



Adsorption of Ni(II) and Cu(II) by Thionyl Chloride and Ethylene-1,2-diamine Modified Coir Fibres

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This study describes the preparation of a new adsorbent for heavy metal ions removal derived from coir fibres. Coir fibres were activated by using thionyl chloride and reacted with ethylene-1,2-diamine in order to obtain modified coir fibres. Adsorption behaviours of coir fibres and modified coir fibres for Ni²⁺ and Cu²⁺ were studied respectively and the capacity of modified coir fibres to adsorb Ni²⁺ and Cu²⁺ from aqueous single metal ion solutions was evaluated at different contact times, pHs and initial metal ion concentrations. The characteristics of coir fibres and modified coir fibres were determined by SEM, XPS and FTIR techniques. The results showed that modified coir fibres had a porous and loose surface covered with amino groups, which helpful for removing Ni²⁺ and Cu²⁺ from wastewater. In the range of the designed experiments, modified coir fibres and coir fibres can reach its maximum saturated adsorption capacity (Q_{max}) of 0.773 mmol/g and 0.096 mmol/g for Ni²⁺; 1.658 mmol/g and 0.392 mmol/g for Cu²⁺, respectively. When the Ni²⁺ and Cu²⁺ adsorbed on modified coir fibres was desorbed by HCl, which showed high desorption efficiency, the optimum concentration of HCl was about 0.15 mol/L and the proper contact time was 20 min. In sequential adsorption and desorption cycles, the heavy metal ions uptake capacity on modified coir fibres was relatively maintained through cycles 1-5.

Key Words: Coir fibers, Thionyl chloride, Ethylene-1,2-diamine, Adsorption, Metal ion, Desorption.

INTRODUCTION

Coir fibres are derived from the coconut husks. Because of its hardwearing quality, durability and other advantages, it is widely used materials in floor-furnishing, yarn, rope, etc¹. However, these traditional coir products consume only a small percentage of the total world production of coconut husk². Coir fibers have metal adsorption capacity as a result of both ion exchange and chemical coordination processes at appropriate sites, however, with low selectivity³⁻⁶. Chemical modification of biomaterials is one way to improve adsorption capacity. A variety of appropriate groups of organic ligands could be used to modify the biomaterials surface through low-cost chemical processes such as amines, acid anhydrides and thiols, to produce materials with higher metal ion adsorption capacity. Up to now, there are a few articles about coir fiber with chemical modification, such as coir fiber modified by oxidizing⁷, the P=S functionalization of coconut (*Cocos nucifera*) fibers⁸.

In this work, a new adsorbent was obtained by modifying coir fibres with thionyl chloride and ethylene-1,2-diamine in sequence. As an evaluation, the adsorption studies of Ni²⁺ and Cu²⁺ ions by modified coir fibres and coir fibres were carried out at different contact times, pHs and initial metal ion concen-

trations. In addition, the desorption characteristics using HCl as desorbing agent for modified coir fibres were studied and modified coir fibres retained the greatest proportions of sorbed metal ions after five sorption-desorption cycles.

EXPERIMENTAL

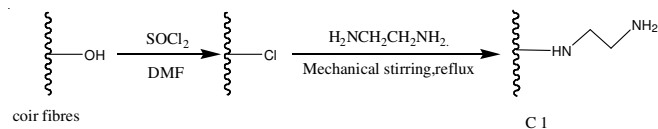
All chemicals are analytical grade. Coir fibres (purchased from Yunnan market of China). Thionyl chloride, *N,N*-dimethylformamide and ethylene-1,2-diamine were used to prepare the adsorbent. Ni²⁺ and Cu²⁺ solutions were prepared from NiSO₄·6H₂O and CuSO₄·5H₂O, respectively.

Preparation of coir fibres (C0): Experimental coir fibres were crushed in mill to pass a 100 mesh sifter, washed and dried to obtain coir fibres.

Coir fibres mercerization: Coir fibres were immersed in 10 % (w/v) NaOH solution for 10 h. Mercerized coir fibres were collected after filtered and dried. Mercerized coir fibres were treated again using the same procedure described above in order to obtain twice-mercerized coir fibres.

