



## Adsorption of Cd(II) and Cu(II) by Epichlorohydrin and Cysteine Modified Bagasse

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A new adsorbent for heavy metal ions removal was obtained by modifying bagasse with epichlorohydrin and cysteine. Bagasse was reacted with epichlorohydrin then grafted with cysteine to produce modified-bagasse. Adsorption behaviours of original-bagasse and modified-bagasse for Cd<sup>2+</sup> and Cu<sup>2+</sup> were studied. The cysteine modification was effective at introducing carboxyl and sulfhydryl groups into bagasse. SEM, XPS and FTIR were used to determine the characteristics of original-bagasse and modified-bagasse. The results showed that modified-bagasse had a porous and loose surface covered with carboxyl and sulfhydryl groups, which was beneficial to removing Cd<sup>2+</sup> and Cu<sup>2+</sup> from wastewater. In the range of experiments, modified-bagasse can reach a maximum saturated adsorption capacity ( $Q_{max}$ ) of 1.092 and 1.122 mmol/g, compared with 0.233 and 0.272 mmol/g of original-bagasse for Cd<sup>2+</sup> and Cu<sup>2+</sup> at 25 °C, respectively. Lower temperature was favourable for the process of adsorption of modified-bagasse. The results indicated that the adsorption property of modified-bagasse had been enhanced obviously, which could be utilized as a potential and promising metal ion adsorbent.

**Key Words:** Bagasse, Epichlorohydrin, Cysteine, Adsorption, Metal ion.

### INTRODUCTION

Bagasse is an abundant and low-cost agricultural byproduct, it can be used as a fuel for the boilers or as a raw material for the manufacture of pulp and paper products, various types of building boards<sup>1</sup>. However, huge quantities of the remaining bagasse are burnt in the fields or on the road and the pollution caused by burning agricultural residues has been a serious problem, particularly in China<sup>2</sup>. The direct utilizations are limited and bagasse needs to be modified for improving value as a renewable material. Chemical modification of agricultural byproduct is one of methods for improving value. Many agricultural byproducts have been utilized for the preparation of different metal ion adsorbents by a series of chemical modification. Such as bagasse was modified with EDTA and carbon disulfide to get the adsorbent contained sulfur and nitrogen<sup>3</sup>, another way modified with different cyclic anhydride for adsorption of metal ion<sup>4</sup>. Marine brown algae was also prepared for an adsorption treated with epichlorohydrin<sup>5</sup>. On the basis of modification with epichlorohydrin, some diverse metal ion adsorbents were prepared by further grafted with polyamine<sup>6</sup>.

Hydroxyl groups are the most abundant in bagasse and can be used for chemical modification. In this study, a new adsorbent was obtained by grafting of epichlorohydrin onto hydroxyl of bagasse and reacted with cysteine. It had carboxyl

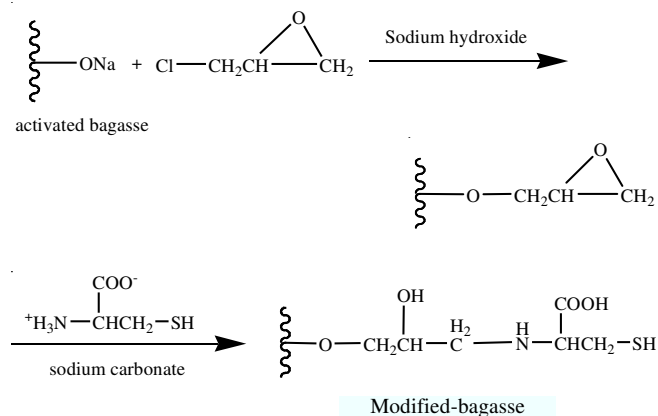
and sulfhydryl groups in their molecules and showed good adsorbent properties for metal ions. To our best of knowledge, the grafting of epichlorohydrin and cysteine on bagasse for heavy metals removal has not been reported. As an evaluation, the adsorbent was examined for their performance in Cd<sup>2+</sup> and Cu<sup>2+</sup> removal.

