Performance of Amphoteric Larch Tannin Derivative Particles for Removal of Azo Acid Dyes

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Two particulate amphoteric larch tannin (CLT) products (CTD and CTB) were prepared by cross-linking reactions, and their acid dyes removal abilities were investigated. The effects of several parameters such as pH, contact time, and particle doses were tested, and the acid dyes removal behaviors of both types of particles were compared. The removal of azo acid dyes on CTD and CTB was pH-dependent, and the maximum removal of ≥90.7% was reached for Acid Black 10 B and 52.6% for Acid Red 14 in aqueous solution at pH 5.0. The effect of particle dosages on the removal of Acid Black 10 B and Acid Red 14 was important for two modified CLT particles. An excessive amount of modified CLT particles increased the chromaticity of water samples and caused the decline of dyes removal. Zeta (ζ) potential data revealed that the main mechanism of removal of the acid dyes on the CTD and CTB particles was charge neutralization.

Keywords: Carboxymethyl larch tannin; Color removal; Adsorption; Acid dye; Charge neutralization

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INTRODUCTION

Most dyes used in the textile industry are stable, non-biodegradable, persistent, and potentially toxic to aquatic life and humans (Bouberka *et al.* 2005). Also, it is estimated that about 70% of industrial dyes are azo dyes. These dyes may be mutagenic and carcinogenic, and can cause severe damage to human beings. This includes damage to the reproductive system, dysfunction of the kidneys and liver, and cancer in the digestive tract, lungs, brain, and central nervous system (Amin 2009). With the increase of environmental awareness among the population, industrial dyeing wastewater is an increasingly major concern and needs to be effectively treated before being discharged into the environment in order to prevent these potential hazards. Various treatment methods including biochemical processes, adsorption, chemical oxidation, flocculation, and membrane treatments have been reported for the removal of dyes from wastewater (Aksu 2005). Among these methods, a combination of sorption and flocculation has been found to be superior to other techniques for wastewater treatment in terms of low costs and ease of operation (Mahmoodi *et al.* 2011; Zohra *et al.* 2008). However, many absorbents and flocculants, apart from being expensive, have disadvantages such as lower removal capacity and difficult regeneration (Vilar *et al.* 2007). Therefore, considerable attention has been focused on the removal of dye from aqueous solutions using biomaterial adsorbents and flocculants derived from low-cost natural materials. In natural materials, tannins are presented as a promising source for novel coagulants and absorbents. Some trees such as quebracho, chestnut, acacia, black wattle, and *Quercus* *aegilops* are well-known tannin sources. From the view of chemical structure, there are three kinds of tannins: hydrolysable, condensed, and combined. Some limited reports about tannin products as adsorbents to remove dyes are listed in Table 1. But most tannin products are prepared used hydrolytic tannin, but not condensed tannin. The main reason is that condensed tannins have a lower chemical reactivity than hydrolytic tannin. As a result, condensed tannin is more difficult to apply in typical situations.

Larch tannin is a condensed tannin with resorcinol A-rings and catechol B-rings (Schofield *et al.* 2001). The adjacent hydroxyl groups on the tannin exhibit a specific affinity to metal ions (Ayhan Sengil and Özaca 2009). Chemical modifications of larch tannin through etherification, esterification, and cross-linking have resulted in new adhesives and adsorbents (Schofield *et al.* 2001). However, there is limited data available on dye removal using modified larch tannin. Each year, about 1000 tons of larch tannin is left unsold at the market in Yakeshi city, China, despite the fact that the price of larch tannin is very low ($1200 to 1500/t). The research and development of new larch tannin products is critical significant.

In the present study, carboxymethyl larch tannin (CLT) was prepared in order to improve the chemical reactivity of larch tannin. Based on the CLT, two CLT products (CTD and CTB) were obtained by cross-linking reaction. As new particulate adsorption materials, the removal of azo acid dyes on CTD and CTB was investigated from aqueous solutions. The effect of different experimental parameters such as pH, contact time, and particle dosage were investigated. Finally, the flocculation mechanism was investigated by zeta (ζ) potential.

