Preparation and Performance of Dimethyl-Acetoxy-(2-Carboxymethyl Ether)-Lignin Ammonium Chloride Amphoteric Surfactant

Jinling Tian, Shixue Ren*, Guizhen Fang, Yanli Ma, and Qing Ai

To improve the added value of the lignin products, dimethyl-acetoxy-(2-carboxymethyl ether)-lignin ammonium chloride (DALAC) amphoteric surfactant was synthesized from wheat straw alkali lignin raw material. The structure was analyzed by Fourier transform infrared spectroscopy (FT-IR), and the solubility in different pH solutions was evaluated. The effect of DALAC on adsorption performance was investigated with a solution of copper ions as simulated wastewater, while its flocculation performance was investigated with acid black ATT and methylene blue (MB) wastewater as simulate dyes. The results showed that carboxyl and quaternary amine groups were successfully grafted, and nitrogen content of DALAC was 3.66%. The adsorption isotherm of copper ions with DALAC fit the Freundlich equation. Optimum adsorption conditions for Cu^{2+} were dosage 0.1 g/L, pH 5.5, and adsorption time 6 h, for which the maximum adsorption capacity was 399 mg/g. The maximum removal rate of Acid black ATT (anionic dye) was 97.8% when the optimum flocculation conditions were dosage 4 g/L, pH 2, and mass concentration of dye 0.1 g/L. The maximum removal rate of methylene blue (cationic dye) was 98.7 %, when the optimum flocculation conditions were dosage 2.5 g/L, pH 9, and mass concentration of dye 0.1 g/L. DALAC will be expected to a novel adsorbent of heavy metal ion and flocculants of dyes in the future.

Keywords: Alkali lignin; DALAC; Amphoteric surfactant; Adsorbent; Flocculants

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INTRODUCTION

Lignin is a natural polymer and is an abundant renewable resource that is non-toxic and low in cost. Industrial lignin is mainly derived from wastewater of the paper industry, and the utilization of industrial lignin as an abundant and available residual biomass has become significant. Developing the alkali lignin products has been an effective way to make the most of lignin (Embree *et al*. 2001). Lignin is a natural amorphous cross-linked resin that has an aromatic three-dimensional polymer structure. However, its composition is not stable and it has a low surface activity. Because of its less hydrophilic functional groups, lignin is practically insoluble in water at a pH value of 7.0. But alkali lignin can acquire excellent surface activity by chemical modification, making the product potentially useful as an adsorbent material for the removal of heavy metal ions from wastewater and as a flocculant material for removal of dye from wastewater.

The development of an alkali lignin-based amphoteric surfactant can improve the added value of alkali lignin products. An amphoteric surfactant, in a narrow sense, refers to a surfactant dissociating positive ions and negative ions at the same time in water.

Amphoteric surfactants, such as an amphoteric leather retanning agent, were developed in the early 1940s, but because of the high cost, production developed slowly (Lan 2001). In recent years, amphoteric surfactants have been used once again, and their application has been extended to water treatment, flocculants, dispersing agents, and water reducing agents (Liu and Zhou 2008). Currently, with the rapid development of the economy, water pollution has become a very serious problem. Many researchers have developed some new adsorbents for the removal of heavy metal ions, such as modified poly (ethylene terephthalate) (PET) fibers (Monier and Abdel-Latif 2013), amine-functionalized nano-magnetic polymer adsorbents (NH_2-NMPs) (Shen *et al.* 2012), and lignite and coconut shell-based activated carbon fiber (Shrestha *et al*. 2013). In addition, there is also much research dealing with color dyes in wastewater and using peach gum (Li *et al*. 2014), activated carbon (Gupta *et al.* 2011), wheat husk (Gupta *et al.* 2007), bottom ash and deoiled soya (Gupta *et al.* 2009), industrial lignin (Suteu and Malutan 2013), and a new amphoteric granular lignin (Liu *et al*. 2005), *etc*. The resource utilization of industrial waste is an important subject during contemporary economic and social development. Lignin amphoteric surfactants not only remove dyes, but they also remove heavy metal ions in wastewater. This product possessing a multifunction effect is worthy of our study. Therefore, using wheat straw alkali lignin as a raw material a new amphoteric surfactant was synthesized that can deal with heavy metal ions and color dyes at a low cost.

In view of its structure, one could expect that dimethyl-acetoxy-(2-carboxymethyl ether)-lignin ammonium chloride (DALAC) should have good adsorption performance for heavy metal ions and good flocculation for anionic and cationic dyes. The synthesis of DALAC amphoteric surfactant was based on the previous research of one of the present authors (Ai 2010). The effect of DALAC on adsorption performance was investigated with copper ions as simulated wastewater, while its flocculation performance was investigated with acid black ATT and methylene blue (MB) wastewater as the simulated dyes. The suitable adsorption and flocculation conditions were determined, and DALAC was investigated as an adsorbent of heavy metal ions and the flocculant of dye wastewater.

