

Modification of jute by use of triethylenetetramine and its adsorption behavior for copper (II)

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Keywords: modified jute fiber; adsorption; copper ions; amino groups;

Abstract. An efficient adsorbent for Cu (II) removal from aqueous solution was synthesized by grafting amino group onto jute fiber. The fiber was chemically modified by two steps, loading of epoxy chloropropane and triethylenetetramine. Properties of the modified jute such as surface chemical structure, tensile strength and adsorption capacity on different environmental conditions were conducted. The results show that the adsorption capacity of the modified jute on Cu (II) is 120.048mg.g⁻¹ at 30°C, and the modified jute has strong anti-interference ability.

Introduction

The removal of heavy metal ions in the emergency water treatment can be achieved by several methods. Among these methods, adsorption method is widely used as disposal technology in our country^[2]. Activated carbon that is available in large quantities, but practical applications required bagging treatment. which can lead to larger fluid resistance, and reduce the adsorption efficiency^[12]. At present, the cotton fiber, straw fiber, corn stalks, sawdust, bagasse^[11/7/4] and other materials have been used to prepare a chelating fiber, but more material prepared as a powder, it is difficult to adapt to the requirements of emergency water treatment. Jute fiber is inexpensive and available in large quantities, and has good ability to resist shear, facilitate direct delivery and recovery in practice, which can realize low flow resistance, high mass transfer adsorption treatment effect. In this paper, jute fiber was studied to determine its efficiency in removing of copper from simulated contaminated samples. In order to increase the adsorption capacities, jute fiber was modified by two-step reaction. The effects of the polyamine type of heavy metal ions adsorbed material has good performance and has important environmental benefits.

Experimental

Materials

Firstly, jute was cleaned to remove surface floating dust, and then boiling for 30 min to make some organic dissolution, after that jute was drying at 70°C. Pretreatment was going with a certain concentration of NaOH solution soaking 30 min and then washing to neutral using deionized water, after that jute was drying at 70°C. In the grafting reaction, the experimental conditions were 1g jute after pretreatment, taking DMF as solvent, under the condition of 90°C water bath conditions. The epoxy chloropropane was joint to the solvent as first step reaction; at second step, adding triethylenetetramine. After grafting, jute was filtrated several times and then dried at 70°C.

Adsorption tests

The effect of experimental parameters such as temperature, pH, coexisting ions, adsorption isotherms and thermodynamics of Cu (II) were investigated. The impact of temperature and pH were studied via adding suitable amount of jute before and after modification at different temperature and pH respectively. After 3h adsorption reaction, Cu (II) concentration of the solution was measured. We chosen K⁺, Na⁺, Ca²⁺, Mg²⁺ as coexisting ions containing different concentrations respectively, the initial concentration of Cu (II) was 300mg.L⁻¹, at the same time, adding suitable amount of modified jute, the adsorption results were measured for 3 h at room

temperature.

Analytical methods

The infrared spectra of the jute before and after modification were analyzed by the Perkin-Elmer Spectrum One B Fourier Transform Infrared (FT-IR) spectrometer. Surface morphology analysis (SEM) was analyzed by field emission environmental scanning electron microscope magnified 5000 times after spraying gold. And mechanical strength test was analyzed by using electronic universal material testing machine. When the adsorption behavior reached equilibrium, biscy clohexanone oxaldihydrazone spectrophotometer ^[12] was used to determine the concentration of Cu ($R^2 = 0.9996$). Jute for Cu (II) adsorption capacity is calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where q_e is the equilibrium adsorption capacity/mg.g⁻¹; C_0 、 C_e is initial solution and adsorption equilibrium Cu (II) concentration/mg.L⁻¹; V is the volume of solution/L; m is the adsorbent dosing quantity/g.

Results and discussion

Preparation of modified Jute

The preparation routes of the modified jute are shown in the following. According to the synthetic route, we designed the L_9 (3^4) level of form factors by modified jute for Cu (II) adsorption. Each set of experiment was performed twice, and the results were compared using analysis of variance.