Table 1. Maximum Capacity (Q_{max}) and Optimum pH of Tannin Adsorbent to Remove Dye

Adsorbent	Dye	Q_{max} (mg/g) and optimum pH	Source
Larch bark tannin	Acid Black 10 Acid Red 14	--;5 --;5-7	This work
Acacia mearnsii tannin	Acid Blue 9	700; 4-5	Sánchez-Martín *et al.* 2011
Tea tannin	Basic Red 12	238.96;3-8	Ekta *et al.* 2011
Quebracho tannin	Methylene Blue	483;10	Sánchez-Martín *et al.* 2010
Acacia mearnsii tannin	Alizarin Violet 3R	490;5	Beltrán-Heredia *et al.* 2011
Caesalpinia spinosa and *C. sativa* tannin	Methylene Blue	300-750;--	Sánchez-Martín *et al.* 2011
Pistachio hull tannin	Methylene Blue	389-602; 3-10	Moussavi and Khosravi 2011

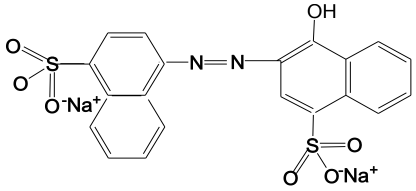
EXPERIMENTAL

Materials

Larch tannin (LT, 78.1% purity) was extracted from the waste bark of *Larix gmelinii* Rupr. in 65 °C water solution, followed by spray drying (Huang *et al*. 2013).

Carboxymethyl larch tannin (CLT, 80% purity) with 0.4742 degree of substitution was prepared by the reaction of carboxymethylation of LT (Huang and Fang 2006). CLT and epoxy propyl trimethyl ammonium chloride (EPTAC) were obtained from Forest chemical laboratory, Northeast Forestry University, Harbin, China. Acrylic amide, dimethyl diallyl ammonium chloride (DMDACC, cationic degree 60%), and $K_2S_2O_8$ were obtained from the chemical reagent development center of Kemiou Engineering, Tianjing, China. The textile dyes Acid Black 10B (AB 10, λmax=517.0 nm) and Acid Red 14 (AR 14, λmax=314.5 nm) were purchased from Sigma-Aldrich, Inc. (American) and used without further purification. Chemical structures of the tested dyes are presented in Fig. 1.

(a)



(b)

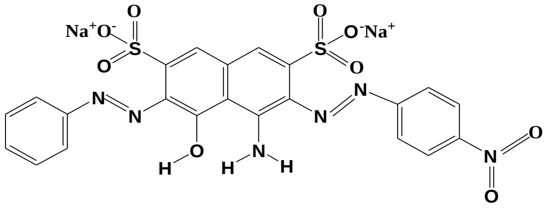


Fig. 1. Chemical structure of (a) AR 14 (λ_{max}=517.0 nm) and (b) AB 10 (λ_{max}=314.5 nm)

Preparation of Amphoteric Larch Tannin Derivative Particles

Five grams of CLT were dissolved in 30 mL of H_2O and then placed into a 250 mL 4-necked round-bottom flask. The mixture was stirred under a nitrogen atmosphere for 15 min. The solutions of 15 g acrylamide (AM), 20 g dimethyldiallylammonium chloride (DMDAAC), and 0.236 g $K_2S_2O_8$ were poured into two drop funnels under constant pressure to provide the monomer and initiator solution systems, respectively. The monomer and initiator solutions were added to the reactor at 50 °C. Then, the cross-linking chemical reaction was maintained at 50 °C for 3 h. The CTD gel (cationic degree 49.27%, grafting ratio 54.39%) was obtained. Another 5 g of CLT was dissolved in 30 mL of H_2O and then placed into a 250 mL 4-necked round-bottom flask. The mixture was stirred under a nitrogen atmosphere for 15 min. Aqueous solution of 10 g acrylamide (AM), 20 g EPTAC, and 0.27 g $K_2S_2O_8$ were poured into two dropping funnels under constant pressure to provide the monomer and initiator solution systems, respectively. The monomer and initiator solutions were added to the reactor at 50 °C. Then, the cross-linking chemical reaction was maintained at 50 °C for 2.5 h. The CTB gel (cationic degree 60.22%, grafting ratio 56.34%) was obtained. The gel was dried under vacuum at 40 °C for 24 h to get CTD and CTB particles. The term “amphoteric” is justified because the tannin derivatives equilibrate in solution to provide both cationic and anionic groups.

