

## Equilibrium, kinetic and mechanism studies on the biosorption of $\text{Cu}^{2+}$ and $\text{Ni}^{2+}$ by sulfur-modified bamboo powder

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**Abstract**—Two biosorbents were prepared using bamboo powder modified with mercaptoacetic acid and carbon disulfide, which exhibits strong adsorption properties for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . The obtained materials were characterized by FTIR. Maximum adsorption for both metals was found to occur around pH 5.0-6.5. The kinetic data followed the pseudo-second-order model. The maximum adsorption capacities of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  on mercaptoacetic acid modified bamboo powder determined from Langmuir isotherm were  $103.97 \text{ mg g}^{-1}$  and  $61.35 \text{ mg g}^{-1}$ , respectively. While on carbon disulfide modified bamboo powder were  $128.21 \text{ mg g}^{-1}$  and  $56.82 \text{ mg g}^{-1}$ , respectively. The adsorption mechanism analysis revealed that the most possible adsorption mode of  $\text{Cu}^{2+}$  was coordination, and  $\text{Ni}^{2+}$  was ion exchange. The obtained adsorbents could effectively remove  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from industrial electroplating wastewater and could be used repeatedly for more than five cycles.

Keywords: Sulfur Modification, Biosorption, Bamboo Powder, Copper, Nickel

### INTRODUCTION

Industrial wastewater discharge is the most important source of water pollution. The objective of water pollution control is to minimize the generation of toxic contaminants such as heavy metals [1]. Among them, industrial electroplating wastewater contains high concentration of heavy metals such as copper, nickel, zinc and chromium [2]. Direct discharge of this wastewater to the environment will be polluted. Even at low concentrations, heavy metal ions are highly toxic and not biodegradable [3,4]. Many studies have shown that these heavy metals may damage human health seriously and natural aqueous environment due to bio-accumulation tendency and persistency [5]. Thus removal of heavy metals from electroplating wastewater is of utmost importance.

The main methods for removal of heavy metal ions from aqueous solutions include chemical precipitation [6], chemical oxidation/reduction [7,8], ion exchange [9], coagulation [10], membrane separation [11], electrolysis [12], and adsorption [13]. Among these, adsorption is a simple and effective technique for water and wastewater treatment; it offers flexibility in design and operation, and desorption processes are of low cost and high efficiency [14,15]. Activated carbon and different types of ion-exchange resins are very often used in adsorption processes. The high capital and regeneration costs of the materials limit their large-scale use for the removal of metal ions [16]. In recent years, there has been considerable interest in the use of agricultural by-products as adsorbents to remove

toxic metals from aqueous solution. Some of the reported adsorbents include sawdust [17], waste tea [18], cork bark [19], rice husk [20], prunus amygdalus shell [21], and garlic powder [22]. The major advantages include relative cheapness, abundance in nature, renewability, large surface area and high adsorption capacity.

Chemical modification of agricultural by-products could enhance their natural ion-exchange and adsorption properties [23]. Meena et al. [24] studied the removal of  $\text{Cr}^{6+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  from aqueous solutions using the treatment of sawdust with NaOH and  $\text{H}_2\text{SO}_4$ . Igwe and Abia [25] reported that treating maize cob with EDTA at an elevated temperature enhanced its metal ions adsorption capacity. Li et al. [26] showed that modified orange peel with citric acid could remove significant amounts of  $\text{Cd}^{2+}$  from aqueous solutions. Wong et al. [27] showed that tartaric acid modified rice husk had high binding capacities for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ . Zheng et al. [28] modified corn stalk with acrylonitrile for the removal of  $\text{Cd}^{2+}$  from aqueous solutions and reported adsorption capacities of raw corn stalk increased from  $3.39$  to  $12.73 \text{ mg g}^{-1}$  after modification.

China is one of the countries with abundant bamboo resources. The advantage of bamboo includes fast growth, high texture quality, various applications, high economic values, and vast planting areas. Bamboo powder is the by-product of bamboo after deep processing, which is constituted of cellulose, lignin and pentosan. Because bamboo powder contains a large amount of hydroxyl groups in the structure, its absorption capability can be improved by chemical modification. In addition, adsorbents containing sulfur-bearing groups have a high affinity for heavy metals. Some sulfur-bearing compounds include sulfides, thiols, dithiocarbamates, dithiophosphates and xanthates [29].

The purpose of this study was to modify bamboo powder with

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mercaptoacetic acid or carbon disulfide to enhance its adsorption properties for the removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from aqueous solutions. Effect of various parameters including equilibrium pH, contact time and initial metal ions concentration on adsorption of both metal ions by the modified adsorbents was also studied. The kinetic parameters were calculated and described. The equilibrium adsorption data were analyzed by the Langmuir and Freundlich isotherm models, and the probable mechanisms explained. Additionally, reusability of the adsorbents used in electroplating wastewater treatment was also investigated through repeated adsorption - desorption experiments.

## MATERIALS AND METHODS

### 1. Chemicals

All chemicals used were of analytical reagent grade. The stock solution ( $1.0 \text{ g L}^{-1}$ ) of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  was prepared by dissolving  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  in double distilled water, respectively. The stock solution was diluted with de-ionized water to obtain the desired concentration range of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  solutions for each test.  $0.1 \text{ mol L}^{-1}$  HCl and  $0.1 \text{ mol L}^{-1}$  NaOH were used for pH adjustment. Mercaptoacetic acid and carbon disulfide were purchased from Shanghai, China, and were used for chemical modification of the adsorbent.