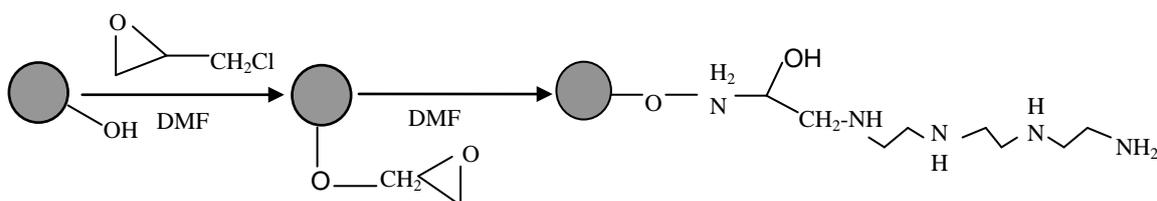


Table 1 Factors and levels table of orthogonal experiment

Factor	A temperature /°C	B Epoxy chloropropane: triethylenetetramine /mL	C Etherification time/h	D Amination time/h
Level				
1	90	10: 5	0.5	0.5
2	70	5:5	1	1
3	50	5:10	3	3

When we analysed the influence of different elements in the grafting reaction, we used the saturated adsorption capacity of Cu (II) to describe the property of modified jute. And the results were shown in Table 2. As shown in Table 2, the effect of the four factors was significant, indicating a successful graft. And at the same time, by comparison k_{ij} values, we chosen A1B1C2D3 as the optimal combination. In order to describe the results significantly, we used variance analysis to analysis the experimental data, and the results were shown in Table 3.

Table 2 Intuitive analysis method

experimental group	A	B	C	D	Q_e / mg.g ⁻¹	Q_e / mg.g ⁻¹
1	90	10:5	0.5	0.5	70.713	72.791
2	90	5:5	1	1	72.045	79.951
3	90	5:10	3	3	82.586	86.272
4	70	10:5	1	3	57.290	52.289
5	70	5:5	3	0.5	20.356	24.983
6	70	5:10	0.5	1	21.561	19.133
7	50	10:5	3	1	29.345	22.071

8	50	5:5	0.5	3	13.640	14.806
9	50	5:10	1	0.5	10.018	16.968
k_{1j}	77.393	50.750	35.441	35.972		
k_{2j}	32.602	37.630	48.093	40.684		
k_{3j}	17.808	39.428	44.269	51.147		
range	59.585	13.120	12.652	15.175		
Factor main->minor	A>D>B>C					

Table 3 Analysis of variance table

Sources of variance	Sum of squares	Freedom of motion	Mean square	F value	$F_{0.05}$	Significant t
A	2887.734	2	1443.867	110.451		***
B	152.416	2	76.208	5.830	4.26	*
C	126.315	2	63.157	4.831		*
D	180.979	2	90.489	6.922		*
Error	117.653	9	13.073			
SS_T	3465.097	17				

F test showed that: the impact of temperature on the grafting reaction is extremely significant, the amination time and reagent ratio on jute modification effect significantly. In summary, after the reaction jute fiber has been connected to the corresponding groups, and optimal reaction conditions are A_1 (grafting temperature 90°C), B_1 (reagent ratio of epoxy chloropropane 10mL: triethylenetetramine 5mL), C_2 (etherification time 1h), D_3 (amination time 3h).

