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Short communication

Synthesis of sesbania gum supported dithiocarbamate chelating resin and studies on its adsorption performance for metal ions

Q. Zhang [a], Y. Gao [b], Y.A. Zhai [a], F.Q. Liu [a], G. Gao [a,*]

[a] *College of Chemistry and MacDiarmid Laboratory, Jilin University, Changchun 130021, PR China*
[b] *Peking University Health Science Center, Beijing 100083, China*

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Abstract

Sesbania gum supported dithiocarbamate chelating resin (SGDSA) was prepared. The epoxy functional groups were introduced into sesbania gum to produce the sesbania gum supported resins and then reacted with triethylenetetramine, and lastly were converted to the respective dithiocarbamates by reacting with carbon disulphide. The structure of functionalized resins was characterized by FT-IR. The influences of various reaction conditions on the epoxidation were discussed. The prepared SGDSA exhibited high adsorption capacity for metal ions and the adsorption equilibrium could be arrived at shorter time.

Keywords: Sesbania gum; Dithiocarbamate polymer; Adsorption capacity; Epoxidation; Synthesis

1. Introduction

Sesbania gum (SG) is a natural polysaccharide growing only in China with an average molecular weight of $2.3 \times 10^5 - 3.4 \times 10^5$. SG is a galactomannan and its main and its main structure involves β $(1 \rightarrow 4)$ glycosidic bonds linked mannose and α $(1 \rightarrow 6)$ glycosidic bonds linked galactose on the side chains (Wang, Zhu, Zhang, Zhao, & Zhu, 1996). The mannose:galactose ratio of the galactomannan is 2:1. Physicochemical properties and chemical construction of SG are similar to guar gum (Ma & Pawlik, 2005; Rwddy & Tammishetti, 2004; Tang, 1995). The molecular structure of SG is shown in the Fig. 1 (Fan, Zhu, Yang, Gu, & Tang, 2000; Wang, Somasundaran, & Nagaraj, 2005). Like other galactomannans, SG is insoluble in organic solvents but partially soluble in water.

The work on SG is mainly concentrated on its modification and applications. Huang et al. performed pioneering studies on modified SG and synthesized carboxymethyl SG, hydroxyethyl SG, and carboxymethyl–hydroxyethyl SG (Huang, Gao, & Shi, 1980). Cui et al. synthesized sesbania gum supported palladium compound and studied catalysis for the Heck reaction (Cui & Zhang, 2005). In addition, they also prepared quaternary ammonium cationic sesbania gum and researched its flocculating properties (Cui, Wang, Li, Li, & Zhou, 2004). Rao et al. synthesized modified SG with sodium hypochlorite and phosphate (Rao, Mao, Wu, & Zeng, 1995). Modified SG was widely used in many industrial areas such as petroleum, pharmaceuticals, ore dressing, paper manufacturing, textiles, printing and dyeing, coating tobacco, construction, pesticide, and cosmetics industries (Sun, Zhang, & Yan, 2001; Wang, Huang, Li, & Hua, 1982). According to the principle and methods of modified starch and cellulose, more kinds of chemically modifying sesbania gum can be produced to increase the range of applications.

Dithiocarbamate is supported by synthetic and natural polymers. Synthetic polymers used include polystyrene, polyvinyl chloride, polyether, and polymethacrylic derivates (Mathew & Pillai, 1992; Minagawa & Takizawa, 1980; Yamagami, Taleishi, & Hashimoto, 1980) and natural polymers used include cellulose, starch, and chitosan (Chen &

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[*] Corresponding author. Tel.: +86 431 82214252; fax: +86 431 8499187.
E-mail address: gaoge@jlu.edu.cn (G. Gao).