EXPERIMENTAL

Materials

Chemical reagents

The alkali lignin used in this study was obtained through solubilization at high pH, after which 1 M HCl was added to the solution to reduce the pH to 4, causing precipitation of the alkali lignin. The solids were then filtering by vacuum-filtration (0.22 µm cellulose acetate membrane filter), the precipitation was washed with distilled water until the pH was 7.0, and finally the material was oven-dried at 50 °C to a constant weight. Industrial alkali lignin was supplied by Shandong Quanlin Paper industry Co., Ltd. (China). Formaldehyde (37 to 40% solution) was obtained from Tianjin Fengchuan Chemical Reagent Co. Ltd. (China). Dimethylamine (33% solution) and sodium chloroacetate were of analytical reagent grade obtained from Tianjin Guangfu Fine Chemical Research Institute (China). Pentahydrate copper sulfate was purchased from Jilin Hengyuan Chemical Reagent Co. Ltd. (China). The NaOH was of analytical reagent grade purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (China).

Synthesis of DALAC

Alkali lignin (5 g) dissolved with 80 mL 10% NaOH solution and 30 mL 4% H_2O_2 were added to a 250 mL three-necked round-bottom flask equipped with a stirrer and a reflux condenser at 80 °C for 2 h. After cooling to room temperature, a Mannich reaction was subsequently performed in the reaction vessel at 80 °C for 3 h. After completing the reaction, 20 mL 40% sodium chloroacetate solution was added to the reaction vessel at 60 °C for 4 h. Then the product was precipitated by HCl (1 mol/L). After filtering by vacuum-filtration (0.22 μm cellulose acetate membrane filter), the residues were washed with distilled water until the pH was 7.0, and then oven-dried at 50 °C to a constant weight (approximately 24 h). The resulting tan color powder was DALAC.

Methods

Fourier transform infrared spectroscopy (FT-IR)

The infrared spectra of lignin and DALAC were recorded between 4000 and 400 cm^{-1} at 4 cm^{-1} resolution with a Spectrum One (Magna-IR560, Nicolet; USA) spectrometer. Testing samples (0.002 g) and KBr (0.2 g) were made into slices to measure.

Elemental analysis

The nitrogen content of DALAC (0.001 g) was determined by a Euro EA-3000 elemental analyzer (Vector Instruments & Software; Italy). DALAC (0.001 g) was put into tin cup, and tin cup that was sealed with tweezers was put into sample tank.

Automatic potentiometric titration

The carboxyl content of lignin and DALAC were determined by automatic potentiometric titration (Hiranuma COM-300, Shanghai Tian Mei Scientific Instrument Co. Ltd.; China). The DALAC (0.06 g) and lignin (0.06 g) were each placed in a 25-mL volumetric flask, followed by 20 mL of calcium acetate solution (0.4 M). The mixture was put in a water bath at 85 °C for 0.5 h. After cooling to room temperature, distilled water was added to the mixture to the mark of 25-mL volumetric flask. After filtering by vacuum-filtration (0.22 μm cellulose acetate membrane filter), 20 mL of the filtrate was measured with a 0.01 M NaOH standard solution by automatic potentiometric titration until pH value was 8. The carboxyl content was calculated according to Eq. 1 as follows,

$$[OH] = \frac{(a - a_0) f \times 1.25 \times 0.85}{A} \times 100\% \tag{1}$$

where a (mL) is the NaOH (0.01 M) volume that the sample consumed, a_0 (mL) is the NaOH (0.01 M) volume that the blank consumed, f is the correction factor, 0.85 is the amount of acid base that the lignin consumed in 1 mL NaOH (0.01 M), and A (mg) is the quality of the sample.

Quaternary ammonium salt structure detection

The solution of the product that was not precipitated by HCl (2 to 3 drops) was added to 10 mL of a bromophenol blue-ethanol solution, which was prepared by bromophenol blue (0.1 g) dissolved in 100 mL of 20% ethanol solution. When the solution of product appeared by eye as a light blue color, this was taken as an indication that the product was an amphoteric surfactant (Tang *et al*. 2007).

Determination of solubility

Lignin (0.005 g) and DALAC (0.005 g) were each placed in three 100-mL beakers, and 75 mL of distilled water was added (1 mg:15 mL). Under constant stirring, NaOH (0.01 M) and HCl (0.01 M) were each added to one of the beakers until lignin and DALAC dissolved. The pH value was measured with a precision pHs-3C (Shanghai Thunder Magnetism Instrument Factory) at this time.