Structural and morphological analysis before and after modification of jute

1) Infrared Characterization of jute before and after modification

The surface modification of the jute fiber before and after modification was confirmed by FT-IR. As shown in Fig.1, peaks of $3200\text{-}3700\text{cm}^{-1}$ were ascribed to the N-H stretching vibration significantly, near the peak of 1600cm^{-1} was the -NH₂ bending vibration, 1568cm^{-1} department to -NH bending vibration absorption peak, 1260cm^{-1} was -CN stretching vibration. Infrared spectrum analysis showed that after reaction amino groups were grafted successfully on the surface of jute [10]

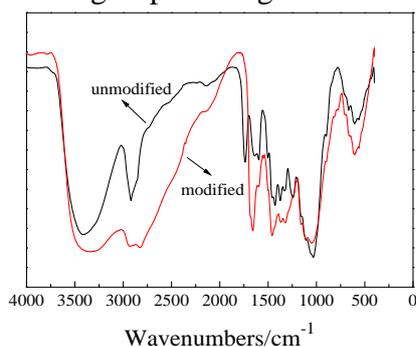


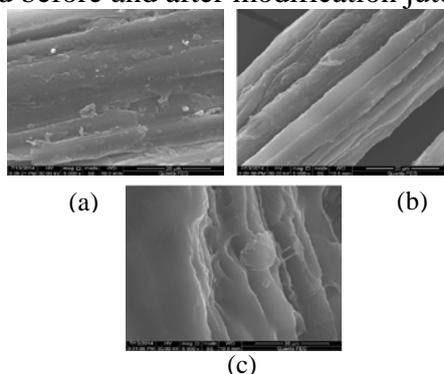
Fig.1 The graph of FTIR analysis

2) SEM analysis

We used the optimal reaction conditions to prepare jute modified materials, and the adsorption capacity was measured obtaining at $120.048\text{mg}\cdot\text{g}^{-1}$, at the same time, the saturated adsorption of the unmodified jute was only $7.694\text{mg}\cdot\text{g}^{-1}$, after the mass fraction of 15% NaOH treatment, jute adsorption capacity was $10.076\text{mg}\cdot\text{g}^{-1}$.

Through the SEM test on unmodified, alkali treatment and modified jute magnified 5000 times, we could directly observe the surface change of different treatment on jute. As can be seen from Figure 2, before modification, the surface of jute (a) was covering a lot of gum; jute after alkali treatment (b) was bundle, the possible reason was because of pretreated with alkaline NaOH solution, the glial layer was damaged, and colloidal low molecular weight materials of jute surface such as pectin, lignin was dissolved, making the inside of the cellulose exposed [5]. That is conducive to the grafting reaction between cellulose and modified material. The surface groove

of modified jute (c) was conducive to the adsorption reaction. This is consistent with the above-described adsorption capacity before and after the modification. The results showed that in pretreatment and grafting reaction, the surface structure of jute was obviously changed, and the adsorption quantity improved greatly. To determine the impact of the grafting reaction, the mechanical strength was measured before and after modification jute.



(a) unmodified (b) alkali treatment; (c) modified;
Figure 2 SEM analysis

3) mechanical strength analysis

Choosing the thickness was relatively uniform and the diameter was around 1mm before and after modification, in the same operating conditions the mechanical properties of jute was test, and each group experiment was repeated 5 times. As apparent from Table 4, after alkali treatment the breaking force of jute changed significantly, the jute strength decreased much less after grafting reaction, which was consistent with the results of SEM image, namely because of pretreatment, the surface structure of jute was damaged, thus reduced its mechanical strength. The maximum load of modified jute was decreased significantly, but still could meet the needs of the hydraulic shear resistance, did not affect the use of the emergency in water treatment. After alkali treatment, the extension performance has a certain increase, probably because colloidal substances on the surface of the jute were destroyed to expose the internal base of cellulose, lignin, etc, making its extension performance improved. Probably because of the chemical reaction that it extends the performance of the modified somewhat lower, but still higher than the pre-modified jute.

Table 4 Jute mechanics index

Jute	Breaking force/N	Breaking elongation /%
unmodified	50.489±7.488	1.779±0.413
alkali treatment	15.105±0.718	3.839±0.894
modified	13.817±4.341	2.161±0.236

Experiment Experiments

1) Effect of Temperature

As shown in Fig.3, the higher adsorption capacity obtained at a relatively higher temperature. Obviously, the temperature rise from 10°C to 30°C, the maximum adsorption capacity of the modified jute increased from 67.984mg.g⁻¹ to 121.045mg.g⁻¹. Adsorption capacity of unmodified jute varies small with temperature, and the adsorption volume in 7mg.g⁻¹, far less than the modified jute. This is consistent with the SEM diagram, namely after the grafting reaction of jute, changes in surface morphology is conducive to adsorption reaction.