Synthesis of modified coir fibres (C1): The synthesis route used to obtain modified coir fibres (C1) is illustrated in **Scheme-I**. 10 g coir fibres was previously activated in DMF at 80 °C for 12 h, then reacted with 35 mL of thionyl chloride

under mechanical stirring for 4 h. The product was washed with dilute ammonium hydroxide solution until neutral pH and dried at 60 °C. After drying, 1 g of coir fibres chloride was reacted with 5 mL of ethylene-1,2-diamine under reflux and with mechanical stirring for 4 h. The filtered sample was washed with distilled water and ethanol alternately and dried at 60 °C to obtain modified coir fibres (C1).



Scheme-I: Synthesis route used to obtain modified coir fibres

Adsorption experiments: Batch experiments were carried out under constant stirring at room temperature (25 °C) using 100 mL conical flask containing 50 mL of metal ion solutions and 50 mg coir fibres, the contact time was ranged from 2 min to 240 min. The process used for coir fibres was the same for modified coir fibres. After being filtered, the filtrates of Cu^{2+} and Ni^{2+} were analyzed with the atomic absorption spectrometer (AAS) (AA-6501, Shimadzu, Japan). Various conditions, including the contact time, the pH, the initial concentration and the ionic strength, were tested.

Desorption experiments: HCl was used as desorbing reagent for previously adsorbed Cu^{2+} and Ni^{2+} on modified coir fibres. It was used in all batch-typed desorption experiments using 100 mL conical flask mixed under constant stirring for 4 h at 25 °C. 4 h was long enough to get an equilibrium state. In order to determine optimal desorption conditions using HCl, effects of concentration, time on desorption efficiency were studied. Also, the reusability of the modified coir fibres was studied in batch experiments. The adsorbed modified coir fibres was thoroughly washed with distilled water and dried at 25 °C and then added to a conical flask containing 50 mL HCl solution. The conical flask was under constant stirring for 4 h at 25 °C. Following desorption, the suspensions were filtered and the metal ion concentration of the filtrate was analyzed with AAS. The desorbed modified coir fibres was used in the next cycle of adsorption and desorption.

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

RESULTS AND DISCUSSION

Characterization of coir fibres and modified coir fibres

Scanning electron microscopy morphological characterization: The characteristic surface aspect of coir fibres (Fig. 1a) and modified coir fibres (Fig. 1b) observed by SEM is shown in Fig. 1. The coir fibres (Fig. 1a) surface is not smooth and covered with globular silicon-rich protrusions. But it was broken after being reacted with thionyl chloride and ethylene-1,2-diamine. The SEM images also show that modified coir fibres is irregular filamentous and loose surface. This structure made modified coir fibres possess more surface area than coir fibres. The modified process improved the adsorption capacity of coir fibres.

FTIR Analyses of coir fibres and modified coir fibres:

The characterization of coir fibres and modified coir fibres was analysed by FTIR spectroscopy and the results are shown in Fig. 2a and b. As shown in Fig. 2, the major chemical group of -OH appeared broad band at the wavenumber region of 3500-3300 cm^{-1} . The important changes can be observed in Fig. 2 of modified coir fibres in relation to coir fibres appears at 1158.64 and 1059.37 cm^{-1} . The band at 1158.64 cm^{-1} attributed to deformation vibration of C-N and the band at 1059.37 cm^{-1} attributed to corresponds to asymmetric stretching of C-N-C.

