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A modified lignin adsorbent for the removal of 2,4,6-trinitrotoluene

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ABSTRACT

Waste water containing 2,4,6-trinitrotoluene (TNT) in industrial production has caused many serious environmental problems worldwide. In this paper, a novel modified lignin adsorbent for TNT, aminated lignin (AmL) was synthesized by a two-step approach. The characterization using FTIR, SEM and XPS suggested that modification of the lignin was successful. Batch adsorption experiments of AmL for TNT were performed on factors of contact time, temperature, initial TNT concentration, initial pH and adsorbent dosage. The results show that the adsorption equilibrium can be achieved in 24 h and the adsorption kinetics is well described by pseudo-second-order model. It was found that the equilibrium data was better represented by the Freundlich isotherm model and the saturated adsorption capacities reach a maximum of 55.7 mg/g at pH 7.0. Thermodynamic parameters were also evaluated and their values indicated that adsorption capacity using AmL. The reusability characteristic has been also investigated and more than 95% recovery was obtained after 8 desorption–adsorption cycles for ethanol eluent. The results showed that the synthesized material is a promising sorbent of TNT in water.

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1. Introduction

2,4,6-Trinitrotoluene (TNT) is a high explosive widely used for military purposes since 1902 [1]. It is also used for industrial purposes including underwater blasting, mining, dyestuffs and as a chemical intermediate in the manufacture of photographic chemicals [2]. Unfortunately, there are various primary and secondary explosive compounds containing in water and soil due to human activities. For instance, World War II are responsible for many serious environmental problems in many regions of the world. Waste water discharged from TNT industry has become a severe environmental problem as well and this has attracted attention from researchers in most countries. Taking toxic, mutagenic and potentially carcinogenic effects of TNT on humans and animals into consideration, removal of TNT from liquid waste from TNT manufacturing plants has become a must [3–5]. At present, destruction and concentration are two typical methods to reduce or remove TNT from liquid waste. Destruction methodology, such as oxidation with hydrogen peroxide/ozone [6-8], photocatalytic oxidation [9-12] and biological degradation [13-17], involves advanced technology to destroy TNT structure. However, these treatments cannot be widely applied due to their own problems, such as high cost,

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long cycle, secondary pollution, etc. Concentration methodology means essentially a mixture of adsorption with various adsorption materials such as activated carbon [5,18], PAM/SiO₂ [19], polyvinylbenzyl acid/SiO₂ (PVBA/SiO₂) [20], etc. Unfortunately, PAM/SiO₂ and PEI/SiO₂ have only a low adsorption capability for TNT. The treatment of activated carbon is expensive because of the high cost of the preparation and regeneration although it is effective to treat TNT-containing water. Consequently, it is urgent to find a low-cost and efficient adsorption material to handle the explosive-laden wastewater.

Byproducts of industrial or agricultural production, such as lignin, sawdust, pine bark, coconut husk, tealeaf and rice hull, are sorts of the low-cost adsorbents [21-23]. Industrial lignin is generally produced as byproduct or waste in large quantities in the process of pulp and biofuel production [24-26]. Lignin is a heterogeneous three-dimensional crosslinked polymer consisting of methoxylated phenylpropane units, which contains a number of functional groups such as phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxyl, and aldehyde groups. In natural lignin, the positions on the aryl ring para- and ortho- to the hydroxyl groups are usually occupied by alkoxy or alkyl substituents [27]. Moreover, lignin is not soluble in water, and has strong resistance to chemical reactions. These properties of lignin demonstrate that it has a potential to be used as a possible adsorption material to remove heavy metals and various organic pollutants from waste waters [28-31]. However, the adsorption capacities of unactivated lignin [32] and lignin-quaternary [33] for TNT are comparatively poor.

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Scheme 1. Preparation of chlorinated lignin.