### EXPERIMENTAL

Bagasse was purchased from Yunnan market of China. Epichlorohydrin (BE), cysteine, CuSO<sub>4</sub>·5H<sub>2</sub>O, 3CdSO<sub>4</sub>·8H<sub>2</sub>O and sodium carbonate were purchased from Shanghai Chemical Reagent Company, China.

**Preparation of original-bagasse, BE and modified-bagasse:** The method for functionalization of bagasse is illustrated in **Scheme-I**. Experimental bagasse was crushed, washed and dried to obtain original-bagasse. The first stage in the preparation was the reaction between epichlorohydrin and the hydroxyl groups on original-bagasse. 1 g of original-bagasse was immersed in 10 % (w/v) NaOH solution for 20 h and it was collected after filtered and dried. Then the material was reacted with 5 mL of BE and 10 mL of 3 mol/L NaOH solution under stirring for 24 h at room temperature. The filtered material was washed with distilled water and ethanol alternately and dried at 60 °C to obtain modified bagasse with epichlorohydrin. The second stage of the preparation procedure is as following:

Epichlorohydrin was mixed with 0.2 g of cysteine, 0.25 g of  $\text{Na}_2\text{CO}_3$  and 25 mL of distilled water and reacted under stirring for 5 h at 50 °C. Finally, the modified-bagasse was obtained after washed with distilled water and ethanol alternately and further dried at 45 °C until constant weight.



**Scheme-I:** Functionalization of modified-bagasse with epichlorohydrin and cysteine

### Adsorption experiments

**Kinetic study of metal ions adsorption:** Experiments with each sample and metal ion were performed to determine the adsorption equilibrium time. The interval times used were from 10-180, 10-150 and 5-80 min for original-bagasse, BE and modified-bagasse, respectively. An amount of 200 mg from original-bagasse and BE, 100 mg from modified-bagasse were placed in a 100 mL conical flask with 25 mL of metal ion solution at fixed concentrations (500, 500 and 500 mg/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; 500, 500 and 500 mg/L  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  for original-bagasse, BE and modified-bagasse, respectively) under constant stirring at room temperature (25 °C). The experiments were done at pH 4.0 for  $\text{Cu}^{2+}$ , 7.0 for  $\text{Cd}^{2+}$ , as optimal values to obtain the best adsorption. After filtered, the filtrates of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  were analyzed with the atomic absorption spectrometer (AA-6501, Shimadzu, Japan).

**pH study of metal ions adsorption:** Experiments with each sample and metal ion were performed to determine the effect of pH on metal ion adsorption. 100 mg of modified-bagasse were placed in a 100 mL conical flask with 25 mL of metal ion solution at fixed concentrations (500 mg/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 500 mg/L  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ) under constant stirring at room temperature (25 °C). The pH range studied was from 1-5 for  $\text{Cu}^{2+}$  and 3-8 for  $\text{Cd}^{2+}$ . The pH was adjusted with HCl or NaOH solutions at 0.01-1.0 mol/L. The reaction times used were obtained from the kinetic study. After filtration, the metal ion concentration was determined as earlier described and the pH was corrected during each experiment.

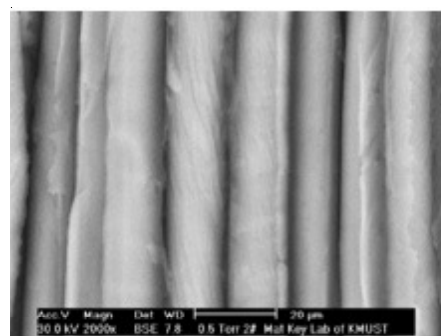
**Adsorption isotherms:** Experiments were performed for each sample and metal ion to determine adsorption isotherms. In the experiment, 100 mg of modified-bagasse was placed in a 100 mL conical flask with 25 mL of metal ion solution at specific concentrations from 300-500 mg/L under constant stirring at different temperatures (25, 35 and 45 °C). 200 mg of original-bagasse and 200 mg of BE were both treated in accordance with modified-bagasse determined at 25 °C. Each

experiment was performed at the pH of the greatest ion adsorption during the time necessary for equilibrium. After filtered, the metal ion concentration was determined as earlier described.