Adsorption performance of DALAC

A standard stock solution of copper(II) at a concentration of 100 mg/L was prepared by dissolving pentahydrate copper(II) sulfate ($CuSO_4 \cdot 5H_2O$) in 0.5 L of ultrapure water. The DALAC (0.002 to 0.08 g) was placed in a flask, and 20 mL of the Cu(II) standard solution was added to the flask and shaken in a water bath at 25 °C for a period of 6 h. When adsorption equilibrium was achieved, the adsorbent was removed through vacuum-filtration, and the concentration of Cu(II) ions in the residual solutions was checked and analyzed by atomic absorption spectrophotometry (AAS) (TAS-990, Beijing Purkinje General Instrument Co. Ltd.; China). The wavelength and slit values used for the Cu(II) detection were fixed at 324.7 nm and 0.4 nm, respectively. The amount of Cu(II) ions adsorbed by the bio-adsorbent at adsorption equilibrium was calculated according to Eq. (2) as follows,

$$Q = \left(\frac{C_0 - C}{m}\right)V \qquad (2)$$

where Q (mg/g) is the amount of Cu(II) adsorbed per gram of adsorbent at equilibrium, C_0 (mg/L) is the initial Cu(II) concentration, C (mg/L) is the equilibrium Cu(II) concentration, V (L) is the volume of the standard solution of Cu(II), and m (g) is the mass of adsorbent.

For the pH-effect experiments, the pH of the solution was initially adjusted with aqueous solutions of acid or base (0.01 mol/L HNO_3 and 0.01 mol/L $NH_3 \cdot H_2O$) to reach pH values of 3.5 to 5.5. The DALAC (0.002 g) was placed in a flask and 20 mL of the Cu(II) standard solution was added; the flask was shaken in a water bath at 25 °C for 6 h. Adsorption kinetic tests were performed using 100 mg/L as initial Cu(II) concentration at 25 °C (t_{ads} = 0 to 10 h). The adsorption isotherms were determined by running the adsorption experiments with various initial Cu(II) concentrations (C_0 = 30 to 200 mg/L) at three different temperatures (25, 35, and 45 °C) for a 12-h contact time.

Flocculation performance of DALAC

The simulated cationic dye (MB) and anionic dye (acid black ATT) wastewaters were prepared by dissolving 0.05 g of each dye in 0.5 L of distilled water. DALAC (0.03 to 0.12 g) was placed in a flask, 20 mL of the dye solution (0.1 g/L) was added, and the flask shaken in a water bath at 25 °C for 4 h. The solution was allowed to settle for 0.5 h after shaking. The light transmittance of the clean supernatant was then measured with a double beam spectrophotometer (Spectrophotometer–TU-1901, Beijing Purkinje General Instrument Co. Ltd.; China) at the maximum adsorption wavelength (315 nm for ATT and 663 nm for MB). The residual dye concentration in the solution was calculated according to the standard curve. The percentage removal of dye (R) was calculated according to Eq. (3) as follows,

$$R = (1 - \frac{C}{C_0}) \times 100\% \tag{3}$$

where C_0 and C are the dye concentrations before and after treatment (mg/L).

The pH was adjusted to a desired value using NaOH (1.0 M) and hydrochloric acid (1.0 M) solutions. The effect of solution pH, dye concentration (C_0), and flocculant dosage (m) on dye removal was studied to determine the optimum operating conditions.

RESULTS AND DISCUSSION

FT-IR Analysis

Figure 1 shows the FT-IR spectra of alkaline lignin and DALAC. In the major peaks, the absorption at 2933 cm^{-1} originated from C-H stretching in methyl and methylene groups, while the absorption at 1597 cm^{-1} and 1454 cm^{-1} arose from DALAC benzene ring skeletal vibration. The lignin peak at about 826 cm^{-1} disappeared, while the DALAC peak at about 837 cm^{-1} appeared, which meant that tri-substituted of lignin benzene ring had been converted into a tetrasubstituted form (Ai 2010). The peak at about 1710 cm^{-1} was attributed to carboxyl symmetric stretching vibration, which demonstrated the presence of a carboxyl group (Zhao *et al*. 2013). The phenolic hydroxyl can generate ether with sodium chloroacetate, which reduced the content of phenolic hydroxyl.

