Removal and Recovery of Cationic Dyes from Aqueous Solutions Using Spherical Sulfonic Lignin Adsorbent

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ABSTRACT: A novel spherical sulfonic lignin adsorbent, denoted as SSLA, was adopted to removal and recover the cationic dyes from aqueous solutions, e.g., Cationic Red GTL, Cationic Turquoise GB, and Cationic Yellow X-5GL, and various affecting factors were optimized. It was found that the adsorption of cationic dyes on the adsorbent was initially concentration- and temperature-dependent, and followed both the Freundlich and Langmuir isothermal adsorption. The positives values for ΔH indicated that the process was endothermic. The breakthrough adsorption capacities for GTL, GB, and X-5GL were 536.0, 550.0, and 582.0 mg/g, respectively, which prevailed over the commercial powdered activated carbon and strongly acidic cation-exchange resin R732 evidently. Additionally, the maximum recovery percentage could reach 93.2, 97.1, and 96.5% separately for GTL, GB, and X-5GL, when a mixture of 3.0 mol/L HCl and alcohol with the volume ratio of 1 : 4 was adopted as eluant. Moreover, the results of the mobile desorption and recovery tests indicated that the maximum concentrations of GTL, GB, and X-5GL in the eluants could reach 13,108, 13,980, and 13,520 mg/L, respectively. Only 6.3, 5.0, and 4.6% of adsorption capacities for GTL, GB, and X-5GL decreases individually after 20 replicates of adsorption and desorption. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2284–2291, 2006

Key words: lignin; adsorption; cationic dye; adsorption isotherm; recovery

INTRODUCTION

Dyeing effluents mainly contain the waste waters from the dye manufacturing processes of the dyeing chemical factories and all of the dyeing processes of various natural celluloses and synthetic celluloses. The dye and dyeing effluents have such characteristics as high chromaticity, high COD_{Cr} content as well as large amount of suspension solid, etc.[1] The processes for the color removal from the dye and dyeing effluents include biological treatment, flocculation, adsorption, oxidation, hyperfiltration, etc. Among the above treatment methods, very high cost-effectiveness of adsorption technology would tend to open new opportunities for the treatment of dyeing effluent.[2] Relatively simple dye adsorption processes can meet the progressively stricter environmental discharge criteria.[3] Recently, numerous investigations have proved the feasibility of use of agricultural products and by-products, industrial byproducts, industrial waste biomass, and natural substances to adsorb and accumulate the dyes. The adsorbents for the color removal include the bamboo dust, coconut shell, groundnut shell, rice husk,[4,5] wheat straw, corn cob, barley husk,[6,7] modified sawdust,[4] peat,[8] activated carbon,[9] chitin,[10–12] chitosan,[10–12] byproducts from the steel and fertilizer plants,[13,14] spent brewery grains,[15] modified cellulose,[16] chromium waste sludge,[17] natural polysaccharides,[18] modified fuller's earth,[19] sulfonated coal,[20] fly ash,[21] sepiolite,[22] synthetic Na-saponite, synthetic Na-hectorites, synthetic swelling mica, natural Na-montmorillonite,[23] etc. Most of these materials are readily available and inexpensive. Among the above adsorbents mentioned, modified fuller's earth,[19] sulfonated coal,[20] fly ash,[21] sepiolite,[22] synthetic Na-saponite, synthetic Na-hectorites, synthetic swelling mica, and natural Na-montmorillonite[23] as well as activated carbon[9] and byproducts from the steel and fertilizer plants[13,14] have been adopted to remove the cationic dyes successfully.

