

# Adsorption Characteristics of Copper (II) onto Ferrocene Modified Resin

Qian Wang, Senlin Tian, Zongliang He, Jiaqi Li, and Ping Ning

**Abstract**—Ferrocene (Fc) modified cation exchange resin (FM CER) was synthesized for copper adsorption process and characterized by XRF and BET analysis. Fc has been successfully impregnated into resin, and Fc loaded on resin was about 0.1792% (w/w). Both surface area and pore width of resin was enlarged. Results from batch experiments indicated that the adsorption kinetics of  $\text{Cu}^{2+}$  obeyed pseudo-second-order kinetic model and the adsorption rate constant was 0.0011 g/mg/min. Langmuir adsorption isotherm model fitted the adsorption of  $\text{Cu}^{2+}$  well. The adsorption process of  $\text{Cu}^{2+}$  was exothermic reaction. The adsorption process was pH dependent and the optimal pH was found to be 4-5, and maximum removal efficiency was 38.59% at pH 4.

**Index Terms**—Ferrocene modified cation exchange resin,  $\text{Cu}^{2+}$ , adsorption kinetics, isotherm study.

## I. INTRODUCTION

Water pollution has been attended for several decades, especially heavy metals pollution. Accumulation of heavy metals in living tissues through food chain has already poses serious health problems [1]-[3]. Copper pollution is common to see in southwest china, it is usually arises from copper mining and smelting, brass manufacture [4], et al. Wastewater containing copper from industries can not be discharged directly before treatment, and the removal and recovery of copper from wastewater is important in the protection of the environment and human health.

Adsorption, biosorption, complexation, chemical precipitation, solvent extraction, ion exchange and membrane processes have been commonly used in heavy metal contained wastewater treatment [5]-[6]. Adsorption is a high efficient and economical method in heavy metal removal from aqueous solutions among all the processes mentioned above [7]. Resin has attracted considerable attention for several years, because of its wide applications in environmental pollution remediation such as the removal of organic or inorganic pollutants from wastewater [8]-[10]. Resin is considered to be economic, and has already been successfully used in recovery of precious metals [11]-[13], such as Au, Ag, Cu, Cr, etc. Fatal drawbacks such as small pH window in the range of 1-1.4 and limitation of surface area and pore width are there, thus, adsorption capacity was not high for heavy metals.

To overcome drawbacks mentioned above, in this study, cation exchange resin was modified with ferrocene (Fc) and

used in copper (II) adsorption. Fc was a kind of organic transition metallic compound, which is considered to have donor-acceptor conjugated structure and rigid skeleton [14]-[16], and the impregnation of Fc may change surface characteristics of cation exchange resin and improve the adsorption capacity. Effects of initial solution pH and contact time on adsorption capacity were investigated. The adsorption isotherms and kinetics of the adsorbent were measured, and equilibrium data were fitted to Langmuir, Freundlich equations to determine the correlation between the isotherm models and experimental data.

## II. MATERIALS AND METHODS

Cation exchange resin was rinsed by acids to remove the mechanical impurities as pretreatment. A given amount of FeCp was dissolved in alcohol, and the pretreated resin was added into the FeCp solution, shaken for 5 h. The clear supernatant was discarded, and the final FeCp modified resin was washed several times with alcohol to remove redundant FeCp. The sample was dried at 70°C and kept in a sealed bottle. Cation exchange resin modified with ferrocene was investigated by XRF and  $\text{N}_2$  adsorption-desorption analysis. The  $\text{Cu}^{2+}$  adsorption data from water solutions were obtained by the immersion method. The adsorption experiments were carried out by agitating 0.25g adsorbent in 250mL  $\text{Cu}^{2+}$  solution having concentrations ranging from 0 mg/L to 640mg/L with the pH of 2-7 and the temperatures (30°C, 40°C, 50°C). The solution and solid phase were separated by filtration, and the  $\text{Cu}^{2+}$  solutions were analyzed using a atomic absorption spectrophotometer (Shimadzu AA6300C). The  $\text{Cu}^{2+}$  adsorption capacity at equilibrium,  $Q_e$ (mg/g), can be calculated from:

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

where  $C_0$  (mg/L) is the initial  $\text{Cu}^{2+}$  concentration in liquid phase,  $C_e$  (mg/L) denotes the  $\text{Cu}^{2+}$  concentration in liquid phase at equilibrium,  $V$ (L) represents the total volume of the  $\text{Cu}^{2+}$  solution, and  $m$ (g) is the mass of the adsorbent.

