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Removal of organic pollutants from red water by magnetic-activated coke

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ABSTRACT

A magnetic adsorbent, magnetic-activated coke (MAC), is incorporated with Fe_3O_4 particles for removal of organic materials from 2,4,6-trinitrotoluene red water. The MAC is characterized by N_2 adsorption, Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscope, and energy dispersive X-ray spectroscopy. Adsorption of organic pollutants is evaluated systematically by varying the adsorbent dosage, exposure time, temperature, pH, and dilution ratios of 2,4,6-trinitrotoluene red water. The equilibrium adsorption data can be better fitted with the Freundlich isotherm than Langmuir isotherm except at 343 K. The adsorption kinetics follows a pseudo-second-order model and thermodynamic analysis indicates an endothermic and spontaneous adsorption process. The settling rate after adsorption suggests that the response of MAC under an external magnetic field is very fast.

Keywords: Adsorption; Magnetic; Activated coke; TNT red water; Organic pollutants

1. Introduction

TNT is an important explosive used in many fields [1]. During production and assembly, a large amount of TNT wastewater is produced and if it is discharged without effective treatment, contamination of soil and underground water will pose health and environmental hazards [2]. Red water produced during purification of crude TNT by sodiumsulfite is dark red and contains hazardous dissolved dinitrotoluene sulfonates (mainly 2,4-dinitrotoluene-3-sulfonate and 2,4-dinitrotoluene-5-sulfonate), trinitrotoluene, nitrotoluene, dinitrotoluene, as well as other chemicals [3]. Several methods are proposed to remove TNT and other organic species from wastewater, for example, adsorption [4], incineration [5], vacuum distillation [6], degradation [7], catalytic destruction such as fenton oxidation [8], photocatalytic oxidation [9], advanced oxidation employing UV and hydrogenperoxide/ozone [10], as well as supercritical water oxidation [11].

Adsorption is one of the commonly used methods but adsorbents can be expensive and so there is much research on developing more efficient and economical adsorbents to treat TNT red water. Activated coke (AC) [12], a common substitute for activated carbon is used because of the lower cost and availability [13–15], is produced from natural carbonaceous materials like lignite, petroleum coke, wood, and other biomass. It is typically macro- and mesoporous with a small micropore volume

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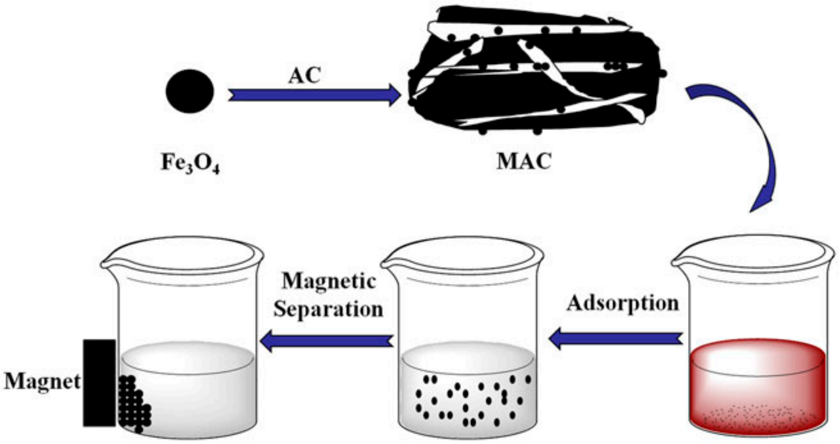

Fig. 1. Synthesis of MAC and removal of organic pollutants from TNT red water under an external magnetic field.

[16] thus boding well for extraction of contaminants from liquids [17,18]. AC has been utilized to extract organic pollutants from TNT red water but using 160 g L^{-1} AC, the relative removal of chemical oxygen demand (COD) is only 64.8% and adsorption efficiency is quite low [19]. Hence, improvement is needed before the process becomes commercially viable.

Magnetic adsorbents [20] have attracted more attention recently because of their capability to treat a large volume of wastewater in a short time. The aim of this study is to investigate the adsorption efficacy and related properties of magnetic-activated coke (MAC) from the perspective of TNT red water treatment. The synthesis of MAC and removal of organic chemicals from TNT red water under an external magnetic field are illustrated in Fig. 1.

2. Experimental

2.1. Materials

TNT red water supplied by Dongfang Chemical Corporation (Hubei Province, China) was dark red with complicated compositions and high COD. The water samples used in the experiments were diluted 1–100 times with distilled water and Table 1 shows the physical and chemical properties. The AC made from lignite was provided by Datang Yima Coke Plant (Henan Province, China). The price was only 0.5 CNY kg^{-1} and Table 2 lists the physical properties. All the other reagents used in this study were analytical grade and distilled water was used to prepare the solutions.

2.2. Preparation of nano-Fe_3O_4

0.4374 g of $FeCl_2{\cdot}4H_2O$, 1.189 g of $FeCl_3{\cdot}6H_2O$, and 25 mL of distilled water were added dropwise to an ammonia solution, which was purged with nitrogen and agitated ultrasonically at 60℃ for 3 h. Magnetic particles in the solution were obtained by magnetic separation.

2.3. Preparation of MAC

The magnetic particle and 100 mL of distilled water were agitated ultrasonically at 60℃ for 1 h in three neck round-bottom flask. 10 g of AC was then added to the solution gradually. It was stirred at 60℃ for 2 h, filtered 3 times, and dried at 100℃. The adsorbents were used separately in the equilibrium isotherm experiments.