In this work, an efficient modified lignin adsorbent was made through a simple chemical modification by introducing functional groups with high affinity and selectivity for TNT contamination of water. Lignin and the modified lignin were characterized by using Fourier transform infrared (FT-IR) spectroscopy, Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The adsorption ability of the modified lignin on TNT in aqueous solutions and the regeneration of the adsorbent were also evaluated in its application.

2. Materials and methods

2.1. Materials

Lignin was purchased from Shandong Yiyuan Xuemei Paper Company, Ltd. (Shangdong, China) and was used without further purification. Ethylenediamine, 1,2-dichloroethane (DCE), N,Ndimethylformamide (DMF), acetone, alcohol, sodium hydroxide, ammonia, sodium sulfite, cetylpyridinium chloride (CPC), KNO₃ and hydrochloric acid used in this work were analytical grade and obtained from Kelong Chemicals Company (Chengdu, China). Anhydrous aluminum chloride (AR grade) was purchased from Shanghai Meixing Chemical Ltd. (Shanghai, China). TNT was obtained from the Department of Materials Science and Engineering of the Southwest University of Science and Technology, China.

2.2. Preparation of modified lignin

2.2.1. Preparation of chlorinated lignin

Scheme 1 shows the synthetic route of Chlorinated lignin (ChL). 10 g of dried lignin and 250 mL of 1,2-dichloroethane were added into a dried three-necked round-bottomed flask with magnetic stirring, reflux condenser equipped with drying pipe, and thermometer. The reactor was immersed into a water bath at 65 °C with stirring for 10 min before adding 35 g of finely powdered anhydrous aluminum chloride. The Friedel–Crafts alkylation reaction continued for 6 h. At the very last minute of the reaction, mixture of ice/water was added followed by dilute hydrochloric acid. The products were thoroughly washed with water to remove any residual free acid. The residue was filtered out and washed with distilled water and then with acetone. At the last stage, the products were dried overnight at 90 °C for further preparation of aminated lignin (AmL). The yield of ChL is about 10.2 g.

2.2.2. Preparation of aminated lignin

The synthetic production of aminated lignin (AmL) is illustrated in Scheme 2. 50 mL of N,N-dimethylform amide (DMF) and 100 mL of ethylenediamine were put into a glass reactor with magnetic stirring, the reactor was immersed into an oil bath at 80 °C with stirring for 10 min prior to addition of 7.0g of ChL. The reaction proceeded for 7 h, the obtained reaction mixture was then filtered



Scheme 2. Preparation of aminated lignin.

and washed with ethanol and then with distilled water until neutral pH was achieved. The AmL product was dried in a convection oven at 80 °C for 24 h. The yield of AmL is about 7.2 g.

2.3. Batch experiment

The samples of AmL were used for TNT adsorption study with different contact time, initial concentration of TNT, initial pH, adsorbent dosage and temperature. All adsorption experiments were conducted in triplicate in a 250 mL stoppered conical flask containing 100 mL of test solution, and mean value of the results (differences less than 3%) were used for data analysis. A stock solution of 100 mg/L TNT was prepared and the desired different initial concentration of TNT was prepared by proper dilution of the stock solution. The pH of initial TNT solution was adjusted by sodium hydroxide (0.1 mol/L) and hydrochloric acid (0.1 mol/L). A fixed amount of the adsorbent was added and the mixture in the flask was shaken in an electrically thermostatic reciprocating shaker at 150 rpm for a predetermined contact time. After that, solid-liquid separation was achieved by filtration, and the residual TNT concentrations of the filtrates were analyzed (1 mL of TNT sample solution was diluted to 10 mL with distilled water, then 3 mL of Na₂SO₃ (100 g/L), 5 mL of cetylpyridinium chloride (CPC) (2.5 g/L) were successively added. Finally the mixture was diluted to 25 mL with distilled water. TNT concentrations were measured by Shimadzu UV-3150-VIS-NIR spectrophotometer (wavelength reproducibility: ± 0.1 ; wavelength accuracy: ± 0.3 nm) at 466 nm [34] using calibration curve (linear equation: Y = 0.09052X + 0.0495, where *Y* is absorbency and *X* is TNT concentration in mg/L; $R^2 = 0.999$) which was established from the known concentration of standard TNT solutions (0.2 mg/L, 0.4 mg/L, 1.2 mg/L, 2.0 mg/L, 2.8 mg/L and 4.0 mg/L, respectively). The standard linear calibration curves were prepared to match closely the composition of the analyzed solutions and the linearity was ensured by Beer-Lambert law. The equilibrium adsorption capacity (q_e) and removal efficiency (E%)was calculated as follows:

$$q_{\rm e} \ ({\rm mg/g}) = \frac{(c_0 - c_{\rm e})V}{1000w} \tag{1}$$

$$E(\%) = \frac{c_0 - c_e}{c_0} \times 100$$
(2)

where C_0 (mg/L) and C_e (mg/L) are the initial TNT concentration and TNT concentration after adsorption, respectively. *V* is the volume of the solution in mL and *w* is the weight of the adsorbent in g.

2.4. Regeneration experiment

Desorption of the adsorbed TNT from AmL was studied by static experiment. AmL (0.5 g) was dispersed in 1000 mL stoppered conical flask containing 500 mL of 100 mg/L TNT solution as is mentioned in the adsorption procedure. Once equilibrium was achieved, the AmL loaded with TNT was filtered out and placed in the 250 mL stoppered conical flask containing 100 mL of ethanol (95%) for desorption, and kept in an orbital shaker at 150 rpm for a period of 4 h at room temperature (25 °C). After filtration (filtrate was recycled by reduced pressure distillation) and washing with distilled water, the solid was dried in a convection oven at 80 °C for 24 h. The regenerated AmL was then used in the next adsorption experiment. The adsorption–desorption process was repeated 8 times using the same material. All the studies illustrated above were also conducted with acetone as an eluent for comparison. All experiments were carried out in duplicate and showed differences less than 3%.

2.5. Characterization

FT-IR spectra of dried samples in potassium bromide discs were recorded at 400-4000 cm⁻¹ using a Nicolet-6700 model FT-IR spectrometer.

The morphologies of Lignin, ChL, AmL, and TNT-loaded AmL were investigated by SEM (S440 Leica Cambridge Ltd.). All dried samples were sputter coated with gold prior to the examination.

The XPS experiments were carried out on a spectrometer (XSAM-800, KRATOS Co) with Mg K_{α} radiation under Ultra High Vacuum (UHV) to conduct surface analysis of the samples. In order to compensate for the charging effects, all spectra were calibrated with graphitic carbon as the reference at a binding energy (BE) of 284.8 eV. Survey scans (0–1100 eV) were carried out with 1.0 eV step size, 150 ms dwell time. High-resolution scans (C 1s, N 1s, O 1s and Cl 2p (if present in survey scan)) were carried out with 0.05 eV step size and 150 ms dwell time.

The zero surface charge (pH_{zpc}) characteristic of AmL was determined by using the solid addition method [35–37]. The experiment was conducted in a series of 50 mL glass-stoppered flasks. Each flask was filled with 20 mL of different initial pH KNO₃ solutions (0.1 mol/L) and 0.20 g of AmL. The pH values of the KNO₃ solutions were adjusted between 2 and 12 by dropping either HCl (0.1 mol/L) or NaOH (0.1 mol/L). The suspensions were then sealed and shaken for 24 h at 150 rpm. The final pH values of the supernatant liquid were noted. The difference between the initial pH (pH₀) and final pH (pH_f) values (pH = pH₀ – pH_f) was plotted against the pH₀. The point of intersection of the resulting curve with abscissa, at which pH of 0, gave the pH_{zpc}.