## III. RESULTS AND DISCUSSION

### A. Characterization of FM CER

Cation exchange resin and FM CER were dried at 40°C and detected using X-Ray Fluorescence (XRF). The components of main elements of both cation exchange resin and FM CER are shown in Table I. As depicted in Table I,

the ratio of Fe contained in FM CER was much higher than that in untreated resin, the ratio of Fe incorporate to resin was about 0.0037%, the ratio increased to 0.0580% after modification by Fe, and the ratio of Fe was calculated to be 0.1792%.

The surface and pore characteristics of untreated resin and FM CER were determined using N<sub>2</sub> adsorption-desorption analysis, and the results were depicted in Table II. The surface area of untreated resin was about 1.7 m<sup>2</sup>/g, while FM CER was 2.4 m<sup>2</sup>/g. Pore diameter of cation exchange resin was enlarged from 2.07 nm to 5.38 nm through the impregnation of Fe.

TABLE I: SQX CALCULATED RESULTS OF UNTREATED RESIN AND FM CER (MASS: %)

Component	Untreated resin	FM CER
C	97.5416	96.0021
S	1.2748	2.7353
O	0.6385	0.6457
Na	0.3668	0.4862
Fe	0.0037	0.0580

TABLE II: FM CER CHARACTERIZATION DATA

	Untreated resin	FM CER
BET surface(m <sup>2</sup> /g)	1.7	2.4
V <sub>total</sub> (cm <sup>3</sup> /g)	10.00	11.73
S <sub>BJH</sub> (m <sup>2</sup> /g)	1.6	1.7
V <sub>BJH</sub> (cm <sup>3</sup> /g)	0.0020	0.0023
Pore diameter BJH (nm)	2.07	5.38
Fe content (%)	0.0037%	0.0580%

### B. Kinetic Study

The kinetic study for the adsorption of Cu<sup>2+</sup> was conducted at pH 3. 0.25 g/L adsorbent was added into 250 mL 640 mg/L CuSO<sub>4</sub> solution, Samples were taken at time intervals of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5 and 7.0 h. The adsorption of Cu<sup>2+</sup> onto FM CER was time dependent and the equilibrium time required for maximum removal of Cu<sup>2+</sup> was about 6 h. The adsorption capacity of FM CER for Cu<sup>2+</sup> was 218 mg/g, as shown in Fig.1.

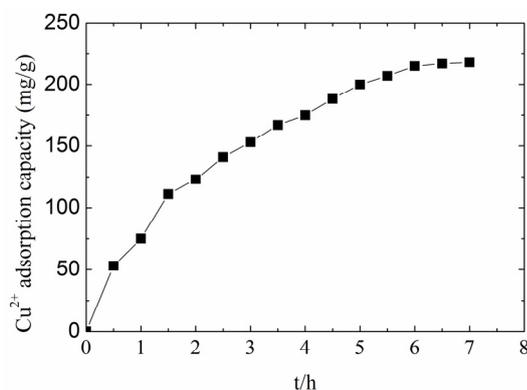


Fig. 1. Adsorption of copper (II) onto FM CER and kept shaking at 30°C.

To describe the kinetic behavior of the adsorption process, pseudo-first-order and pseudo-second-order equations depicted in Eq(2)-(3) were used to analyze the experiment data.

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where  $q_e$  and  $q_t$  (mg/g) are the amount of Cu<sup>2+</sup> adsorbed at the equilibrium time and time  $t$  (h), respectively.  $k_1$  (min<sup>-1</sup>),  $k_2$  (g·mg<sup>-1</sup>·min<sup>-1</sup>) are the rate constants of adsorption of the pseudo-first-order equation and pseudo-second-order equation, respectively. Fig. 2 shows the linearized form of the pseudo-first-order and pseudo-second-order models for Cu<sup>2+</sup> adsorption on FM CER. The pseudo-first-order rate constants  $k_1$ ,  $q_e$  and pseudo-second-order rate constants  $k_2$ ,  $q_e$  for Cu<sup>2+</sup> were calculated from the slope and intercept of the linear plots of  $\log(q_e - q_t)$  versus  $t$  and  $t/q_t$  versus  $t$ , and the results were summarized in Table III.

