

Adsorption/desorption behavior between a novel amphoteric granular lignin adsorbent and reactive red K-3B in aqueous solutions

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Abstract: A novel amphoteric granular lignin adsorbent (AGLA) was prepared using magnesium lignosulfonate as a raw material which was provided by a straw sulfite pulp mill in Guangdong Province, China. A reactive dye (red K-3B) was used as an adsorbate to investigate the adsorption behavior by static and mobile ways. The removal of reactive red K-3B was found to be initially pH and concentration dependent. Moreover, an increase of solution temperature ranging from 5°C to 60°C helped to enhance the rate of intraparticle diffusion of adsorbate and changes in the size of the pores of the adsorbent and thus to reduce the adsorption time. The total breakthrough adsorption capacity was 531 mg/g, and the saturated adsorption capacity was 560 mg/g, which prevailed over the activated carbons evidently. The reactive red K-3B adsorbed on AGLA could be recovered with a mixture of alcohol, NaCl and HCl aqueous solutions. The recovery percentage could reach 92.4%.

Keywords: lignin; amphoteric; granular adsorbent; adsorption; desorption; dyeing effluent

Introduction

Dyeing effluents mainly contain the wastewater from all of the dyeing processes of various natural celluloses and synthetic celluloses. The dyeing effluents have such characteristics as high chromaticity, high COD_C content as well as large amount of suspension solid etc. (Huang, 1987). The process for color removal from dyeing effluents include biological treatment, flocculation, adsorption, oxidation and hyper-filtration etc. Among the above treatment methods, very high cost-effectiveness of adsorption technology would tend to open new opportunities for the treatment of dyeing effluents, especially for the reactive dye wastewaters (Khattri, 1999). And, relatively simple reactive-dye adsorption processes can meet the progressively stricter environmental discharge criteria (Liu, 2001; 2002).

Recently, numerous investigations have been proved the feasibility of use of agricultural products and by-products, industrial waste biomass and natural substances to adsorb and accumulate the dyes (Wu, 2000; Mohan, 2002; Nassar, 1997; McKay, 1999). And, these materials are readily available and inexpensive. Lignin is one of the most abundant renewable materials on earth, and it is exceeded in nature abundance only by cellulose. It has been found to adsorb the halides (Vakurova, 1988) and heavy metal ions, e.g., lead (II), copper (II), zinc (II), nickel (II), cadmium (II), chromium (III) and iron (III) ions etc. (Koch, 2001; Carrillo-Morales, 2001).

In this study, a novel amphoteric granular lignin adsorbent (denoted as AGLA) was prepared using magnesium lignosulfonate as a raw material which was provided by a straw sulfite pulp mill in Guangdong, China. Then a reactive dye (red K-3B) was used as an adsorbate to investigate the adsorption behavior by static and mobile ways. The effects of concentration, initial pH value, and temperature on the adsorption and ion-exchange processes of the removal of reactive red K-3B were also investigated.

1 Experimental

1.1 Materials

The magnesium lignosulfonate aqueous solution with 45% of content was kindly provided a straw sulfite pulp mill in Guangdong, China. 3-chloro-2-hydroxypropyl trimethyl ammonium chloride, denoted as CHPTA (55% aqueous solution) was synthesized from the procedure described by Langher *et al.* (Langher, 1970). Transformer oil, granular activated carbon (GAC) and powdered activated carbon (PAC) were industrially pure. Epichlorohydrin, trimethylamine, formaldehyde, reactive red K-

3B, acetone, ether, sodium hydroxide, hydrochloric acid, sodium chloride, lithium hydroxide, alcohol, toluene, chlorobenzene, methanol, Tween20, Span60 and sodium oleate etc. (Shanghai Chemical Co., China) were chemically pure. The water used was distilled water.

1.2 Instruments

A model UV-2001 Recording Spectrophotometer (Shimadzu, Japan) was used to determine the chromaticity of reactive red K-3B aqueous solution and the content of K-3B before and after adsorption with AGLA. And a Model Precisa XT 120A electronic analytical balance (Swiss) and a model PHS-25 pH meter (Shanghai Hongyi Instrumental Plant, China) were used.