3. Results and discussion

3.1. Structure and morphology of the modified lignin adsorbent

The FTIR spectra of lignin, ChL and AmL are shown in Fig. 1(a)–(c), respectively. Compared to lignin, the main changes of the FTIR spectrum of ChL is the appearance of three new bands at 639, 1420 and 843 cm⁻¹, respectively. The former two bands are characteristic absorptions of -CH₂Cl group, and are assigned to stretching vibration absorption of the C-Cl bond and in-plane bending vibration absorption of the C-H bond in the -CH₂Cl group, respectively. Furthermore, the peak at 843 cm⁻¹ is due to the out of plane bending vibration absorption of the =C-H bond of the benzene ring after tetrasubstituted at 1, 2, 3 and 5 positions. These suggest that the Friedel-Crafts alkylation reaction on lignin was successfully performed. There are some characteristic peaks for AmL: a broad band of strong intensity with a peak at 3410 cm⁻¹ can be observed, this is caused by vibrations of N-H bonds in NH₂ groups. The peak at 1360 cm⁻¹ is ascribed to stretching vibration of C–N, and the C–NH₂ in-plane and out of plane bending modes of AmL are observed at 469 cm⁻¹ in the infrared [38]. All these indicate that the amidogen functional groups with high affinity and selectivity for TNT were successfully introduced on lignin.

SEM micrographs of lignin, ChL, AmL and TNT-loaded AmL are displayed in Fig. 2(a)–(d). Comparing the surface morphology of



the lignin with that of the ChL, we can easily find some changes of surface morphologies among the mentioned lignins. For instance, the surface of ChL turned slightly rough, which indicates that ChL could form different packing structure as comparing to lignin itself after the alkylation reaction. Similarly, the surface of AmL has porous structure, and this special structure contributes to the higher adsorption of TNT molecules comparing to its counterparts (a) and (b) in Fig. 2. The micrograph of the AmL exhibited significant difference after adsorbing of TNT (Fig. 2(d)), which is not clearly understood, it might be due to TNT adsorption and solvent induced morphological change.

XPS has been utilized as a convenient and sensitive probing method for tracking the surface composition variations before and after chemical modification and analyzing the interactions between adsorbate and adsorbents. The relative percentage of surface composition and atomic ratios determined from the wide scan XPS spectra are summarized in Table 1 and the typical wide scan spectrum is presented in Fig. 3. Fig. 3(a) shows the results of the survey scan XPS spectra of the lignin surface, the characteristic signals for carbon (C 1s at 284.8 eV) and oxygen (O 1s at 532.9 eV) are clearly observed. Silicon (Si 2p at 104.4 eV and Si 2s at 156 eV) is also detected, due to adventitious and unavoidable dust contamination adsorbed spontaneously from ambient air onto the surface [39]. In comparison with surfaces of lignin, ChL has an additional signals assigned to chlorine Cl 2p at 200.5 eV, together with increased ratio of carbon to oxygen (C/O) in Table 1 from 2.9 to 4.8, which indicates that chloroethene groups have been grafted successfully onto the lignin surfaces (Fig. 3(b)). It is obvious that the Cl 2p peak disappears in AmL, while a new peak at the binding energy of 400.0 eV appeared (Fig. 3(c)), which is assigned to N 1s. It confirms that chlorine atoms of ChL have been substituted successfully by ethylenediamine. We must bear in mind that there are three -NO2 groups in each TNT molecule. The N 1s and O 1s peak in Fig. 3(d) have increased compared to those peaks in Fig. 3(c) since the AmL

Table 1

Atomic concentrations on the lignin, ChL, AmL and TNT-loaded AmL surfaces obtained using XPS (data precision is \pm 5%).