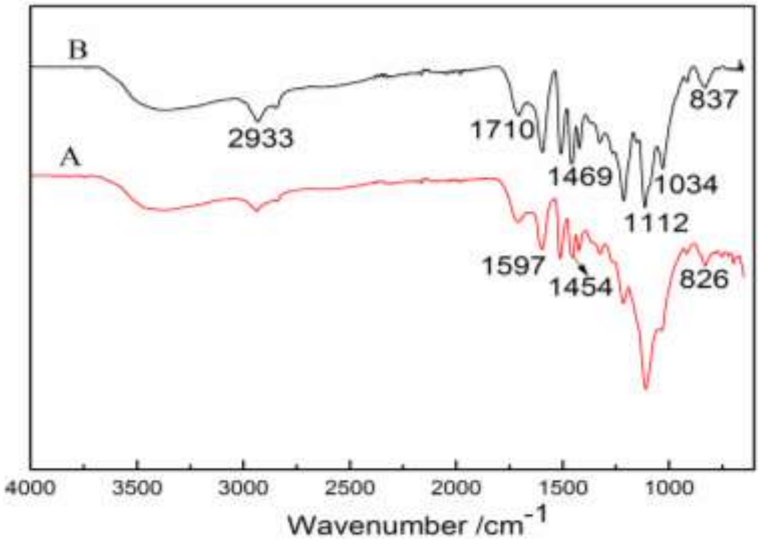

Fig. 1. FT-IR spectra of (A) alkali lignin and (B) DALAC

Compared to the FT-IR spectra of lignin, the peak of DALAC at 1112 cm^{-1} was weakened significantly, and a new absorption peak appeared at 1034 cm^{-1} due to aromatic C-O-C symmetric stretching vibrations (Hegde *et al*. 2006). The absorption peak at 1469 cm^{-1} was the C-N stretching vibration of quaternary ammonium (Xia and Gu 2010), which proved that quaternary the amine group was successfully grafted.

Nitrogen Content and Carboxyl Content Analysis

Table 1 depicts the nitrogen and carboxyl content of DALAC and alkaline lignin. In relation to the determination of nitrogen content, the theoretical nitrogen content of DALAC was 4.96%, while the actual nitrogen content was 3.66%. The theoretical nitrogen content of DALAC was calculated by assuming guaiacyl propane as the basic unit structure, so the result may be much larger. Lignin is a three-dimensional network structure, and the steric hindrance is large. It was difficult for the formaldehyde to have a nucleophilic reaction with the benzene ring; as a result, the actual nitrogen content of DALAC was lower than its theoretical nitrogen content. However, the carboxyl content of DALAC was greater than the alkali lignin carboxyl content (Table 1). The product carboxyl content was improved by chemical modification, which indicates that the lignin had reacted with the sodium chloroacetate. As mentioned above, each characterization mutually supported and demonstrated that the carboxyl group and quaternary amine group were successfully grafted.

Table 1. Nitrogen Content and Carboxyl Content of DALAC and Alkaline Lignin

	Alkaline Lignin	**DALAC**
Actual nitrogen content	0	3.66%
Theoretical nitrogen content	0	4.96%
Carboxyl content(mmol/g)	0.6108	1.3721

Quaternary Ammonium Salt Structure Detection Analysis

Bromophenol blue is a common way to test organic compounds containing a quaternary ammonium structure. The positive charge of quaternary amine and the negative charge of bromophenol blue can form electron pairs when the increase of product concentration is greater than the critical micelle concentration, and because of the compatibilization bromophenol blue presents an indigo fluorescence. The bromophenol blue-ethanol solution and DALAC solution were mixed, showing light blue to indicate that the product possessed the structure of quaternary ammonium.

Dissolution Performance Analysis

Table 2 shows the solubility of alkaline lignin and DALAC. Alkaline lignin can dissolve at pH 10.64, while DALAC can dissolve at pH 7.35. Alkaline lignin is a type of natural polymer, and its structure has a number of polar groups, in particular hydroxyl. It can cause lignin to have a strong molecular internal energy and intermolecular hydrogen bond, so alkaline lignin does not dissolve in water. A higher pH value is necessary for alkaline lignin to dissolve. The DALAC is an amphoteric ionic surfactant and simultaneously contains anionic (carboxyl) and cationic (quaternary amine) groups. The DALAC can dissolve under partial neutral conditions, since the pH needed to dissolve DALAC was lower than that of lignin.