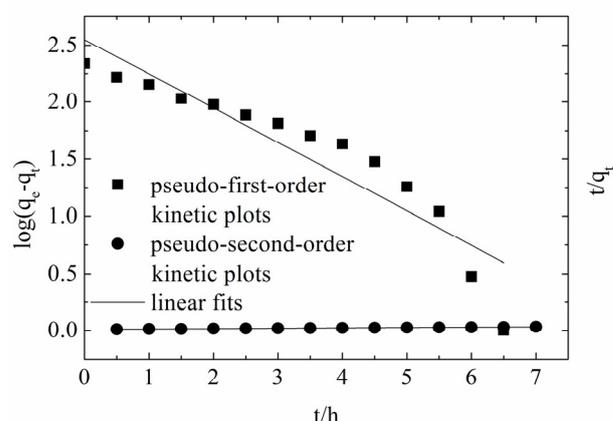


Fig. 2. Kinetic study of adsorption Cu<sup>2+</sup> onto FM CER (initial concentration of Cu<sup>2+</sup> 640g/L, FM CER 1g/L, pH=3, 30°C)

TABLE III: KINETIC PARAMETERS FOR Cu<sup>2+</sup> ADSORPTION ONTO FM CER

sam ple	Pseudo-first-order equation			Pseudo-second-order equation		
	k <sub>1</sub> (min <sup>-1</sup> )	q <sub>e</sub> (mg/g)	R <sup>2</sup>	k <sub>2</sub> (g/mg/min)	q <sub>e</sub> (mg/g)	R <sup>2</sup>
Cu <sup>2+</sup>	0.6920	353.6959	0.8610	0.0011	231.4	0.9908

The coefficients R<sup>2</sup> for the pseudo-first-order model was only 0.8610, and the theoretical values of  $q_e$  deviated from experiment data obviously. For the pseudo-second-order kinetic model, the correlation coefficients were 0.9908 and the theoretical  $q_e$  was 231.4 g, which agreed well with the experimental  $q_e$  in comparison. The results indicated that the pseudo-second-order model could adequately describe the adsorption kinetics for Cu<sup>2+</sup>.

### C. Adsorption Isotherm of FM CER

The adsorption isotherms were established at 20°C, 30°C and 40°C by batch experiments with initial Cu<sup>2+</sup> concentrations varying from 0 to 640 mg/L under the condition of 1g/L adsorbent at pH 3. The isotherm of Cu<sup>2+</sup> on FM CER is shown in Fig. 3. The Cu<sup>2+</sup> adsorption capacity increased considerably with the equilibrium concentration increasing from 0 to 422 mg/L.

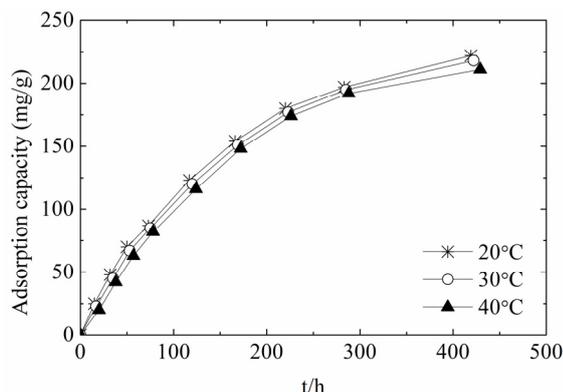


Fig. 3. adsorption isotherm of  $\text{Cu}^{2+}$  onto FM CER (initial  $\text{Cu}^{2+}$  concentration 0-640 mg/L, 250mL, FM CER 1g/L, pH =3, shaking 7 h, temperature 20°C, 30°C, 40°C)

Equilibrium adsorption data of  $\text{Cu}^{2+}$  onto FM CER were fitted to Langmuir, Freundlich models, and the two linear isotherm model equations were described in Eq(4)-(7):

$$q_e = \frac{bq_m c_e}{1 + bc_e} \quad (4)$$

The linear from the equation is:

$$\frac{1}{q_e} = \frac{1}{bq_m} \frac{1}{c} + \frac{1}{q_m} \quad (5)$$

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

The linear from the equation is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

where  $q_e$  is the adsorption capacity at equilibrium (mg/g) and  $C_e$  is the equilibrium concentration of  $\text{Cu}^{2+}$  in solution (mg/L),  $K_F$  and  $n$  are Freundlich constants. The estimated isotherm model parameters and linear regression coefficient ( $R^2$ ) values obtained are listed in Table IV.