Lignin is one of the most abundant renewable materials on earth, and it is exceeded in natural abundance only by cellulose. Lignin accounts for 24–33% of the dry matter of softwood and 16–24% of the hardwood usually in pulping process.[24] Agriculture residuals such as straw contain 12–18% lignin.[24] During the chemical pulping (in the Kraft, soda, organosolv, or

sulfite process), the partially degraded lignin is dissolved in the black or red liquor, from which it can be isolated by various methods.[24,25] Currently, the annual global production of lignin in pulp mills amounts to some 50 million tons.[24] In China, for the large-scale pulp and paper mills, the black liquors were used to recycle the alkali liquor by the procedures of concentration, combustion, and causticization, and the lignin was combusted. Consequently, the Silvola recovery process is only a good way to avoid the black-liquor pollution. It is not an economic method that causes the tremendous resources waste. For the medium and small pulp and paper mills, the black liquors from the pulping process were discharged directly without any treatments, which caused the severe environmental pollution. Therefore, how to prepare the lignin-based products that yield a high added value and thus to avoid the environmental pollution has aroused the increasing interests of the many chemists and technologists. As one of the modified products, the lignin adsorbent has been found to adsorb the halides[26] and heavy metal ions, e.g., lead (II), cadmium (II), copper (II), zinc (II), nickel (II), cadmium (II), chromium (III), iron (III) ions, etc.[27,28] However, few literatures have reported on the adsorption treatment of simulating dye effluents with modified spherical lignin adsorbent.

To improve the surface area, permeability, and hydraulic performance of the cellulose adsorbent, a new kind of adsorbent, spherical sulfonic lignin adsorbent (denoted as SSLA), was developed in this article to meet the needs of bed adsorption and thus to further increase the adsorption efficiency. This spherical sulfonic lignin adsorbent was prepared by using the sodium lignosulfonate as raw material, which was provided by a bamboo pulp mill in Sichuan, China. Then three kinds of cationic dyes, e.g., Cationic Red GTL (denoted as GTL), Cationic Turquoise GB (denoted as GB), and Cationic Yellow X-5GL (denoted as X-5GL), were used as adsorbates to investigate the adsorption behaviors by the static and mobile ways. The effects of adsorption time, solution pH, and initial concentration of the adsorbate on the adsorption process of the removal of the cationic dyes were discussed, and the Langmuir constant and thermodynamic parameters of adsorption in a temperature range of 26–45°C, as well as Freundlich parameters, were also investigated. Moreover, the recovery and regeneration tests and comparison tests were conducted to assess the practical utility of the adsorbent.

EXPERIMENTAL

Materials and chemicals

The sodium lignosulfonate with 4.5% of moisture content was kindly provided by a bamboo pulp mill in

TABLE I
Some Physicochemical Properties of SSLA

Particle diameter (μm)	200–600
Specific surface area (m^2/g)	106.5
Specific density (g/mL)	1.036
Apparent density (g/mL)	0.521
Pore volume (mL/g)	0.954
Mean pore diameter (nm)	35.83
Porosity (%)	52.17
Moisture content (%)	50.03
Capacity (mmol/g)	2.01

Sichuan, China. Transformer oil and powdered activated carbon (PAC) were industrially pure. A strongly acidic cation-exchange resin 732 (denoted as R732) was provided by Chengdu Chemical. Three kinds of cationic dyes, i.e., Cationic Red GTL (denoted as GTL), Cationic Turquoise GB (denoted as GB), and Cationic Yellow X-5GL (denoted as X-5GL), were provided by Shanghai Luojing Dyeing Chemical, Shanghai, China. Formaldehyde, chlorobenzene, acetone, ether, sodium hydroxide, hydrochloric acid, sodium chloride, lithium hydroxide, alcohol, toluene, chlorobenzene, methanol, Tween 20, Span 60, neopelex, lauryl sodium sulfate, lauryl sodium sulfonate, sodium oleate, etc. (Shanghai Chemical Reagent, Shanghai, China) were chemically pure. The water used was distilled water.

Instruments

A UV-2001 Recording Spectrophotometer (Shimadzu, Japan) was used to determine the chromaticity of the cationic dye solution and the content of the cationic dye before and after adsorption with SSLA.