### 2. Adsorbent Preparation

#### 2-1. Raw Bamboo Powder

Bamboo powder (BP) was procured from a moso bamboo fabricating plant of Lishui, Zhejiang, China. The BP was washed thoroughly with tap water and double distilled water, and then dried at  $70^\circ\text{C}$  inside a convection oven for 24 h. The product was sieved to obtain a particle size lower than  $0.42 \text{ mm}$ .

#### 2-2. Washing with Sodium Hydroxide and Ethanol

About 25 g of dried BP was dipped in  $250 \text{ mL}$   $0.1 \text{ mol L}^{-1}$  NaOH solution and  $250 \text{ mL}$  ethanol, and stirred at  $120 \text{ r min}^{-1}$  at  $25^\circ\text{C}$  for 24 h. Then the obtained sample was washed with double distilled water until the pH of solution reached neutral, and also dried at  $70^\circ\text{C}$  for 24 h. This dried product was abbreviated as SBP thereafter, and prepared as the raw material for modification.

#### 2-3. Modified with Mercaptoacetic Acid

$80 \text{ mL}$  mercaptoacetic acid,  $50 \text{ mL}$  acetic anhydride and  $0.5 \text{ mL}$  sulfuric acid were added and mixed in a brown wide mouth flask, respectively. After cooling to room temperature,  $10 \text{ g}$  of SBP was added to the mixture, soaked completely, affixed with a seal, then treated in the convection oven at  $80^\circ\text{C}$  for 12 h. Then obtained sample was washed with double distilled water until the pH of solution reached neutral, and dried in the vacuum drying oven at  $30\text{--}35^\circ\text{C}$  to constant weight. The product was stored away from light and thereafter named as MBP.

#### 2-4. Modified with Carbon Disulfide

$10 \text{ g}$  of SBP was added to  $100 \text{ mL}$   $1 \text{ mol L}^{-1}$  NaOH solution in a  $250 \text{ mL}$  Erlenmeyer flask, and stirred for 3 h at room temperature. About  $10 \text{ mL}$  carbon disulfide ( $\text{CS}_2$ ) was added to the mixture and reaction continued for another 3 h. This mixture stood for 1 h and the supernatant decanted. The modified sample was washed with double distilled water to remove excess alkali, and then washed with acetone. Finally, the sample was dried and stored at

low temperature ( $5\text{--}8^\circ\text{C}$ ), hereafter abbreviated as XBP.

### 3. Biosorption Experiments and Analysis

All of the adsorption tests were batch wise;  $0.1 \text{ g}$  of adsorbent was taken into a  $100 \text{ mL}$  conical flask together with a  $20 \text{ mL}$  single metal ion ( $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$ ) solution. The mixture was shaken at  $120 \text{ r min}^{-1}$  on an orbital shaker. After adsorption, the samples were centrifuged at  $4,000 \text{ rpm}$  for 10 min. The residual metal ion concentrations in the supernatant liquor were determined by using an atomic absorption spectrophotometer, model Perkin Elmer AAnalyst 200.

The effect of solution pH on the equilibrium adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  was investigated at an initial concentration of  $50 \text{ mg L}^{-1}$  metal solution at  $25^\circ\text{C}$  for 120 min between pH 2.0 and 6.5. The adsorption kinetics and isotherms were studied as well. The adsorption kinetic experiments were varied between 0 min and 240 min. In the adsorption isotherm experiments, adsorbent was added in metal solution at various concentrations ( $25\text{--}1,000 \text{ mg L}^{-1}$ ). Each adsorption experiment was repeated three times, and the mean values were used in data analysis. The experimental data of the adsorption process were analyzed to study the adsorption mechanism. The percentage metal uptake and the amount of metal adsorbed ( $q_e$ ) were determined by using the following equations:

$$\text{Sorption \%} = \frac{(C_0 - C_e) \times 100}{C_0} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial and equilibrium metal ions concentrations, respectively.  $V$  ( $\text{mL}$ ) is the volume of the solution, and  $m$  ( $\text{g}$ ) is the dry weight of adsorbent.

### 4. The Practical Application of the Adsorbents and Desorption Studies

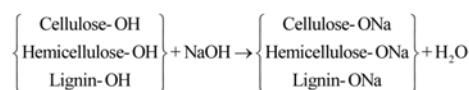
Desorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from electroplating wastewater and regeneration of the adsorbents were also investigated.  $0.5 \text{ g}$  MBP or XBP was added to a conical flask containing  $100 \text{ mL}$  of electroplating wastewater sample and shaken at  $25^\circ\text{C}$  for 2 h. After centrifugation, the filtered residue was then transferred to another conical flask and stirred with  $50 \text{ mL}$  of  $0.1 \text{ mol L}^{-1}$  HCl solution for 2 h. After stirring, the residue was washed several times with double distilled water to remove excess acid, and then dried at  $70^\circ\text{C}$  for 24 h. The regenerated adsorbent was further used for the next adsorption process. The consecutive adsorption-desorption cycles were repeated five times using the same adsorbent.

