treatment efficiency of TNT red water by potassium dichromate oxidation (Hach Heating System, Hach Corporation, USA).

The concentrations of 2,4-DNT-3-SO$_3^-$ and 2,4-DNT-5-SO$_3^-$ before and after adsorption were determined by HPLC (Agilent 1100 liquid chromatography, Agilent Corporation, USA). The sample was detected at 230 nm, with the Agilent SB-Aq column (250 mm × 4.6 mm, 5 μm). The sample amount of injection was 20 μL and the flow rate was 1.0 mL/min (Preiss et al., 2009). After being filtered by a 0.45-μm membrane and diluted 30 times, all samples were detected by HPLC.

The UV-Vis spectra of the TNT red water samples before and after adsorption were measured in the range of 190–1100 nm using a UV-Visible spectrophotometer (UV-1800, Shimazu, Japan) with a 1 cm quartz cell.

A 6890N/5973 GC/MS system (Agilent Corporation, USA) 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 of 1.0 μL was injected, operated from 40 to 280°C at a programming rate of 2.0°C/min with the DB-35MS capillary column (30 m × 0.25 mm × 0.25 μm). Pure helium gas was used as the carrier gas at a flow rate of 1.0 mL/min.

1.5 Acute toxicity test

A BHP9511 water quality toxicity analyzer (Beijing Hamatsu Photon Techniques Inc., China) was used to detect the acute toxicity of TNT red water before and after adsorption by determining the luminescence inhibition ratio of *Vibrio qinghaiensis* sp. Nov. (Ma et al., 1999), a freshwater luminescent bacterium separated from body surfaces of *Gymnocypris przewalskii* living in Qinghai Lake, China.

The luminescence inhibition ratio (LIR) was calculated according to Eq. (1):

$$LIR = \frac{RLI_{ref} - RLI_s}{RLI_{ref}} \times 100\% \qquad (1)$$

where, RLI is the relative light intensity of the luminescence emitted from luminescent bacteria, and ref and s represent the reference and sample, respectively.

2 Results and discussion

2.1 Sorption kinetics of COD in TNT red water

In this study, the pseudo first- and second-order models and the intraparticle diffusion model were used to analyze the adsorption mechanism of COD onto AC from TNT red water.

The pseudo first-order model (Ho and McKay, 1998a) can be expressed as Eq. (2):

$$\log(q_1 - q_t) = \log q_1 - \frac{k_1 t}{2.303} \qquad (2)$$

where, q_1 (mg/g) and q_t (mg/g) are the amount of COD adsorbed at equilibrium and at time t (min), respectively; and k_1 (min^{-1}) is the rate constant of the pseudo first-order sorption. The straight line plots of $\log(q_1 - q_t)$ against t have been tested to obtain parameters of k_1 and q_1.

The pseudo second-order model (Ho and McKay, 1999) can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \qquad (3)$$

The initial sorption rate h (mg/(g·min)) can be calculated by Eq. (4):

$$h = k_2 q_2^2 \qquad (4)$$

where, q_2 (mg/g) is the amount of COD adsorbed at equilibrium; and k_2 (g/(mg·min)) is the rate constant of pseudo-second order sorption. The straight line plots of t/q_t against t have been tested to obtain parameters of k_2, h and q_2.

Intraparticle diffusion (Weber and Morris, 1963) was determined by Eq. (5):

$$q_t = k_3 t^{0.5} \qquad (5)$$

where, k_3 (mg/(g·min$^{0.5}$)) is the intraparticle diffusion rate constant.

Figure 1 presents the dependence of sorption capacity on contact time at different temperatures. It shows that the sorption capacity at different temperatures increased with contact time, quickly in the first 30 min and then gradually with increasing contact time until the adsorption reached equilibrium at 3 hr. It can also be observed that the lower the temperature, the higher the saturated sorption capacity. When adsorption reached equilibrium at 20°C, the saturated sorption capacity was 60.5 mg/g. Generally, if adsorption is a chemical process, sorption capacity increases with increasing temperature due to some chemical adsorptions with a chemical reaction or bond being involved in the adsorption process (Acemioğu, 2004; Mittal et al., 2005). The results showed that sorption capacity increased with the decreasing temperature, indicating that the adsorption of COD on AC might be an exothermic process.

