Adsorption Behavior of Reactive Turquoise Blue KN-G in Aqueous Solutions on a Novel Spherical Lignin-based Adsorbent*

LIU Ming-hua[1], *HONG Shu-nan*[1], *HUANG Jian-hui*[1], *Ye Qing*[1], *LIU Qian-jun*[2]
(1. College of Environment & Resources, Fuzhou University, Fuzhou 350002, China
2. College of Environmental Science & Engineering, Guangdong University of Technology, Guangzhou 510090, China)

Abstract: A novel spherical lignin-based adsorbent, denoted as SLBA, was prepared using alkali lignin as a raw material which was provided by a masson pine pulp mill in Fujian, China. Then an investigation was conducted regarding the adsorption behavior of a reactive dye (Turquoise Blue KN-G) from aqueous solutions with the above new spherical lignin-based adsorbent containing the quaternary ammonium cationic group. Moreover, various affecting factors on the adsorption were optimized. It was found that the adsorption of reactive Turquoise Blue KN-G on the adsorbent was found to be initially pH and concentration dependent. The concentration helped to increase the equilibrium adsorption capacity. With an increase in solution pH ranging from 3 to 8, the removal percentage increased sharply from 12.3% to 98.6%, and at pH= 10, the removal rate reached 100%. The adsorption process followed the Langmuir adsorption isotherm, i.e., $C_e/q_e = 0.0002136 + 0.001225C_e$. Moreover, R_L, a dimensionless separation factor of an equilibrium parameter, was 8.711×10^{-4}, which was far less than 0.1 indicating the favorable adsorption. The saturated adsorption capacity was 816.3 mg/g, and the total breakthrough removal capacity was 761 mg/g, which prevailed over the commercial activated carbons evidently. The reactive Turquoise Blue KN-G adsorbed on SLBA could be recovered with a mixture of alcohol, dicyandiamide-formaldehyde polycondensate and HCl aqueous solutions. And, the maximum desorption efficiency could reach 98.7%.

Key words: lignin; spherical adsorbent; adsorption; reactive dye; Langmuir adsorption isotherm
CLC number: O636.2; O647.3 **Document code**: A **Article ID**: 0529-6579 (2005) S2-0001-06

1 Introduction

Dyeing effluents mainly contain the waste waters from all of the dyeing processes of various natural celluloses and synthetic celluloses. The dyeing effluents have such characteristics as high chromaticity, high CODCr content as well as large amount of suspension solid etc.[1] 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[2]. And, relatively simple reactive-dye adsorption processes can meet the progressively stricter environmental discharge criteria[3,4].

Recently, numerous investigations have been proved the feasibility of use of agricultural products and byproducts, industrial waste biomass and natural substances to adsorb and accumulate the dyes[5—8]. 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[9] and heavy metal ions, e.g., lead (Ⅱ), cadmium (Ⅱ), copper (Ⅱ), zinc (Ⅱ), nickel (Ⅱ), cadmium (Ⅱ), chromium (Ⅲ) and iron (Ⅲ) ions etc.[10,11]

In this study, a new spherical lignin-based adsorbent containing the quaternary ammonium cationic group (denoted as SLBA) was prepared using alkali lignin as a raw material which was provided by a masson pine pulp mill in Fujian, China. Then a reactive dye (Turquoise Blue KN-G) was used as an adsorbate to investigate the adsorption behavior by static and mobile ways. The effects of adsorption time, solution pH and initial concentration of KN-G on the adsorption processe of the removal of Turquoise Blue KN-G were also investigated. Moreover, the desorption tests were conducted to assess the practical utility of

* 收稿日期: 2005—07—10
基金项目: 国家自然科学基金资助项目（50203003）；福建省青年科技创新基金资助项目（2002J002）；福建教育厅基金资助项目（JA03012）；福州大学科技发展基金资助项目（2003-XQ-28）
作者简介: 刘明华（1970 年生），男，博士，教授；E-mail: mhliu2000@236.net

the adsorbent.