## RESULTS AND DISCUSSION

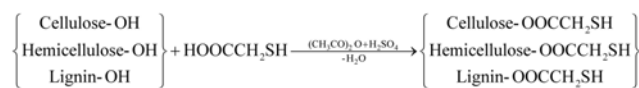
### 1. Characterization of the Adsorbent

According to the structural features of BP, adding ethanol could remove the small molecular compounds; adding sodium hydroxide could increase the number of hydroxyl in BP, and it also could react with hydroxyl groups in cellulose, hemicellulose and lignin to form sodium alkoxide simultaneously. Additionally, soaking processing (treatment) of sodium hydroxide could make the structure of cellulose expand and increase the porosity and specific surface area. All of these were beneficial for improving the adsorption effi-

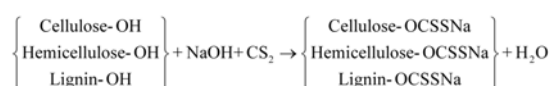
## Pretreatment



## Modification of mercaptoacetic acid



## Modification of carbon disulfide



Scheme 1. Proposed modification mechanism of BP using mercaptoacetic acid and carbon disulfide.

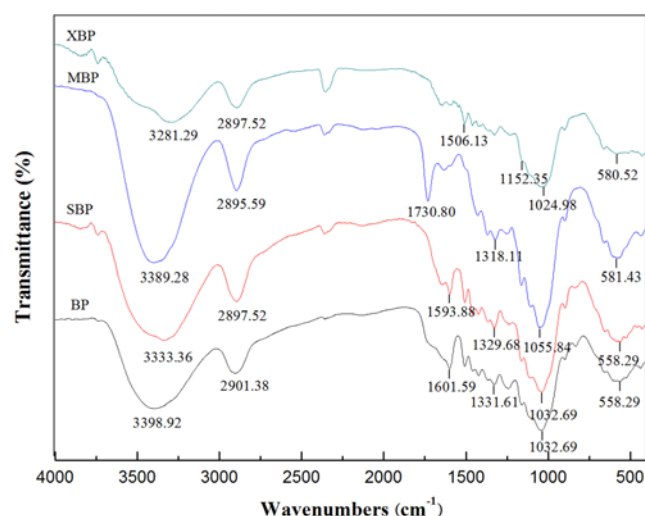


Fig. 1. FTIR spectra of BP, SBP, MBP and XBP.

ciency of BP for heavy metal ions in aqueous solution. The modification of mercaptoacetic acid and carbon disulfide aims at that sulfur and heavy metal ions have a strong binding ability and hydroxyl in BP are the main reaction sites of modification [29]. Scheme 1 shows the proposed modification mechanism of BP using mercaptoacetic acid or carbon disulfide; the possible chemical reactions are shown below.

The FTIR spectra of BP, SBP, MBP and XBP are shown in Fig. 1. From these figures, the spectra display a number of absorption peaks, indicating the complex nature of these materials. In the spectrum of BP and SBP, the broad and intense absorption peaks around  $3350\text{ cm}^{-1}$  correspond to the hydroxyl groups stretching vibrations, confirming the presence of free and intermolecular bonded hydroxyl groups on the adsorbent surfaces. The peaks observed around  $1600\text{ cm}^{-1}$  are due to the  $\text{C}=\text{C}$  stretching vibration that can be attributed to the aromatic  $\text{C}-\text{C}$  bonds, and the peaks around  $1330\text{ cm}^{-1}$  can be assigned to bending vibration of the  $\text{O}-\text{H}$  group. The strong  $\text{C}-\text{O}$  band at  $1032\text{ cm}^{-1}$  is characteristic of the stretching vibrations of carboxylic acids and alcohols. For FTIR spectrum of MBP, a new peak at  $1730\text{ cm}^{-1}$  is attributed to  $\text{C}=\text{O}$  stretching vibration of the carboxylic ester, and the peak at  $581\text{ cm}^{-1}$  can be assigned to stretch-

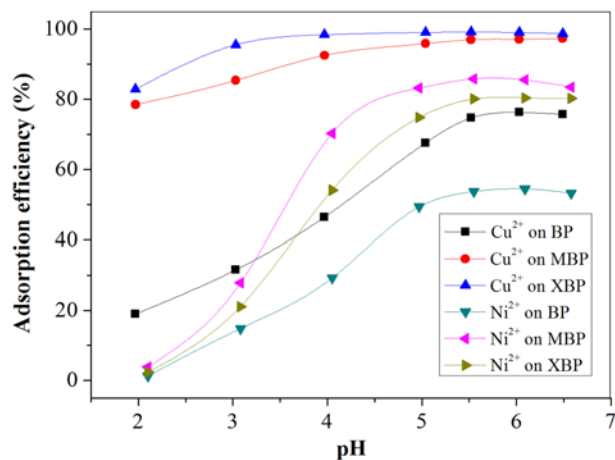


Fig. 2. Effect of equilibrium pH on adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  by BP, MBP and XBP. Conditions: initial metal ion concentrations  $50\text{ mg L}^{-1}$ , adsorbent concentrations  $2.5\text{ g L}^{-1}$ , temperature  $25^\circ\text{C}$ , contact time 2 h.

ing vibrations of the  $\text{C}-\text{S}$  bonds, which indicates the existence of sulfur groups in MBP. Compared to the spectrum BP and SBP, some different functional groups in the spectrum XBP are noted. The strong  $\text{O}-\text{H}$  band adsorption peak at  $3398\text{ cm}^{-1}$  in the pristine BP is observed to shift to  $3281\text{ cm}^{-1}$  in the XBP, which shows that the hydroxyl groups have combined with  $\text{CS}_2$ . The three new peaks at  $580\text{ cm}^{-1}$ ,  $1024\text{ cm}^{-1}$  and  $1152\text{ cm}^{-1}$  correspond to  $\gamma_{\text{C-S}}$ ,  $\gamma_{\text{C-S}}$  and  $\gamma_{\text{S-C-S}}$  in the FTIR spectrum of the XBP.