Characterizations

Fourier transform-infrared (FTIR) spectra of the CTD and CTB were recorded with a MAGNA 560 FTIR spectrometer from Thermo Nicolet Corporation (USA). A pressed pellet was prepared by grinding the sample powder with IR grade KBr with an agate mortar and pestle. The wavelength scan range was 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and an interval of 1.0 cm^{-1}. Scanning electron microscope (SEM) images were taken with an FEI QUANTA 200 microscope (USA). The zeta potential of products was measured with the aid of a Model ZM-75 from Zeta-meter Incorporated (Ningbo, China). Surface tensions were measured with JK99C Automatic Tensiometer from Beijing Shangdetong Corporation, China. A certain amount of CTD and CTB were dissolved in 50 mL of DMF and then placed into a special beaker. The method of Du Nouy ring was used to test the surface tensions at room temperature.

Flocculation Experiments

The effect of important parameters such as pH, contact time, initial dye concentration, and temperature on the removal of acid dye was studied. Batch adsorption experiments were carried out in a 250 mL stoppered conical flask at room temperature. Stock solutions of 1 g/L of all the selected dyes were prepared and used for obtaining solutions of known concentrations. 50 mL of acid dyes solution of known concentration, known pH, and a known dosage of the flocculants were taken in a 250 mL stoppered conical flask. Effect of pH on dye removal was studied over a pH range of 1 to 11. The initial pH of the solution was adjusted by addition of dilute aqueous solutions of HCl or NaOH (0.1 M). The time-dependent behavior of the dye removal was tested by varying the contact time, with concentrations of 25 mg/L, 50 mg/L, 75 mg/L, and 100 mg/L. Samples were withdrawn at different contact time intervals (0 to 120 min), filtrated, and analyzed for remaining dye concentration by UV-1901 spectrophotometer (Puxi Corporation, Beijing, China) at λ_{max}. The calibration curves of AB 10 and AR 14 were obtained as follows,

$$Y_{(AB\ 10)} = 1.76\times10^{-2}X + 2.53\times10^{-2} \quad R^2=0.9999 \tag{1}$$

$$Y_{(AR\ 14)} = 2.18\times10^{-2}X + 2.98\times10^{-2} \quad R^2=0.9997 \tag{2}$$

where X (mg L^{-1}) and Y are the dye concentration and the absorbance of solution at λ_{max}, respectively. R^2 is the coefficient of determination.

The percentage removal of dye was calculated as follows:

$$\%\ \text{Dye removal} = \frac{C_0 - C_t}{C_0}\times100 \tag{3}$$

where C_o and C_t (mg L^{-1}) are the initial dye concentration and concentration at time t, respectively.

RESULTS AND DISCUSSION

Morphological Investigation

Scanning electron microscope (SEM) images of CTD and CTB are shown in Fig. 2. SEM is useful for revealing the surface morphology, porosity, and the distribution of the flocculants size. It is clear that the main structure of the polymer was particulate. The size of particle was about 30 to 40 µm for CTD and 10 to 20 µm for CTB. However, there was no obvious regularity between compounds. There are some impurities, such as starch, soluble sugar, and ash in CLT (Schofield *et al.* 2001). So, the size of particles of CTD and CTB was nonuniform, and the primary reaction should be an unordered terpolymerization cross-linked reaction.

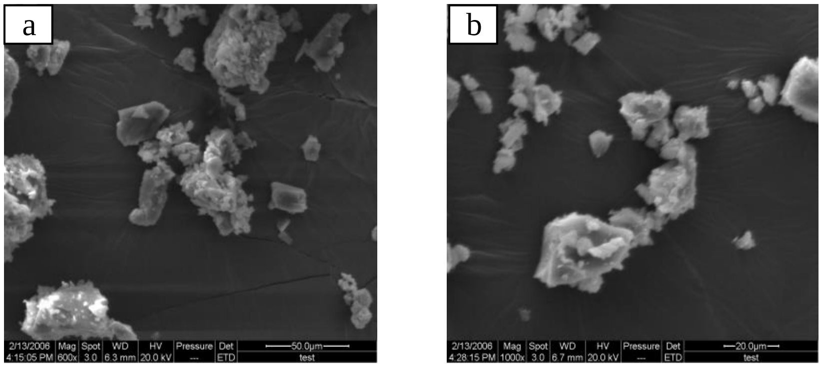


Fig. 2. SEM images of CTD (a) and CTB (b)

Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra of CTD and CTB are shown in Fig. 3. The strong, overlapping peaks that occurred at 3500 to 3250 cm^{-1} can be attributed to the N–H and –OH stretching vibration peaks. The –C–H vibration peaks of alkyl group appear at 2927 cm^{-1} and 1384 cm^{-1} in Fig. 3. The sharp peak that occurred at 1384 cm^{-1} was mainly due to the formation of $–CH_3$ come from DMDACC in the CTD, and the source of $–CH_3$ in the CTB was EPTAC. The vibration peaks at 1616 cm^{-1} and 1519 cm^{-1} in the CTD can be attributed to the skeleton of benzene. In CTB however, the vibration peak at 1616 cm^{-1} was covered by the –C=O stretching vibration peak at 1731 cm^{-1} (Huang *et al*. 2006), thus becoming a strong and overlapping peak (Oo *et al.* 2009). The strong stretching peak that occurred at 1660 cm^{-1} in the CTD can be attributed to the -C=O stretching vibration peaks in acid amides (Sánchez-Martín *et al.* 2010). In the CTB, this peak was covered by the –C=O stretching vibration peaks at 1731 cm^{-1}. Based on these results, it can be concluded that $–CH_3$, $–CH_2$, –C=O, and $–NH_2$ were introduced to the modified CLT product, indicating that a polymerization reaction had occurred.

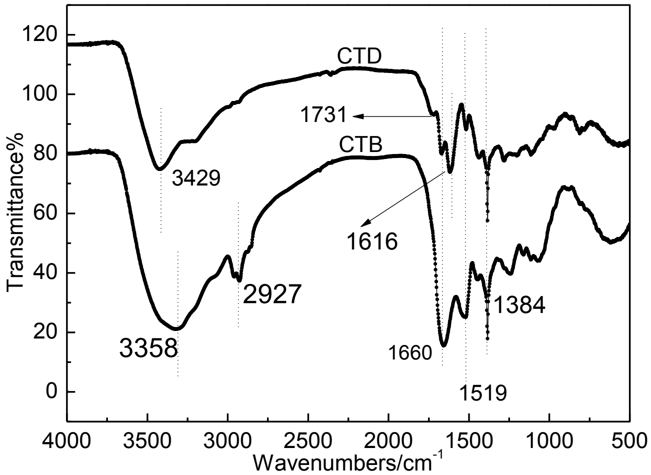


Fig. 3. FTIR spectra of CTD and CTB

Surface Tension

The effect of the concentration of solution on surface tension is shown in Fig. 4. The surface tension data of CTD and CTB followed a decreasing trend when the concentration was increased from 2.0×10^{-3} g/L to 8.0×10^{-3} g/L. In contrast, the surface tension of CTD and CTB suddenly decreased from 30.68 mN/m to 25.37 mN/m, and 31.59 mN/m to 25.02 mN/m as the concentration of solution went from 6.0×10^{-3}g/L to 8.0×10^{-3}g/L and 4.0×10^{-3}g/L to 6.0×10^{-3}g/L, respectively. The surface tension did not vary when the concentration of solution was increased from 8.0×10^{-3}g/L to 12.0×10^{-3}g/L. The results indicate that the Critical Micelle Concentration (CMC) of CTD and CTB were 8.0×10^{-3}g/L and 6.0×10^{-3}g/L, respectively. The decreased surface tensions can be attributed to low interaction energy between liquid molecules of CTB and CTD. The surface tension no longer falls when the concentration of surfactant is greater than the CMC because any additional molecules will immediately become associated in micelles. At the same time, CTB and CTD in the solution form micelles, which is a lot of surfactant molecules together. Many micelles are very useful for adsorption. Based on these results, it can be concluded that CTB and CTD were amphoteric surfactants.