2 Experimental

2.1 Materials

The black liqour with 45% of solid content was kindly provided by a masson pine pulp mill in Sanming Qinshan Pulp Industry Group Co., Ltd. in Fujian, China. 3-chloro-2-hydropropyl trimethyl ammonium chloride, denoted as CHPTA, (55% aqueous solution) was synthesized from the procedure described by Langher et al[12]. Transformer oil, granular activated carbon (GAC) and powdered activated carbon (PAC) was industrially pure. Epichlorohydrin, trimethylamine, formaldehyde, Turquoise Blue KN-G, 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 sulphonate and sodium oleate etc. (purchased from shanghai Chemical Co., Shanghai, China) were chemically pure. The water used was distilled water.

2.2 Instruments

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

2.3 Preparation of SLBA

2.3.1 Preparation of spherical cross-linked lignin beads 500 mL of the mixture of transformer oil and chlorobenzene with 1∶1.5 of volume ratio was used as disperse phase. Then 165 ml 45% of black liquor was slowly added into the above oil phase. After stirring for 20 min at a speed of 300 r/min, the calculated amounts of dispersant agent and epichlorohydrin were slowly added respectively. The mixture was stirred at 65 ℃ for 1.0 h. Then the reaction temperature was raised to 90 ℃. After 1.0 h of reaction, the slurry was cooled to room temperature. Then the slurry was filtered and the pH adjusted to 6.5 with a 1.0 mol/L NaOH aqueous solution. The spherical cross-linked lignin beads (GCLB) were washed with water, acetone and ether, and then dried.

2.3.2 Quaternization 100 g of GCLB (moisture content 70.6%) was suspended in 250 mL water containing 5.0 g sodium chloride. 25 g 20% of sodium hydroxide aqueous solution was added into the above mixture. Then the reaction temperature was raised to 85 ℃ and 35.0 g of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTMA) was added slowly over 30 min, and the mixture was stirred for 3 h at 85 ℃. The mixture was cooled, filtered and washed with water, acetone and ether, and then dried to obtain the spherical lignin-based adsorbent containing the quaternary ammonium cationic group (SLBA).

2.4 Static adsorption experiments

Batch adsorption experiments were carried out by shaking the calculated amount of SLBA adsorbent (moisture content 72.5%) with 100 mL aqueous solution of Turquoise Blue KN-G 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 KN-G was analyzed by UV-2001 Recording Spectrophotometer. The concentration of KN-G adsorbed was calculated by the difference of the concentration of KN-G in solution before and after adsorption.

2.5 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 KN-G aqueous solution was pumped through the adsorption at a flow rate of 5.0 ml/min until the effluent concentration of KN-G reach 100 mg/L. The effluent concentration of KN-G was analyzed at various predetermined time intervals by UV-2001 Recording Spectrophotometer.

2.6 Desorption tests

In order to assess the practical utility of the adsorbent, the desorption experiments were conducted by treating the SLBA with adsorbed KN-G with 10 mL of the desired concentration of alcohol, NaCl aqueous solution, dicyandiamide-formaldehyde polycondensate aqueous solution and HCl aqueous solutions or their mixed solutions for a predetermined time. The concentration of KN-G was analyzed by the difference of the concentration of KN-G in the solution before and after desorption.

3 Results and discussion

3.1 Establishment of linear equation of KN-G

The concentration of KN-G was determined by UV-2001 Recording Spectrophotometer at a wavelength of 670 nm, the following equation was obtained by linear regression analysis of the determination results.

$$y = 0.0141A, \qquad \gamma = 0.9981 \qquad (1)$$

Where is the concentration of KN-G, mg/L; A is absorbance; γ is the correlation coefficient indicating the linear relationship between A and γ among the concentration range of 0 and 50 mg/L

3.2 Effect of adsorption time

Fig. 1 illustrates the effect of adsorption time on the adsorption efficiency. The removal rate of KN-G increases

with an 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.