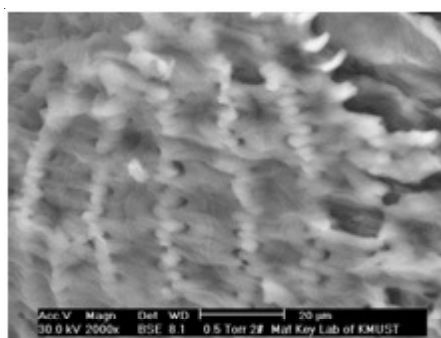
**Characterization:** Scanning electron microscopy (XL30SEM), X-ray photoelectron spectroscopy (PHI5600) and FT-IR (4000-400  $\text{cm}^{-1}$ , WQF-200) were used to characterize the properties of modified-bagasse and show the differences with original-bagasse.

## RESULTS AND DISCUSSION

**Characterization of original-bagasse and modified-bagasse:** As shown in Fig. 1, there existed obvious distinguish between original-bagasse (Fig. 1a) and modified-bagasse (Fig. 1b). Before modification, original-bagasse (Fig. 1a) showed fibrous tubular structure and was smooth and orderly. But it became broken and rough after grafted by epichlorohydrin and cysteine. Part of the original groups of surface were replaced and bagasse became to be a concave convex modified-bagasse (Fig. 1b) showed with porous and loose structure. Compared to original-bagasse, the surface area of modified-bagasse was increased. The modified process improved the adsorption capacity of bagasse.



(a)



(b)

Fig. 1. SEM images of original-bagasse (a) and modified-bagasse (b)

The modified-bagasse was confirmed by IR analysis and the results are shown in Fig. 2. As shown in Fig. 2(a), the major chemical group of original-bagasse appeared broad band at the wavenumber region of 3500-3300  $\text{cm}^{-1}$ , which was the hydroxyl group. There existed the same strong broad band with modified-bagasse observed in Fig. 2(b), but the absorbance was increased due to the introduction of N-H of cysteine, overlapping between the N-H and the O-H stretching vibrations.

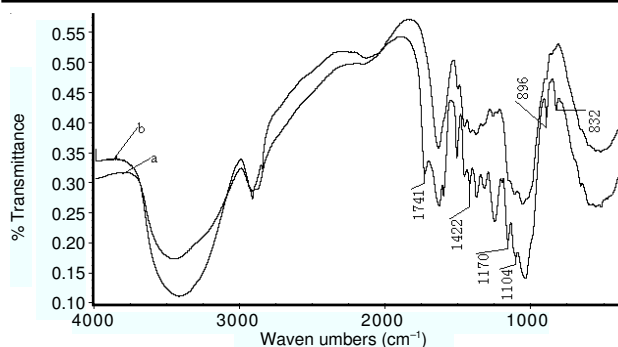


Fig. 2. FTIR spectra of original-bagasse (a) and modified-bagasse (b)

Compared to that of original-bagasse (Fig. 2a), the spectrum of modified-bagasse (Fig. 2b) has characteristic peaks of epoxy group at 896 and 832  $\text{cm}^{-1}$  and the absorption intensity of methylene at 1422  $\text{cm}^{-1}$  was enhanced. It proved that epichlorohydrin had been successfully grafted into original-bagasse through etherification. But not all of epoxy groups participated in the following reaction. Moreover, the characteristic peak of carboxyl was observed at 1741  $\text{cm}^{-1}$  (Fig. 2b) while no absorbance found with original-bagasse (Fig. 2a). And the absorption peak intensity at 1170  $\text{cm}^{-1}$  (C-O) and 1104  $\text{cm}^{-1}$  (C-N) of modified-bagasse were obviously enhanced from original-bagasse, which suggested that cysteine participated in the reaction and successfully grafted.