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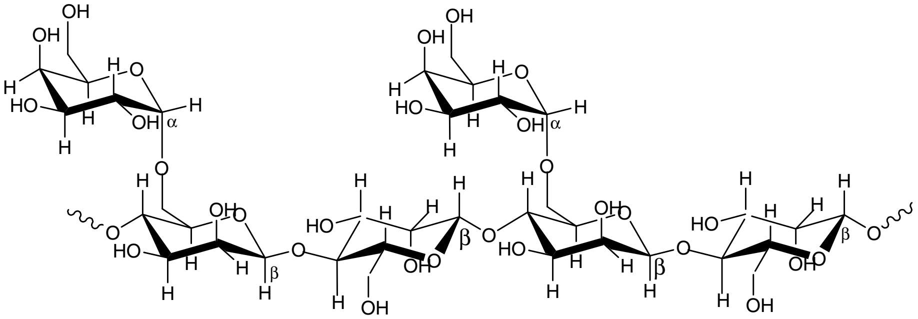


Fig. 1. Molecular structure of SG.

Gu, 1982; Xiang, Li, & Ni, 2003). As far as we know, the work on the preparation and characterization of SG supported dithiocarbamate derivates has not been reported. In this paper, dithiocarbamates were introduced onto the side chain of SG by epoxidation to obtain a type of chelating resin. The structure of the functionalized resin was characterized by FT-IR. The influences of various reaction conditions on the epoxidation were discussed. The prepared SGDSA exhibited high adsorption capacity for metal ions and the adsorption equilibrium could be arrived in shorter time.

2. Experimental

2.1. Materials

SG was commercially obtained from Hongtu Plant Adhesive Factory, epichlorohydrin, triethylenetetramine, and tetramethylammonium bromide were purchased from the First Reagent Factory of Shanghai, carbon disulphide, tetrahydrofuran, and sodium hydroxide were purchased from Tianjin Tiantai Fine Chemical Limited Co., glacial acetic acid, hydrochloric acid, and absolute alcohol were obtained from the Beijing Chemical Plant.

2.2. Instrument

2.2.1. FT-IR spectra

FT-IR spectra were determined by a Vector 22 infrared spectrometer (Bruker Ltd. Co.). The dried sample power was mixed with KBr and pressed into pellets. The FT-IR spectra were obtained by scanning between 4000 cm^{-1} and 400 cm^{-1}.

2.2.2. UV–Vis spectra

UV–Vis spectra were recorded on a Cary 50 UV–Vis spectrophotometer (Varian Ltd. Co.). The measurements were processed in a quartz cell of 1 cm path length at room temperature.

2.3. Synthesis of SGDSA

One gram of water-immiscible SG was added to 36 mL of aqueous solution of sodium hydroxide (2.75 mol/L) and the reaction was processed with stirring at room temperature for about 3 h. Then 1 mL of aqueous solution of tetramethylammonium bromide (1%) and 1 mL of epichlorohydrin were added to the above solution and the reaction continued with stirring for another 3 h. The pH value of the resulting solution was adjusted to 7–8 and the epoxidized SG (EP-SG) was obtained. Some samples were taken from the mixture solution, precipitated repeatedly with absolute alcohol, washed thoroughly with distilled water, and dried under a vacuum oven for the determination of epoxide number and characterization.

A volume of 1 mL of triethylenetetramine was added slowly to the epoxidized SG solution with stirring, and then the reaction was conducted at 60 °C for 12 h. Some samples were taken out, and precipitated repeatedly with absolute alcohol to remove unreacted triethylenetetramine, and dried under a vacuum oven for the measurement of IR spectra.

After the aminated EP-SG solution was cooled to room temperature, the mixture of 7.5 mL of tetrahydrofuran, and 0.5 mL of carbon disulphide were added slowly to it using an injector and the reaction was stirred for 24 h at 8–10 °C. At last the resulting solution was precipitated repeatedly with absolute alcohol and washed thoroughly with distilled water in order to remove unreacted carbon disulphide, and was dried in a vacuum oven.

2.4. Determination of epoxide number

The epoxide number was determined by acid–alkali titration with phenolphthalein as an indicator. The epoxide number E was calculated as

$$E = \frac{100C(V_b - V)}{w}$$

where C, V_b, V, and w are concentration of standard aqueous solution of sodium hydroxide (mol/L), volume of aqueous solution of sodium hydroxide consumed by the blank sample (L), volume of aqueous solution of sodium hydroxide consumed by sample (L), and weight of sample (g), respectively.