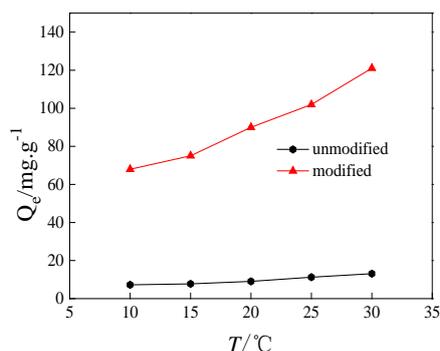


Fig.3 Effect of temperatures T on removal of Cu (II)

2) Effect of pH

Modified jute for Cu (II) adsorption effect along with the change of solution pH is shown in figure 4. As can be seen from Figure 4, when pH ranged from 4 to 6, the adsorption capacity of modified jute for Cu (II) was higher. May be due to lower pH, there was a large number of protons in the solution, part of the amino modified jute could proton reaction with water and hydrogen ions, then produced $-NH^{3+}$ with a positive charge, and produced an electrostatic repulsion with Cu (II) ^[3/9], resulting in low adsorption on Cu (II); when pH was about 5, the free Cu (II) ion was abundance in solution, that was conducive to modified jute adsorption Cu (II). When the pH was too high, Cu (II) was adsorbed by water and formed Cu (OH)₂, that was not conducive to Cu (II) complex with amino. The pH about Cu (II) solution is generally between 4 and 6, so in experimental operation, we can not adjust the pH of solution.

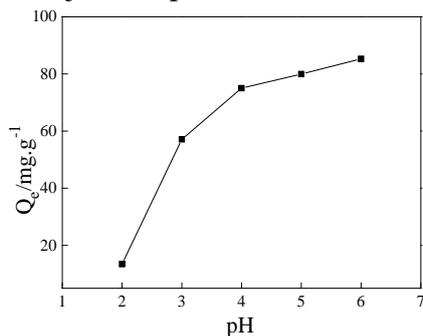


Fig.4 Effect of pH on removal of Cu (II)

3) Effect of coexisting ions

In order to determine the influence of coexisting ions on the adsorption of modified jute, we choose K^+ , Na^+ , Ca^{2+} and Mg^{2+} four kinds of common interfering ions in natural water as the experiment. These coexisting ions on Cu (II) removal efficiency is shown in figure 5. The figure 5 shown that when there were no interference ions, the saturated adsorption capacity of modified jute for Cu (II) was 81.717 $mg.g^{-1}$; and there were interfering ions coexisting, modified jute for Cu (II) adsorption capacity remained at higher levels. Possibly because these ions were no empty tracks available to complex ions.

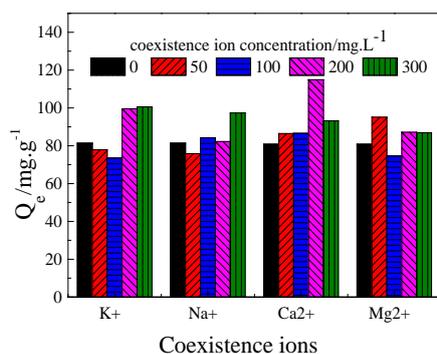


Fig.5 Effect of coexistence ion on removal of Cu (II)

The adsorption kinetics study

Jute before and after modification on Cu (II) adsorption kinetic curve are shown in figure 6. The

figure 6 shown that adsorption quantity on modified jute increased sharply in 20min, after 20min became slowly, until stable, that is modified jute adsorbed Cu (II) in about 20min to reach equilibrium. The modified jute on Cu (II) adsorption equilibrium quantity is 97.512mg.g⁻¹, much higher than the unmodified jute equilibrium adsorption capacity of 7.694mg.g⁻¹.