Sample	Atomic concentration (%)					Atomic ratios	
	С	0	Ν	Cl	Si	C:N	C:0
Lignin	70.9	24.7	_	-	4.4	-	2.9
ChL	80.5	16.7	-	1.0	1.9	-	4.8
AmL	83.0	12.5	4.2	-	0.3	19.8	6.6
TNT-loaded AmL	81.3	13.5	4.9	-	0.3	16.6	6.0





Fig. 2. SEM of (a) lignin, (b) ChL, (c) AmL and (d) TNT-loaded AmL (magnification: ×20,000).

in Fig. 3(d) had adsorbed TNT molecules. In addition, the surface carbon to nitrogen (C/N) ratio in Table 1 changed from 19.8 (AmL) to 16.6 (the TNT-loaded AmL), which provides insight evidence that the surface of the AmL was overlaid with the adsorbed TNT.

3.2. Effect of contact time and adsorption kinetics

Fig. 4 shows the effect of contact time on the adsorption extent of TNT on AmL. It is observed that adsorption yield gradually increases with the increasing of contact time at 25 °C. Adsorption equilibrium was established at about 24 h and after that saturation plateau at around adsorption capacity of 55.7 mg/g was established. It implies that AmL possesses strong adsorption ability and affinity for TNT.

According to the data obtained from this experiment, different kinetic models including pseudo-first-order, pseudo-second-order model and intraparticle diffusion models have been employed to elucidate the potential rate-controlling steps and predict the adsorption kinetics. The kinetics of TNT adsorption on AmL were analyzed using pseudo-first-order Eq. (3) given by Lagergren [40] and pseudo-second-order Eq. (4) as follows [41,42]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(4)

where *t* is the contact time (h), q_t and q_e are the amounts of TNT absorbed at time *t* and at equilibrium (mg/g), respectively, and k_1



Fig. 3. XPS survey spectra of (a) lignin, (b) ChL, (c) AmL, and (d) TNT-loaded AmL surfaces.

Table 2

Comparison of pseudo-first-order kinetics and pseudo-second-order kinetics constants and experimental and calculated q_e values.





Fig. 4. Effect of contact time on adsorption of TNT on AmL (TNT: 100 mg/L, adsorbent dose: 1 g/L, pH: 7.0, and temperature: $25 \degree$ C).

(1/h) and k_2 (g/mg h) are the rate constant. The results are listed in Table 2. As the calculated equilibrium adsorption capacity q_e (58.2 mg/g) is closer to the experimental value (55.7 mg/g), it is clear that the adsorption kinetics of TNT on AmL fit better into the pseudo-second-order kinetics model in contrast to the pseudofirst-order model. Moreover, the R^2 value of pseudo-second-order kinetics model is higher than that of pseudo-first-order kinetics model. It means that the rate adsorbed TNT on AmL is heavily dependent on the amount of TNT on the AmL surface.

The kinetic experimental data were also applied to the intraparticle diffusion model which is given in the following form [43].

$$q_t = k_i t^{1/2} + C (5)$$

where k_i (mg/(gh^{1/2})) is intraparticle diffusion rate constant and C (mg/g) is the intercept. If intraparticle diffusion is a rate-limiting step, q_t versus $t^{1/2}$ should be linear and the plot should pass through the origin. Fig. 5 shows the plot of the amount of TNT adsorbed (q_t) versus the square root of time ($t^{1/2}$). The intraparticle diffusion plot in this case is not linear over the whole time range. This indicates that intraparticle diffusion is applicable to this system to a certain extent but is not the only rate-controlling step in the adsorption.

3.3. Effect of equilibrium concentration and isotherm model

The adsorption isotherms of TNT on AmL at different temperatures are displayed in Fig. 6. Obviously, the equilibrium adsorption amount (q_e) increased significantly along with the increase of TNT equilibrium concentration (C_e) in aqueous solution.

The equilibrium data for this present study were analyzed in the light of two well-known models: Langmuir and Freundlich models. The Freundlich isotherm assumes non-ideal sorption on heterogeneous surfaces and multilayer sorption, whereas Langmuir isotherm is used for the monolayer adsorption on a homogenous surface. The adsorption equilibrium data presented in Fig. 6 are applied to Freundlich isotherms Eq. (6) and Langmuir Eq. (7) [44].