Preparation of SSLA

Transformer oil (600 mL) was used as disperse phase. Then, 150.0 g of 65% sodium lignosulfonate aqueous solution was slowly added into the above oil phase. After stirring for 20 min at a speed of 300 rpm, the calculated amounts of dispersant agent and 6.0 mol/L HCl aqueous solution were slowly added into the reactor. The mixture was stirred at ambient temperature for 30 min and 50.0 g of 37% formaldehyde aqueous solution was added into the above reaction mixture over 30 min. Then the reaction temperature was raised to 95°C. After 3.0 h of reaction, the slurry was cooled to room temperature. Then the slurry was filtered to recover the transformer oil. After adjusting the pH to 6.5 with a 0.5 mol/L NaCl aqueous solution, the spherical sulfonic lignin adsorbent product was washed with water, acetone, and ether, and then dried. Some physicochemical properties of SSLA are listed in Table I.

Static adsorption experiments

Batch adsorption experiments were carried out by shaking the calculated amount of SSLA adsorbent (50.03% of moisture content) with 200 mL cationic-dye aqueous solution of the desired concentration, pH, and temperature in different glass-stoppered Erlenmeyer flasks at a constant speed of 80 rpm for predetermined time intervals. The concentration of cationic dye was analyzed with a UV-2001 Recording Spectrophotometer. The concentration of cationic dye adsorbed was calculated by the difference of the concentration of cationic dye in solution before and after adsorption. The equilibrium adsorption capacity, q_e, of SSLA can be calculated according to the following formula:

$$q_e = \frac{V(C_0 - C_e)}{W(1 - X)} \tag{1}$$

where C_0 and C_e are the initial and equilibrium solution concentrations, mg/L; V is the solution volume, L; q_e is the equilibrium adsorption capacity of adsorbent, mg/g; W is the adsorbent dosage, g; X is the moisture content of the adsorbent, %.

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 (dry basis). Cationic dye solution (100 mg/L) was pumped through the adsorption at a flow rate of 5.0 mL/min until the solution concentration of cationic dye reach 100 mg/L. The concentration of the cationic dye was analyzed at various predetermined time intervals with a UV-2001 Recording Spectrophotometer.

Desorption and readsorption experiments

Recovery of adsorbate and regeneration of adsorbent is a key process in wastewater process. To achieve these two purposes and to assess the practical utility of the adsorbent, desorption experiments were conducted in two ways. The static desorption experiments were carried out by treating the SSLA with adsorbed cationic dye with 20 mL of the desired concentration of HCl aqueous solution, alcohol, or their mixtures for a predetermined time. The mobile desorption experiments were conducted by pumping the above eluant into the adsorption column at a flow rate of 0.5 mL/min. The concentration of the desorbed cationic dye was analyzed at various predetermined time intervals with a UV-2001 Recording Spectrophotometer. The readsorption experiments were conducted by using the SSLA desorbed according to the procedures of adsorption experiments. The concentration of the cat-
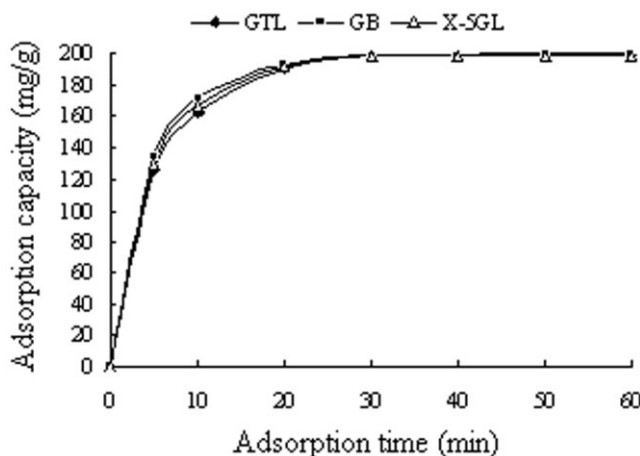

Figure 1 The effect of the adsorption time on the adsorption of cationic dyes on SSLA at pH 7.0 and 26°C with 200 mg/L of GTL, GB, and X-5GL with 0.2 g of adsorbent (dry basis).

ionic dye was analyzed by the difference of the cationic-dye concentration in the solution before and after desorption.