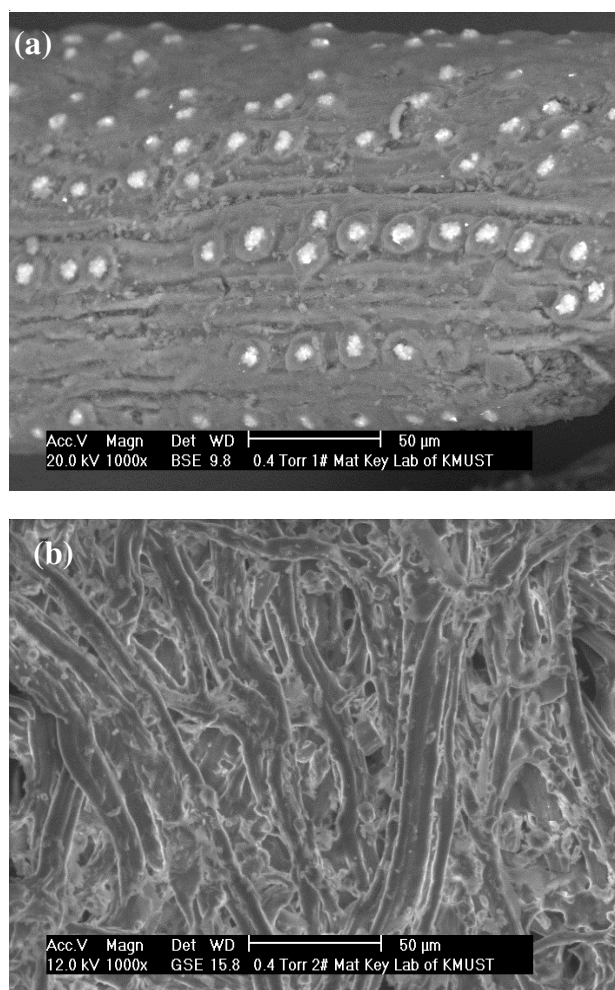


Fig. 1. SEM images of coir fibres (a) and modified coir fibres (b)

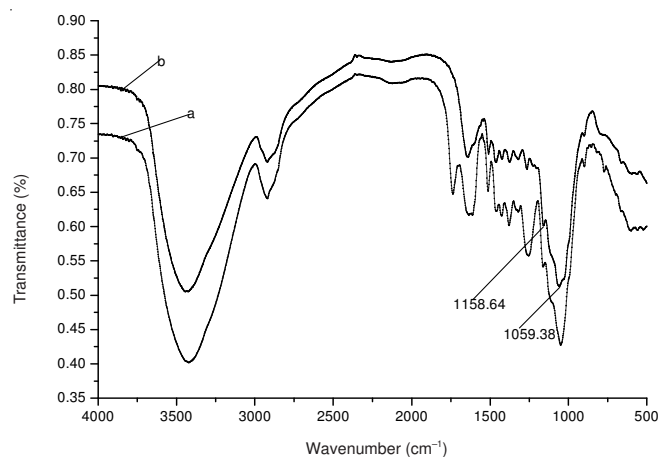


Fig. 2. FTIR spectra of coir fibres (a) and modified coir fibres (b)

XPS Analyses coir fibres and modified coir fibres: XPS N1s spectra of coir fibres and modified coir fibres are shown in Fig. 3. The most intense component centered at 400 eV is due to electrons from nitrogen atoms that are bonded to carbon atoms (N-C) or non-protonated amino groups. The area of signal at 399.74 eV showed in Fig. 3b was larger than that of signal at 400.36 eV showed in Fig. 3a. The atomic concentration of nitrogen groups of coir fibres and modified coir fibres is 1.21 and 2.29 %, as indicated in Table-1. It indicates that ethylene-1,2-diamine had been grafted with coir fibres.