Fig. 5. Intraparticle diffusion model for the adsorption of TNT on AmL.

Their expressions can be presented by the following equations:

$$\ln q_e = \ln K_F + n \ln C_e \tag{6}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}}b} \tag{7}$$

where $q_e (mg/g)$ and $C_e (mg/L)$ are the amount of adsorbed TNT per unit weight of adsorbent and TNT concentration in solution at equilibrium, respectively. $K_F (mg/g)$ indicates the multilayer adsorption capacity and n an empirical parameter related to the intensity of adsorption. K_F and n are determined by the intercept and slope of linear plot of $\ln q_e$ and $\ln C_e$, respectively. b (L/mg) is Langmuir constant relating the free energy of adsorption. q_{max} is the monolayer uptake capacity of the adsorbent. q_{max} and b are calculated from slope and intercept of the linear plot of C_e/q_e and C_e , respectively.

The analysis of equilibrium data according to Freundlich and Langmuir-type equations allowed us to obtain the parameters pre-



Fig. 6. Adsorption isotherms of TNT on AmL (adsorbent dose: 1 g/L, pH: 7.0, contact time: 24 h).

Table 3

Characteristic parameters obtained by the Freundlich and Langmuir equations, where R is the correlation coefficient.

Temperature	Freund	Freundlich constant			Langmuir constant			
<i>T</i> (°C)	n	$K_{\rm F} ({\rm mg/g})$	R^2	b (L/mg)	$q_{\rm max}~({\rm mg/g})$	R^2		
15	0.562	5.915	0.997	0.0466	71.58	0.925		
25	0.517	7.589	0.995	0.0602	71.02	0.926		
35	0.478	9.090	0.994	0.0752	69.06	0.926		
45	0.431	11.193	0.994	0.1027	65.96	0.941		
55	0.381	14.373	0.992	0.1559	64.27	0.959		



Fig. 7. Freundlich model for the adsorption of TNT on AmL.

sented in Table 3. Fig. 7 shows Freundlich model for the adsorption of TNT on AmL at different temperature. The Freundlich constant *n* obtained between 0.381 and 0.562 indicated that the adsorption process is favorable on our conditions [45]. The linear plot of C_e/q_e versus C_e shows that the adsorption also obeys Langmuir isotherm (figure not shown here). The results confirm that the equilibrium is better described by a Freundlich isotherm at the temperature range from 15 to 55 °C, since the correlation coefficients R^2 are higher than 0.99 when compared to the Langmuir isotherm ($R^2 > 0.92$).

3.4. Effect of temperature and adsorption thermodynamics

Fig. 6 also gives the information of temperature on TNT adsorption. It clearly shows that the adsorption capacity of AmL for adsorption of TNT increases with the increasing of temperature. The data obtained from the sorption isotherms are used to evaluate the thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS), and they are given in Table 4. ΔG is calculated by using the following equation [46]:

$$\Delta G = -RT \quad \ln \quad K_0 \tag{8}$$

where K_0 is the thermodynamic equilibrium constant (m³/mol) [47], *T* is the absolute temperature (K). The relationship between K_0

Thermodynamic parameters for the adsorption process of TNT on AmL.

<i>T</i> (°C)	K_0 (m ³ /mol)	$\Delta G (kJ/mol)$	$\Delta H (kJ/mol)^a$	$\Delta S (J/(mol K))^a$	R^2
15	10.578	-5.651			
25	13.665	-6.482			
35	17.070	-7.269	23.06	99.16	0.987
45	23.313	-8.329			
55	35.389	-9.730			

^a Measured between 288 and 328 K.

Table 4



Fig. 8. The relationship of InK and 1/T for TNT adsorption on AmL.

and the thermodynamic parameters of ΔH and ΔS can be described by Van't Hoff correlation in the following equation [47,48]:

$$\ln K_0 = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$
(9)

According to Eq. (9), it is shown in Fig. 8 that the parameters of ΔH and ΔS can be calculated from the slope and the intercept of the plot of $\ln K_0$ versus 1/T, respectively.