RESULTS AND DISCUSSION

Establishment of linear equations of the cationic dyes

The concentrations of the cationic dyes, i.e., GTL, GB, and X-5GL, were determined with a UV-2001 Recording Spectrophotometer at a wavelength of 515, 650, and 435 nm, respectively. Then the following equations of GTL, GB, and X-5GL were obtained by linear regression analysis of the determined results.

$$\text{GTL: } y = 0.0356A + 0.0379 \quad \gamma = 0.9973 \tag{2}$$

$$\text{GB: } y = 0.0861A + 0.0526 \quad \gamma = 0.9957 \tag{3}$$

$$\text{X-5GL: } y = 0.0198A + 0.0013 \quad \gamma = 0.9985 \tag{4}$$

where y is the concentration of the cationic dye, mg/L; A is absorbance; γ is the correlation coefficient indicating the linear relationship between A and y within the concentration range of 0–50 mg/L.

Effect of adsorption time

Figure 1 illustrates the effect of adsorption time on the adsorption efficiency. The adsorption capacities for GTL, GB, and X-5GL increase with the increase of the adsorption time. After the equilibrium adsorption time of 30 min, the adsorption capacities for GTL, GB, and X-5GL reach 198.6, 199.0, and 199.1 mg/g, respectively, and they remain constant when the adsorption time exceeds 30 min, which indicates that the adsorp-
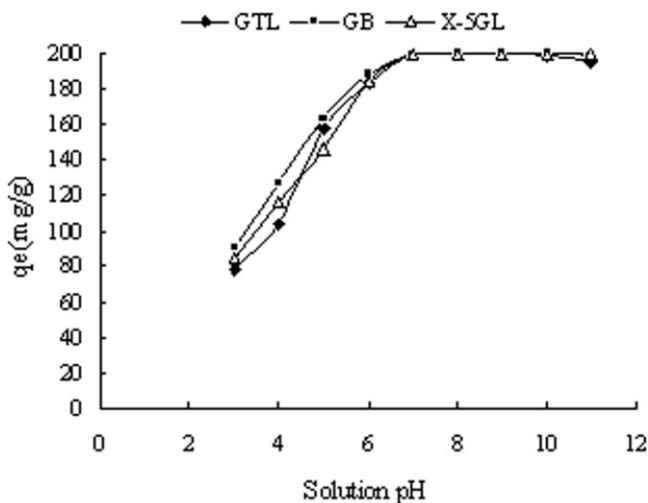
Figure 2 The effect of solution pH on the adsorption of cationic dyes on SSLA at 26°C for 30 min with 200 mg/L of GTL, GB, and X-5GL with 0.2 g of adsorbent (dry basis).

tion tends toward saturation at 30 min. Therefore, the adsorption time was set to 30 min in each experiment.

Effect of solution pH

The effect of solution pH on the adsorption of cationic dyes on SSLA is presented in Figure 2. Solution pH is an important controlling parameter in the adsorption process, and thus the role of solution pH was examined at different pH value covering a range of 3.0–11.0. Figure 2 shows that with an increase in solution pH ranging from 3.0 to 11.0, the equilibrium adsorption capacities for GTL, GB, and X-5GL increase from 77.6 to 199.8 mg/g. The equilibrium adsorption capacities of SSLA are higher in the neutral and alkaline solutions than those in the acidic conditions. However, when the solution pH reaches 11, some Cationic Yellow X-5GL precipitates from the solution. Moreover, the color of the Cationic Red GTL and Cationic Turquoise GB changes evidently. In general, the pH values of the cationic-dye solutions are below 6.0, and the cationic dyes become stable in the acidic mediums instead of alkaline mediums. Furthermore, the pH values of the cationic dye effluents from the dyeing processes range from 4.0 to 7.0. Consequently, the pH of the simulating effluents of the cationic dyes was adjusted to 7.0 to conduct the adsorption experiments.