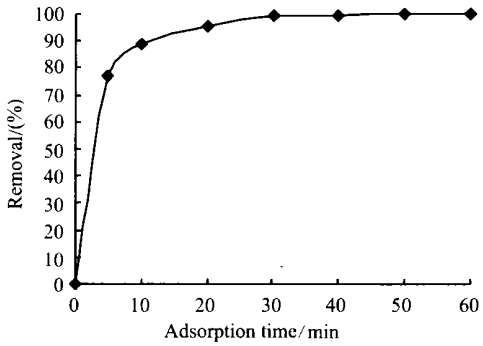

Fig 1　Effect of adsorption time
pH 9.0, 25 ℃, 200 mg/L KN-G, 1.0 g of SLBA adsorbent

3.3　Effect of solution pH

The effect of solution pH on the adsorption of KN-G on SLBA is presented in Fig. 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 ~ 12.0. Fig. 2 shows that with an increase in solution pH ranging from 3 to 8, the removal percentage increased sharply from 12.3 % to 98.6 % and at pH = 9, the removal rate reached 99.3%. At pH=10, the removal rate reached 100%. In general, the pH values of the reactive dye effluents from the printing and dyeing mills range from 9.0 to 12. Consequently, the pH of the simulating effluents of the Turquoise Blue KN－G was adjusted to 9. 0 to conduct the adsorption experiments.

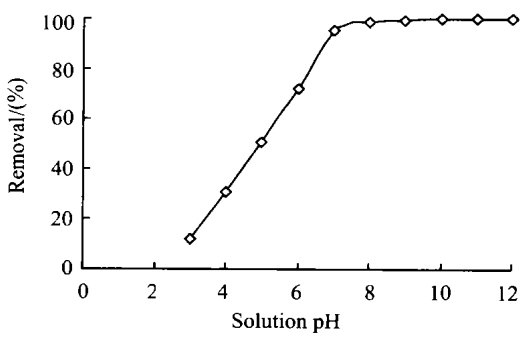

Fig 2　Effect of solution pH on the adsorption of KN-G on SLBA
200 mg/L KN-G, 25 ℃, 30 min, 1.0 g of SLBA adsorbent

3.4　Effect of initial concentration

The removal rates and the equilibrium adsorption capacity q_e of SLBA for the initial concentration of KN-G ranging from 50 to 400 mg/L at 25 ℃ are shown in Fig. 3. Under otherwise identical conditions, the removal rate of SLBA decreases with an increase of the initial concentration of KN-G, the results indicates that the removal of KN-G is initial concentration dependent. The equilibrium adsorption capacity q_e increases sharply among the concentration range of 0 and 250 mg/L. When the concentration exceeds 250 mg/L, the increase curve of q_e becomes smooth gradually indicating the adsorption capacity of SLBA tends towards saturation.

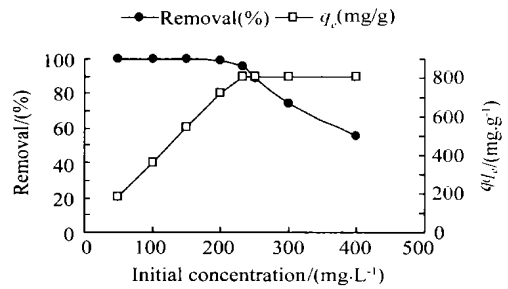

Fig 3　Effect of initial concentration on the adsorption of KN-G on SLBA
25 ℃, 30 min, pH 9.0, 1.0 g of SLBA adsorbent

3.5　Adsorption isotherm

The linear representation of the Langmuir isotherm can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \qquad (2)$$

Where $q_e = \dfrac{C_0 - C_e}{W}$

C_0 and C_e are the initial and equilibrium concentrations of the Turquoise Blue KN-G in solution respectively, mg/L; q_e is the mg of adsorbed KN－G per g of adsorbent, mg/g; W is the amount of adsorbent required to adsorb KN－G, g; Q_0 is the maximum amount of adsorbed KN－G per g of adsorbent, mg/g; and b is the Langmuir constant, L/mg. Thus. A plot of $\dfrac{C_e}{q_e}$ versus C_e should yield a straight line having a slope $\dfrac{1}{Q_0}$ and an intercept of $\dfrac{1}{Q_0 b}$ from which the values of Q_0 and may be readily obtained.