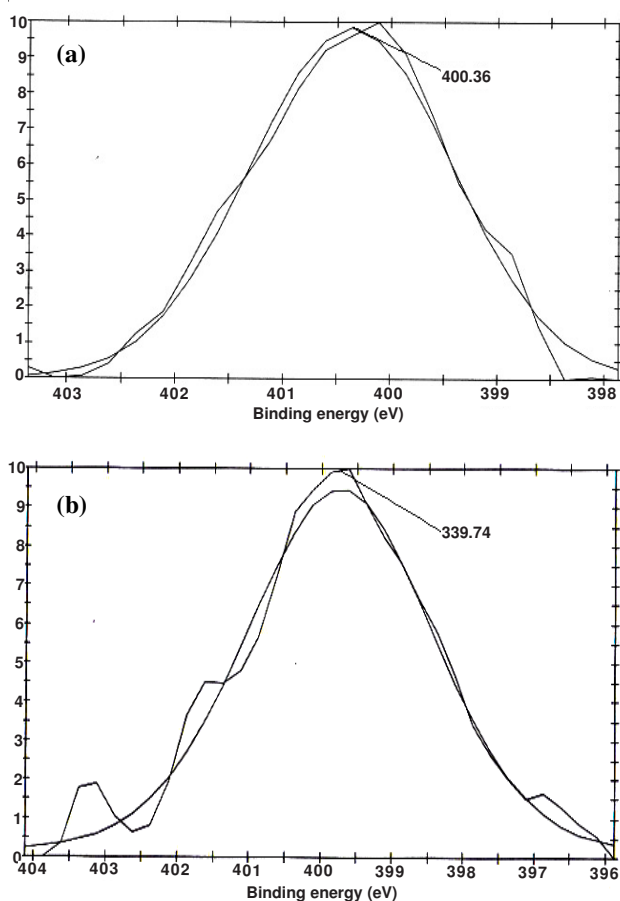


Fig. 3. XPS N1s spectra of coir fibres (a) and modified coir fibres (b)

TABLE-1
SEMI-QUANTIFIED ATOMIC CONCENTRATION FOR
COIR FIBRES AND MODIFIED COIR FIBRES

Sample	Concentration (atomic %)		
	C	N	O
Coir fibres	73.97	1.21	24.82
Modified coir fibres	70.48	2.29	27.23

Study of adsorption of metal ions

Adsorption kinetics: Based on the experiments about the kinetic study of metal ions adsorption, equilibrium time was achieved that is 2 h for modified coir fibres and 150 min for coir fibres. Compared with coir fibres, the adsorption equilibrium time of modified coir fibres was shorter. The adsorption equilibrium times mentioned above were chosen for pH and concentration dependent experiments. The equilibrium time further confirms that the readily available and easily accessible

organic groups on modified coir fibres were probably due to the facilitated transportation of metal ions during the adsorption.

Effect of pH on metal ion adsorption: The pH of metal solutions has been recognized by many scientists as the major parameter controlling metal adsorption processes⁹⁻¹¹. This is due to the pH of a solution affecting adsorbent surface charge, the degree of ionization and the species of adsorbates. The effect of pH on the adsorption of Cu²⁺ and Ni²⁺ on modified coir fibres was shown in Fig. 4. The adsorption of Cu²⁺ and Ni²⁺ both increased significantly with the increase of solution pH in certain extent. The maximum adsorption of Cu²⁺ and Ni²⁺ was observed at pH 5 and 6.5, respectively.

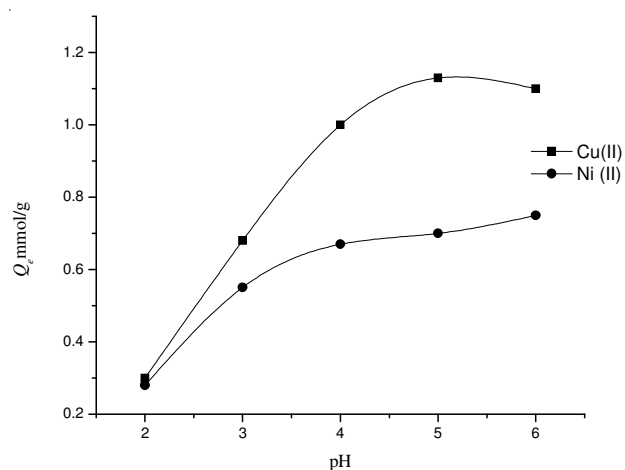


Fig. 4. Effect of pH value on adsorption capacity

The pH effects on metal ion adsorption that may be explained in relation to competition effect between the hydronium ions and metal ions¹². At low pH, the concentration of hydronium ions is higher than that of the metal ions and the hydronium ions is easily bound to modified coir fibres compared with the metal ions. At high pH, the concentration of hydronium ions decreases and the adsorption capacities of modified coir fibres were promoted with the metal ions. However, adsorption experiments could not be carried out at pH > 6 and 8 for Cu²⁺ and Ni²⁺ due to the insolubility of metal hydroxide, respectively. The working pH for adsorption was determined as 5 for Cu²⁺ and 6.5 for Ni²⁺.