## 2. Effect of pH

The pH of the aqueous solution is an important controlling parameter affecting the adsorption process since it determines the surface charge of the adsorbent, the degree of ionization and the species of adsorbate [30]. The effect of pH range from 2.0 to 6.5 on adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from aqueous solution by BP, MBP and XBP was studied and the results are shown in Fig. 2. MBP and XBP exhibit higher adsorption efficiencies of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  than BP under the same conditions.

Also, the adsorption process of  $\text{Ni}^{2+}$  was obviously affected by the pH value. The adsorption efficiency of  $\text{Ni}^{2+}$  increased rapidly as the pH was increased in the pH range 2.0-4.0, and changed relatively slowly in the pH range 4.0-6.5. The maximum adsorption of  $\text{Ni}^{2+}$  using MBP and XBP occurred at pH 5.5 and 6.0, respectively, the adsorption percentages were 85.83% and 80.37%. The pH value had little effect on the adsorption of  $\text{Cu}^{2+}$ . The adsorption efficiency of  $\text{Cu}^{2+}$  adsorbed on MBP and XBP was minimum at pH 2.0 and increased as the pH increased, and then became almost stable at pH range 5.0-6.5. The maximum adsorption of  $\text{Cu}^{2+}$  using MBP and XBP occurred at pH 6.5 and 5.5, respectively; the adsorption percentages were 97.31% and 99.12%.

Obviously, the adsorption of metal ions increased with increasing pH and a plateau was reached at pH range 5.0-6.5. Other authors also have reported the same trend by some other materials [16,20,31]. We will be discussing mechanism of adsorption in detail.

## 3. Adsorption Kinetics

One of the most important features of the adsorbent material is the rate with which the solid phase adsorbs metal ions from the

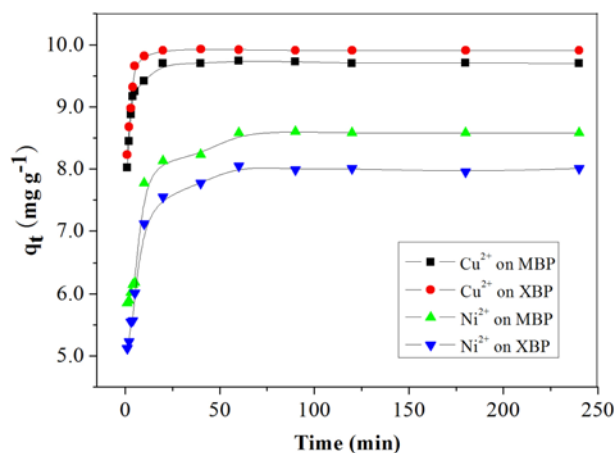


Fig. 3. Effect of contact time on adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  by MBP and XBP. Conditions: pH 5.5, initial metal ion concentrations  $50 \text{ mg L}^{-1}$ , adsorbent concentrations  $5 \text{ g L}^{-1}$ , temperature  $25^\circ\text{C}$ .

aqueous solutions and attains equilibrium [32]. Fig. 3 shows the effect of contact time on the batch adsorption of  $50 \text{ mg L}^{-1} \text{ Cu}^{2+}$  and  $\text{Ni}^{2+}$  at  $25^\circ\text{C}$  and pH 5.5. The adsorption process on  $\text{Cu}^{2+}$  proceeds rapidly and adsorption equilibrium can be attained within 20 min; in 20 min the amount of  $\text{Cu}^{2+}$  adsorbed on MBP and XBP was  $9.70 \text{ mg g}^{-1}$  and  $9.91 \text{ mg g}^{-1}$ , respectively. Therefore, the XBP shows better adsorption ability for  $\text{Cu}^{2+}$  than MBP. The amount of  $\text{Ni}^{2+}$  adsorbed on MBP and XBP sharply increased with increasing contact time in the initial stage (0–10 min), and the equilibrium values were attained in 60 min, and, respectively, were  $8.58 \text{ mg g}^{-1}$  and  $8.05 \text{ mg g}^{-1}$ . It is obvious that the MBP shows better adsorption ability for  $\text{Ni}^{2+}$  than XBP.

To analyze the adsorption kinetics of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , examine the rate of the adsorption process and to propose the potential rate-controlling step, the pseudo-first-order and pseudo-second-order kinetic models were applied to evaluate the experimental data.

The pseudo-first-order rate equation is

$$\log(q_e - q_t) - \log q_e = -k_1 t \quad (3)$$

where  $k_1$  ( $\text{min}^{-1}$ ) refers to the constant of the pseudo-first-order rate,  $q_e$  ( $\text{mg g}^{-1}$ ) and  $q_t$  ( $\text{mg g}^{-1}$ ) are the amount of  $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$  adsorbed at equilibrium and time  $t$  (min), respectively. The plots of the pseudo-first-order rate equation are shown in Fig. 4(a) and the