Table 2. Determination of Solubility of Alkaline Lignin and DALAC

Sample	0.01 M NaOH	0.01 M HCl	Distilled water	Soluble pH value
Alkaline lignin	Easily soluble	Insoluble	Insoluble	10.64
DALAC	Easily soluble	Insoluble	Slight soluble	7.35

Adsorption Performance of DALAC for Cu^{2+}

There are a number of heavy ions in industrial wastewater and also many methods to deal with heavy ions, such as mining, metallurgy, ion exchange, electronic, and electroplating (Bessbousse *et al*. 2008; González-Muñoz *et al*. 2006; Satapathy and Natarajan 2006). However, several methods such as ion exchange are expensive and the processes of the product more complex. The DALAC of the synthesis was simple and low cost and placed directly in water to achieve the adsorption in this experiment. Adsorption (or bio-sorption) has received much attention in recent years and used in wastewater treatment has the advantages of simplicity in operation and low lost (Ma *et al.* 2014). The adsorption of DALAC is primarily a combination of chemical and physical adsorption. The carboxyl group of DALAC for Cu^{2+} adsorption in an aqueous solution was mainly due to chemical adsorption, with the adsorption mechanism chemical chelating and ion exchange adsorption. The chelating adsorption was the main adsorption mechanism. Therefore, the effectiveness of DALAC on the adsorption performance was investigated with copper ions as simulate wastewater.

Adsorption kinetics

Figure 2 shows the kinetics of the adsorption of Cu^{2+} by DALAC. When the adsorption time was 0 to 6 h, the adsorption capacity rapidly improved and it tended to level off after 6 h. Because the DALAC surface possesses carboxyl, amino, and phenolic hydroxyl groups, the chemical chelating reaction with Cu^{2+} occurs in a short time (Yang *et al*. 1997). In addition, the effect of electrostatic force allows the adsorption capacity to reach equilibrium more easily. In order to ensure that the Cu^{2+} adsorption on DALAC was achieved completely in the experiment, oscillation time should be more than 6 h.

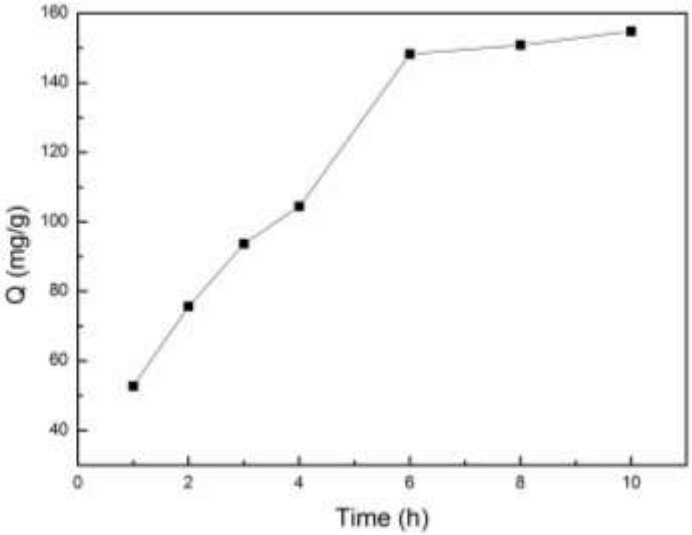

Fig. 2. Effect of contact time on the adsorption of Cu^{2+} by DALAC (initial concentration 100 mg/L, DALAC 0.1 g/L, 25 °C)

Effect of pH on adsorption

The adsorption capacity as a function of equilibrium pH is shown in Fig. 3. The copper existed mainly in the form of the ions in the acidic waste water. When the pH value was greater than or equal to 6, the solution generates copper hydroxide precipitant. Therefore, the pH range used in this experiment was less than 6. When the pH value was low, the -OH, -COOH, -N$^+$ on the DALAC surface and hydrogen ions in the aqueous solution cause protonation to weaken the electrostatic force between DALAC and Cu^{2+} and thus decrease the adsorption capacity. With an increase of pH, protonation was weakened but ion exchange was strengthened. Metal ions gradually replaced the hydrogen ions of the functional groups and generated a lignin complex, thereby increasing the adsorption capacity. Therefore, DALAC adsorption of Cu^{2+} was optimum at pH 5.5.

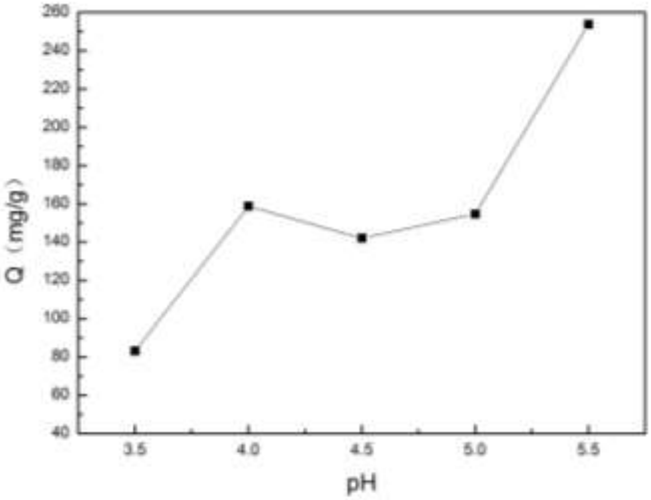

Fig. 3. Effect of pH on the adsorption of Cu^{2+} by DALAC (initial concentration 100 mg/L, DALAC 0.1 g/L, 25 °C)

Effect of dosage on adsorption

As illustrated in Fig. 4, the adsorption capacity gradually decreased with an increase in DALAC dosage from 0.1 g/L to 4 g/L.