As is evident in Table 4, the ΔH parameter is found to be 23.06 kJ/mol, which are typical values for the energy (2–40 kJ/mol) of adsorption from typical hydrogen bond forces [49]. The results indicate that physical forces such as hydrogen bonding interaction between TNT and AmL act as the dominant role in adsorption process. In addition, the positive values of ΔH indicate that the adsorption of TNT on the AmL is an endothermic process.

The negative sign of ΔG suggests the spontaneous nature of TNT adsorption onto the AmL. In addition, with the increasing of temperature, ΔG increases, which reveals that the sorption process of TNT on AmL is more favorable at higher temperatures. This is in good agreement with their adsorption capacities. The positive value of ΔS suggests the increasing randomness at the solid/solution interface during the adsorption of TNT on AmL. The adsorbed solvent molecules, which are displaced by TNT, gain more translational entropy than is lost by TNT molecules, thus leading to enhanced randomness in the system [50].

3.5. Effect of pH on adsorption

Generally, the effect of pH is considered to be an important factor because the chemical structures of TNT and AmL (Scheme 2). The adsorption of TNT was therefore studied from the aqueous solutions of different pH values covering a range of 2-11. The adsorption isotherms at different pH values are shown in Fig. 9. The effect of pH value on the adsorption amount of AmL is given in Fig. 10. As is shown from Figs. 9 and 10, respectively, at low pH range, with the increase in solution pH, the adsorption capacity of TNT increases, and the maximum adsorption of TNT on AmL occurred around the neutral pH (about 6.0–8.0), whereas the adsorption amounts decreased dramatically with increasing pH at pH > 8. It is reasonable to assume that the functional group -NH₂ or -NH- of AmL interact with the O atom of TNT at a molecular state via hydrogen bond interaction. Due to the protonation at low pH and deprotonation at high pH of the amino groups of AmL, the ionization of amine breaks the H-bondings. Opposite to that, when the pH approaches to neutral, more of the -NH₂ and -NH- group are freed from the



Fig. 9. Adsorption isotherms of TNT on AmL (adsorbent dose: $1\,g/L$, temperature: $25\,^\circ C$, contact time: $24\,h).$



Fig. 10. Effect of pH on adsorption of TNT on AmL(TNT: 100 mg/L, dose: 1 g/L, contact time: 24 h, and temperature: $25 \degree$ C).

protonation [20], the hydrogen bond interaction between amino group of AmL and TNT is gradually becoming the strongest. Therefore, the adsorption capacities depend markedly on pH variation. Eqs. (10)–(11) represent the protonation/deprotonation reactions of the amine groups of the AmL with varying pHs.

 $Lignin-(CH_2)_2-NH-(CH_2)_2-NH_2+2H^+ \leftrightarrow Lignin-(CH_2)_2$

$$-NH_2^+ - (CH_2)_2 - NH_3^+$$
(10)

Due to AmL amine ionization at low or high pHs, the hydrogen bond interaction between amino group of AmL and TNT was weakened. In addition, in alkaline condition (Scheme 3), TNT forms the



Scheme 3. Formation of Janovsky complexes.



Fig. 11. Determination of the point of zero charge of AmL by the solid addition method.

Janovsky complexes [51] which may hinder the adsorption due to steric barrier. Hence, the uptake declines sharply at high pH.

The effect of pH on adsorption of TNT can also be explained in terms of pH_{zpc} . In the present study, pH_{zpc} of AmL was determined as 6.62 (Fig. 11). At $pH < pH_{zpc}$, there more H^+ are present thus the AmL chains take up more H^+ , suppressing TNT molecules to bind on the AmL chains. At $pH > pH_{zpc}$, the AmL chains are negatively charged, the increasing electrostatic repulsion between electronegative sorbate species and adsorbent particles would lead to decrease adsorption capacity of TNT. Therefore, at around neutral condition, the charge of AmL chains is almost zero, hydrogen bond interaction between AmL and TNT increased dramatically. It is therefore important to suggest a neutral condition for adsorption of TNT using AmL.

