

# Kinetic studies on the adsorption of Cu(II) onto alginate-carboxymethyl cellulose membrane

Xihui Zhao, Xiaolu Sun, Qun Li, Xiaowen Li & Yanzhi Xia

Collaborative Innovation Center for Marine Biomass Fibers, Materials and Textiles of Shandong Province, Qingdao University, Qingdao, China

College of chemistry and chemical engineering, Qingdao University, Qingdao, China

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**Abstract.** Alginate-carboxymethyl cellulose membrane (AC membrane) was prepared. The adsorption behavior of Cu(II) on AC membrane was studied. The adsorption mechanisms were investigated with three different kinds of kinetic models (Lagergren's pseudo-first-order, Ho's pseudo-second-order equations). The results indicated that the experimental data of the Cu(II) adsorption on AC membrane could be well described by the Ho's pseudo-second-order model, the correlation coefficients  $R^2$  all reached 0.99. The adsorption process is a complex and heterogeneous chemical adsorption process.

## Introduction

The pollution of heavy metal ions in water resources is a critical problem because of their toxicity and other adverse effects to plants, animals and human beings <sup>[1]</sup>. Copper is one of the most widespread heavy metal contaminants. Excessive intake of copper results in serious problems to human beings <sup>[2]</sup>. Many methods have been reported to remove heavy metals from water and wastewater. Among all these methods, the adsorption technique has been proved to be an excellent way due to its low cost, ready availability, easy operation and high efficiency <sup>[3]</sup>. Different adsorbents such as clay minerals <sup>[4]</sup>, active carbon <sup>[5]</sup>, agricultural by-products <sup>[6]</sup> have been studied. However, some limitations including incomplete metal removal, high cost, and difficult treatment to the polluted forms still exist in these adsorbents. Therefore, it is indeed necessary to explore low cost, environmentally friendly, and high effective adsorbent materials.

Sodium alginate (SA) and carboxymethyl cellulose (CMC) are well known as safe and biodegradable materials. SA has attracted considerable attentions and has been used as an adsorbent for heavy metal ions <sup>[7]</sup>. CMC has also been reported as adsorbent for metal ions such as Cu, Cd, and Pb <sup>[8-10]</sup>. However, to our knowledge, no work has been done with alginate-carboxymethyl cellulose membranes (AC membranes) as an adsorbent. The objectives of this study were to prepare AC membranes and evaluate the adsorption performance of the membranes for Cu(II) ions. In order to understand the adsorption process, adsorption kinetics were also determined.

## Experimental

**Materials.** Sodium alginate (SA) was supplied by Jiejing Seaweed Co. Ltd., Shandong Province, P. R. China. Carboxymethyl cellulose (CMC) was purchased from Shanghai Chemical Reagents Company, chemical grade. All other reagents were of analytical grade.

**Preparation of AC membranes.** The membranes were prepared by the solution casting method. SA (2.0%) and CMC (2.0 %) were mixed with the weight ratio of 80:20 (SA: CMC). The mixed

solution was degassed and spread over a glass plate and coagulated in the air. The formed membrane was immersed in a 3 wt%  $\text{CaCl}_2$  for 1 h, followed by washing in distilled water, drying and labeling as AC membranes.

**Adsorption experiments.** The batch adsorption experiments were carried out using a series of 250 mL volumetric flasks, in which a determined amount of membrane and copper solution were added. After agitation, the phase was separated by filtration. The concentration of Cu(II) in the filtrates was determined using an Atomic Absorption Spectrometer (TAS-986, Purkinje General, China). The amount of Cu(II) adsorbed  $q_t$  (mg/g) at time  $t$  (min), adsorption capacity  $q_e$  (mg/g) at equilibrium were calculated as follows:

where  $C_0$  (mg/L),  $C_t$  (mg/L) and  $C_e$  (mg/L) are Cu(II) concentrations at initial, time  $t$  and equilibrium in the solution, respectively,  $V$  (mL) is the volume of Cu(II) solution and  $W$  (mg) is the amount of adsorbent employed.

**Characterization.** Fourier transform infrared spectra (FTIR) were obtained with NICOLET5700 spectrometer by KBr tablet method. The micrograph of the AC membranes before and after Cu(II) adsorption were taken by using SEM (JEM-200EX, JEOL, Ltd.).