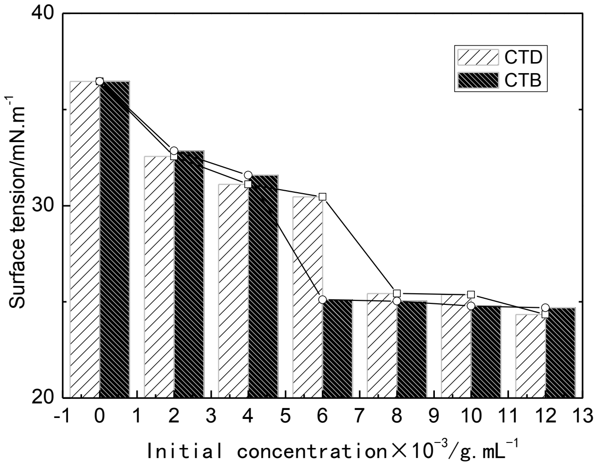


Fig. 4. Effect of the concentration of flocculants on the surface tension

Dye Removal Studies

Effect of flocculants dosage

The effect of flocculants dosage on the removal of azo acid dyes was evaluated. As shown in Fig. 5, the dye removal of AR 14 increased when the particle dosage was increased from 0.2 to 1.0 g. As indicated, 51.67% and 42.28% of AR 14 was removed at 1.0 g CTB and 1.0 g CTD, respectively. It was observed that the dye removal of AB 10 increased with increasing particle dosage up to 0.6 g and reached to over 90.7% for both CTB and CTD. However, the dye removal of AB 10 decreased when the particle dosage was increased from 0.6 to 1.0 g. This phenomenon indicates that charge neutralization is very important in the process (Yang *et al*. 2013). The increase in dye removal with increasing the particle dosage can be attributed to the increase of surface charges and the sorption sites. The flocculants neutralize the net charges on the surface of dyes, and some kinds of insoluble complexes were formed which will further aggregate together and fall. If the dosage of the flocculants was lower, it was not enough for neutralization. However, excessive flocculants was lead to the instability of the flocs due to the electrostatic repulsion. In this study, the effect of excessive flocculants on the stabilization of flocs was remarkable. And, the chromaticity of water samples was increased and cause of the dye removal was decreased due to excessive flocculants. As a result, the dosage of flocculants was an important factor in the dye removal.

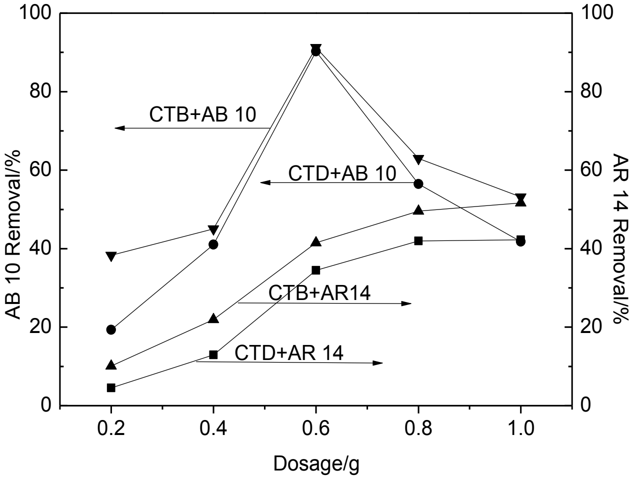


Fig. 5. Effect of the flocculants dosage on the dye removal (initial pH 5, 50 mg/L of acid dyes, shaking time 2 h, temperature 25 °C)

Effect of pH

The effect of the initial pH on the dye removal is shown in Fig. 6. The dye removal increased when the pH was increased. Maximum removal of acid dyes occurred at pH 5. CTD and CTB are comprised of various functional groups such as hydroxyl groups and amino groups that are affected by the pH of solutions. As a result, the surface acidity of dye suspended particles was high. However, the cationic groups on the surface of CTD and CTB are subject to neutralization by sulfonic groups.

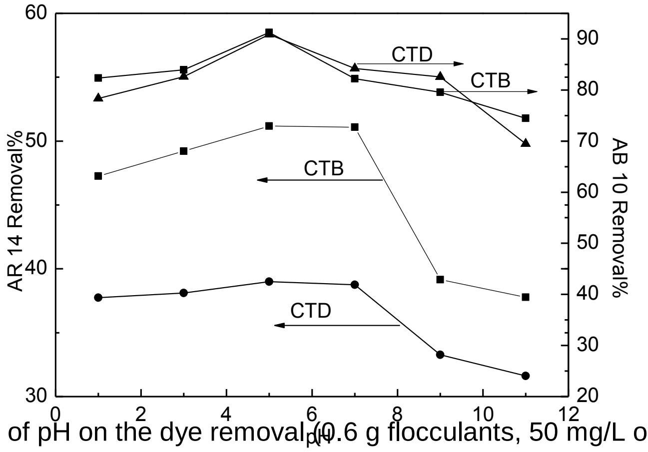


Fig. 6. The effect of pH on the dye removal (0.6 g flocculants, 50 mg/L of acid dyes, shaking time 2 h, temperature 25 °C)

When there is an excess of negative charge groups, the system will become stabilized by electrostatic repulsion. At the same time, under acid condition, a network structure can be formed between the cationic groups and anionic groups of CTD and CTB. The network structure will benefit the enmeshment and adsorption (Hameed *et al.* 2007).