2.4. Adsorption experiments

The adsorption experiments were conducted using 2 g of MAC as the adsorbent in a 100 mL flask containing 25 mL of TNT red water. The bottles were shaken in a digital water bath oscillator at 150 rpm. In order to determine the optimal adsorbent dosage, time, pH value, temperature, and concentration of TNT red water, experiments were performed systematically. The effects of pH were studied in the range of 1.0–14.0. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl and measured by CLEAN water quality analyzers (pH 500 pH/TEMP Meter). The effects of temperature on the MAC adsorption capacity were studied at 298, 313, 323, 333, 343, and 353 ± 0.2 K in TNT red water diluted 0–100 times. The effects of the exposure time on the removal degree of COD were determined from 5 to 360 min in TNT red water diluted 30 times. After equilibrium had been reached, the suspension was filtered rapidly and the filtrate was analyzed by a COD rapid detector with a

Table 1
Properties of red water diluted 30 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
6.78	855.2	1900	186	330	50.3	63.2	Reddish brown 1 × 30 times

Table 2
Properties of AC

Particle size (mm)	BET (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Aperture (um)	Bulk density (gcm^{-3})	Porosity (%)
0.90–2.0	439.7	0.271	≤403.0	0.70	45

precision of ±5% to determine the adsorption efficiency. The relative removal of COD of the organic pollutants and q_e (mg g^{-1}) in the TNT red water adsorbed by MAC was calculated by Eqs. (1) and (2):

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

$$q_e = \frac{(\text{COD}_o - \text{COD}_e)V}{W} \quad (2)$$

where COD$_o$ (mg L^{-1}) is the COD of the initial TNT red water and COD$_e$ is the COD of the TNT red water treated by the adsorbents until 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 absorbed, q_t (mg g^{-1}), by the MAC was calculated by a similar relationship based on Eq. (2).

Fourier transform infrared spectra (FT-IR, PerkinElmer Spectrum 100), X-ray diffraction (XRD, Rigaku D/max-rA), scanning electron microscope (SEM, JSM-6301F), and energy dispersive X-ray spectroscopy (EDS) were performed to characterize the structure and morphologies of MAC and AC. The COD of red water was determined by a COD rapid detector (5B-6, Lian-Hua Tech. Co., China).

3. Results and discussion

3.1 Characterization of MAC

3.1.1. FT-IR of MAC

In order to study the functional groups before and after magnetic modification of AC, FT-IR spectra are acquired. Fig. 2 shows the FT-IR spectra of the AC (Fig. 2(a)) and MAC (Fig. 2(b)). The FT-IR spectrum of MAC shows new peaks. The peak at 3,436 cm^{-1} is assigned to O–H stretching indicating that the surface of the MAC particles is hydroxylated. The peaks at 1,446 and 1,080 cm^{-1} can be attributed to the axial deformation vibrations of C–H bonds and C–O bonds, respectively [21].

3.1.2. XRD and SEM of MAC

XRD and SEM were conducted to examine the surface morphology of AC, MAC, and MAC after adsorption. The XRD patterns in Fig. 3 reveal the existence of iron oxide particles (Fe_3O_4) in MAC before and after adsorption. They have magnetic properties and can be used in magnetic separation. The SEM image of MAC

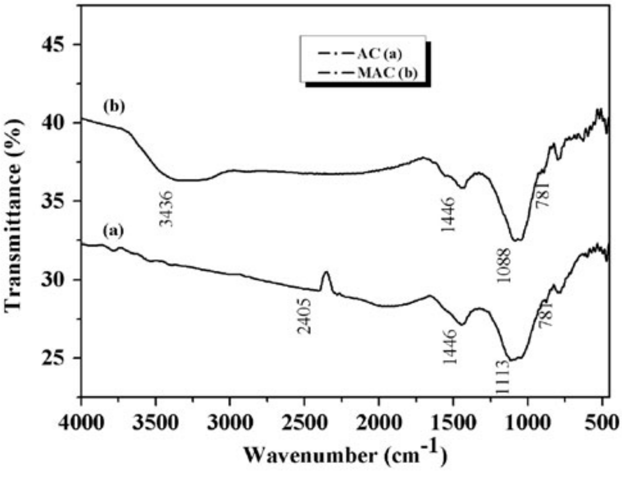

Fig. 2. FTIR spectra: (a) AC and (b) MAC.

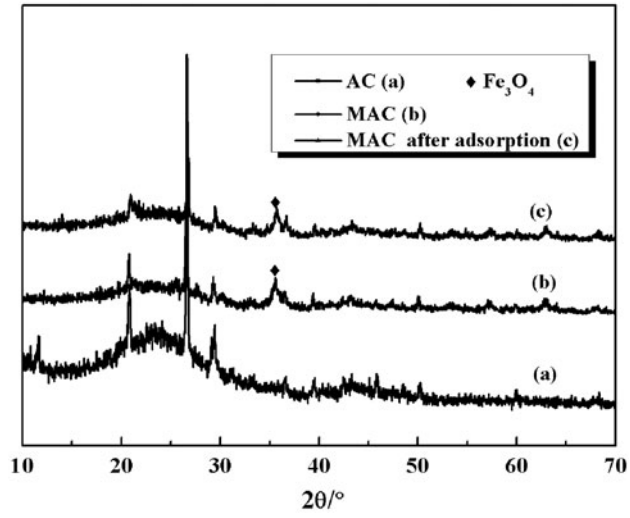

Fig. 3. XRD patterns: (a) AC, (b) MAC, and (c) MAC after adsorption.

(Fig. 4) shows that the MAC before adsorption had a porous and coarse surface (Fig. 4(a)–(c)). There are many Fe_3O_4 particles on the surface and in the channel of MAC as revealed by EDS (Fig. 4(c)). After adsorption, the porosity of the MAC (Fig. 4(d)–(f)) decreases or disappears because the surfaces and pores of MAC are covered by organic chemicals. However, as shown in Figs. 3 and 4(f), the Fe_3O_4 particles still exist on the MAC after adsorption as indicated by XRD and EDS. Hence, the MAC after adsorption is still magnetic.