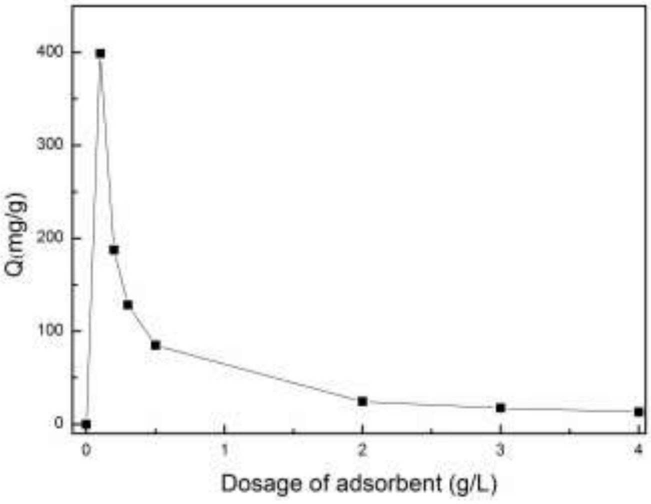

Fig. 4. Effect of dosage on the adsorption of Cu^{2+} by DALAC (initial concentration 100 mg/L, DALAC 0.1 g/L, pH 5.5, 25 °C)

The adsorption capacity was greatest at 0.1 g/L, when the DALAC could fully contact the Cu^{2+}. With the increase of DALAC dosage, because of the influence of factors such as diffusion and adsorption saturation, the adsorption capacity gradually decreased. Therefore, a concentration of 0.1 g/L was considered the optimal adsorbent dosage for DALAC. The maximum adsorption capacity was 399.0 mg/g.

Table 3 compares the maximum adsorption capacities of Cu(II) on various adsorbents. Although these data were obtained under different experimental conditions, they will still be useful as a criterion for comparing the adsorption capacities. As can be seen from Table 3, the maximum adsorption capacities of DALAC for Cu(II) is higher than those of most previous studies.

Table 3. Comparison of Adsorption Capacity for Cu(II) with Various Adsorbents

Ion	Adsorbent	Q_{max} (mg/g)	Refs.
Cu(II)	DALAC	399.0	This work
	Sodium lignosulfonate-chitosan polyelectrolyte	12.5	Wang *et al*. 2012
	Wheat straw amphoteric adsorbent	73.53	Zhong *et al*. 2013
	Pyromellitic dianhydride	60.21	Qi *et al.* 2013
	Ethylenediamine tetraacetic acid dianhydride	33.45	Qi *et al.* 2013

Adsorption isotherms

Figure 5 depicts the adsorption isotherms of Cu(II) on DALAC at three different temperatures (25, 35, and 45 °C).

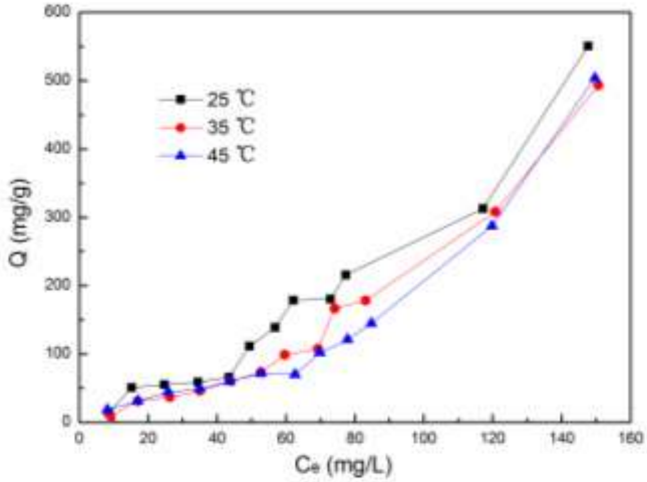

Fig. 5. Adsorption isotherms of Cu^{2+} by DALAC (DALAC 0.1g/L, adsorption time 12 h)