Effect of initial concentration

The equilibrium adsorption capacities of SSLA for the initial concentration of cationic dyes ranging from 100 to 700 mg/L at 26°C are shown in Figure 3. Under otherwise identical conditions, the equilibrium adsorption capacities of SSLA increase with an increase of the initial cationic-dye concentration, the results

indicates that the removal of cationic dye is initial concentration-dependent. The equilibrium adsorption capacity, q_e, increases sharply among the concentration range of 100 and 700 mg/L. When the concentration exceeds 700 mg/L, the increase curve of q_e becomes smooth gradually indicating that the adsorption of GTL, GB, and X-5GL on SSLA tends toward saturation.

Adsorption isotherms

The adsorption isotherms for the adsorbed cationic dyes on SSLA can be analyzed by both the Langmuir and Freundlich isotherms.

The linear representation of the Langmuir isotherm can be expressed as:[29,30]

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \tag{5}$$

where Q_0 is the maximum amount of the adsorbed cationic dye per gram of adsorbent, mg/g; b is the Langmuir constant, L/mg. Thus, a plot of $\frac{C_e}{q_e}$ versus C_e should yield a straight line having a slope of $\frac{1}{Q_0}$ and an intercept at $\frac{1}{Q_0 b}$, from which the values of Q_0 and b may be readily obtained.

The linear representation of the Friundlich adsorption equation is expressed as:[29,30]

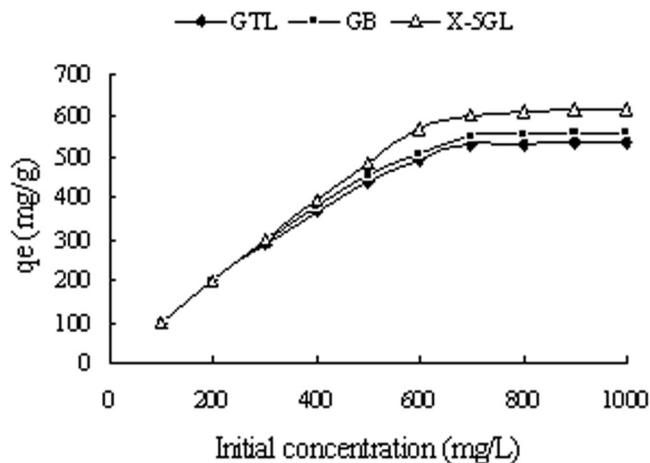$$\log q_e = \log k + \frac{1}{n} \log c_e \tag{6}$$

Figure 3 The effect of initial concentration on the adsorption of cationic dyes on SSLA at pH 7.0 and 26°C for 30 min with 0.2 g of SSLA adsorbent (dry basis).

TABLE II
Langmuir and Freundlich Constants for Cationic Dyes at pH 7.0 and 26°C

Cationic dyes	Langmuir constants			Freundlich constants		
	Q_0	b	γ	k	$1/n$	γ
GTL	576.0	0.3506	0.9990	240.4	0.1692	0.9144
GB	582.4	0.5017	0.9989	303.1	0.1282	0.9609
X-5GL	640.8	0.4715	0.9992	319.8	0.1276	0.9549

where k and $\dfrac{1}{n}$ are the empirical constants (Freundlich parameters). The values of k and $\dfrac{1}{n}$ are equal to the intercept and slope of the capacity and intensity of adsorption, respectively.

Through the linear regression of $\dfrac{C_e}{q_e}$ against C_e as well as $\log q_e$ against $\log C_e$, the regression results are summarized in Table II. Table II indicates that the Langmuir adsorption isotherm fits quite well with the experimental data (the correlation coefficient $\gamma = 0.9990$ for GTL, $\gamma = 0.9989$ for GB, and $\gamma = 0.9992$ for GTL). Moreover, the adsorption of cationic dyes on SSLA was also found to correspond with the Freundlich adsorption isotherm, because the correlation coefficients for three kinds of the cationic dyes exceed 0.9144. The adsorption of cationic dyes on SSLA is feasible ($\dfrac{1}{n} \leq 0.1692$). It also can be seen from Table II that the computed maximum monolayer adsorption capacities Q_0 of SSLA for GTL, GB, and X-5GL are 576.0, 582.4, and 640.8 mg/g, respectively.