3.2. *Effects of adsorbent dosage on extraction of pollutants*

In order to determine the optimal adsorbent dosage, different values are studied at 298 K for 3 h in water diluted 30 times. As shown in Fig. 5, adsorption of organic materials by AC and MAC reaches equilibrium when the dosage is 2 g/25 mL. The adsorption rate of MAC is obviously faster than that of AC and the relative removal of COD reaches 50.13 and 74.41%, respectively. MAC possesses stronger adsorption ability than AC for organic pollutants and 2 g/25 mL is the experimentally determined optical dosage.

3.3. *Effects of exposure time and temperature on extraction of organic chemicals*

Fig. 6 shows the effects of the exposure time on adsorption of organic pollutants from TNT red water diluted 30 times with a dosage of 2 g/25 mL between 298 and 353 K. The adsorption rate increases quickly in the initial 30 min and then does not change obviously, finally it reaches equilibrium after 30 min. A similar phenomenon has been reported for extraction of organic pollutants from TNT red water using AC and bamboo charcoal [22]. In this study, the relative removal of COD on MAC can reach 84.89% instead of 45% on AC at a dosage of 2 g/25 mL. The results indicate that many vacant sites and active sites are available to organic materials on the surface of MAC and AC in the initial stage. Our results suggest that the optimal exposure time is 30 min.

Fig. 6 shows the relative removal of COD increases with temperature in this range and the adsorption process is controlled by diffusion and endothermic [23]. The surface of MAC is loaded with Fe_3O_4 particles. At a higher temperature, the kinetic energy of magnetic particles is larger and therefore, contact between the magnetic particles and active sites on the MAC are sufficient to increase the loading efficiency. Similar trends pertaining to aqueous adsorption have been reported [24]. At the same time, chemical interactions also take place between magnetic particles on the MAC and organic materials in the TNT red water to promote adsorption. As a result, the relative removal of COD of MAC is higher than that of AC. Additionally, the increased loading capacity on MAC at a higher temperature may be attributed to the enlarged pore size [25]. However, the trend does not continue after reaching a certain temperature and the increase in the relative removal of COD is no longer obvious. This can be explained by the commencement of desorption if the temperature exceeds a threshold [26].

Fig. 7 shows the effects of TNT red water diluted 10, 20, 30, 50, and 100 times at temperature (298, 313, 323, 333, 343, and 353 K) at an adsorbent dosage of 2 g/25 mL. The results show that the removal of COD is appropriate when TNT red water is diluted 30 times.

3.4. *Effects of pH on adsorption of organic pollutants*

The pH is one of the most important parameter determining the adsorption capacity of MAC [27]. Adsorption of organic materials involves electrostatic interactions between the organic pollutants in TNT red water and functional groups on the MAC. The TNT red water contains dinitrotoluene-sulfonate (Ph-SO_3Na), α-TNT, several α-nitrophenols (NBCs-OH), α-nitrobenzoic acid (NBCs-COOH), and other nitrobenzene compounds (NBCs) [28]. In the aqueous medium, dinitrotoluene-sulfonate is dissociated and converted to anionic forms as shown in Eq. (3):