Adsorption isotherms: Adsorption isotherms describe how metal ions interact with adsorbents. Adsorption isotherms of coir fibres and modified coir fibres are determined at the equilibrium time. The experimental data were obtained by Langmuir and Freundlich isotherms. The experimental data were well correlated to the Langmuir model. Langmuir equation is expressed as:

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

where, Q_e (mmol/g) is the equilibrium loading capacity, Q_{\max} (mmol/g) represents the maximum uptake of metal ion, C_e (mmol/L) and b (L/mmol) are the equilibrium concentration of solutions and Langmuir constant.

Adsorption isotherms of modified coir fibres at different temperatures are shown in Table-2. The result shows that the temperature of 30 °C was in favour of adsorption capacity for

modified coir fibres. As can be seen from Table-3, the obtained Q_{\max} (mmol/g) values for the removal of Cu^{2+} and Ni^{2+} by modified coir fibres were greater than coir fibres. Modified coir fibres and coir fibres can reach its maximum saturated adsorption capacity (Q_{\max}) of 0.773 and 0.096 mmol/g for Ni^{2+} ; 1.658 and 0.392 mmol/g for Cu^{2+} , respectively. The increase of the adsorption capacity (Q_{\max}) of modified coir fibres in relation to coir fibres for Cu^{2+} and Ni^{2+} due to the introduction of amino groups on modified coir fibres.

TABLE-2
ADSORPTION ISOTHERMS OF MODIFIED COIR FIBRES AT DIFFERENT TEMPERATURES

Metal ion	TM (°C)	Fitting curves of the Langmuir isotherm	R^2	Q_{\max} (mmol/g)
Ni(II)	30	$1/Q_e = 0.128/C_e + 1.293$	0.997	0.773
	40	$1/Q_e = 0.025/C_e + 1.394$	0.993	0.717
	50	$1/Q_e = 0.097/C_e + 1.334$	0.990	0.749
Cu(II)	30	$1/Q_e = 0.239/C_e + 0.603$	0.992	1.658
	40	$1/Q_e = 0.075/C_e + 0.864$	0.994	1.157
	50	$1/Q_e = 0.227/C_e + 0.648$	0.994	1.543

TABLE-3
ADSORPTION ISOTHERMS OF COIR FIBRES AND MODIFIED COIR FIBRES AT 30 °C

Metal ion	Sample	Fitting curves of the Langmuir isotherm	R^2	Q_{\max} (mmol/g)
Ni(II)	C0	$1/Q_e = 32.5/C_e + 10.33$	0.998	0.096
	C1	$1/Q_e = 0.128/C_e + 1.293$	0.997	0.773
Cu(II)	C0	$1/Q_e = 1.367/C_e + 2.546$	0.994	0.392
	C1	$1/Q_e = 0.239/C_e + 0.603$	0.992	1.658

C0: coir fibres; C1: modified coir fibres

Adsorption mechanism of metal Ion onto modified coir fibres:

The principal mechanism for the removal of metal ion onto modified coir fibres can be interpreted due to the transference of cation from solution to the basic centers of the anchored ethylene-1,2-diamine molecule, by complexation of the cations through the available amino groups. Coir fibres consist mainly of cellulose, hemicelluloses and lignin and those compounds have active sites- hydroxyl groups. Part of hydroxyl groups of coir fibres were grafted with ethylene-1,2-diamine, so the modified coir fibres have hydroxyl and amino groups in their molecules. To illustrate the possible cation complexation on this surface, the structures are proposed as shown in Fig. 5.

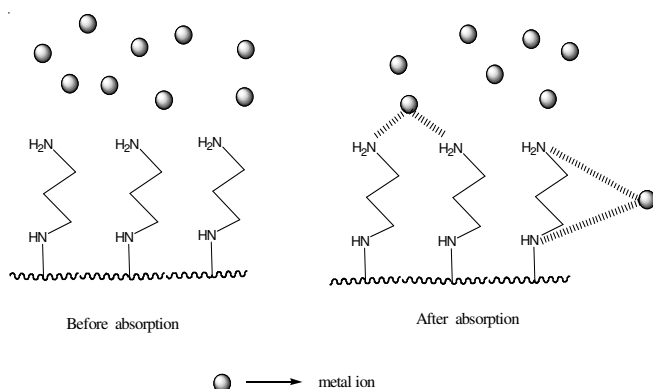


Fig. 5. Adsorption of metal ion onto modified coir fibres

Desorption study: The study for the optimal concentration of HCl was performed. Various concentrations of HCl including 0.01, 0.05, 0.1, 0.15 and 0.2 mol/L were tested for elution of adsorbed Cu^{2+} and Ni^{2+} using modified coir fibres. Fig. 6 shows that desorption efficiency of Cu^{2+} and Ni^{2+} was about 96 % and was almost same in the range over the 0.15 mol/L HCl concentration. Therefore, the optimum concentration of HCl was determined as 0.15 mol/L for desorption process.