The favorable nature of adsorption can be expressed in terms of a dimensionless separation factor of an equilibrium parameter, which is defined by:[31,32]

$$R_L = \frac{1}{(1 + bC_0)} \quad (7)$$

where b is the Langmuir constant introduced in eq. (5) and C_0 is the initial concentration of the adsorbate in solution. The R_L values for the cationic dyes of GTL, GB, and X-5GL uptake are 1.406×10^{-2}, 9.868×10^{-2}, and 1.049×10^{-2}, respectively, which is far less than 0.1 indicating the favorable adsorption.

Effect of temperature

The adsorption behaviors of adsorbed cationic dyes on SSLA at 26, 35, and 45°C also follow the Langmuir adsorption isotherm. The adsorption capacities, Q_0, of SSLA for the uptake of cationic dyes increase by increasing the temperature from 26 to 45°C indicating the process to be endothermic (Table III). The increase in uptake of cationic dyes with temperature may be due to the enhanced rate of intraparticle diffusion of adsorbate and changes in the size of the pores.

The change in apparent enthalpy (ΔH), free energy (ΔG), and entropy (ΔS) of adsorption were calculated using the following equations:[29,30]

$$\ln b = \ln b' - \frac{\Delta H}{RT} \quad (8)$$

$$\ln b = -\frac{\Delta G}{RT} \quad (9)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (10)$$

The values for the enthalpy (ΔH) change of adsorption, as determined from the slope of $\ln b$ versus $\dfrac{1}{T}$ are

TABLE III
Langmuir Constants and Thermodynamic Parameters at Different Temperatures

Cationic dyes	Temperature (°C)	Langmuir constant		Thermodynamic parameter		
		Q_0 (mg/g)	b (L/mg)	$-\Delta G$ (kJ/mol)	ΔS (J/mol)	ΔH (kJ/mol)
	26	576.0	0.3506	29.32	145.3	
GTL	35	587.1	0.4153	30.64	145.4	14.15
	45	592.7	0.5027	32.14	145.5	
	26	582.4	0.5017	30.10	154.4	
GB	35	590.1	0.6273	31.58	154.7	16.08
	45	596.2	0.7389	33.04	154.4	
	26	640.8	0.4715	30.23	140.8	
X-5GL	35	647.1	0.5362	31.47	140.7	11.89
	45	652.0	0.6276	32.91	140.8	

TABLE IV
Results of Mobile Experiments and Comparison Tests at pH 7.0 and 25°C

Adsorbent	GTL		GB		X-5GL	
	V_B (L)	Q_B (mg/g)	V_B (L)	Q_B (mg/g)	V_B (L)	Q_B (mg/g)
SSLA	26.8	536.0	27.5	550.0	29.1	582.0
R732	14.0	280.0	17.3	346.0	17.2	344.0
PAC	6.45	129.0	8.60	172.0	8.05	161.0

V_B, breakthrough volume; and Q_B, breakthrough adsorption capacity.

equal to 14.15, 16.08, and 11.89 kJ/mol for GTL, GB, and X-5GL individually, which suggests the possibility of bonding between the adsorbate and adsorbent. Moreover, the results indicate that the adsorption process is endothermic, and is temperature dependent. The values of ΔG are negative and decreases with increasing temperature demonstrating increase in the feasibility of adsorption at higher temperatures. The positive value of ΔS suggests some structural changes in the adsorbate and adsorbent. And, it also reflects the affinity of the adsorbent for such cationic dyes as GTL, GB, X-5GL, etc.

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 concentrations of the cationic dyes, and they are inversely proportional to the initial concentration. The tests were carried out by pumping a single synthetic cationic dye solution containing 100 mg/L of cationic dye into the adsorption column at a flow rate of 5.0 mL/min. The residual cationic dye in the simulating effluent was determined with a UV-2001 Recording Spectrophotometer for predetermined time intervals. The results are summarized in Table IV.