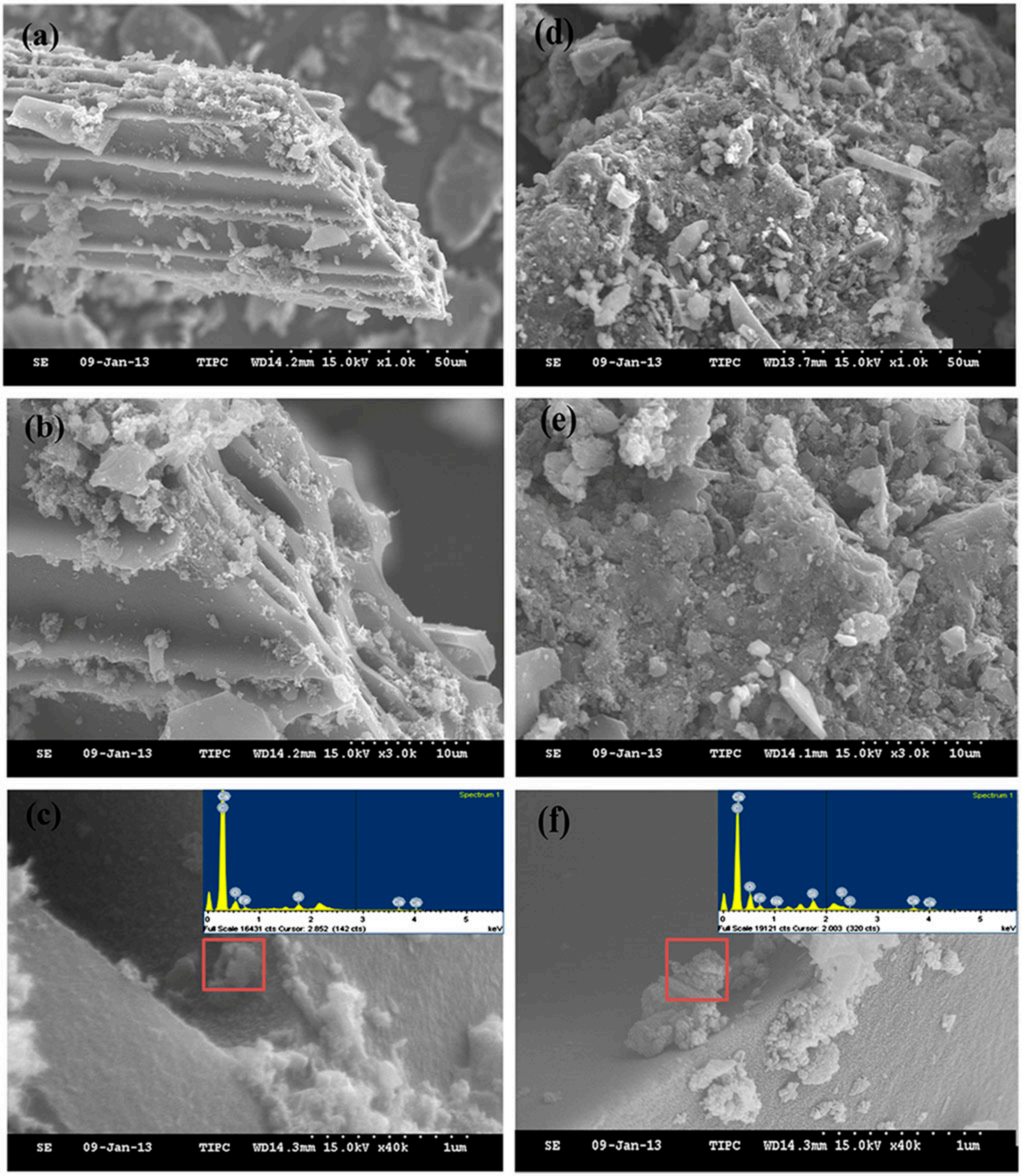

Fig. 4. SEM of MAC: Before adsorption: (a) ×1,000, (b) ×3,000, and (c) ×40,000. After adsorption: (d) ×1,000, (e) ×3,000, and (f) ×40,000.

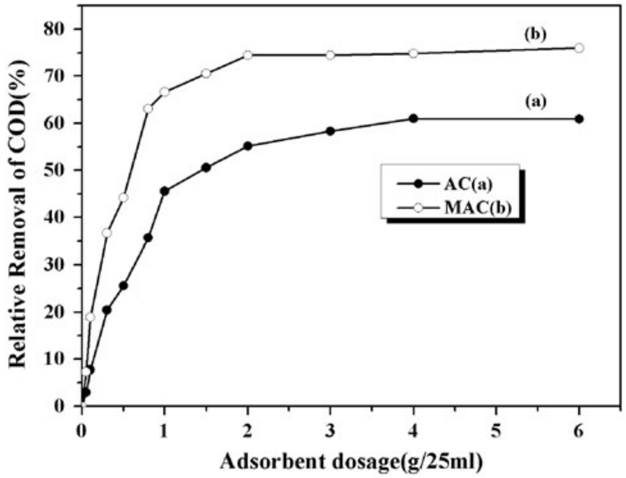

Fig. 5. Effects of adsorbent dosage on adsorption of organic pollutants in TNT red water on (a) AC and (b) MAC.

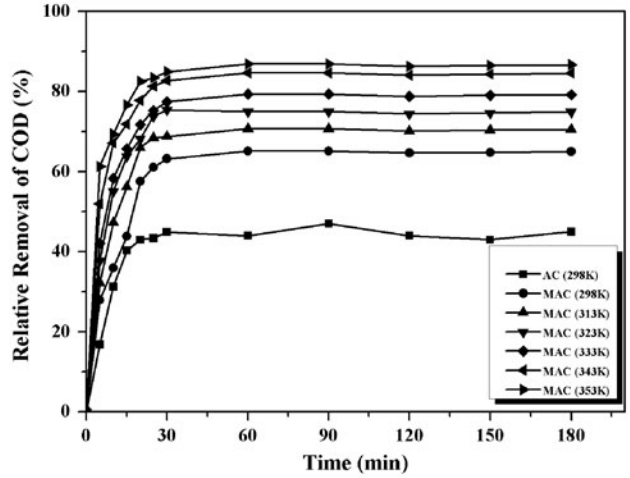

Fig. 6. Effects of exposure time and temperature on adsorption of organic pollutants in TNT red water on AC and MAC.

$$Ph - SO_3Na \xrightarrow{H_2O} Ph - SO_3^- + Na^+ \tag{3}$$

Under acidic conditions, most of the organic pollutants in TNT red water exist in the molecular form because they are difficult to ionize. In addition, Fe_3O_4 can be dissolved in an acidic solution as shown by Eq. (4).

$$Fe_3O_4 \xrightarrow{H^+} 2Fe^{2+} + Fe^{3+} + 4H_2O \tag{4}$$

In a basic medium, α-TNT forms the Janovsky complexes [29] (Fig. 8). In addition, the α-nitrophenols and α-nitrobenzoic acid in TNT red water easily ionize to anionic forms [30], as shown by Eqs. (5) and (6).

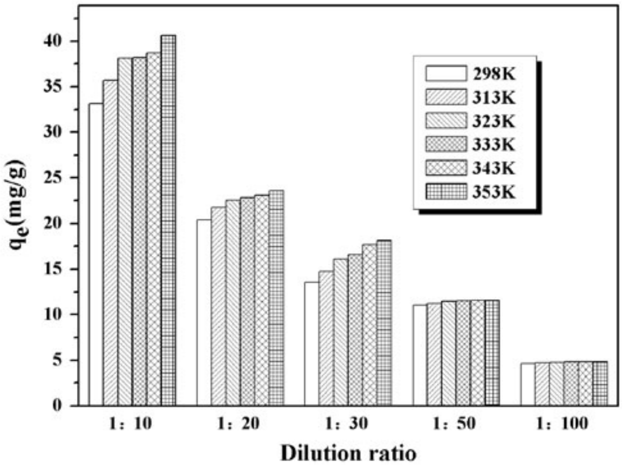

Fig. 7. Effects of dilution ratios of TNT red water on MAC (adsorbent dosage = 2 g/25 mL).