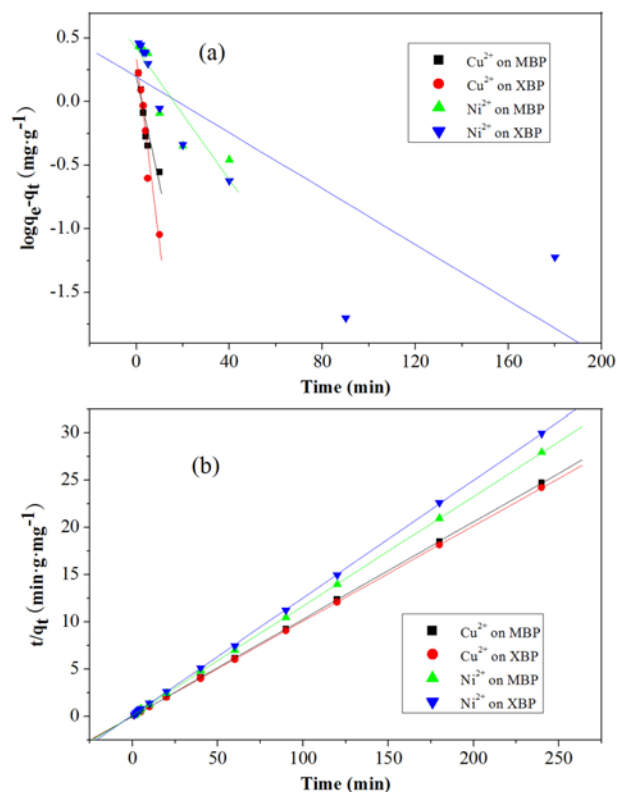


Fig. 4. Pseudo-first-order (a) and pseudo-second-order (b) kinetics plots.

values of  $k_1$  were determined from the slopes of the plots  $\log(q_e - q_t)$  against  $t$ .

The corresponding parameters of the pseudo-first-order kinetic equation are given in Table 1. The results show that the values of correlation coefficient ( $R^2$ ) were lower than 0.95; and  $q_{e, \text{cal}}$  for the theoretical  $q_e$  values calculated from pseudo-first-order kinetic model were not in agreement with  $q_{e, \text{exp}}$  for the experimental  $q_e$  values, so the adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  on MBP and XBP was not a pseudo-first-order reaction.

The pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) refers to the constant of the pseudo-second-order

Table 1. The pseudo-first-order and pseudo-second-order kinetic parameters for the adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$

Metal ions	Adsorbent	$q_{e, \text{exp}}$ ( $\text{mg g}^{-1}$ )	Pseudo-first-order model			Pseudo-second-order model		
			$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_{e, \text{cal}}$ ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g mg}^{-1} \text{ min}^{-1}$ )	$R^2$	$q_{e, \text{cal}}$ ( $\text{mg g}^{-1}$ )
$\text{Cu}^{2+}$	MBP	9.70	0.0844	0.8574	1.57	0.6338	1	9.72
	XBP	9.91	0.1463	0.9495	2.21	0.6960	1	9.92
$\text{Ni}^{2+}$	MBP	8.58	0.0258	0.8273	2.61	0.0995	0.9999	8.64
	XBP	8.01	0.0110	0.6843	1.57	0.1084	0.9999	8.05

$q_{e, \text{exp}}$  ( $\text{mg g}^{-1}$ ) is the experimental value of equilibrium adsorption capacity,  $q_{e, \text{cal}}$  ( $\text{mg g}^{-1}$ ) is the calculated value of equilibrium adsorption capacity,  $k_1$  and  $k_2$  are respectively the rate constants of the pseudo-first-order and pseudo-second-order kinetic equation,  $R^2$  is the coefficient of determination

ond-order rate. The plots of the pseudo-second-order rate equation are shown in Fig. 4(b) and the values of  $k_2$  were determined from the slopes of the plots  $t/q_t$  against  $t$ .

The corresponding parameters of the pseudo-second-order kinetic equation are given in Table 1. The results show that the values of correlation coefficient ( $R^2$ ) were very close to 1; and  $q_{e,cal}$  for the

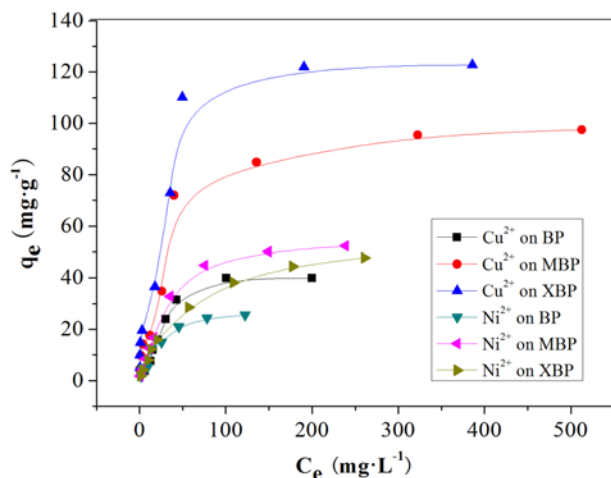


Fig. 5. Adsorption isotherms of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  on MBP and XBP. Conditions: pH 5.5, adsorbent concentrations  $5 \text{ g L}^{-1}$ , temperature  $25^\circ\text{C}$ , contact time 2 h.