Kinetics of adsorption process is mainly used to describe the adsorption of solute rate, the data can be fitted by a kinetic model to infer its adsorption mechanism. Both of the unmodified and modified jute were analyzed by pseudo-first-order, pseudo-second order [8], and the results are shown in table 5. Quasi secondary dynamics equation has the significance level to describe the adsorption kinetics, and can well describe the adsorption process; theoretical equilibrium adsorption capacity before and after modification of jute were 7.959 mg.g⁻¹ and 100.705mg.g⁻¹, in accordance with the experimental data.

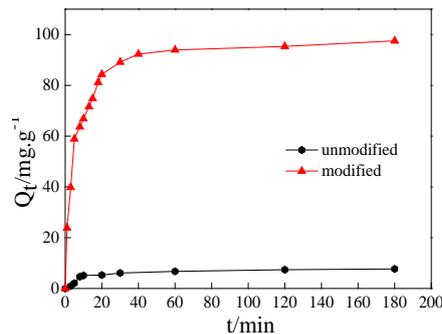


Fig.6 Cu (II) adsorption kinetics of jute

Adsorption isotherms study

At 25⁰C, we configured a series of different concentrations of Cu (II) solution, adding suitable amount of modified jute to 100ml Cu (II) solution, and the adsorption process designed for 12 h at constant temperature water. After adsorption we determined the concentration of Cu (II) solution, and obtained the adsorption isotherm of modified jute, and its Langmuir isotherm and Frundlich fitting results shown in Figure 7 and Table 6. The figure 7 shown that modified jute for Cu (II) adsorption quantity increased with the initial concentration, and the maximum adsorption capacity can reach 112.981mg.g⁻¹, The table 6 shows that the adsorption process conforms to the Langmuir theory [2], which is more homogeneous modification of the surface properties of materials; the adsorption process is single dynamic adsorption.

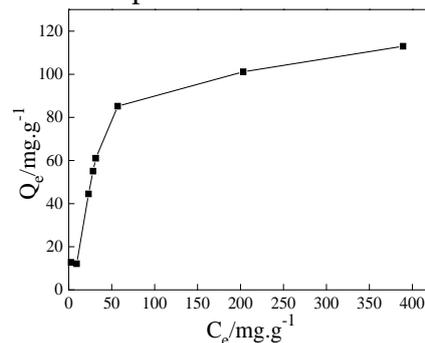


Fig.7 The isothermal line of adsorption of modified jute against Cu (II)

Table 5 Regression coefficient of Cu²⁺ adsorption kinetics

Jute fiber	First order kinetic model			Second order kinetic model		
	q _e /mg.g ⁻¹	k ₁ /min ⁻¹	R ²	q _e /mg.g ⁻¹	k ₂ /g.(mg.min) ⁻¹	R ²
unmodified	4.828	0.0274	0.871	7.959	0.0154	0.998
modification	47.785	0.0416	0.872	100.705	0.00431	0.997

Table 6 Regression coefficient of Cu²⁺ adsorption isotherm

Q _m / mg.g ⁻¹	Langmuir		Freundlich		
	K _L /L.mg ⁻¹	R ²	K _F	n	R ²

Conclusions

The grafting reaction temperature on jute fiber modification effect bigger, and under the condition of optimum modification, modified jute for Cu (II) adsorption capacity can reach 120mg. g⁻¹, far higher than the 7 mg. g⁻¹ before modification. The mechanical strength of modified jute has decreased, but still meets the actual needs. Heating is conducive to the adsorption reaction; neutral acidic environment on modified jute removing Cu (II) advantageously; water common coexist ions such as K⁺, Na⁺, Ca²⁺, Mg²⁺, modified jute for Cu (II) adsorption has certain promoting effect.

Acknowledgements

This work was funded by National water pollution control and management technology major projects (2012ZX07205-005). *Corresponding authors is T. ZHENG, associate Professor. Email address: zhengtong@hit.edu.cn.

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