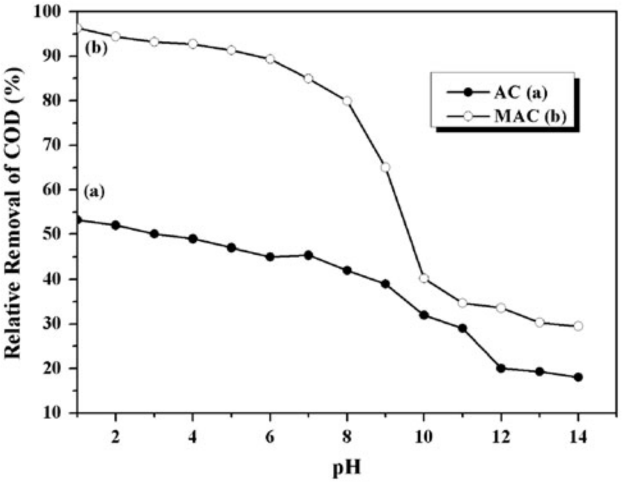

Fig. 8. Effects of pH on adsorption of organic pollutants in TNT red water on AC and MAC.

$$NBCs - OH \xrightarrow{OH^-} NCBs - O^- + H_2O \tag{5}$$

$$NBCs - COOH \xrightarrow{OH^-} NCBs - COO^- + H_2O \tag{6}$$

The effects of pH on the adsorption of organic materials on the MAC are illustrated in Fig. 9. The optimal pH value is determined to be 1.0 at which the relative removal of COD is 96.3%. When $pH < 8$ ($pH_{PZC} = 6.2$

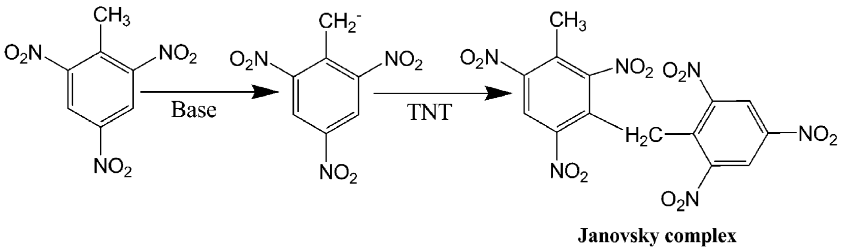

Fig. 9. Formation of Janovsky complex.

for Fe_3O_4, $pH_{PZC} = 8.2$ for AC), the surface charges on AC and Fe_3O_4 particles are positive [31]. The relative removal of COD increases with the decrease of pH due to the electrostatic attraction. Furthermore, under acidic conditions, most of the organic pollutants in TNT red water exist in the molecular form because they are difficult to ionize. The lower the pH, the better the organic molecules are absorbed, as shown in Fig. 9. The relative removal of COD reaches a maximum at pH of 1.0. However, at $pH > 8$, the surface charges of AC and Fe_3O_4 particles are negative. Meanwhile, the organic materials in TNT red water are ionized forming anions in the basic medium. Consequently, the relative removal of COD is smaller because of electrostatic repulsion. The Janovsky complexes and the low solubility of α-TNT also affect adsorption negatively.

3.5. Sorption isotherm models

The sorption equilibrium data of organic materials in TNT red water on MAC are analyzed by the Langmuir and Freundlich isotherm models. The linear form of the Langmuir's isotherm model is given by the following Eq. (7):

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \tag{7}$$

where q_e (mg g^{-1}) is the amount of COD absorbed per unit mass by MAC at equilibrium, c_e (mg L^{-1}) is the COD of the TNT red water treated by MAC until reaching equilibrium, q_m (mg g^{-1}) is the amount of maximum COD adsorbed per unit mass by the MAC, and b (L mg^{-1}) is the Langmuir constant related to the rate of adsorption. The specific isotherm parameters, q_m and b, can be calculated from the slope and intercept of the plots $\frac{c_e}{q_e}$ vs. c_e (Fig. 10(a)) and they are listed in Table 3. The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, defined in Eq. (8):

$$R_L = \frac{1}{1 + bC_0} \tag{8}$$

where b is the Langmuir constant and C_0 is the initial COD of TNT red water. The value of R_L indicates whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [32]. Its values determined from this study are given in Table 3. Since they are within the range of 0–1, adsorption on MAC appears to be a favorable process. In addition, the small R_L values (<0.1) imply that the interaction between organic pollutants in TNT red water and MAC is relatively strong.

The Freundlich [33] isotherm equation is given in Eq. (9):

$$q_e = K_f c_e^{1/n} \tag{9}$$

The linear form of the Freundlich model is expressed in Eq. (10):

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \tag{10}$$

where q_e (mg g^{-1}) is the amount of absorbed per unit mass on the MAC at equilibrium, c_e (mg L^{-1}) is the COD of the TNT red water treated by MAC until reaching equilibrium, and K_f (mg g^{-1} (L mg^{-1})$^{1/n}$) and n are the Freundlich constant and intensity factors, respectively. The plot of log q_e vs. log c_e (Fig. 10(b)) yields a straight line with a slope of $1/n$.

The experimental isotherm data are fitted according to the corresponding isotherm equation. Table 3 lists the parameters of the equations and correlation coefficient values. It can be observed that the fitting is better when the Freundlich isotherm is used than Langmuir isotherm, except at 343 K. The results may be due to the specific homogeneous nature of the MAC surface.