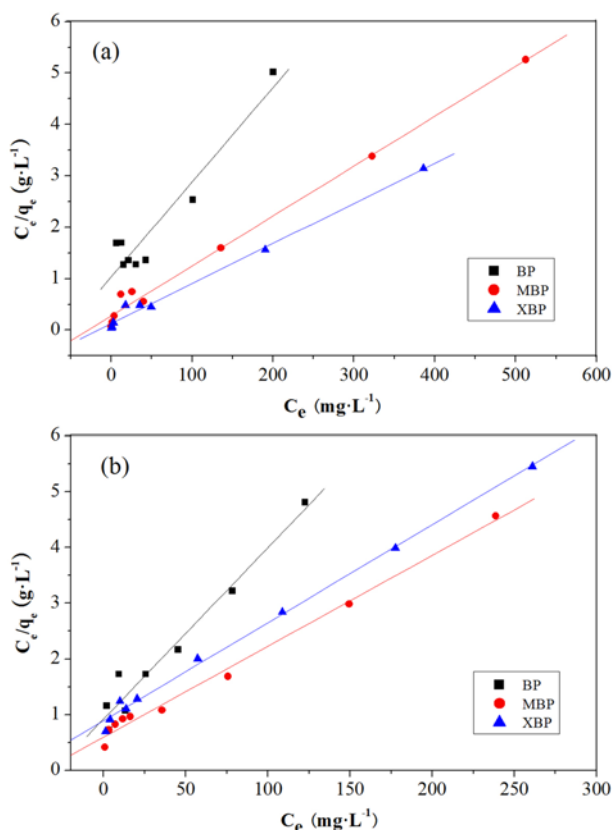


Fig. 6. Langmuir isotherms plot for the adsorption of  $\text{Cu}^{2+}$  (a) and  $\text{Ni}^{2+}$  (b) by MBP and XBP.

theoretical  $q_e$  values calculated from pseudo-second-order kinetic model agree very well with  $q_{e,exp}$  for the experimental  $q_e$  values. These indicate that the adsorption processes of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  on MBP and XBP could be well described by the pseudo-second-order kinetic model, and the adsorption rate was controlled by chemical adsorption.

#### 4. Adsorption Isotherms

Fig. 5 shows the adsorption isotherms of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  on BP, MBP and XBP. The amount of both metals adsorbed increased with the increase of metal ion concentration in the equilibrium solution at a certain range of concentration until an equilibrium was reached.

Adsorption isotherms indicate the partition of adsorbate between solution and adsorbent at equilibrium; it is important to describe how solutes interact with adsorbent [4]. The Langmuir and Freundlich adsorption isotherms equations were adopted in this study. Both these analytical methods are suitable for describing short-term and mono component adsorption of metal ions by different adsorbents.

The Langmuir isotherm assumes that the sorption takes place at specific homogeneous sites within the adsorbent and represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (5)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $q_m$  ( $\text{mg g}^{-1}$ ) are the equilibrium and maxi-

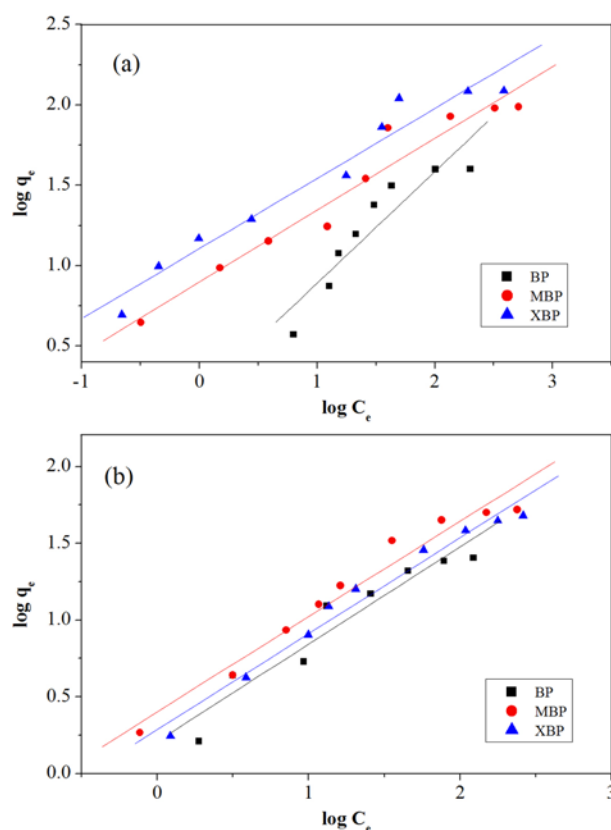


Fig. 7. Freundlich isotherms plot for the adsorption of  $\text{Cu}^{2+}$  (a) and  $\text{Ni}^{2+}$  (b) by MBP and XBP.

**Table 2. The isotherm parameters for the adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> on BP, MBP and XBP**

Metal ions	Adsorbent	Adsorption isotherms					
		Langmuir			Freundlich		
		q <sub>m</sub> (mg g <sup>-1</sup> )	b (L mg <sup>-1</sup> )	R <sup>2</sup>	K <sub>F</sub> (mg g <sup>-1</sup> )	1/n	R <sup>2</sup>
Cu <sup>2+</sup>	BP	54.35	0.018	0.9118	1.58	0.69	0.8547
	MBP	103.97	0.035	0.9915	7.92	0.45	0.9479
	XBP	128.21	0.064	0.9905	12.78	0.44	0.9557
Ni <sup>2+</sup>	BP	32.57	0.033	0.9603	1.62	0.63	0.9171
	MBP	61.35	0.027	0.9915	9.21	0.62	0.9644
	XBP	56.82	0.020	0.9954	1.93	0.63	0.9749

maximum metal uptake capacities, respectively. C<sub>e</sub> (mg L<sup>-1</sup>) is the equilibrium concentration and b (L mg<sup>-1</sup>) is the Langmuir constant termed as apparent energy of adsorption. According to this equation, the values of q<sub>m</sub> and b were calculated from the slope (1/q<sub>m</sub>) and intercept (1/q<sub>m</sub>b) of the linear plots C<sub>e</sub>/q<sub>e</sub> versus C<sub>e</sub> (Fig. 6).