The fitting results presented a better compliance with the pseudo second-order model, as shown in Table 1. The regression coefficients were higher than 0.993 and
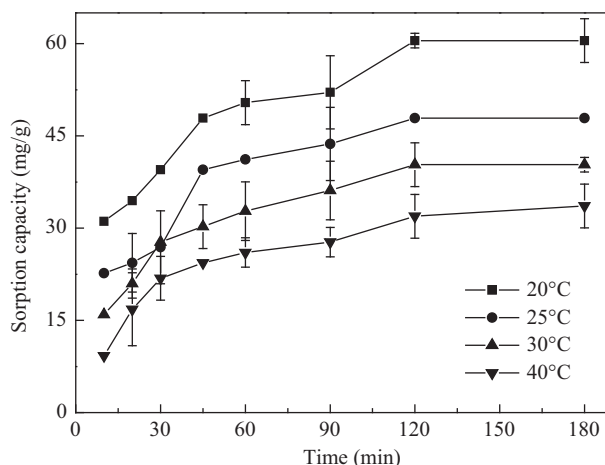

Fig. 1 Kinetic curves of COD onto AC at various temperatures.

the initial sorption rate h decreased from 3.54 to 1.46 mg/(g·min) when the temperature increased from 20 to 40°C, which suggested that chemisorption reaction was not predominant in the rate controlling step. Therefore, the adsorption process was a physical one rather than a chemical one (Ho and McKay, 1998b).

Figure 2 plots the amount of COD adsorbed per unit weight of AC against the square root of time. The plot in the initial 30 min was due to the diffusion of adsorbate through the solution to the external surface of the adsorbent or the boundary layer diffusion of solute molecules (Kumar et al., 2003). Good linearization of the data, as shown in Table 1, was observed for the initial phase of the reaction in accordance with expected behavior, which indicated that intraparticle diffusion was the rate limiting step (Weber and Morris, 1963).

2.2 Equilibrium isotherms

Langmuir, Freundlich and Redlich-Peterson isotherms were used to examine the adsorption mechanism of COD onto AC from TNT red water.

At constant temperature, COD adsorbed onto AC will be in equilibrium with COD in bulk solution. The saturated monolayer isotherm can be represented as Langmuir isotherm (Langmuir, 1916; Kinniburgh, 1986):
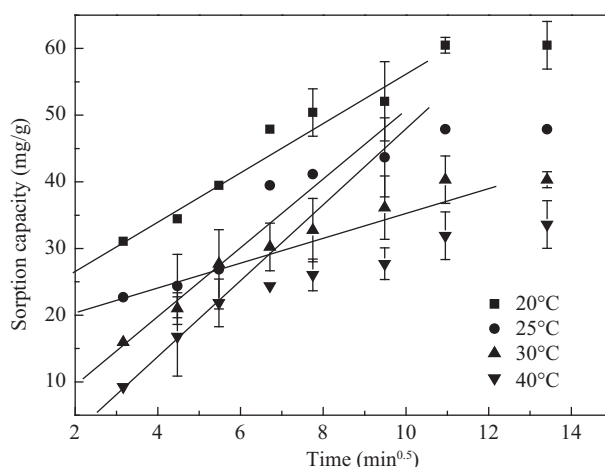

Fig. 2 Intraparticle diffusion plots for the adsorption of COD onto AC at various temperatures.

Table 1   Kinetics parameters for the adsorption of COD onto AC

T (°C)	$q_{e, exp}$ (mg/g)	Pseudo first-order model				Pseudo second-order model				Intraparticle diffusion	
		q_1 (mg/g)	k_1 (min^{-1})	R_1^2		q_2 (mg/g)	k_2 (g/(mg·min))	h (mg/(g·min))	R_2^2	k_3 (mg/(g·min$^{0.5}$))	R_3^2
20	58.8	33.2	1.71×10^{-2}	0.900		64.7	8.44×10^{-4}	3.54	0.993	0.691	0.928
25	46.2	36.0	3.08×10^{-2}	0.933		54.1	9.00×10^{-4}	2.63	0.990	0.345	0.928
30	40.3	25.0	2.00×10^{-2}	0.992		45.8	9.82×10^{-4}	2.06	0.997	0.801	0.950
40	33.6	26.4	2.11×10^{-2}	0.928		38.1	1.01×10^{-2}	1.46	0.995	0.214	0.997

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \tag{6}$$

where, C_e (mg/L) is the equilibrium concentration; q_e (mg/g) is the equilibrium amount of COD adsorbed; q_m (mg/g) is q_e for a complete monolayer, and K_a (L/mg) is the sorption equilibrium constant.