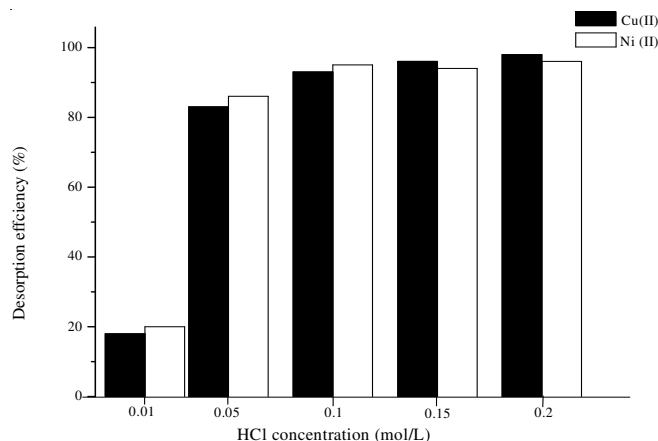


Fig. 6. Effect of HCl concentration on desorption efficiency for modified coir fibres

The study on the effect of contact time on desorption efficiency for modified coir fibres were performed using 0.15 mol/L HCl as desorption agent. As shown in Fig. 7, desorption efficiency increased with reaction time. But, most of desorption processes were completed within 20 min. It shows that desorption processes were performed very quickly.

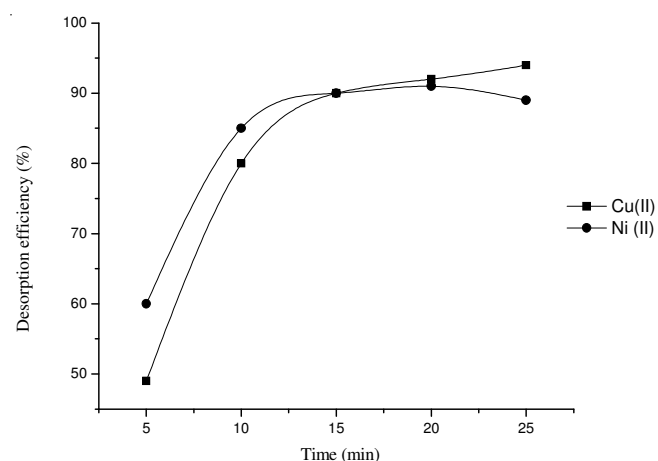


Fig. 7. Effect of contact time on desorption efficiency for modified coir fibres

Conclusion

Through the chlorination reaction and nucleophilic reaction, the ethylene-1,2-diamine molecule was successfully introduced into coir fibres. Based on the maximum adsorption of Cu^{2+} , the pretreatment of twice-mercerized show better properties after the introduction of the ethylene-1,2-diamine. modified coir fibres have more efficiency than the unmodified

coir fibres in adsorbing metal ions like Ni²⁺ and Cu²⁺ from their aqueous solutions. The loading capacity was significantly increased by coupling with ethylene-1,2-diamine. Compared to coir fibres, the saturated adsorption capacity of modified coir fibres achieved 0.773 mmol/g for Ni²⁺ and 1.658 mmol/g for Cu²⁺ at 40 °C, respectively. Furthermore, the desorption characterization using HCl as desorbing agent for modified coir fibres showed good desorption efficiency at a concentration of 0.15 mol/L and the desorption processes was completed within 20 min. In sequential adsorption and desorption cycles, the heavy metal ions uptake capacity on modified coir fibres was relatively maintained through cycles 1-5. The results reveal that modified coir fibres is an efficient and economic adsorbent for the treatment of industrial wastewaters contaminated with heavy metal ions.

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