Table IV indicates that, under the breakthrough volume, cationic dyes can be completely removed, which indicates that the adsorbent and adsorption column can be continuously used to remove the cationic dyes in the practical application, and the breakthrough volume for GTL, GB, and X-5GL are 26.8, 27.5, and 19.1 L separately. The breakthrough adsorption capacities are 536.0, 550.0, and 582.0 mg/g, respectively.

It can also be seen from Table IV that the breakthrough adsorption capacities of SSLA increases 1.0–1.5 times as those of strongly acidic cation-exchange resin R732, and 3.0–4.5 times as those of powdered activated carbon (PAC). The results indicate that SSLA has a potential application foreground in the cationic-dye effluent treatment.

Desorption and recovery tests

The static desorption and recovery tests were carried out by utilizing the various concentrations of alcohol, and HCl aqueous solutions or their mixed solutions for 2.0 h. The results are listed in Table V. Table V shows that the cationic dyes adsorbed on SSLA can be recovered with a mixture of HCl aqueous solution and absolute alcohol. The maximum recovery percentage could reach 95.3, 97.1, and 96.5% separately for GTL, GB, and X-5GL when a mixture of 3.0 mol/L HCl and alcohol with the volume ratio of 1 : 4 was adopted as eluant. Then the mobile desorption and recovery experiments were conducted by pumping the above eluant into the adsorption column at a flow rate of 0.5 mL/min. The results are illustrated in Figure 4. Figure 4 shows that the eluants used to regenerate the SSLA contain high content of cationic dyes, and the maxi-

TABLE V
Results of Desorption and Recovery Tests

Eluant	Recovery percentage (%)		
	GTL	GB	X-5GL
1.0 mol/L HCl	46.7	53.3	48.9
2.0 mol/L HCl	68.9	75.2	70.2
3.0 mol/L HCl	73.2	81.6	75.1
Mixture of 2.0 mol/L HCl with Alcohol[a] (V : V = 1 : 4)	90.2	93.5	91.5
Mixture of 3.0 mol/L HCl with Alcohol[a] (V : V = 1 : 4)	95.3	97.1	96.5
Mixture of 3.0 mol/L HCl with Alcohol[a] (V : V = 1 : 9)	93.6	95.9	95.9

[a] Alcohol used is the absolute alcohol.
Desorption time, 2.0 h; desorption temperature, 22°C.

mum concentrations of GTL, GB, and X-5GL can reach 13,108, 13,980, and 13,520 mg/L, respectively. Therefore, it is feasible for SSLA to recover the cationic dyes and alcohol by further distillation process for the single cationic-dye effluents from the dye-manufacturing process. However, for the effluents containing multi-kinds of cationic dyes, the recovery of the adsorbed cationic dyes from SSLA becomes impossible and impractical.

Readsorption tests

Readsorption tests were also carried out to evaluate the practical utility of SSLA. After 10 replicates of adsorption and desorption, the equilibrium adsorption capacities for GTL, GB, and X-5GL are 197.8, 198.0, and 198.5 mg/g, and almost no loss of adsorption capacity is observed. Only 6.3, 5.0, and 4.6% of adsorption capacities for GTL, GB, and X-5GL decreases individually after 20 cycles. After 30 cycles, the lost adsorption capacities reach 19.4, 18.1, and 16.1% separately for GTL, GB, and X-5GL (Fig. 5). The results indicate that SSLA is a promising adsorbent in the treatment of cationic-dye effluents.