XPS C 1s spectra of original-bagasse and modified-bagasse are shown in Fig. 3. The area of signal at 286.15 eV (Fig. 3b), which was attributed<sup>7</sup> to carbon of C-O, was larger than that of signal at 286.30 eV showed in Fig. 3a. It indicated that epichlorohydrin had been grafted to bagasse by etherifi-

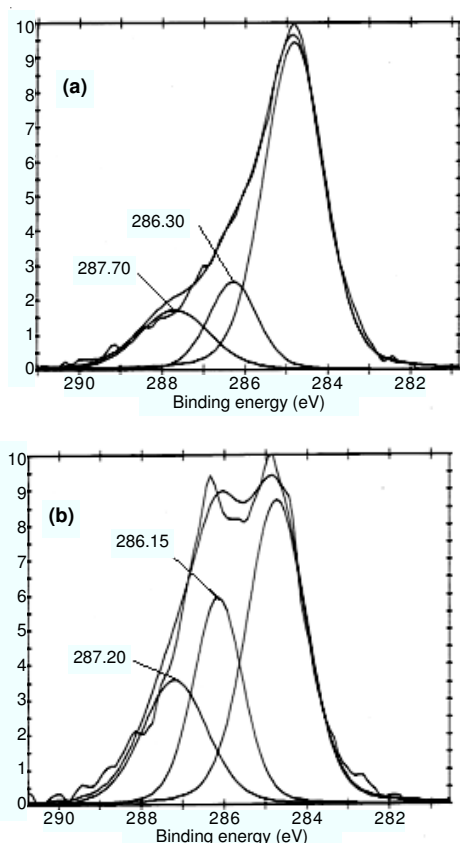


Fig. 3. XPS C 1s spectra of original-bagasse (a) and modified-bagasse (b)

cation, enhanced the content of carbon of C-OH. Moreover, the signal at 287.2 eV (Fig. 3b) was stronger than that at 287.70 eV (Fig. 3a), which indicated the content of carbon in C=O was increased. It was due to the introduction of cysteine containing carboxyl group. Furthermore, there was a signal at 164.65 eV in S 1s spectra of modified-bagasse, but not found with original-bagasse. It confirmed furtherly the introduction of cysteine.

### Study of adsorption of metal ions

**Adsorption kinetics:** The adsorption equilibrium time experiments were carried out for different contact times with a fixed adsorbent quantity (200 mg original-bagasse, 200 mg BE and 100 mg modified-bagasse) with 25 mL of metal ion solution at a pH of 4.0 for  $\text{Cu}^{2+}$  and 7.0 for  $\text{Cd}^{2+}$  at a fixed concentration. The adsorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions increased with contact time up. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles<sup>8</sup>. The equilibrium time was achieved after 150, 130 and 60 min for  $\text{Cu}^{2+}$ ; 150, 120 and 60 min for  $\text{Cd}^{2+}$  for original-bagasse, BE and modified-bagasse, respectively. In contrast with original-bagasse and BE, the adsorption equilibrium time of modified-bagasse was shortened obviously. It indicated that the readily available and easily accessible organic groups on modified-bagasse were probably due to the facilitated transportation of metal ions during the adsorption. The adsorption equilibrium times mentioned above were chosen for pH and concentration dependent experiments.

**Effect of pH on metal ion adsorption:** The removal of metal ions from aqueous solutions by adsorption is dependent on the solution pH, as it affects adsorbent surface charge, the degree of ionization and the species of adsorbates. Adsorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  in modified-bagasse as a function of pH was shown in Fig. 4. The adsorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  increased significantly with the increase of solution pH. The maximum removal of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  was observed at pH 4.0 and 7.0, respectively.