The Langmuir (Eq. 4) and Freundlich (Eq. 5) isotherm models (Kitagawa and Suzuki 1983; Özer 2007) were used in the current study to describe the adsorption process. The relative parameters calculated on the basis of the Langmuir and Freundlich equations are listed in Table 4. With an increase in temperature, the adsorption capacity gradually decreases; by contrast, the adsorption capacity was higher at 25 °C.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m \times K_L \times C_e} \tag{4}$$

$$\lg q_e = \lg K + \frac{1}{n} \lg C_e \quad (5)$$

where q_e (mg/g) is the adsorption capacity of adsorbent at equilibrium, C_e (mg/L) is the equilibrium Cu(II) concentration, q_m (mg/g) is the saturated adsorption capacity of adsorbent, K_L (L/mg) is Langmuir constant, and K and $1/n$ are Freundlich parameters.

As shown in Table 4, the linear coefficient of determination R^2 values of the Freundlich equation at three different temperatures were all greater than 0.90 and its value was stable. However, the linear correlation coefficient R^2 of the Langmuir equation at three different temperatures were not all greater than 0.90 and its value was unstable. The results show that DALAC adsorption isotherms of copper ions can be fitted well by the Freundlich equation, and the adsorption was a heterogeneous adsorption process under the condition of an uneven surface. The Cu^{2+} adsorption by DALAC was not a monolayer adsorption, and there existed physical adsorption and chemical adsorption at the same time. The mechanism of adsorption of metal ions is very complicated, to mainly include electrostatic forces, hydrogen bonding, van Der Waals force, and the coordination effect.

Table 4. Adsorption Isotherm Fitting Parameters

Temperature (K)	**Langmuir**			**Freundlich**		
	q_m **(mg/g)**	K_L **(L/mg)**	R^2	K	n	R^2
298 K	625	0.0029	0.8858	0.5708	0.7400	0.9468
308 K	270.2702	0.0044	0.9824	0.1193	0.6546	0.9740
318 K	232.5581	0.0050	0.9348	0.2456	0.6709	0.9606

Flocculation Performances of DALAC for Various Dyes

The DALAC amphoteric surfactant molecule exists as hydrophilic groups that are anionic (carboxyl group) and cationic (quaternary ammonium group). Due to this feature of DALAC, its flocculation performance was investigated with acid black ATT and MB wastewater as the simulate dyes. The pH, the concentration of dyes, and the dosage factors were investigated for the effect of flocculation performance.

Effect of dosage on flocculation

As shown in Fig. 6, acid black ATT removal first increased and then decreased with the increase of the dosage. For acid black ATT, 4 g/L was considered as optimal flocculant dosage for DALAC. It is evident from Fig. 6 that the removal of MB increased sharply with the increase of flocculant dosage from 0.5 g/L to 2.5 g/L. There was no change in the percentage of MB removal above 2.5 g/L of adsorbent loading. So, in regards to MB, 2.5 g/L was considered the optimal flocculant dosage for DALAC.

Effect of dye concentration on flocculation

Figure 7 shows the effect of different initial concentration of simulate dyes. With an increase in the concentration of dyes, the removal rate of acid black ATT and MB dyes first increased and then decreased, with the optimum removal rate at 0.1 g/L. When the concentration of acid black ATT was 0.1 g/L, the best removal rate was 88.0%. Gupta *et al.* (2014) recently studied removal of MB by guar gum-cerium (IV) tungstate hybrid cationic exchangers and found the removal rate was more than 90%.