The Freundlich isotherm is suitable for a highly heterogeneous surface, which is presented by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

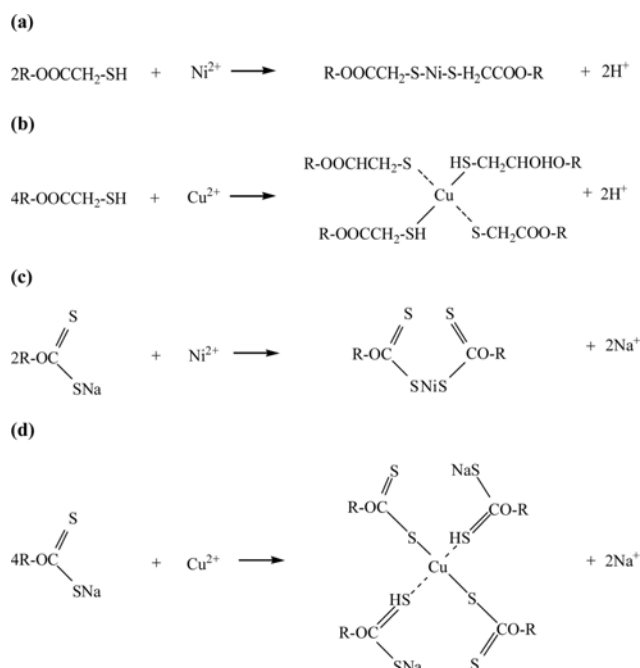
where K<sub>F</sub> (mg g<sup>-1</sup>) and n are the Freundlich constants, indicating the adsorption capacity and adsorption intensity, respectively. They were calculated from the slope (1/n) and intercept (log K<sub>F</sub>) of the plots log q<sub>e</sub> versus log C<sub>e</sub> (Fig. 7).

Both the Langmuir and Freundlich isotherm equations were applied to the adsorption experimental data. The isotherm parameters (q<sub>m</sub>, b, K<sub>F</sub> and n) and the regression coefficient (R<sup>2</sup>) are given in Table 2. It is clear that the Langmuir isotherm exhibited a better fit to the experimental data than the Freundlich isotherm. This outcome reflects that the adsorption of Cu<sup>2+</sup> and Cd<sup>2+</sup> on surface of BP, MBP and XBP was monolayer adsorption. In addition, values in the range 0.1 < 1/n < 1 indicate favorable adsorption of Cu<sup>2+</sup>

and Ni<sup>2+</sup> onto BP, MBP and XBP. For Cu<sup>2+</sup>, values of q<sub>m</sub> calculated by Langmuir isotherm equation on BP, MBP and XBP were 54.35, 103.97 and 128.21 mg g<sup>-1</sup>, respectively. While for Ni<sup>2+</sup>, values of q<sub>m</sub> were 32.57, 61.35 and 56.82 mg g<sup>-1</sup>, respectively. Thus, bamboo powder with mercaptoacetic acid and carbon disulfide, the adsorption capacities of Cu<sup>2+</sup> and Ni<sup>2+</sup> have been greatly enhanced. The maximum copper and nickel uptake capacities (q<sub>m</sub>) obtained from this study with those of some other biosorbents reported in the literature are given in Table 3. Comparison of Cu<sup>2+</sup> and Ni<sup>2+</sup> adsorption on MBP and XBP with the literature data indicates that sulfur-modified bamboo powder presents higher adsorption capacity than other adsorbents, and has very broad application prospects.

### 5. Mechanism of Adsorption

Scheme 2 shows the possible reaction mechanism of MBP and XBP, which adsorb Cu<sup>2+</sup> and Ni<sup>2+</sup> through coordination or ion exchange. Combined with the analysis of Fig. 2, we can draw the following conclusions.



**Scheme 2. The possible adsorption mechanisms of MBP (R-OOC-CH<sub>2</sub>SH) and XBP (R-OCSSNa): (a) and (c) ion exchange; (b) and (d) coordination.**

**Table 3. The list of some agriculture by-products for adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> in the literature**

Adsorbent	q <sub>m</sub> (mg g <sup>-1</sup> )		References
	Cu <sup>2+</sup>	Ni <sup>2+</sup>	
Grape stalks	10.12	10.67	16
Wheat bran	14.5	13.3	17
Cork bark	2.96	4.10	19
Yohimbe bark	9.42	8.91	19
Rice husk	10.9	5.52	20
Pine bark	9.47	6.28	33
Black gram husk	27.73	19.56	34
Cocoa shell	2.87	2.63	35
Orange peel	3.65	6.01	36
Banana peel	4.75	6.88	36
Peanut hull	7.09	2.22	37
Sugar beet pulp	21.16	11.86	38
MBP	103.97	61.35	This study
XBP	128.21	56.82	This study

In the case of  $\text{Ni}^{2+}$ , the pH value has remarkable influence on the adsorption of  $\text{Ni}^{2+}$  by MBP and XBP. At lower pH values (pH 2.0–4.0) the  $\text{H}_3\text{O}^+$  concentration is high, which can compete strongly with  $\text{Ni}^{2+}$  for the active sites of the adsorbents. At higher pH values (pH 4.0–6.5) the  $\text{H}_3\text{O}^+$  concentration decreases, the adsorbent surface provides greater number of negative charge sites, which are conducive to the adsorption of  $\text{Ni}^{2+}$  and thus the adsorption efficiency of  $\text{Ni}^{2+}$  increases. But with further increase in pH, the formation of anionic hydroxide complexes decreases the concentration of  $\text{Ni}^{2+}$ , so as to reach adsorption equilibrium. Therefore, the most possible adsorption mode of  $\text{Ni}^{2+}$  was ion exchange; (a) and (c) are the most possible adsorption process.