At pH>7, -COOH groups of CTD (CTB) were dissociated into the carboxylate $–COO^-$ form. Quaternary ammonium ions were adsorbed to the surface of suspended particles by electrical neutralization. This led to less effective removal. Based on these results, it can be concluded that the removal of acid dye on CTD and CTB was achieved by neutralization and enmeshment mechanism.

Effect of contact time and initial dye concentrations

The effect of the contact time and initial dye concentrations on the dye removal is shown in Fig. 7, and the % dye removal, the removal rate of dye, and correlation values are listed in Table 3. It can be seen from Fig. 7 that the removal of acid dyes on CTD and CTB at different concentrations increased with an increase of contact time, and equilibrium was reached in 60 min.

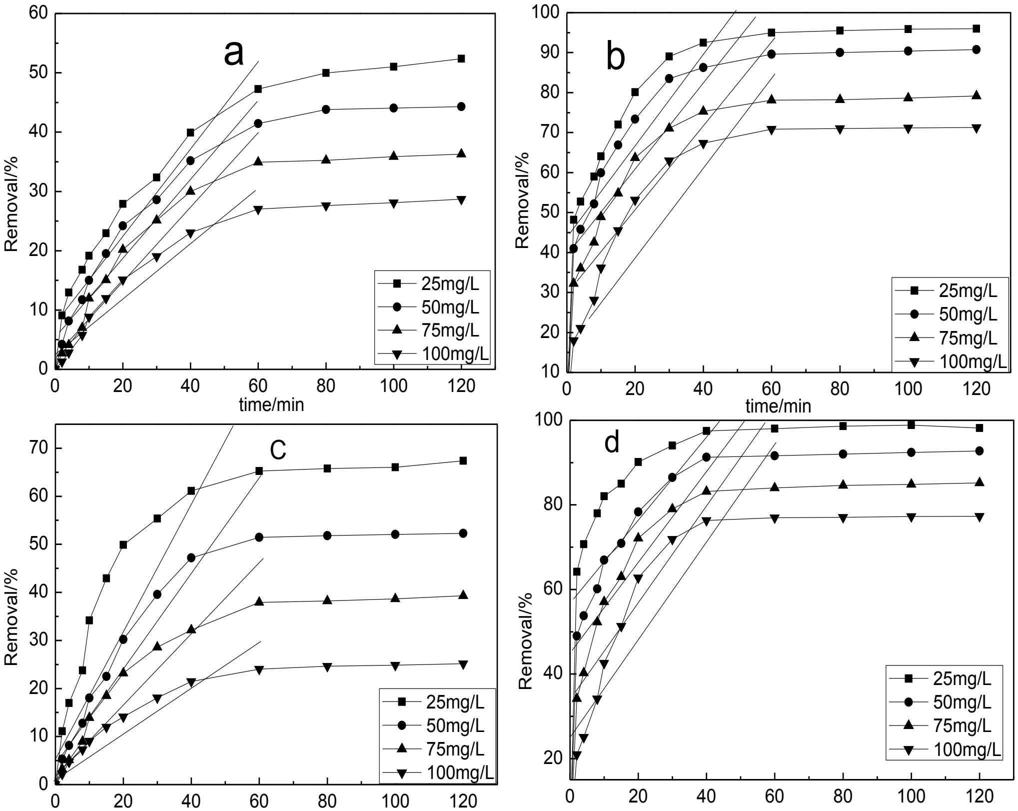


Fig. 7. Effect of the contact time on the dye removal (a) CTD+AR14, (b) CTD+AB10, (c) CTB+AR14, and (d) CTB+AB10 (0.6 g flocculants, 50 mg/L of acid dyes, shaking time 2 h, temperature 25 °C, initial pH 5)