It is obvious that, the value of  $R^2$  for adsorption of  $\text{Cu}^{2+}$  based on Freundlich was 0.9400, which was much lower than 0.9990 based on Langmuir. The Langmuir isotherm model describes the adsorption data for  $\text{Cu}^{2+}$  much better than Freundlich. The adsorption capacity ( $K_F$ ) was 1639.2597mg/g in the Freundlich equation, while the value of adsorption capacity ( $q_e$ ) was about 250mg/g in Langmuir, according to which, the Langmuir constant  $b$  was 0.0058.

TABLE IV: ESTIMATED ISOTHERM PARAMETERS FOR  $\text{Cu}^{2+}$  ADSORPTION ON FM CER

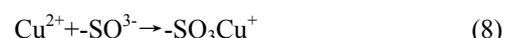
Model	parameters	Fc modified resin
Langmuir Equation	$q_m$	250.00
	$b$	0.0058
	$R^2$	0.9990
Freundlich	$K_F$	1639. 26
	$n$	4.0650
	$R^2$	0.9400

The adsorption capacity obtained from Langmuir agreed much better with the data obtained experimentally.

In the Langmuir equation, the value for maximum adsorption capacity ( $q_e$ ) for  $\text{Cu}^{2+}$  adsorption onto FM CER decreased with the increasing of temperature which also shows an exothermic process in the adsorption process.

#### D. Effect of pH on $\text{Cu}^{2+}$ adsorption

The effect of pH on  $\text{Cu}^{2+}$  adsorption was studied, ranging from 2 to 7, and the results were shown in Fig. 4. The results indicated that the pH of the aqueous solution plays a major role in determining the amount of  $\text{Cu}^{2+}$  adsorbed onto FM CER. The adsorption capacity of  $\text{Cu}^{2+}$  onto FM CER increased as the initial solution pH value increased, and pH ranging from 4 to 5 was the optimum pH for the adsorption process. The adsorption capacities of FM CER at pH 4, 5 were 247 and 245 mg/g, respectively. The effect of pH may be explained in relation to the interaction of  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{OH})^+$ , and  $\text{Cu}(\text{OH})_2$  with functional group  $-\text{HSO}_3$  present in surface of FM CER as follows:



It can be seen that at low pH values,  $\text{H}^+$  competes with the Cu ions for the active surface sites. On the other side, less  $-\text{SO}_3^-$  are ionized at this range of initial solution pH. Moreover,  $\text{Cu}^{2+}$  and  $\text{Cu}(\text{OH})^+$  are the dominant species involved in adsorption process below pH 5, and  $\text{Cu}(\text{OH})_2$  was the leading at pH values higher than 6, thus, the removal of  $\text{Cu}^{2+}$  was not only attributed to the adsorption process, but also the precipitation at neutral condition.

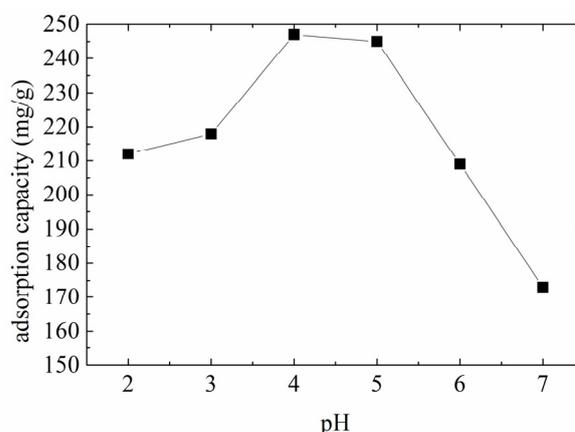


Fig. 4. Effect of pH on  $\text{Cu}^{2+}$  adsorption by FM CER ( $\text{Cu}^{2+}$  initial concentration 640 mg/L, 250 mL, FM CER 1g/L, temperature 30°C)

## IV. CONCLUSION

Ferrocene modified cation exchange resin was prepared using immersion method, and used in  $\text{Cu}^{2+}$  adsorption process. Fc was successfully loaded onto cation exchange resin, pore width and surface area of the resin was enlarged, and the ratio of Fc on resin (w/w) was 0.1792%. The  $\text{Cu}^{2+}$  adsorption process obeyed pseudo-second-order kinetic model. The adsorption of  $\text{Cu}^{2+}$  followed the Langmuir adsorption isotherm model and the adsorption process was an exothermic reaction. The adsorption of  $\text{Cu}^{2+}$  was found to be pH dependent and the optimal pH was found to be 4-5.

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