The empirical Freundlich isotherm (Freundlich, 1906), based on adsorption on heterogeneous surface, can be derived by assuming a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites, and is as follows

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

where, K_F and $1/n$ are the Freundlich constant characteristics of the system, indicating the sorption capacity and sorption intensity, respectively.

The Redlich-Peterson isotherm (Redlich and Peterson, 1959) incorporates the features of the Langmuir and Freundlich isotherms, which has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be expressed as follows:

$$q_e = \frac{A C_e}{1 + B C_e^g} \tag{8}$$

where, three isotherm constants, namely, A (L/mg)^g, B (L/g), and g ($0 < g < 1$), characterize the isotherm. Eq. (8) can be linearized by taking logarithms:

$$\ln(A \frac{C_e}{q_e} - 1) = g \ln(C_e) + \ln(B) \tag{9}$$

where, A, B, and g can be evaluated from the linear plot represented by Eq. (9) using the solver add-in with Microsoft's spreadsheet, Microsoft Excel (Ho and Ofomaja, 2006).

Figure 3 presents the isotherm curves of COD onto AC at different initial concentrations and temperatures. The equilibrium sorption capacity increased with decreasing temperature and increased with increasing initial concentration. Table 2 shows the fitting results of the experimental data by different isotherms. The correlation coefficients for the Redlich-Peterson isotherm were higher than those for the Langmuir and Freundlich isotherms, which might be due to the complexity of TNT red water composition. Therefore, the Redlich-Peterson isotherm might be more useful for simulating the complicated adsorption process of TNT red water by AC.
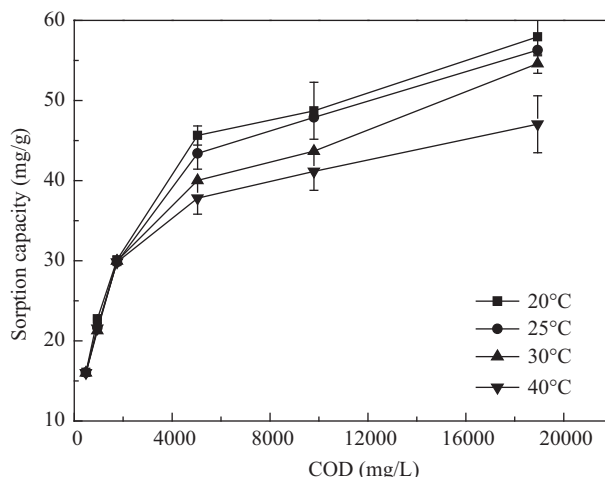
Fig. 3 Isotherm curves of sorption equilibrium COD onto AC at various temperatures.

2.3 Effect of AC dose on COD removal

Figure 4 presents the effect of AC dose on equilibrium sorption capacity and COD removal efficiency. The removal efficiency of COD increased quickly from 7.93% to 64.8%, when the concentration of AC increased from 10 to 160 g/L. This was because the number of active sites and surface areas increased with the increase in AC, which was helpful for removal of COD. The sorption capacity gradually decreased from 80.6 to 40.1 mg/g, indicating that the addition of AC in the solution decreased the sorption capacity of AC. After adsorption, the pH of effluents did not change. The changes in 2,4-DNT-3-SO$_3^-$ and 2,4-DNT-5-SO$_3^-$ in the samples before and after adsorption were detected by HPLC, indicating that most of the two dinitrotoluene sulfonates were removed. The concentrations of 2,4-DNT-3-SO$_3^-$ and 2,4-DNT-5-SO$_3^-$ decreased from 2.11×10^3 and 3.40×10^3 mg/L to 412 and 533 mg/L, and the removal efficiencies were 80.5% and 84.3%, respectively. Thus, AC effectively removed the 2,4-DNT-3-SO$_3^-$ and 2,4-DNT-5-SO$_3^-$ from TNT red water.