3.6. Effect of adsorbent dosage

The adsorbent dosage is an important parameter because it determines the removal ability of AmL for TNT. Experimental studies were carried out at temperature 25 °C with varying amounts (0–8 g/L) of AmL using 100 mL of initial concentration of TNT at 100 mg/L at pH 7.0. The effect of adsorbent dosage on the removal extent of TNT is shown in Fig. 12. In general, removal efficiency increases with increasing adsorbent dosage, which may be attributed to increasing surface area and more active sites available for hydrogen bonding and adsorption [52]. After adsorbent dosage



Fig. 12. Effect of dosage on adsorption of TNT on AmL (TNT: 100 mg/L, pH: 7.0, contact time: 24 h, temperature: $25 \degree$ C).



Fig. 13. Relationship between q_e and adsorption-desorption cycle of AmL.

increases to approximate 4 g/L, the removal efficiency approaches to 90% and then increases slightly with adsorbent dosage. The maximum removal efficiency is over 95% when adsorbent dosage reaches 8 g/L. So we may assume that it is possible to remove TNT completely if there is sufficient AmL in solution. On the other hand, the adsorption capacity (q_e) decreases with an increase in adsorbent dose. The observed decrease in adsorption capacity is due to adsorption sites remaining unsaturated during the adsorption process [21,23].

3.7. Desorption and regeneration studies

It is very important to regenerate the waste adsorbent for repeated use and to keep the adsorption process cost down in industrial treatment. When ethanol (or acetone) is used as eluent, the hydrogen bond interaction between TNT and AmL is replaced by the hydrogen bonding interactions between AmL and ethanol (or acetone), TNT is thus released into the eluent.

The adsorption-desorption cycle of AmL is shown in Fig. 13. As can be seen, AmL could be used repeatedly and the adsorption capacity undergoes a slight decline, demonstrating that the AmL is very suitable for the design of a continuous sorption process. Furthermore, ethanol was shown to be a better eluent compared to acetone (the recovery percentage is 95.2% and 91.9% after 8 desorption-adsorption cycle, respectively). Compared to other adsorbents such as activated carbon or zeolites, the greatest advantages of this modified lignin are: (1) lignin-based material is a low cost polymer which can be reproducible; (2) can be completely regenerated for recycling and repeatable usage without a significant loss of its adsorption capacity, which is significant for practical applications. Desorption of the adsorbed TNT from AmL is able to take place in ethanol, indicating that ethanol has a good affinity with TNT or with AmL where there is a competitive relationship of H-bonding between ethanol, TNT and AmL. The facile removal of TNT adsorbed on AmL also can be explained that the hydrogen bonding interactions between AmL and ethanol are stronger than hydrogen bonding between AmL and TNT.

4. Conclusions

In the study, a lignin derivative, aminated lignin was prepared successfully by a simple method. It has great adsorption capacity for the adsorption of TNT. The adsorption process depended significantly on the pH and temperature of solution. The strongest adsorption capacity was found in the solution at around the neutral pH. The saturated adsorption capacity could reach to 55.7 mg/g at 298 K and at pH of 7. Equilibrium data are best described by the Freundlich isotherms model. The negative sign of ΔG confirms the spontaneous nature of the adsorption process. The lower value of enthalpy (ΔH) indicates that hydrogen bonding interactions play an important role in adsorption process, and the positive sign of ΔH indicates that the adsorption process is endothermic. Furthermore, the biosorbent has admirable capability of regeneration. All these indicated that AmL is a promising sorbent of TNT in water and it is worthy studying its dynamic adsorption for further industrial application.

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