In addition, the valence shell electron configuration of the central ion  $\text{Cu}^{2+}$  is  $3d^9$ , so negative charged sulfur atoms of adsorbents and  $\text{Cu}^{2+}$  are easy to form quadridentate ( $\text{sp}^3$ ) complexes; (b) and (d) is the most possible adsorption process. On the other hand, due to the differences in the coefficient of adsorption equation, the ability of the adsorbents to capture  $\text{Cu}^{2+}$  is better than  $\text{Ni}^{2+}$ . It seems that pH has little influence on adsorption of  $\text{Cu}^{2+}$ .

MBP and XBP, respectively, contain sulfhydryl groups and xanthate group. On the one hand, MBP showed stronger ionic character compared with XBP. Consequently, MBP adsorbing  $\text{Ni}^{2+}$  was better than XBP through ion exchange. On the other hand,  $\text{Cu}^{2+}$  is a soft metal ion, and the xanthate group can be classified as soft bases. According to the Pearson rule, soft bases are likely to form stable complexes with soft metal ion, and therefore the xanthate group is very easy to form coordination bonds with  $\text{Cu}^{2+}$ , so XBP shows stronger coordination ability of  $\text{Cu}^{2+}$  than MBP. We can get the same results from Table 1 and Table 2.

## 6. The Removal of $\text{Cu}^{2+}$ and $\text{Ni}^{2+}$ from Electroplating Wastewater and Reuse of the Adsorbent

The availability of reusable biosorbent is the key to the commercialization of biosorption technology. MBP and XBP were applied to the removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in electroplating wastewater sample. Chemical characteristics of electroplating wastewater sample are as follows: pH 5.5, conductivity  $2.17 \text{ mS cm}^{-1}$ ,  $C_{\text{Cu}^{2+}}$   $172 \text{ mg L}^{-1}$ ,  $C_{\text{Ni}^{2+}}$   $85 \text{ mg L}^{-1}$ . Fig. 8 shows the variation of adsorption efficiencies of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in electroplating wastewater sample with respect

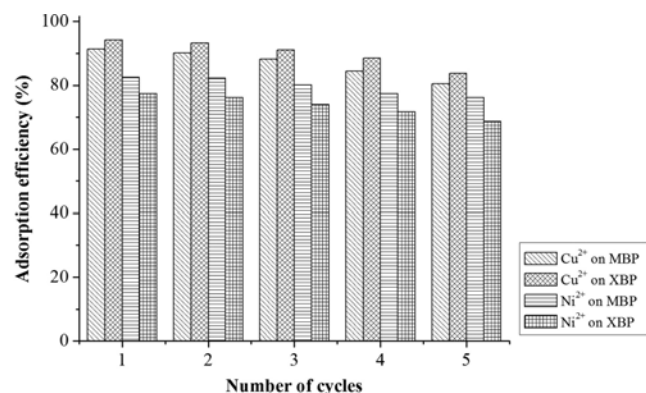


Fig. 8. Adsorption-desorption cycles of MBP and XBP. Conditions: pH 5.5, initial metal ion concentrations  $50 \text{ mg L}^{-1}$ , adsorbent concentrations  $5 \text{ g L}^{-1}$ , temperature  $25^\circ\text{C}$ , contact time 2 h.

to the number of adsorption-desorption cycles. The experimental results clearly indicate that MBP and XBP could effectively remove  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from the electroplating wastewater sample. After five cycles, adsorption efficiencies of these two metals decreased slightly after each successive cycle, so it is clear that MBP and XBP can be used repeatedly for removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in electroplating wastewater.

## CONCLUSIONS

Mercaptoacetic acid and carbon disulfide were used for modifying bamboo powder, which could be used as efficient and useful adsorbents for the removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from aqueous solutions. FTIR spectra demonstrated the presence of the sulfur groups in MBP and XBP after modification. The adsorption efficiencies of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  increased with an increase in pH, and the maximum adsorption was found to occur at pH range 5.0–6.5. Kinetics studies showed that the adsorption process followed the pseudo-second-order model, indicating that the chemical adsorption was the rate-limiting step. Compared to the Freundlich isotherm equation, the Langmuir isotherm equation could better describe MBP and XBP on the adsorption behavior of metal ions, and it was a monolayer adsorption reaction. The maximum adsorption capacity for  $\text{Cu}^{2+}$  on MBP and XBP was found to be  $103.97$  and  $128.21 \text{ mg g}^{-1}$ , respectively. While for  $\text{Ni}^{2+}$ , it respectively was  $61.35$  and  $56.82 \text{ mg/g}$ . According to experimental data, the maximum adsorption capacity of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  for MBP increased by 91.3% and 88.4% compared to BP, while for XBP increased by 135.9% and 74.5%. In addition, the adsorption mechanism also was discussed, indicating that adsorbents and  $\text{Cu}^{2+}$  easily form quadridentate ( $\text{sp}^3$ ) complexes; however, ion exchange is the most possible mode of adsorbing  $\text{Ni}^{2+}$ . Finally, adsorption-desorption tests showed that MBP and XBP can be reused for at least five cycles for removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in electroplating wastewater. The investigation shows that the bamboo powder modified with mercaptoacetic acid and carbon disulfide is more favorable for adsorption of metal ions with positive charge, and it is a promising biosorbent for the removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from aqueous solutions.

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