2.4 Chemical variations of TNT red water before and after adsorption

2.4.1 UV-Vis spectra

Figure 5 presents the UV-Vis spectra of samples before and after adsorption with the dilution ratio of 10,000. An absorption peak at 290 nm was observed in TNT red water, indicating that it might contain large amounts of aromatic compounds (Hao et al., 1993b). Absorbing light in the visible region (400–800 nm) mean that compounds in TNT red water looked colored. After adsorption, the absorbance at 290 nm was reduced from 0.141 to 0.046, indicating

Table 2   Isotherm parameters for the adsorption of COD on AC

T (°C)	q_m (mg/g)	Langmuir			Freundlich			Redlich-Peterson		
		K_a (L/mg)	R_4^2	K_F	n	R_5^2	A (L/mg)^g	B (L/g)	g	R_6^2
20	59.5	9.94×10^{-4}	0.991	4.17	3.64	0.980	0.484	−2.51	0.762	0.998
25	57.9	9.62×10^{-4}	0.992	4.12	3.67	0.983	0.989	−1.55	0.737	0.998
30	55.5	8.78×10^{-4}	0.982	4.44	3.88	0.980	1.40	−1.28	0.755	0.997
40	47.4	1.27×10^{-3}	0.994	5.35	4.40	0.964	0.357	−3.24	0.830	0.998
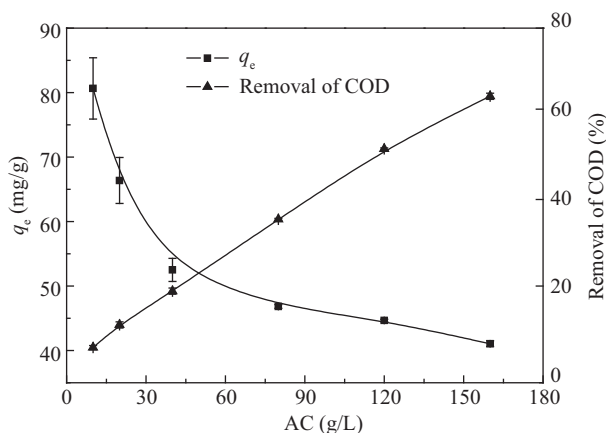
Fig. 4   Effect of AC dose on COD removal efficiency and equilibrium sorption capacity.

that most aromatic compounds might be removed after adsorption.

2.4.2 GC/MS analysis

The GC/MS was used to detect volatile and semi-volatile organic compounds (VOCs and SVOCs) with molecular weights less than 500 atomic mass units (amu). Figure 6a illustrates gas chromatography of TNT red water before adsorption by GC/MS. Eleven non-polar organic compounds were detected, with the relative content of 1,3,5-trinitrobenzene the highest at 66.6% (Table 3). After adsorption, as shown in Fig. 6b, many non-polar organic pollutants were removed. Only seven organic compounds were detected and the relative content of 4-methyl-2,6-dinitro-phenol was 19.3%, higher than that of 1,3,5-trinitrobenzene at 4.71%. From the above results, it can be concluded that the concentrations of most non-polar organic compounds were reduced to different extents after

adsorption, especially 1,3,5-trinitrobenzene which was the most easily adsorbed onto AC.

2.5 Acute toxicity test

Due to the complicated composition of toxic organic pollutants in TNT red water, the dilution ratio was determined to evaluate the variations of acute toxicity before and after adsorption. The greater the dilution ratio at certain LIR, the higher the toxicity of the water sample. In this study, the dilution ratio at 50% LIR was used as the evaluation criteria.