2.5. Determination of the adsorption performance of SGDSA

Aqueous solutions of Co (II) (0.01 mol/L, pH 6.0) and Cr (III)) (0.01 mol/L, pH 4.4) were prepared by dissolving 0.2910 g of $Co(NO_3)_2{\cdot}6H_2O$ and 0.4002 g of

$Cr(NO_3)_3{\cdot}9H_2O$ in 100 mL of water, respectively. A set amount of SGDSA was added to the solutions of metal ion (Co (II), Cr (III)) with a concentration of 0.01 mol/L under stirring at room temperature for setting time, and then the solution was filtered. Absorbance of metal ion solution was determined at the maximum absorption wavelength (514 nm for Co (II) and 580 nm for Cr (III)) by UV–Vis. In addition, blank corrections were taken before the absorption measurement, and it was proved that the resin itself does not release any soluble organic components that strongly absorb at the maximum absorption wavelength.

Adsorption capability labeled as Q was calculated as

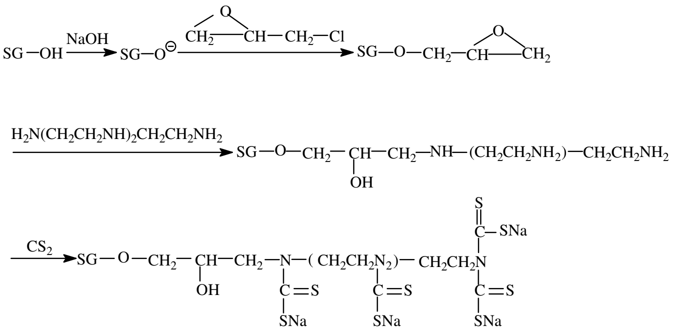
$$Q = \frac{V(C_0 - C)}{w}$$

where V, C_0, C, and w are volume of metal ion solution (L), initial concentration of metal ion solution (mol/L), equilibrium concentration of metal ion solution (mol/L) and weight of sample (g), respectively. The variation of Q with adsorption time t was determined as follows: 0.01 g of SGDSA was added to 10 mL of Cr (III) or Co (II) ion solution (0.01 mo1/L) with stirring. The samples were taken out for analysis periodically and the Q–T curve was plotted.

3. Results and discussion

3.1. Synthetic and characterization

Generally speaking, only the primary hydroxyl group possesses higher reaction activity (Sun, Gu, Ma, & Liang, 2003) and the secondary hydroxyl can react only at severe condition, so functional groups with chelating performance can be introduced to the primary hydroxyl of SG. The synthetic route is showed as follows:



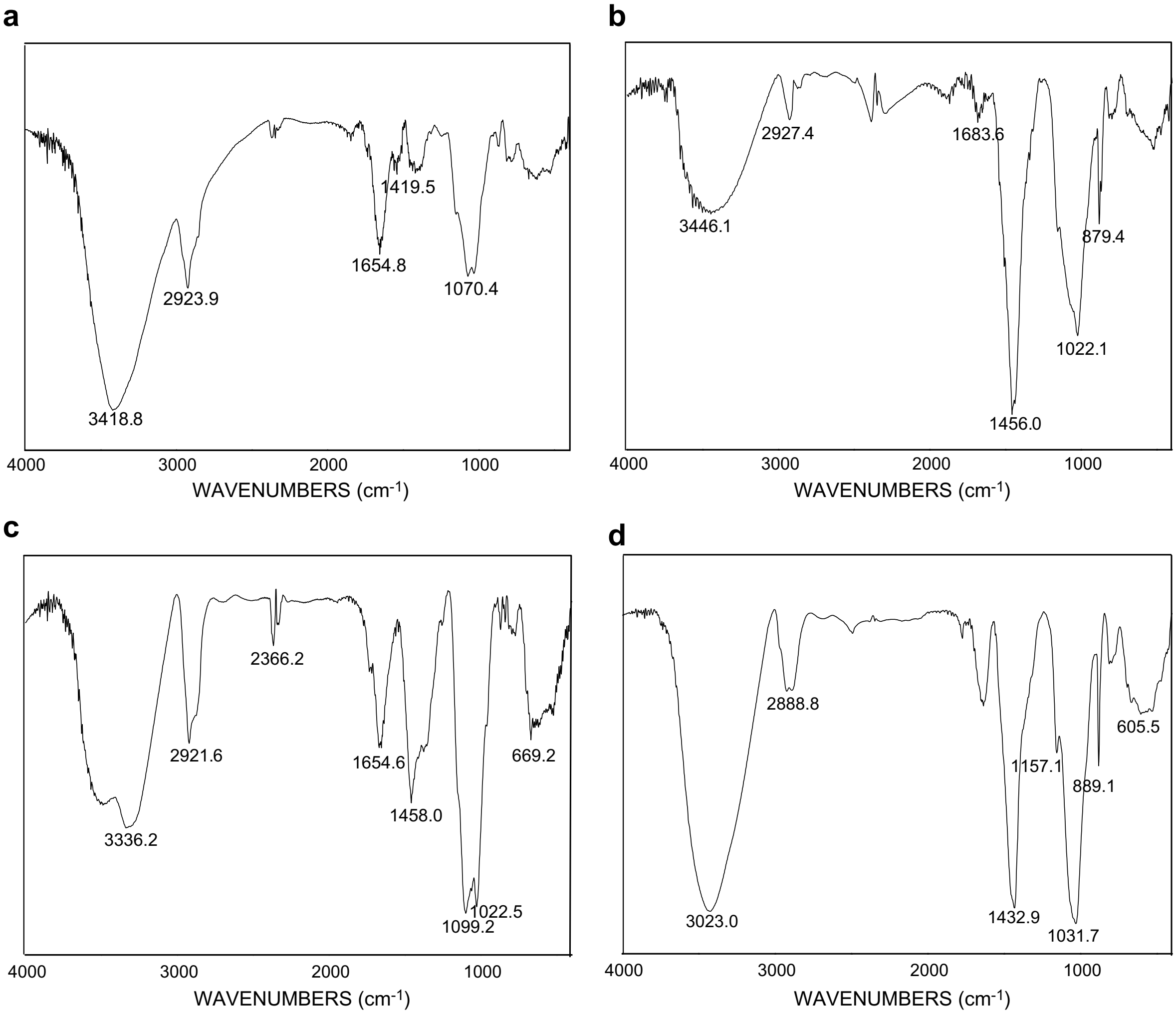


Fig. 2. IR spectra (a) SG, (b) epoxidized SG, (c) aminated EP-SG, (d) SGDSA.

Fig. 2 shows the IR spectra of intermediate products and SGDSA. The peaks at 3418.8 cm^{-1}, 1070.4 cm^{-1}, and 2923.9 cm^{-1} are assigned to O—H stretching, C—O bending and C—H stretching, respectively (Fig. 2(a)). The absorption band of O—H weakens obviously and epoxy absorption band appears at 879.4 cm^{-1}, which demonstrates the formation of the epoxidized SG. The peaks at 1022.1 cm^{-1} and 1456.0 cm^{-1} could be assigned to C—O deformation vibrations and C—H deformation vibrations of methylene, respectively (Fig. 2(b)). The peaks at 3336.2 cm^{-1} and 1458.0 cm^{-1} are attributed to N—H stretching and C—H deformation vibrations of methylene, respectively, in the IR spectra of aminated EP-SG (Fig. 2(c)). The peaks at 1157.1 cm^{-1}, 1432.9 cm^{-1}, 1031.7 cm^{-1}, and 2088.8 cm^{-1} could be assigned to C═S stretching, N—C═S characteristic peak, C—O deformation vibrations, and C—H deformation vibrations of methyl, respectively (Fig. 2(d)) (Wang, He, & Sun, 1990).