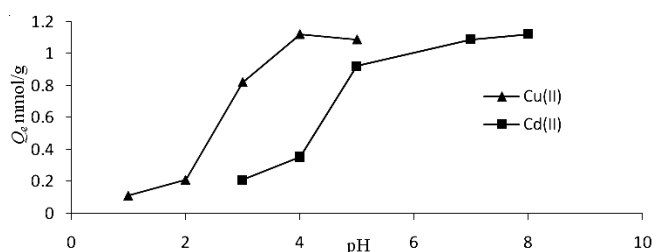


Fig. 4. Effect of pH value on adsorption capacity

The dependence of metal ions uptake on pH is related to the surface functional groups of the adsorbent. At low pH (e.g., pH 1), the -SH and  $-\text{COO}^-$  groups in modified-bagasse are protonated where metal ion must compete with the proton<sup>9</sup>. At high pH, -OH, -SH and -COOH are ionized, therefore, the formation of specific interaction with metal ions is more pronounced. In addition, the surface charge density also played a significant role on metal ions adsorption. At pH > 3.0 and 4.0 the negative charge of modified-bagasse was favourable to the removal of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , respectively. However, adsorption experiments could not be performed at pH > 6.0 and 8.0 for

Cu<sup>2+</sup> and Cd<sup>2+</sup>, respectively due to the insolubility of metal hydroxide.

**Adsorption isotherms:** Adsorption isotherms provided valuable information on the interactions between metal ions and adsorbents. Adsorption isotherm of original-bagasse, BE and modified-bagasse was determined on the basis of the equilibrium time. Langmuir and Freundlich isotherms were used to fit the experimental data. The results suggested that Langmuir isotherm showed better agreement with the real adsorption processes for original-bagasse, BE and modified-bagasse and it is expressed as:

$$\frac{1}{Q_e} = \frac{1}{(bQ_{\max}C_e)} + \frac{1}{Q_{\max}} \quad (1)$$

where  $C_e$  (mmol/L) is the equilibrium concentration of solutions,  $Q_e$  (mmol/g) and  $Q_{\max}$  (mmol/g) are the equilibrium loading capacity and the saturated adsorption capacity, respectively.  $b$  (L/mmol) is Langmuir constant.

Langmuir isotherm fits well with the experimental data. This may be due to homogenous distribution of active sites on the sample, since the Langmuir equation assumes that the surface is homogenous<sup>10</sup>. Adsorption isotherms of modified-bagasse at different temperatures were listed in Table-1. The results indicated that lower temperature was in favour of adsorption for modified-bagasse and the saturated adsorption capacity reduced when increasing temperature. As shown in Table-2. Modified-bagasse presented greater saturated adsorption capacity ( $Q_{\max}$ ) and larger bond energy between metal and sample than BE and original-bagasse for Cu<sup>2+</sup> and Cd<sup>2+</sup>. It achieved the saturated adsorption capacity ( $Q_{\max}$ ) of 1.092 and 1.122 mmol/g for Cu<sup>2+</sup> and Cd<sup>2+</sup> at 25 °C, respectively. The increase of the adsorption capacity ( $Q_{\max}$ ) of modified-bagasse in relation to original-bagasse and BE for Cu<sup>2+</sup> and Cd<sup>2+</sup> can be explained by the fact that modified-bagasse had carboxyl and sulfhydryl groups in their molecules.