Figure 7 presents the dependence of luminescence inhibition ratio on dilution ratio before and after adsorption. It is shown that even though TNT red water samples were diluted ten times, almost 100% of LIR was obtained, which shows its high acute toxicity. When the dilution ratio was greater than 25.1, however, it began to decrease obviously. For effluent adsorbed by AC, LIR decreased quickly when the dilution ratio was greater than ten. Before and after
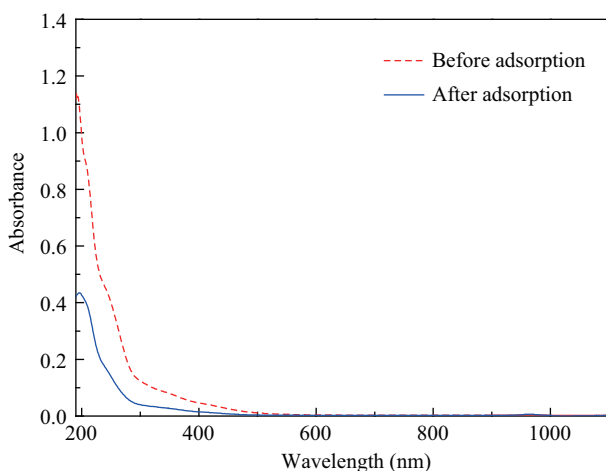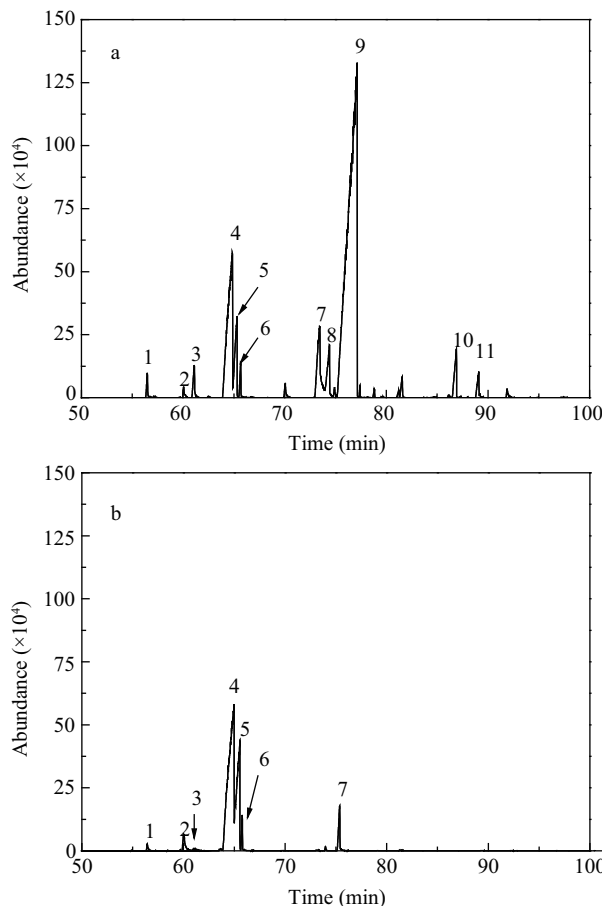

Fig. 6   Gas chromatography of TNT red water before (a) and after (b) adsorption.

Fig. 5   UV-Vis spectra before and after adsorption.

Table 3   Organic compounds analysis before and after adsorption on AC

	Before adsorption				After adsorption		
Peak	Retention time (min)	Relative content (%)	Compound	Peak	Retention time (min)	Relative content (%)	Compound
1	56.5	0.61	2-Methyl-1,3-dinitro-benzene	1	56.4	0.65	2-Methyl-1,3-dinitro-benzene
2	60.0	0.26	1-Methyl-2,4-dinitro-phenol	2	60.0	2.75	1-Methyl-2,4-dinitro-phenol
3	61.1	1.11	1-Methyl-2,4-dinitro-benzene	3	61.1	0.43	1-Methyl-2,4-dinitro-benzene
4	64.3	2.57	2,3-Dihydro-6-nitro-1,4-benzodioxin	4	64.3	15.7	2,3-Dihydro-6-nitro-1,4-benzodioxin
5	65.3	3.93	4-Methyl-2,6-dinitro-phenol	5	65.3	19.3	4-Methyl-2,6-dinitro-phenol
6	65.7	0.82	2-Methyl-4,6-dinitro-phenol	6	65.7	6.60	2-Methyl-4,6-dinitro-phenol
7	73.5	5.18	2,4,6-Trinitrotoluene	7	77.0	4.71	1,3,5-Trinitrobenzene
8	74.4	2.92	2,4,6-Trinitrotoluene				
9	77.0	66.6	1,3,5-Trinitrobenzene				
10	86.9	2.13	1-Azido-4-nitro-benzene				
11	89.1	0.65	3,5-Dinitro-p-toluidine				

adsorption, the dilution ratio at 50% LIR were 250 and 45.4, respectively, indicating that the acute toxicity of TNT red water was greatly reduced compared with that of unprocessed TNT red water.

2.6 Cost analysis

Three other commercial adsorbents, 1# granular activated carbon (GAC), 2# GAC, and RS-50B adsorption resin, produced by Beijing Dali Fine Chemical Company, Tianjing Fuchen Chemical Regent Company and Xi'an Putian Biological Technology Company, respectively, were also tested in this study. Table 4 shows the sorption capacity and the sorption cost of COD for the four adsorbents. It can be seen that the sorption capacity of RS-50B was the highest and 1# GAC was a little higher than that of AC. However, the costs of RS-50B and 1# GAC were 45 and

Table 4   Comparison of different adsorbents

Adsorbent	Sorption capacity (mg COD/g)	Price (CNY/kg)	Sorption cost (CNY/g COD)
1# GAC	85.3	31	0.36
2# GAC	10.4	10	0.96
RS-50B	136	45	0.33
AC	60.5	0.50	0.0083