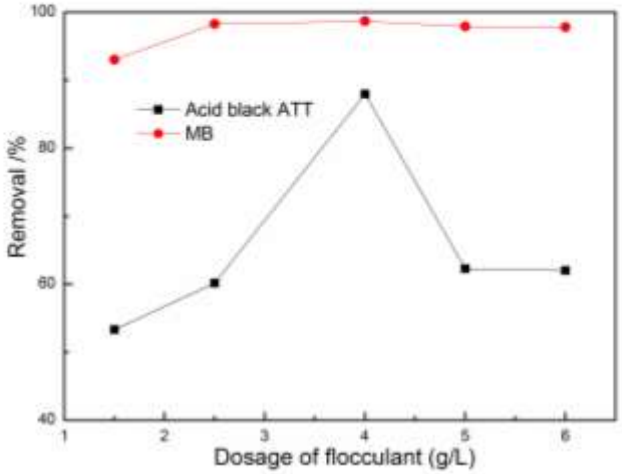

Fig. 6. Effect of flocculant dosage on the flocculation of acid black ATT and MB

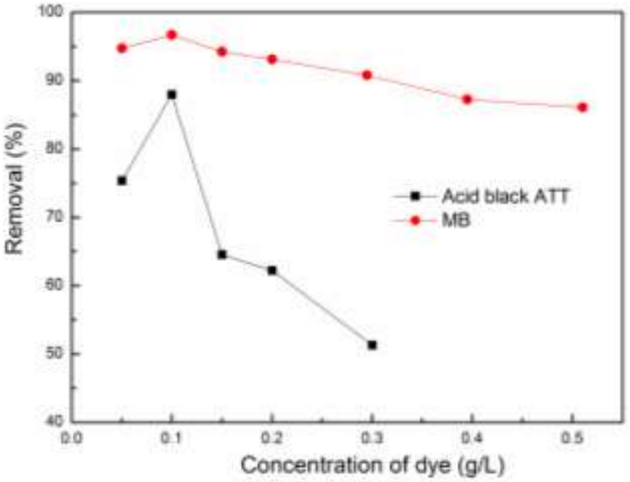

Fig. 7. Effect of concentration on the flocculation of Acid black ATT and MB

Effect of pH value on flocculation

Figure 8 shows the effect of pH value on flocculation performance of DALAC. It was found that acid black ATT removal decreased as the pH value was increased from 2 to 6, while the MB removal first increased then decreased as the pH value was increased from 6 to 10. The flocculation performance of acid black ATT was optimum when the pH value was 2, and the best removal rate was 97.8%. When the pH value was lower, DALAC presented a positively charged hydrophilic group -N$^+$ and the reticular structure of lignin was exposed in solution at the moment by forming a bridge between the lignin molecules so that the colloid and suspended particles were strongly adsorbed (Lei and Lu 1997). Compared to Zhang *et al.* (2012) preparing the trimethyl quaternary ammonium salt based on lignin (SL-QA), was able to achieve a maximum removal rate of Acid Black ATT of 94.0%. However, the optimum removal rate of Zhang *et al.* (2012) preparing the trimethyl quaternary ammonium salt based on lignin (L-QA) was 78.8%. The preparation of L-QA having a spherical form increased its specific surface area, so the removal rate of Acid black ATT was obviously improved. In regards to MB, the flocculation performance was optimum when the pH value was 8. As a result of the three-dimensional network structure of lignin coupled with lignin surface connecting the carboxylic acid group and quaternary ammonium group, DALAC can adsorb more suspended particles and colloid particles under the dual function. Thus, DALAC possessed excellent flocculation properties and caused the dye removal rate to increase. The highest removal rate for MB was 98.7%.

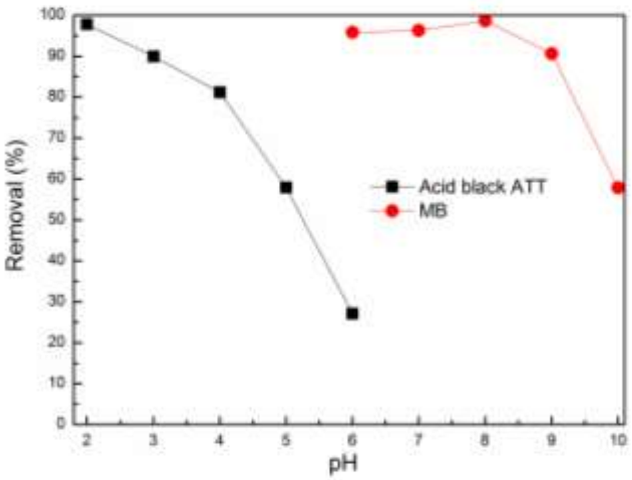

Fig. 8. Effect of pH on the flocculation of acid black ATT and MB

CONCLUSIONS

1. The DALAC was synthesized with wheat straw alkali lignin as a raw material. The analysis results of FT-IR and element analysis revealed that carboxyl and quaternary amine groups were successfully grafted, and the nitrogen content of DALAC was 3.66%. The solubility of DALAC was greater than that of the source lignin.
2. The DALAC on the adsorption isotherm of copper ions could be fitted well by the Freundlich equation. Under the optimum adsorption conditions for Cu^{2+}, with a dosage of 0.1 g/L, pH 5.5, and adsorption time 6 h, the maximum adsorption capacity was 399.0 mg/g.
3. The flocculation performance of DALAC for dyes (acid black ATT and MB) removal was better than the adsorption performance. The maximum removal rate of acid black ATT (anionic dye) was 97.8% under the optimum flocculation conditions of 4 g/L, pH 2, and concentration of dye 0.1 g/L. The maximum removal rate of MB (cationic dye) was 98.7% when the optimum flocculation conditions were 2.5 g/L, pH 8, and concentration of dye 0.1 g/L.

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