1.3 Preparation of AGLA

1.3.1 Preparation of granular cross-linked lignin beads

300 ml of the mixture of transformer oil and chlorobenzene with 1:1 of volume ratio was used as disperse phase. Then 100 ml 45% of magnesium lignosulfonate aqueous solution was slowly added into the above oil phase. After stirring for 15 min at a speed of 200 r/min, the calculated amounts of dispersant agent, 37% formaldehyde solution and concentrated HCl solution were slowly added respectively. The mixture was stirred at 80°C for 2.0 h. Then the slurry was filtered and the pH adjusted to 6.5 with a 1.0 mol/L NaOH solution. The granular cross-linked lignin beads (GCLB) were washed with water, acetone and ether, and then dried.

1.3.2 Quaternization

50 g of GCLB (moisture content 26.8%) was suspended in 100 ml water containing 3.0 g sodium chloride. 10 ml 20% of sodium hydroxide solution was added into the above mixture. Then the reaction temperature was raised to 70°C and 40.0 g of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTMA) was added slowly over 20 min, and the mixture was stirred for 3 h at 70°C. The mixture was cooled, filtered and washed with water, acetone and ether, and then dried to obtain amphoteric granular lignin adsorbent (AGLA).

1.4 Static adsorption experiments

Batch adsorption experiments were carried out by shaking 0.1 g of AGLA adsorbent with 100 ml aqueous solution of reactive red K-3B of the desired concentration, pH and temperature in different glass-stoppered Erlenmeyer flasks at a constant speed of 80 r/min for predetermined time intervals. The concentration of K-3B was analyzed by UV-2001 Recording Spectrophotometer. The concentration of K-3B adsorbed was calculated by the difference of the concentration of K-3B in solution before and after adsorption.

1.5 Mobile adsorption experiments

Each adsorption column(20.0 cm in length and 1.0 cm in internal diameter) was packed with 5.0 g of adsorbents. And, 100 mg/L of K-3B aqueous solution was pumped through the adsorption at a flow rate of 5.0 ml/min until the effluent concentration of K-3B reach 100 mg/L. The effluent concentration of K-3B was analyzed at various predetermined time intervals by UV-2001 Recording Spectrophotometer.

1.6 Desorption and recovery tests

Recovery of adsorbate and regeneration of adsorbent is a key process in the wastewater treatment process. In order to achieve these two purposes and to assess the practical utility of the adsorbent, desorption experiments were conducted by treating 0.1 g of AGLA with adsorbed K-3B with 10 ml of the desired concentration of alcohol, NaCl and HCl aqueous solutions or their mixed solutions for a predetermined time. The concentration of K-3B was analyzed by the difference of the concentration of K-3B in the solution before and after desorption.

2 Results and discussion

2.1 Establishment of linear equation of K-3B

The concentration of K-3B was determined by UV-2001 Recording Spectrophotometer at a wavelength of 520 nm, the following equation was obtained by linear regression analysis of the determination results.

$$y = 37.9876A, \gamma = 0.9916. \quad (1)$$

Where y is the concentration of K-3B, mg/L; A is the absorbance; γ is the correlation coefficient indicating the linear relationship between A and γ in the concentration ranged of 0.5 and 50 mg/L.

2.2 Effect of adsorption time

Fig. 1 illustrates the effect of adsorption time on the adsorption efficiency. The removal rate of K-3B increases with the increase of adsorption time. But it remains constant after the equilibrium time of 30 min, which indicates that the adsorption tends towards saturation at 30 min. Therefore, the adsorption time was set to 30 min in each experiment.

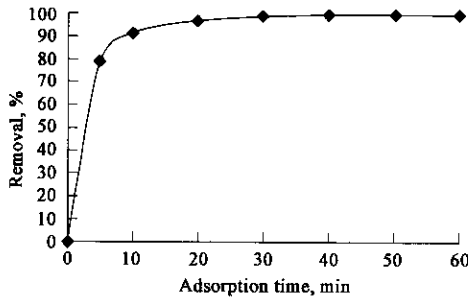


Fig. 1 Effect of adsorption time
Conditions: pH 8.0, 20°C, 250 mg/L K-3B, 0.1 g of AGLA adsorbent

2.3 Effect of concentration

The removal rate and the equilibrium adsorption capacity q_e of AGLA for the initial concentration of K-3B ranging from 50 to 1000 mg/L at 20°C are shown in Fig. 2. Under the identical conditions, the removal rate of AGLA decreases with an increase of concentration of K-3B, the results indicated that the removal of K-3B is the concentration dependent. The equilibrium adsorption capacity q_e increases sharply in the concentration ranged from 0 to 500 mg/L. When the concentration exceeds 500 mg/L, the increase curve of q_e becomes smooth gradually indicating the adsorption capacity of AGLA tends towards saturation.