31 CNY/kg, respectively, which were much higher than that of AC (0.5 CNY/kg). The sorption cost for AC was only 0.0083 CNY/g COD, which was much lower than that of RS-50B (0.33 CNY/g COD), GAC (0.36 CNY/g COD), and 2# GAC (0.96 CNY/g COD). Thereby, it can be concluded that AC is a cheap and effective absorbent for the treatment of TNT red water.
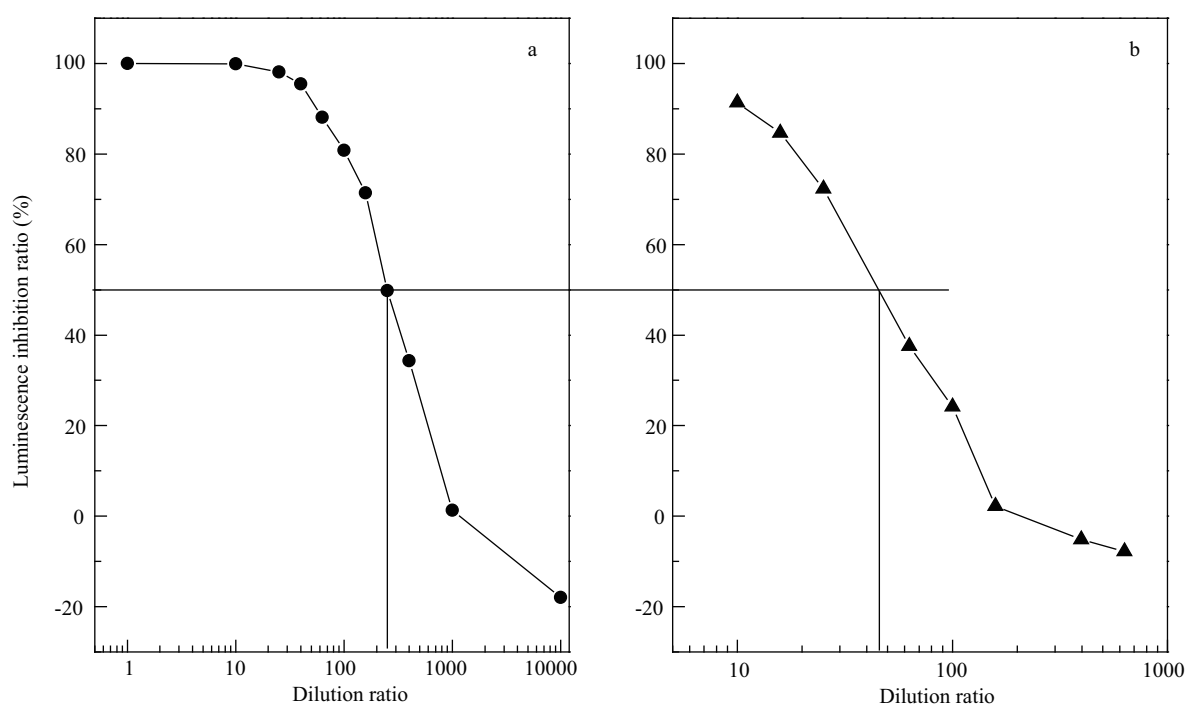
Fig. 7   Dependence of luminescence inhibition ratio on dilution ratio before (a) and after (b) adsorption.

3 Conclusions

Activated coke is a low cost adsorbent for organic pollutants in TNT red water. The sorption kinetics of COD removal from TNT red water on AC fit well with the pseudo-second order model, and the intraparticle diffusion of COD onto AC was the rate limiting step. The results showed that the adsorption process was exothermic and the adsorption of COD onto AC was a physical process rather than a chemical one. In addition, the adsorption isotherm was in agreement with the Redlich-Peterson isotherm, which might be more suitable for simulating the complicated adsorption process of TNT red water by AC. With a 160 g/L AC dose and under conditions of pH 6.28, 20°C and 3 hr of agitation, 64.8% of COD, 80.5% of 2,4-DNT-3-SO$_3^-$, and 84.3% of 2,4-DNT-5-SO$_3^-$ were removed. The GC/MS results showed that most non-polar organic pollutants were removed by AC, especially 1,3,5-trinitrobenzene. In addition, the acute toxicity of the effluent after adsorption was greatly reduced compared with that of unprocessed TNT red water. In summary, the results indicated that AC is a promising adsorbent for the adsorption treatment of organic pollutants from TNT red water.

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