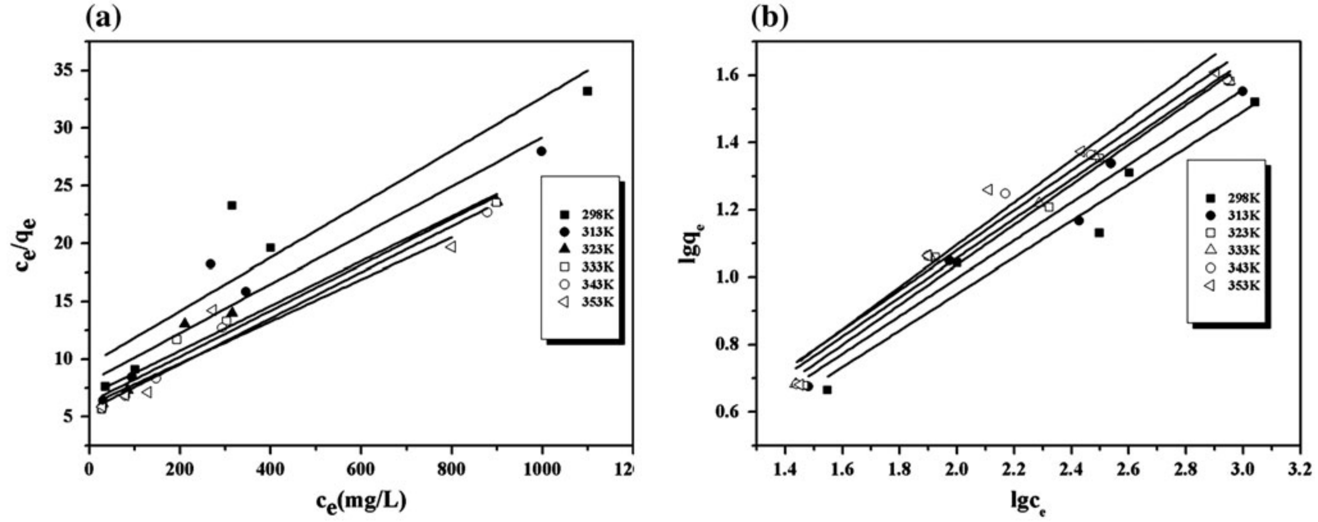

Fig. 10. Adsorption isotherms of organic pollutants extraction from TNT red water by MAC: (a) Langmuir adsorption isotherms, (b) Freundlich adsorption isotherms, adsorbent dosage = 2.0 g/25 mL, dilution ratio = 0–1:100, temperature = 298–353 ± 0.2 K, and contact time = 180 min.

Table 3
Parameters of Langmuir and Freundlich isotherm models for extraction of organic materials from TNT red water by MAC (adsorbent dosage = 2 g/25 mL, ratio of dilution = 1:10–1:100, temperature = 298–353 ± 0.2 K, and contact time = 180 min)

		Temperature (K)					
Isotherm		298	313	323	333	343	353
Langmuir	q_m (mg g^{-1})	43.21521	47.28132	51.62623	50.37783	50.32713	55.12679
	b (L mg^{-1})	4.532709	5.891343	7.521018	8.050522	8.998315	9.170604
	R_L	0.00009	0.00014	0.000155	0.000145	0.000205	0.000495
	R^2	0.81875	0.86523	0.93764	0.96034	0.98551	0.8722
Freundlich	K_f (mg g^{-1} (L $mg^{-1})^{1/n}$)	0.875325	0.883018	0.861681	0.898544	0.903264	0.854678
	n	1.845665	1.783135	1.686198	1.717918	1.691904	1.595303
	R^2	0.93758	0.96389	0.97821	0.97913	0.96182	0.95209

3.6. Adsorption kinetics

Adsorption is a physicochemical process that involves mass transfer of a solute from a liquid phase to the adsorbent surface [34]. A kinetics study imparts important information to facilitate better understanding of the adsorption rate and control of the process. The kinetics is investigated based on two kinetic models, namely the Lagergren pseudo-first-order and pseudo-second-order model [35]. The linear form of the pseudo-first-order kinetic model is expressed by Eq. (11):

$$\log(q_e - q_t) = \log q_e - \frac{K_f}{2.303} t \quad (11)$$

where K_f (L min^{-1}) is the rate constant of pseudo-first-order adsorption, and q_e (mg g^{-1}) and q_t (mg g^{-1}) 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 MAC can be determined from the plot of log $(q_e - q_t)$ vs. t in Fig. 11(a).

The pseudo- second-order equation is expressed as Eq. (12) [36]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order constant and q_e and k_2 can be determined experimen-

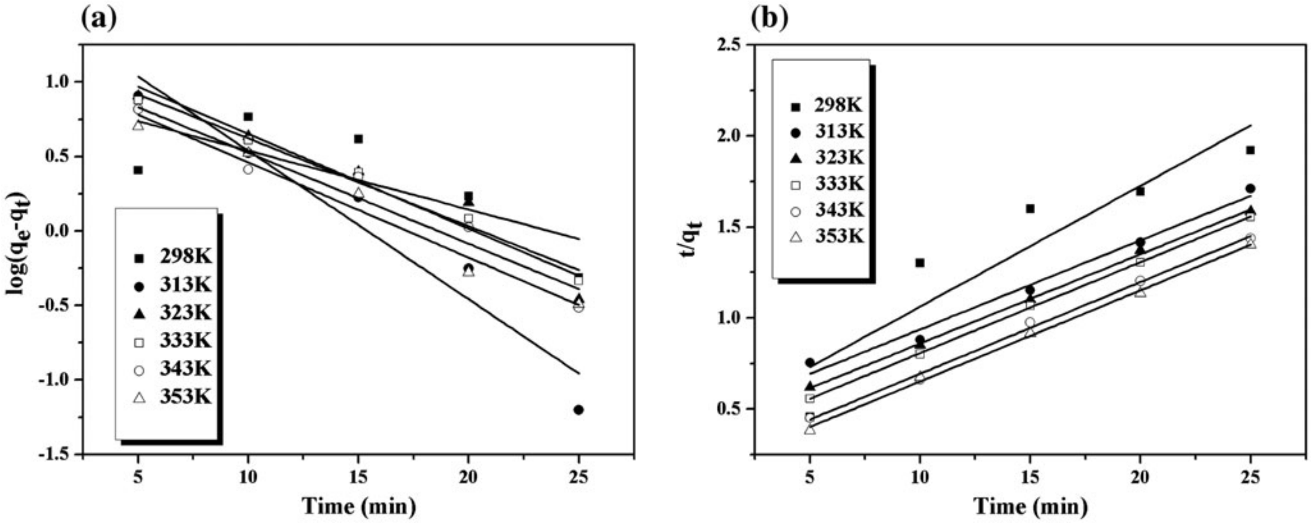

Fig. 11. Kinetics plots: (a) pseudo-first order and (b) pseudo-second order pertaining to adsorption of organic pollutants on MAC.

tally from the slope and intercept of the plot $\frac{t}{q_t}$ vs. t (Fig. 11(b)).