Table 2 shows that as the dye concentration increased, at equilibrium, the dye removal of CTD and CTB for AR14 and AB10 gradually decreased, and the corresponding slope values also show a gradually decreasing trend. For example, the removal of AB 10 on CTB was 98.08% for a dye concentration of 25 mg/L, and the removal was 77.26% when the dye concentration was 100 mg/L. The removal rate of dye was 1.1867 and 0.9524 for the dye concentration of 25 mg/L and 100 mg/L, respectively. In this study, the change of the settling rate of flocs was opposite with the removal rate of dye. When the dye concentration was lower, flocs were small. And, the size of flocs was increased with the increased of the dye concentration. The results can be explained as follows: (i) Lots of insoluble flocculants/dye complexes can be formed more easily through charge neutralization at higher dye concentration, which will aggregate further and form larger flocs through the bridging effect. (ii) Larger flocs can further capture small flocs and residual dyes in water through the sweeping effects (Yang *et al*. 2013; Mahmoodi *et al*. 2011). From the view of adsorption, when the initial dye concentration was lower, the adsorption active site was more. As a result, the rate of dye removal was higher. About 60% uptake of dyes was achieved during the first 20 min and 98% of dyes were achieved at 60 min. Based on the dye removal curves, the removal of acid dye onto CTD and CTB can be divided into two phases: the rapid adsorption phase and the slow adsorption phase (Han *et al.* 2009). During the first phase, the initial removal rate was rapid. Because there are a large number of active sites on the surface of the CTD and CTB, the concentration differences caused a fast mass transfer during the initial phase and the dye molecules was easily absorbed by the CTD and CTB particles. The second phase was a slow stage in which the contribution to the total acid dyes removal efficiency was relatively small, and finally the removal of acid dyes reached equilibrium.

Table 2. Dye Removal Data

Water sample	Concentration (mg • L^{-1})	Removal (%)		Rate of dye removal (Removal%/min)
		60 min	120 min	
CTD+AR 14	25	47.25	52.36	0.7145
	50	41.40	44.28	0.6770
	75	34.92	36.24	0.6051
	100	27.01	28.67	0.4713
CTD+AB10	25	95.01	95.98	1.1505
	50	89.63	90.74	1.1309
	75	78.13	79.18	1.0377
	100	70.84	71.49	1.0184
CTB+AR 14	25	65.35	67.41	1.0399
	50	51.46	52.25	0.8943
	75	37.92	39.23	0.6461
	100	24.01	25.16	0.4021
CTB+AB 10	25	97.47	98.08	1.1867
	50	91.63	92.74	1.0981
	75	84.01	85.37	1.0730
	100	76.94	77.26	0.9524

Zeta potential data

The zeta (ζ) potential data of tested water samples is shown in Table 3. From Table 3 it can be seen that the ζ potential values of AR 14 and AB 10 were negative. After adding CTD or CTB in acid dye water samples, the cationic groups (quaternary ammonium groups) on the surface of CTD or CTB underwent electrical neutralization with colloidal particles of the dye water samples (Espinosa-Jiménez *et al.* 1998). Charges on the surface of the colloidal particles were close to zero and even had the opposite charges. As a result, the ζ potential values of AR 14 and AB 10 was increased. It is speculated that the primary removal mechanism of the acid dye on the CTD and CTB particles may be charge neutralization.

Table 3. Zeta Potential for Each Water Sample (0.6 g Flocculants, 50 mg/L Acid dyes, Shaking time 2 h, Temperature 25 °C, Initial pH 5)

Water sample	ζ/mV	Water sample	ζ/mV
AR 14	-9.132	AB 10	-30.113
CTD+ AR 14	-2.116	CTD+AB 10	+1.110
CTB+ AR 14	-1.727	CTB+AB 10	+0.911

CONCLUSIONS

1. Two particulate amphoteric larch tannin (CLT) products (CTD and CTB) were prepared by cross-linking reactions.
2. The removal of azo acid dyes on CTD and CTB depended on the pH. The optimum removal was observed at pH 5.0, and the maximum removal capacity of ≥90.7% was achieved for AB 10 and 52.6% for AR 14.
3. The effect of flocculants dosage on the removal of azo acid dyes was important. An overabundance of flocculants increased the chromaticity of water samples and caused the decline of dyes removal.
4. It was found that CTD and CTB had good surface tension behavior, and based on their zeta potential *vs.* pH they can be classed as amphoteric surfactants. The primary flocculation mechanism of the acid dyes on the CTD and CTB particles may be charge neutralization.

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