The plot of $\dfrac{C_e}{q_e}$ against C_e gave a straight ling (Fig. 4). Fig. 4 shows that the adsorption behavior follows the Langmuir adsorption isotherm. The Langmuir isothermal adsorption equation is as follows:

$$\frac{C_e}{q_e} = 0.0002136 + 0.001225C_e \qquad (3)$$

Where

Hence, the values of $\frac{1}{Q_0 b}$ and b are 816.3 mg/g and 5.735 L/mg, respectively.

The validity of Langmuir isotherm was further confirmed by regression analysis of the data at 25 ℃. The regression relating $\frac{C_e}{q_e}$ and C_e at 25 ℃ is found as:

$$\frac{C_e}{q_e} = 0.0002131 + 0.001224 C_e \quad (4)$$

By comparing equation (2) and (4), the values of Q_0 and b are 817.1 mg/g and 5.743 L/mg separately, which are in good agreement with the graphical values at 25 ℃.

The favorable nature of adsorption can be expressed in terms of a dimensionless separation factor of a equilibrium parameter, Which is defined by[4]:

$$R_L = \frac{1}{(1 + bC_0)} \quad (5)$$

Where b is the Langmure constant introduced in equation 3 and is the initial concentration of the adsorbate in solution. The R_L value for KN-G ion uptake is 8.711×10^{-4}, which is less than 0.1 indicating favorable adsorption.

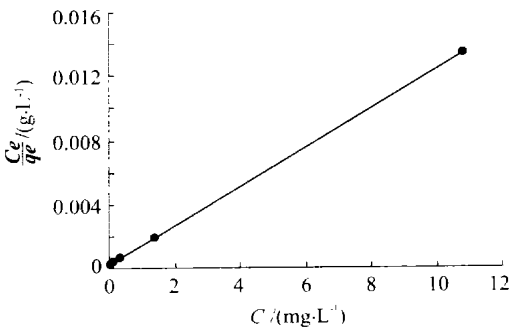

Fig 4 Langmuir plot for the adsorption of KN-G on SLBA
pH 5.0, 20 ℃, 200 mg/L KN-G

3.6 Mobile adsorption experiments and comparison tests

The tests of breakthrough parameters of adsorption column were conducted toassess the practical utility and durability of the adsorbent. The breakthrough parameters vary with the initial concentration of KN-G. And, they are inversely proportional to the initial concentration. The tests were carried out by pumping a synthetic KN-G solution containing 100 mg/L KN-G into the adsorption column at a flow rate of 5.0 ml/min. The residual KN-G in the effluent was determined by UV-2001 Recording Spectrophotometer for predetermined time intervals. The resul0ts are illustrated in Fig. 5 and summarized in Tab. 1.

Fig. 5 shows that under the breakthrough volume (V_B = 10.46 L), KN-G can be completely removed, which indicates that the adsorbent and adsorption column can be continuously used to remove KB-1 in the practical application.

From Table 1, we can see the breakthrough removal capacity and saturated removal capacity of KN-G increase 4~6 times as those of granular activated carbon (GAC) and powdered activated carbon (PAC). The results indicate that the SLBA has a potential application foreground in the reactive dyeing effluent treatment. The breakthrough removal capacity and saturated removal capacity of PAC prevail over those of GAC indicating the surface area also plays an important part in the reactive-dye removal.