3.2. *Influencing factors of epoxide number*

Influencing factors on epoxide number mainly involve alkalizing time, epoxidizing time, and the amount of epichlorohydrin used. In addition, using phase transfer catalyst can increase epoxide number (He, Meng, Chen, Hu, & Chen, 1998; Liu, Tian, & Jiang, 1999). In our experiments tetramethylammonium bromide was selected as a phase transfer catalyst.

Fig. 3(a–c) show the variations of epoxide number with alkalizing time, epoxidizing time, and the amount of epichlorohydrin used, respectively. From the figures we can see that the optimal alkalizing time, epoxidizing time, and the amount of epichlorohydrin used are about 3.5 h, 2.5 h, and 1 mL per 1 g of water-immiscible SG, respectively. When alkalizing time was shorter, SG was only swelled by alkali and it was difficult to form a sodium salt. However, when the alkalizing time was too long the degradation of SG was aggravated, which resulted in the reduc-

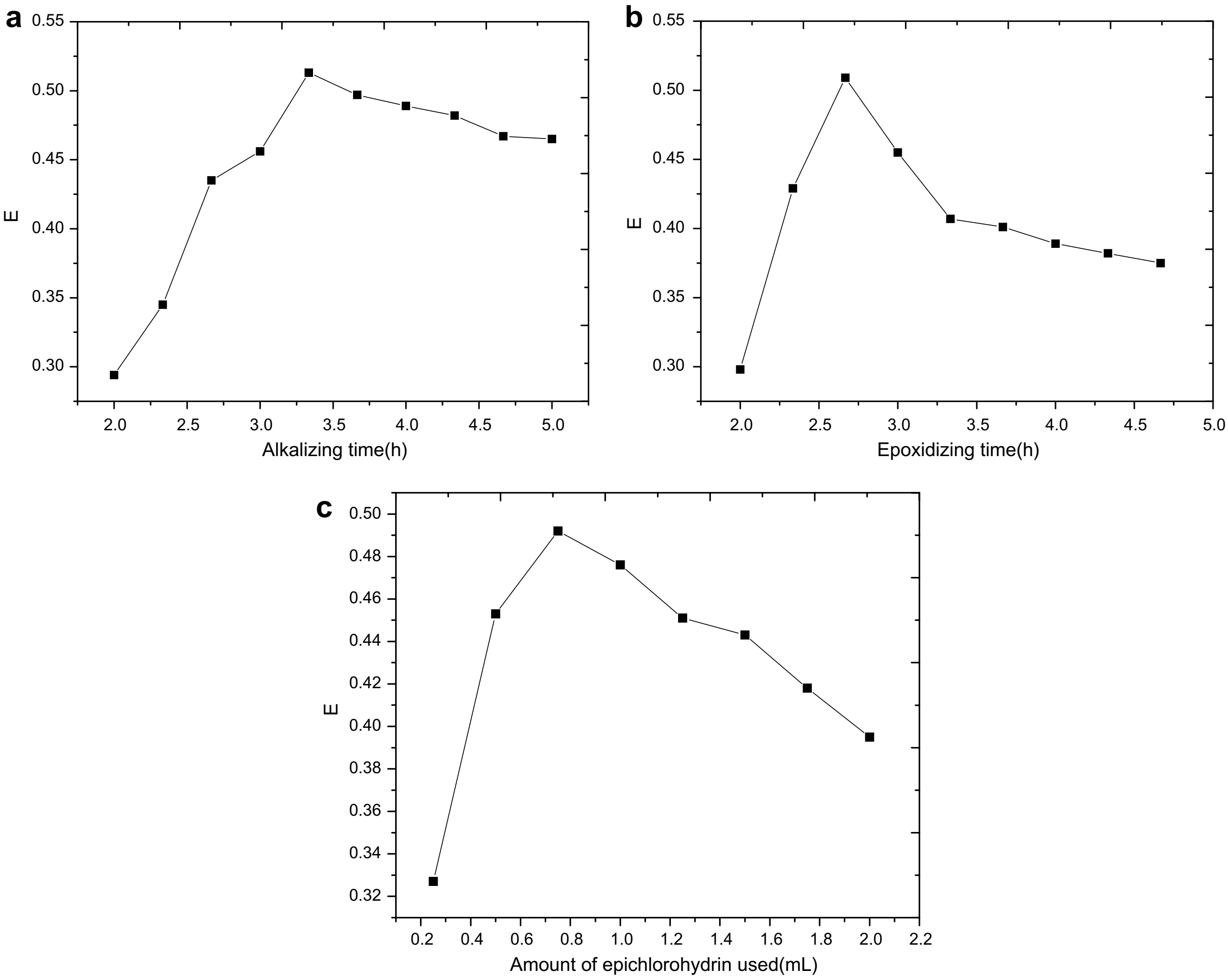


Fig. 3. (a) Variation of epoxide number (*E*) with alkalizing time. (b) Variation of epoxide number (*E*) with epoxidizing time. (c) Variation of epoxide number (*E*) with amount of epichlorohydrin.

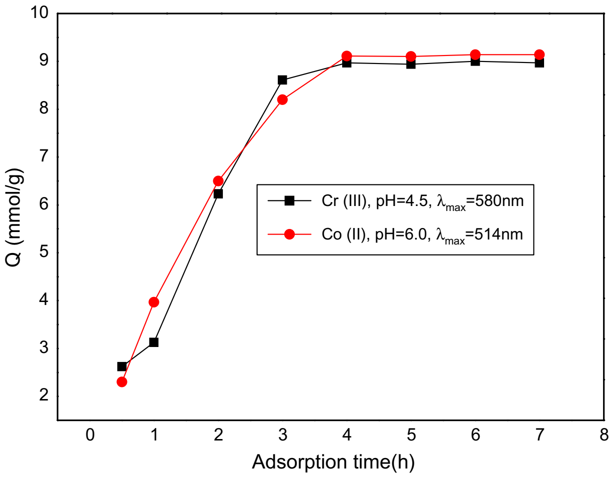


Fig. 4. Kinetics curve of adsorption.

tion of the epoxide number. And too short epoxidizing time would cause incomplete epoxidizing reaction, but too long epoxidizing time could make reactants existing in the system homopolymerize, which thereby will disturb the measurement of epoxide number. In addition, too much of epichlorohydrin could cause a small molecule homopolymer increasing, and they may be adsorbed to surface of alkalized SG, which will reduce the reaction activity.