To compare the validity of each model, a normalized standard deviation is calculated using Eq. (13):

$$\Delta q\ (\%) = 100\sqrt{\frac{\Sigma\left|\frac{(q_{\text{exp}} - q_{\text{cal}})}{q_{\text{exp}}}\right|^2}{N-1}} \tag{13}$$

where q_{exp} and q_{cal} (mg g^{-1}) are the experimental and calculated amounts of absorbed COD and N is the number of measurements. If the data from a model are similar to the experimental data, Δq (%) will be small, but if they differ, Δq (%) will be large. To confirm whether the adsorption system fits a kinetics model, it is necessary to analyze the data using Δq (%) in conjunction with the determined coefficient R^2.

The constants of kinetic models for the adsorption of organic pollutants from TNT red water on MAC are listed in Table 4. The calculated adsorption capacity ($q_{e,\text{cal}}$) values estimated by the pseudo-first-order model differ substantially from those measured experimentally, whereas the $q_{e,\text{cal}}$ values obtained from the pseudo-second-order kinetic model are very close to experimental data. Compared to pseudo-first-order model, Δq of the pseudo-second-order model is smaller. Moreover, the correlation coefficients in the pseudo-second-order model are much larger than those of pseudo-first-order-model confirming the mechanism that follows the pseudo-second-order kinetic model.

3.7. Adsorption thermodynamics

Changes in the free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) can be calculated according to Eqs. (14), (15), and (16) in equilibrium [37–39]:

$$K_c = \frac{c_0 - c_e}{c_e} \times \frac{\rho V}{m} \tag{14}$$

Table 4
Parameters of kinetic and intraparticle diffusion models for extraction of organic pollutants from TNT red water by MAC (adsorbent dosage = 2.0g/25mL, dilution ratio = 1:30, temperature = 303–353 ± 0.2 K, and contact time = 25 min)

Kinetic models	Parameters	298	313	323	333	343	353
Pseudo-first-order kinetic	$q_{e,\text{cal}}$ (mg g^{-1})	0.0909	0.2297	0.1464	0.1359	0.1406	0.1470
	k_f (L min^{-1})	2.545	4.647	3.624	3.360	3.114	3.001
	R^2	0.4079	0.9228	0.9223	0.9783	0.9175	0.9597
	Δq (%)	109.54					
Pseudo-second-order kinetic	$q_{e,\text{cal}}$ (mg g^{-1})	15.06	20.44	20.38	19.99	19.85	19.99

Table 5
Thermodynamic parameters for adsorption of organic pollutants in TNT red water on MAC (adsorbent dosage = 2 g/25 mL, dilution ratio = 1:30, temperature = 298–353, and contact time = 30 min)

	Temperature					
Parameters	298	313	323	333	343	353
K_c	40.00	54.91	76.59	85.57	119.75	140.54
ΔG (kJ mol^{-1})	−9.14	−10.42	−11.65	−12.32	−13.65	−14.51
ΔH (kJ mol^{-1})	20.36					
ΔS (J mol^{-1} K)	98.74					

$$\Delta G = -RT \ln K_c \qquad (15)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (16)$$

where K_c is the distribution coefficient, $\rho = 1$ g L^{-1} is the density of the solution mixture, c_e (mg L^{-1}) is the COD of the TNT red water treated by MAC until reaching equilibrium, q_e is the COD amount of adsorption at equilibrium (mg g^{-1}), T is the solution temperature (K), and R is the gas constant and is equal to 8.314 J mol^{-1} K^{-1}). ΔH and ΔS are calculated from the slope and intercept of the linear plot of $\frac{1}{T}$. vs. ln K_c. The values and thermodynamic parameters of MAC are given in Table 5. The ΔG values (kJ mol^{-1}) (−9.14, −10.42, −11.65, −12.32, −13.65, −14.51) under the experimental conditions indicate that adsorption of organic materials is spontaneous. The positive ΔH indicates that adsorption on the MAC is an endothermic process. In addition, ΔH (15.46 kJ mol^{-1}) is between 2 and 40 kJ mol^{-1} indicative of physical adsorption characteristics [40]. The entropy change ΔS is positive suggesting that the randomness increases during adsorption [41].

3.8. Settling rate after adsorption onto MAC

Magnetic adsorbents can treat a large amount of wastewater in a short time and can also be separated from wastewater conveniently. MAC is a satisfactory

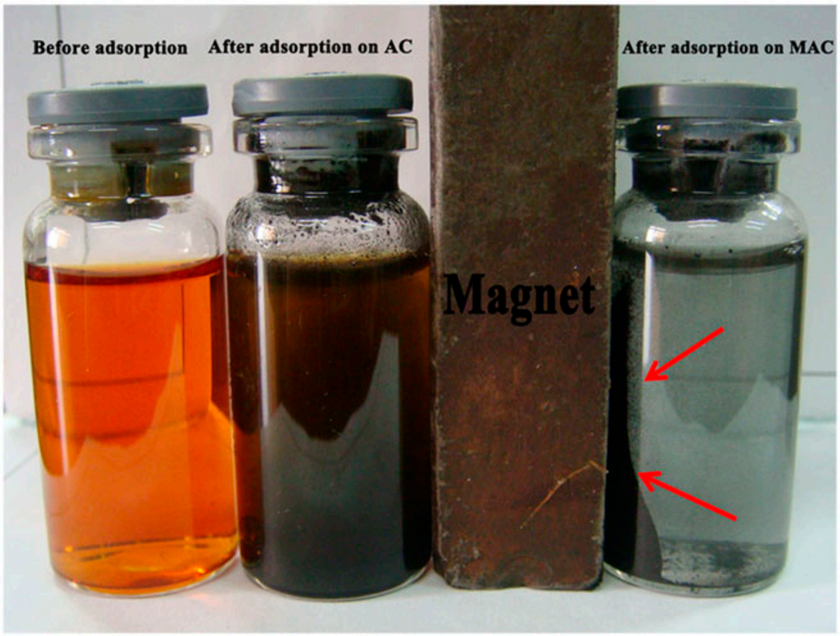

Fig. 12. Comparative study on the before adsorption and after adsorption on AC and MAC.