CONCLUSIONS

The adsorption of cationic dyes on the adsorbent was found to be initially concentration- and temperature-dependent, and followed both the Freundlich and Langmuir isothermal adsorption. Moreover, R_L, a dimensionless separation factor of an equilibrium parameter, was far less than 0.1 indicating the favorable adsorption. The concentration helped to increase the equilibrium adsorption capacity, and higher tempera-
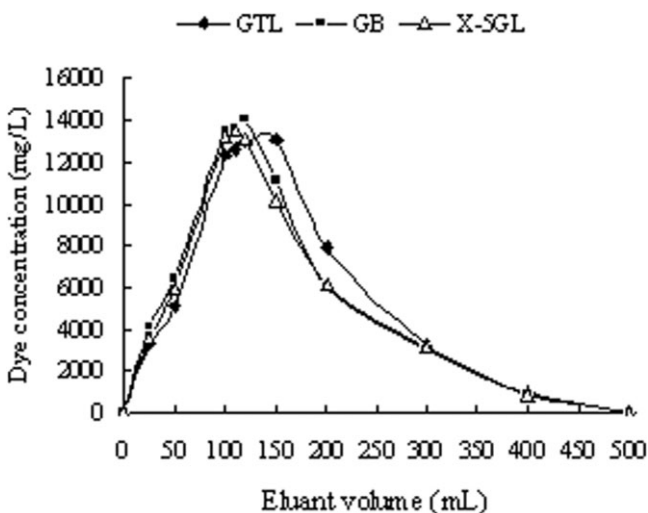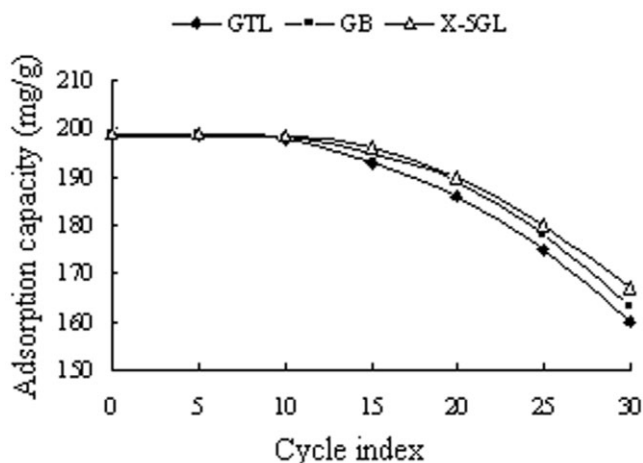

Figure 5 Adsorption–desorption cycles of cationic dyes on SSLA. The adsorption conditions are pH 7.0 and 26°C for 30 min with 200 mg/L of GTL, GB, and X-5GL; The desorption conditions are 20 mL of eluant mixture of 3.0 mol/L HCl and alcohol with the volume ratio of 1 : 4 for 120 min.

ture favored the adsorption. The positives values for ΔH indicated that the process was endothermic. The positive values of entropy ΔS suggested some structural changes in the adsorbate and adsorbent, and it also reflected the affinity of the adsorbent for such cationic dyes as GTL, GB, X-5GL, etc. The breakthrough adsorption capacities for GTL, GB, and X-5GL were 536.0, 550.0, and 582.0 mg/g, respectively, which prevailed over the commercial powdered activated carbon and strongly acidic cation-exchange resin R732 evidently. Additionally, the maximum recovery percentage could reach 93.2, 97.1, and 96.5% separately for GTL, GB, and X-5GL, when a mixture of 3.0 mol/L HCl and alcohol with the volume ratio of 1 : 4 was adopted as eluant. Moreover, the results of the mobile desorption and recovery tests indicated that the maximum concentrations of GTL, GB, and X-5GL in the eluants could reach 13,108, 13,980, and 13,520 mg/L, respectively. Therefore, it was feasible for SSLA to recover the cationic dyes and alcohol by further distillation process for the single cationic-dye effluents from the dye-manufacturing process. Only 6.3, 5.0, and 4.6% of adsorption capacities for GTL, GB, and X-5GL decreases individually after 20 replicates of adsorption and desorption. The above results further proved that SSLA was a prospective adsorbent in the removal of cationic-dye wastewaters.

Figure 4 The elution curve at 25°C with a eluant mixture of 3.0 mol/L HCl and alcohol with the volume ratio of 1 : 4 at a flow rate of 0.5 mL/min.

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