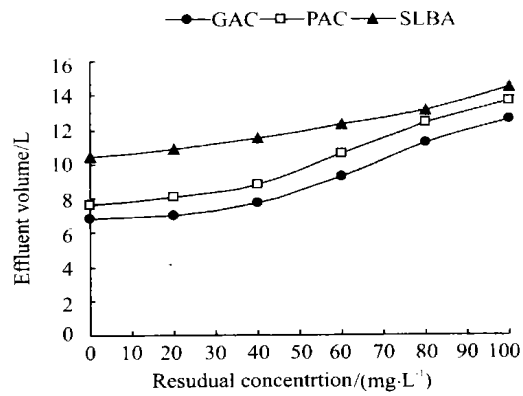

Fig 5 Breakthrough curve
100 mg/L KN-G; pH 9.0; Flow rate 5.0 ml/min; 25 ℃.

Tab 1 Results of mobile adsorption experiments and comparison tests

Adsorbent	SLBA	PAC	GAC
Breakthrough volume /L	10.46	7.63	6.81
Total volume /L	14.5	13.7	12.6
Breakthrough removal capacity/(mg·g^{-1})	761	153	136

3.7 Desorption tests

The desorption tests were carry out by utilizing various concentrations of alcohol, NaCl aqueous solution, dicyandiamide—formaldehyde polycondensate aqueous solution and HCl aqueous solutions or their mixed solutions for 2.0 h / The results are listed in Table 2. Table 2 shows that the Turquoise Blue KN—G adsorbed on SLBA can be recovered with a mixture of alcohol, dicyandiamide—formaldehyde polycondensate and HCl aqueous solutions. And, the maximum recovery percentage could reach 98.7%.

Tab. 2　Results of desorption and recovery tests

Eluant	Desorption efficiency/(%)
10% of NaCl aqueous solution	9.8
10% of HCl aqueous solution	55.1
Mixture of 10% of HCl aqueous solution and Alcohol (The mass ratio is 1∶1)[1)]	70.2
Mixture of 10% of HCl aqueous solution, Alcohol[1)] and 10% of NaCl (The mass ratio is 1∶1∶1)	71.6
65% of DFP aqueous solution	82.3
Mixture of 65% of DFP aqueous solution, 10% of HCl aqueous solution and Alcohol[1)] (The mass ratio is 8∶1∶1)	98.7

Note: 1) Alcohol used is the absolute alcohol. And, the dicyandiamide-formaldehyde polycondensate is denoted as DFP. The desorption time 2.0 h, and the desorption temperature is 25 ℃.

4　Conclusions

The adsorption of reactive Turquoise Blue KN-G on the adsorbent was found to be initially pH and concentration dependent. The concentration helped to increase the equilibrium adsorption capacity. With an increase in solution pH ranging from 3 to 10, the removal percentage increased sharply from 12.3 % to 100%. The adsorption process followed the Langmuir adsorption isotherm, i.e., $\frac{C_e}{q_e}=0.0002136+0.001225C_e$. Moreover, R_L, a dimensionless separation factor of an equilibrium parameter, was 8.711×10^{-4}, which was far less than 0.1 indicating the favorable adsorption. The saturated adsorption capacity was 816.3 mg/g, and the total breakthrough removal capacity was 761 mg/g, which prevailed over the commercial activated carbons evidently. The reactive Turquoise Blue KN-G adsorbed on SLBA could be recovered with a mixture of alcohol, dicyandiamide-formaldehyde polycondensate and HCl aqueous solutions. And, the maximum desorption efficiency could reach 98.7%.