TABLE-1  
ADSORPTION ISOTHERMS OF MODIFIED-BAGASSE  
AT DIFFERENT TEMPERATURES

Metal ion	Temp. (°C)	Fitting curves of the Langmuir isotherm	R <sup>2</sup>	Q <sub>max</sub> (mmol/g)
Cd(II)	25	1/Q <sub>e</sub> = 0.273/C <sub>e</sub> + 0.916	0.997	1.092
	35	1/Q <sub>e</sub> = 0.401/C <sub>e</sub> + 1.260	0.992	0.794
	45	1/Q <sub>e</sub> = 0.538/C <sub>e</sub> + 1.592	0.997	0.628
Cu(II)	25	1/Q <sub>e</sub> = 0.276/C <sub>e</sub> + 0.891	0.998	1.122
	35	1/Q <sub>e</sub> = 0.411/C <sub>e</sub> + 1.200	0.995	0.833
	45	1/Q <sub>e</sub> = 0.543/C <sub>e</sub> + 1.576	0.998	0.634

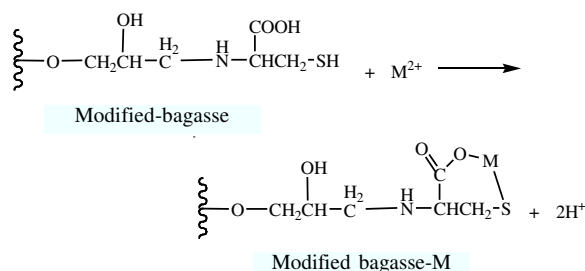
TABLE-2  
ADSORPTION ISOTHERMS OF MODIFIED-BAGASSE (MB),  
BE AND ORIGINAL BAGASSE (OB) AT 25 °C

Metal ion	Sample	Fitting curves of the Langmuir isotherm	R <sup>2</sup>	Q <sub>max</sub> (mmol/g)
Cd(II)	MB	1/Q <sub>e</sub> = 0.273/C <sub>e</sub> + 0.916	0.997	1.092
	BE	1/Q <sub>e</sub> = 9.888/C <sub>e</sub> + 3.098	0.994	0.323
	OB	1/Q <sub>e</sub> = 11.37/C <sub>e</sub> + 4.293	0.994	0.233
Cu(II)	MB	1/Q <sub>e</sub> = 0.276/C <sub>e</sub> + 0.891	0.998	1.122
	BE	1/Q <sub>e</sub> = 10.02/C <sub>e</sub> + 2.929	0.995	0.341
	OB	1/Q <sub>e</sub> = 11.90/C <sub>e</sub> + 3.672	0.997	0.272

**Adsorption mechanism of metal ion onto modified-bagasse:** Langmuir isotherm corresponds to a dominant ion exchange mechanism and which may be the principal mechanism for the removal of metal ion onto modified-bagasse. Bagasse

consists mainly of cellulose, hemicelluloses and lignin. From the nature of material which have certain adsorption of heavy metal ions, it can be speculated that cellulose, hemicelluloses and lignin are the active ion exchange compounds and that active sites are the hydroxyl groups of those compounds.

Part of hydroxyl groups of bagasse were used for the modification with epichlorohydrin and cysteine. So the modified-bagasse had hydroxyl, carboxyl and sulfhydryl groups in their molecules. Based on the structure of these groups, a possible mechanism could be considered as a divalent heavy metal ion (M<sup>2+</sup>) attaches itself to adjacent carboxyl and sulfhydryl groups, sulfur and one of two oxygens of carboxyl groups could donate two pairs of electrons to metal ions, forming six coordination number compounds and releasing two hydrogen ions into solution (**Scheme-II**)<sup>11,12</sup>.



**Scheme-II:** Adsorption of metal ion onto modified-bagasse

## Conclusion

Base on the above results, it can be concluded that the incorporation of epichlorohydrin and cysteine into original-bagasse at alkaline condition was an efficient chemical modification for obtaining modified-bagasse with carboxy groups and sulfhydryl groups. And modified-bagasse can be utilized as a new metal ion adsorbent. The loading capacity was significantly increased by coupling with cysteine. Compared to original-bagasse, the saturated adsorption capacity of modified-bagasse increased about 5 times and achieved 1.092 and 1.122 mmol/g for Cd<sup>2+</sup> and Cu<sup>2+</sup> at 25 °C, respectively. The result revealed that modified-bagasse was a potential metal ion adsorbent.

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