2.4 Effect of adsorbent dose

Increasing the dose of AGLA helps to reduce the adsorption time. However, the equilibrium adsorption capacity q_e is inversely proportional to the adsorbent dose(Fig. 3). The results indicated that the time for reaching adsorption equilibrium can be greatly reduced by increasing the

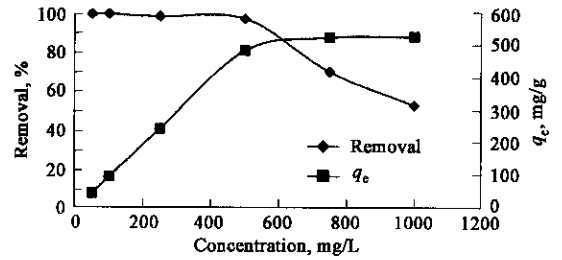


Fig. 2 Effect of concentration on the adsorption of K-3B on AGLA
Conditions: 20°C, 30 min, pH 8.0, 0.1 g of AGLA adsorbent

adsorbent dose, which makes it feasible for AGLA in the practical and plot dyeing effluent treatment.

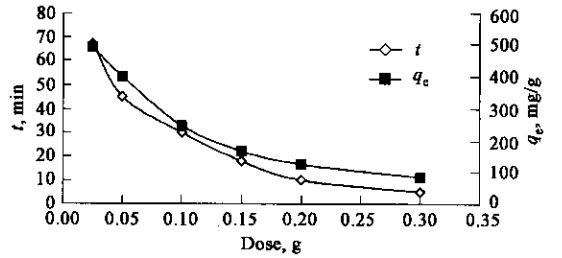


Fig. 3 Effect of the adsorbent dose on the adsorption efficiency
Conditions: 250 mg/L K-3B, 20°C, pH 8.0

2.5 Effect of temperature

The adsorption time decreases with a increase of solution temperature ranging from 5°C to 60°C. The results are summarized in Table 1. Table 1 illuminates that the decrease in adsorption time with an increase of temperature may be due to the enhanced rate of intraparticle diffusion of adsorbate and changes in the size of the pores of the adsorbent(Liu, 2001; 2002).

Table 1 Effect of temperature on the adsorption of K-3B on AGLA

Temperature, °C	5	10	20	30	40	50	60
Time, min	41	37	30	24.5	18	14	12

2.6 Effect of solution pH

Solution pH is an important effective parameter in the adsorption process. The effect of solution pH on the adsorption of K-3B on AGLA is presented in Fig. 4. Fig. 4 shows that with an increase in solution pH ranging from 3 to 8, the removal percentage increases sharply from 12.3% to 98.6%. When the solution pH increases from 8 to 12, the removal rate increases slowly, and at pH = 10, the removal rate reaches 100%.

2.7 Mobile adsorption experiments and comparison tests

The tests of breakthrough parameters of adsorption column were conducted to assess the practical utility and durability of the adsorbent. The breakthrough parameters vary with the initial concentration of K-3B. And they are inversely proportional to the initial concentration. The tests were carried out by pumping a synthetic K-3B solution containing 100 mg/L K-3B into the adsorption column at a flow rate of 5.0 ml/min. The residual K-3B in the effluent was determined by UV-2001 Recording Spectrophotometer for the predetermined time intervals. The results are illustrated in Fig. 5 and summarized in Table 2.