3.3. Adsorption performance of SGDSA

The adsorption capacity of SGDSA for Cr (III) and Co (II) ions was determined with values of 9.14 mmoL/g for Cr (III) and 8.99 mmoL/g for Co (II). Fig. 4 shows the relationship between the adsorption amount with the adsorption time. The nearly identical adsorption density of the ions on SGDSA suggests that the same functional groups of SGDSA participate in the binding of the metals to the resin. For two kinds of metal ions the adsorption equilibrium can be reached in about 4 h.

4. Conclusion

Sesbania gum supported dithiocarbamate chelating resin was prepared. It is evident that the epoxidation reaction is a key step during the preparation of SGDSA. The influencing factors on the epoxide number mainly comprise alkalizing time, epoxidizing time, and the amount of epichlorohydrin used. In addition, using phase transfer catalyst can increase epoxide number. Based on our experiment results the optimal reaction condition is as following: the concentration of aqueous solution of sodium hydroxide, the alkalizing time, the epoxidizing time and the amount of epichlorohydrin used are 2.75 mol/L, 3.5 h, 2.5 h, and 1.0 mL per 1 g of SG, respectively. The resulting resin exhibits high adsorption capacity for some metal ions and the adsorption equilibrium could be arrived in shorter time.

Acknowledgments

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References

Chen, Y. P., & Gu, Z. M. (1982). Preparation and properties of macroporous chelate resins of crosslinked polystyrene bearing dithiocarboxylated polyethylene polyamines. *Polymer Communications, 6*, 443.