References:

[1] HUANG C D. Dyeing effluent treatment [M]. Beijing, China: Textile Industry Press, 1987

[2] KHATTRI S D, SINGH M K. Color removal from dye wastewater using sugar cane dust as an adsorbent [J]. Adsorp Sci Technol, 1999, 17: 269—282

[3] LIU M, ZHANG X, DENG Y, et al. Removal and recovery of chromium (III) from aqueous solutions by a spheroidal cellulose adsorbent [J]. Water Environment Research, 2001, 73 (3): 322—328

[4] LIU M, DENG Y, ZHAN H, et al. Adsorption and desorption of copper (II) from solutions on a new spherical cellulose adsorbent [J]. J Appl Polym Sci, 2002, 84: 478—485

[5] WU F C, TSENG R L, JUANG R S. Comparative adsorption of metal and dye on flake— and bead-types of chitosans prepared from fishery wastes [J]. J Hazard Mater, 2000, 73: 63—75

[6] MOHAN D, SINGH K P, SINGH G, et al. Removal of dyes from wastewater using fly ash, a low-cost adsorbent [J]. Industrial and Engineering Chemistry Research, 2002, 41 (15): 3688—3695

[7] NASSAR M H, MAGDY Y H. Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles [J]. Chemical Engineering Journal, 1997, 66 (3): 223—226

[8] McKAY G, PORTER J F, PRASAD G F. Removal of dye colours from aqueous solutions by adsorption on low-cost materials [J]. Water, Air and Soil Pollution, 1999, 114 (3, 4): 423—438

[9] VAKUROVA I K, DIAROV M D. Removing halides from waste water [J]. Soviet Journal of Water Chemistry and Technology (English Translation of Khimiya i Tekhnologiya Vody), 1988, 10 (5): 111—112

[10] KOCH H F, ROUNDHILL D M. Removal of mercury (II) nitrate and other heavy metal ions from aqueous solution by a thiomethylated lignin material [J]. Separation Science and Technology, 2001, 36 (1): 137—143

[11] CARRILLO-MORALES G, DAVILA-JIMENEZ M M, ELIZALDE-GONZALEZ M P, et al. Removal of metal ions from aqueous solution by adsorption on the natural adsorbent CACMM2 [J]. Journal of Chromatography A, 2001, 938: 237—242

[12] LANGHER R R, JACKSON L, WALLING J C, et al. Synthesis of 3-chloro-2-hydroxypropyl quaternary ammonium salts [M]. US3, 532, 751, 1970

水溶液中的活性翠兰 KN-G 在一种新型球形木质素吸附剂上吸附特性研究

刘明华[1]，洪树楠[1]，黄建辉[1]，叶 庆[1]，刘千钧[2]

（1. 福州大学环境与资源学院，福建 福州 350002；
2. 广东工业大学环境科学与工程学院，广东 广州 510090）

摘 要：以马尾松浆厂提供的碱木素为原料研制出一种新型的球形木质素吸附剂 SLBA。然后以活性翠兰 KN-G 为吸附质研究其在这种含有季铵基团的球形木质素吸附剂上的吸附特性。并进行吸附影响因素的优选实验。实验结果表明：活性翠兰 KN-G 在吸附剂上的吸附效果取决于吸附质溶液的 pH 值和吸附质的初始浓度。初始浓度的增大有利于提高平衡吸附容量。在 3～8 的 pH 范围内，去除率从 12.3% 迅速升至 98.6%，当溶液的 pH 值为 10.0 时，去除率达 100%。吸附过程符合 Langmuir 吸附等温式，即 $\frac{C_e}{q_e}=0.0002136+0.001225C_e$。而且，平衡常数的无量纲系数 R_L 为 8.711×10^{-4}，远小于 0.1，说明活性翠兰 KN-G 在 SLBA 上的吸附很容易进行。而且，SLBA 吸附剂的饱和吸附容量为 816.3 mg/g，总的穿透容量为 761 mg/g，吸附效果明显优于活性炭。吸附在 SLBA 吸附剂上的活性翠兰可用乙醇、双氰胺—甲醛缩聚物和盐酸混合物解析，解析率可达 98.7%。

关键词：木质素；球形吸附剂；吸附；活性染料；Langmuir 吸附等温式

中图分类号：O636.2；O647.3