Table 2 Results of mobile adsorption experiments and comparison tests

Adsorbent	Breakthrough volume, L	Total volume, L	Breakthrough adsorption capacity, mg/g	Saturated adsorption capacity, mg/g
AGLA	26.54	34.1	531	560
PAC	8.13	15.5	163	192.5
GAC	7.32	14.1	146	173.1

Fig. 5 shows that under the breakthrough volume ($V_B = 26.54$ L),

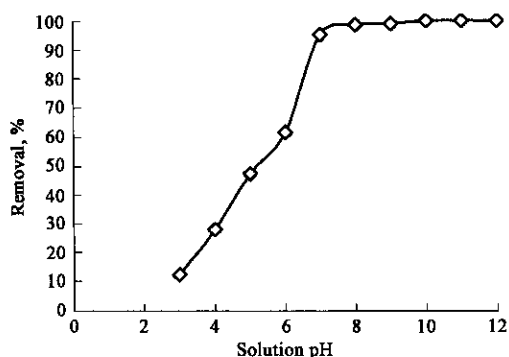


Fig. 4 Effect of the solution pH on the adsorption of K-3B on AGLA
Conditions: 250 mg/L K-3B, 20 °C, 30 min, 0.1 g of AGLA adsorbent

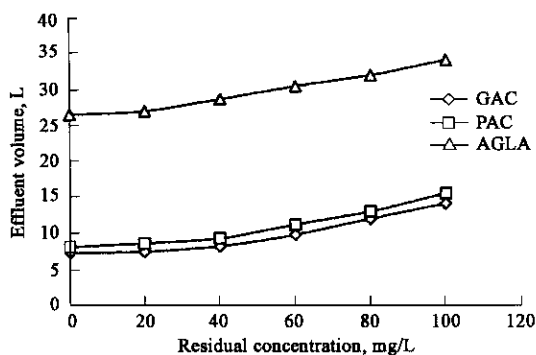


Fig. 5 Breakthrough curve
Conditions: 100 mg/L K-3B; pH 8.0; flow rate 5.0 ml/min; 20 °C.

K-3B can be completely removed, which indicates that the adsorbent and adsorption column can be continuously used to remove K-3B in the practical application.

From Table 2, we can see the breakthrough adsorption capacity and saturated adsorption capacity of K-3B increase 2–3 times as those of granular activated carbon (GAC) and powdered activated carbon (PAC). The results indicated that the AGLA has a potential application foreground in the reactive dyeing effluent treatment. The breakthrough adsorption capacity and saturated adsorption capacity of PAC prevail over those of GAC indicating that the surface area also plays an important part in the reactive dye removal.

We have reported that the anion-exchange capacity of the AGLA obtained was 0.65 mmol/g (Liu, 2003). Then the theoretical adsorption

capacity of the AGLA is 536.6 mg/g. Nevertheless, the practical saturated adsorption capacity is 560 mg/g, which exceeds the theoretical value indicating the removal of K-3B depends on the co-action of adsorption and ion exchange processes at pH = 8. The results proved that the adsorption mechanism can be explained on the basis of adsorption and ion exchange.

2.8 Desorption and recovery tests

The desorption and recovery tests were carried out by utilizing various concentrations of alcohol, NaCl and HCl aqueous solutions or their mixed solutions for 2.0 h. The results are listed in Table 3. Table 3 shows that the reactive red K-3B adsorbed on AGLA can be recovered with a mixture of alcohol, NaCl and HCl aqueous solutions. And, the recovery percentage can reach 92.4%.

3 Conclusions

The removal of reactive red K-3B was found to be initially pH and concentration dependent. Moreover, an increase of solution temperature ranging from 5 °C to 60 °C helped to enhance the rate of intraparticle diffusion of adsorbate and changes in the size of the pores of the adsorbent and thus to reduce the adsorption time. The total breakthrough adsorption capacity was 531 mg/g, and the saturated adsorption capacity was 560 mg/g, which prevailed over the activated carbons evidently. And, the reactive red K-3B adsorbed on AGLA could be recovered with a mixture of alcohol, NaCl and HCl aqueous solutions. The recovery percentage could reach 92.4%.

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Eluant	Recovery percentage, %		
	1.0 mol/L	2.0 mol/L	4.0 mol/L
NaCl aqueous solution	12.6	21.5	23.1
HCl	41.3	67.5	73.2
HCl and NaCl (V:V = 1:1)	52.6	71.8	76.7
HCl and alcohol* (V:V = 1:20)	63.9	81.6	88.5
HCl and alcohol* (V:V = 1:50)	77.9	89.2	91.3
HCl, alcohol* and NaCl (V:V:V = 1:50:1)	83.2	92.4	92.4

Notes: * Alcohol used is the absolute alcohol. Desorption time 2.0 h, desorption temperature 20 °C

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