Cui, Y. C., Wang, X. H., Li, D. L., Li, M. Y., & Zhou, D. P. (2004). Preparation and flocculating effect of quaternary ammonium cationic sesbania gum. *Chinese Journal of Applied Chemistry, 21*(7), 717.

Cui, Y. C., & Zhang, L. (2005). Studies on the catalysis of sesbania gum supported palladium compound for Heck reaction. *Acta Polymerica Sinica, 3*, 423.

Fan, C. L., Zhu, L. F., Yang, Y. X., Gu, H. W., & Tang, M. S. (2000). Quantum chemistry calculation of sesbania gum molecule. *Journal of Biology, 17*(5), 24.

He, Y. B., Meng, L. Z., Chen, F. J., Hu, L., & Chen, Y. Y. (1998). Preparation and adsorptive property of nitrogen containing cotton stalk cellulose derivatives. *Applied Chemistry, 3*, 94.

Huang, Q. H., Gao, W. S., & Shi, W. Y. (1980). Studies on molecular weight and chemical modification of sesbania gum. *Acta Botanica Sinica, 22*, 379.

Liu, Z., Tian, X. L., & Jiang, X. M. (1999). The synthesis and adsorption properties of the chelating resin of crosslinking chitosan condense with salilylaldehyde. *Ionic Interchange and Adsorption, 15*, 432.

Ma, X. D., & Pawlik, M. (2005). Effect of alkali metal cations on adsorption of guar gum onto quartz. *Journal of Colloid and Interface Science, 289*, 48.

Mathew, B., & Pillai, V. N. R. (1992). *N, N*-methylene-bis-acrylamide-crosslinked polyacrylamides as supports for dithiocarbamate ligands for metal ion complexation. *Polymer International, 3*, 28.

Minagawa, K., & Takizawa, Y. (1980). Determination of very low levels of inorganic and organic mercury in natural waters by cold-vapor atomic adsorption spectrometry after preconcentration on a chelating resin. *Analytica Chimica Acta, 115*, 103.

Rao, G. H., Mao, Y. H., Wu, N. P., & Zeng, L. J. (1995). Study on chemical modification of sesbania gum. *Hydrometallurgy, 54*, 10.

Rwddy, T. T., & Tammishetti, S. (2004). Free radical degradation of guar gum. *Polymer Degradation and Stability, 86*, 455.

Sun, B., Gu, C. J., Ma, J. H., & Liang, B. R. (2003). Characterization of structure and properties of the oxidized regenerated cellulose. *Journal of Donghua University, 29*(1), 98.

Sun, Y. K., Zhang, J., & Yan, X. L. (2001). Application investigation of sesbania gum in cigarette paper. *Paper Sinensis, 22*, 44.

Tang, Y. X. (1995). Development of study on chemical modification of guar gum and sesbania gum. *Mining and Metallurgy, 4*, 67.

Wang, Z. M., He, X. X., & Sun, D. Q. (1990). *Practical infrared adsorption spectroscopy*. Beijing: Oil Industry Press (p. 313).

Wang, C. S., Huang, Q. H., Li, X., & Hua, J. (1982). *Sesbania gum and its applications*. Beijing: Science Press (p. 20).

Wang, J., Somasundaran, P., & Nagaraj, D. R. (2005). Adsorption mechanism of guar gum at solid–liquid interfaces. *Minerals Engineering, 18*, 77.

Wang, Z., Zhu, L. F., Zhang, G. B., Zhao, G. S., & Zhu, Y. (1996). Investigation of the thermal decomposition kinetics of modified carboxyl hydroxypropyl sesbania gum. *Acta Physico-Chimica Sinica, 12*(7), 598.

Xiang, B., Li, Y. J., & Ni, Y. M. (2003). Adsorption properties of DTC-starch for copper. *Nonferrous Metals, 55*(4), 54.

Yamagami, E., Taleishi, S., & Hashimoto, A. (1980). Application of a chelation of trace amounts of mercury in natural waters. *Analyst, 105*, 491.