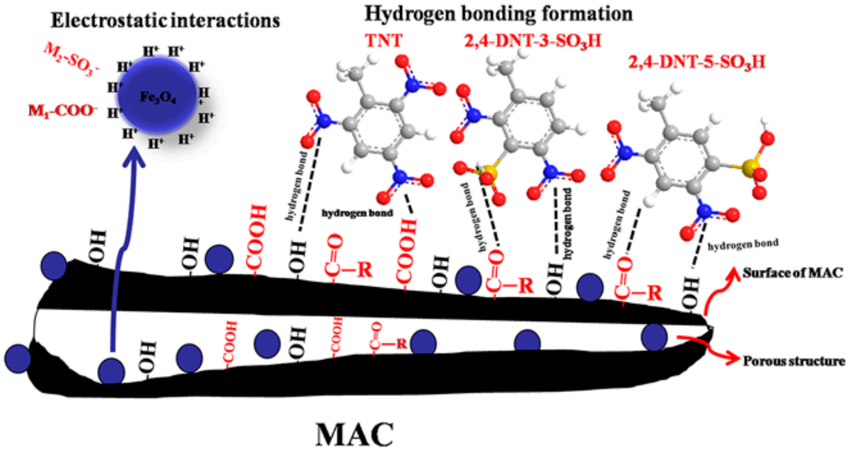

Fig. 13. Adsorption mechanism for organic pollutants on MAC in TNT red water.

magnetic adsorbent in this respect. The settling rate after adsorption in Fig. 12 shows the response of MAC under an external magnetic field. The attraction and re-dispersion processes can be readily altered by switching the external magnetic field. The good water dispersion and magnetic separation characteristics favor effective separation.

3.9. Mechanism of adsorption

Thermodynamic analysis illustrates that the adsorption process is related to electrostatic interactions, hydrogen bond formation, and electron donor–acceptor interaction [42]. As shown by our previous study, electrostatic interactions are the major factor from the perspective of the effects of pH on adsorption. Hydrogen bonding between organic pollutants and MAC also plays the dominant role in the adsorption process. The results can be explained by the functional groups on the MAC that can form hydrogen bonds with nitrogen and oxygen atoms on the organic materials in TNT red water. On the other hand, oxygen on the MAC can also form hydrogen bonds with hydrogen atoms of –COOH, –OH, $-HSO_3^-$and $-NO_2$ on the organic materials in TNT red water. Based on our analysis, the adsorption mechanism is illustrated in Fig. 13.

3.10. Reusability

It has been reported that hydroxypropyl-β-cyclodextrin can increase the solubility of nitro-compounds in water because of the formation of inclusion compounds [43]. Adsorption on MAC proceeds by regeneration of hydroxypropyl-β-cyclodextrin. The organic pollutants are released into the eluent and the active sites on the adsorbent are partly recovered. Therefore, MAC can be recycled. In order to demonstrate the reusability of MAC, the adsorption–desorption cycle is repeated eight times using the same materials. As shown in Fig. 14 MAC can indeed be used repeatedly without significant loss in the adsorption capacity. Meanwhile, the organic pollutants released into the eluent are very dangerous if handled improperly and the organic pollutants can cause secondary pollution. It has been reported that the enriched organic compounds from TNT red water are used for preparation of viscosifier for drilling fluid [44] and hence, the problem associated with secondary pollution can be effectively circumvented.

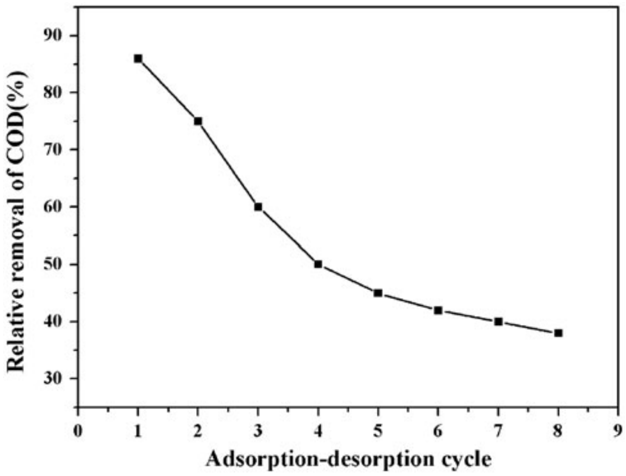

Fig. 14. Adsorption–desorption cycle of MAC.

4. Conclusion

AC is modified with magnetic Fe_3O_4 particles and the efficacy to extract organic pollutants from TNT red water is investigated. Under conditions including an optimal MAC dosage of $2\,g\,25\,mL^{-1}$, initial pH of 1.0, temperature of 353 K, and exposure time of 30 min, 96.3% of COD can be removed. Adsorption isotherm models, adsorption kinetics, adsorption thermodynamics, settling rate after adsorption, mechanism of adsorption, and reusability are studied. Our results demonstrate that MAC has excellent adsorption characteristics and can be used in the removal of organic pollutants from TNT red water.

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