## Results and discussion

**Characterization of AC membrane.** FT-IR spectra of AC membranes before and after Cu(II) adsorption are presented in Fig. 1. Fig. 1A shows characteristic peaks at 3420, 2925, 1608, 1422, 1083  $\text{cm}^{-1}$ . The broad and strong band at 3420  $\text{cm}^{-1}$  is attributed to the  $-\text{OH}$  stretching vibration, the strong peak around 1608  $\text{cm}^{-1}$  shows the carbonyl ( $\text{C}=\text{O}$ ) stretching vibration of the carboxyl groups, while the peaks at 1422  $\text{cm}^{-1}$  can be assigned to carboxylate group ( $-\text{COO}-$ ) stretching. The peak at 1083  $\text{cm}^{-1}$  is ascribed generally to the  $\text{C}-\text{O}$  stretching vibration in carboxylic acids and alcohols. After adsorption Cu(II), FTIR spectrum (Fig. 1B) shows the shifts on the characteristic peak locations from 3420, 1608, 1422 and 1083  $\text{cm}^{-1}$  to 3406, 1605, 1423 and 1036  $\text{cm}^{-1}$ , respectively, which may be attributed to the bond energy of  $-\text{OH}$ ,  $\text{C}=\text{O}$ ,  $-\text{COO}-$  and  $\text{C}-\text{O}$  was impacted by chemical action generated in adsorption process. Hence, FTIR spectra reveals that functional groups like  $-\text{OH}$  and  $-\text{COO}-$  are involved in the adsorption of Cu(II) ions onto the AC membrane.

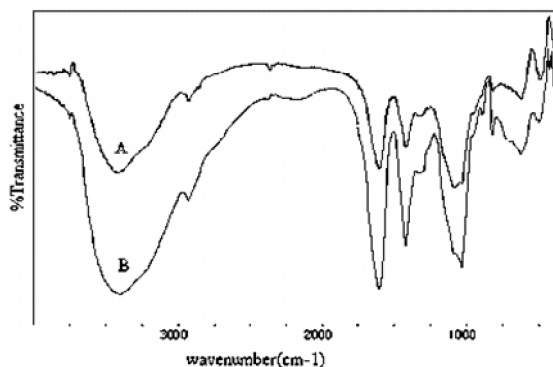


Fig. 1. FTIR spectra of the AC membrane before adsorption (A) and after adsorption of Cu(II) (B).

The SEM images of the surface of the AC membranes before and after Cu(II) ions adsorption are shown in Fig. 2(a) and (b). It can be seen that the adsorption of Cu(II) ions on the AC membranes made the surface smoother and caused the interspaces among protrusions to become smaller than that of pristine AC membranes.

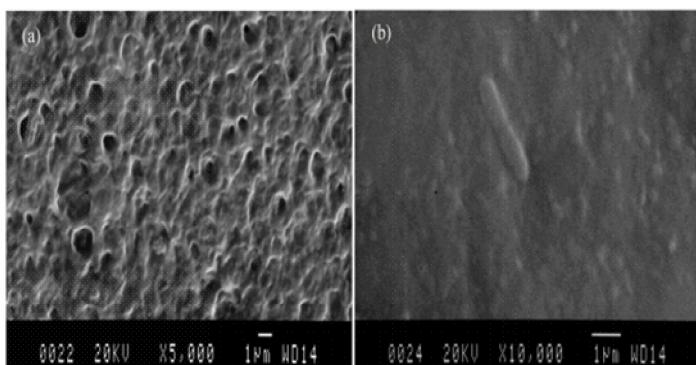


Fig. 2. SEM images of the AC membranes: (a) before adsorption and (b) after adsorption.

**Effects of contact time and initial Cu(II) ion concentration on adsorption.** Effects of contact time and initial Cu(II) ion concentration on adsorption are shown in Fig. 3. It can be seen from Fig. 3 that the adsorption profile was time-dependent and consisted of two-stage. They first experienced a fast increase between 0 and 30 min, followed by a slow increase to reach an equilibrium value after 90 min. The change in the sorption capacity after 90 min was negligible. Therefore, the adsorption time was set on 90 min in all following experiments to ensure that the equilibrium had been reached. In addition, when the initial Cu(II) ion concentration increased from 50 to 200 mg/L, the adsorption capacity increased from 13.83 to 56.75 mg/g. The reason can be explained from the following aspects. Firstly, a higher initial Cu(II) ions concentration increased driving force to overcome the mass transfer resistance of Cu(II) ions between the aqueous and solid phase resulting in higher chance of collision between the Cu(II) ions and the AC membranes. Secondly, with the increase of the Cu(II) ions concentration, the active sorption sites on the AC membranes were surrounded by more Cu(II) ions leading to more intensity interaction between the Cu(II) ions and AC membranes. Similar results have been reported by other authors<sup>[11]</sup>.

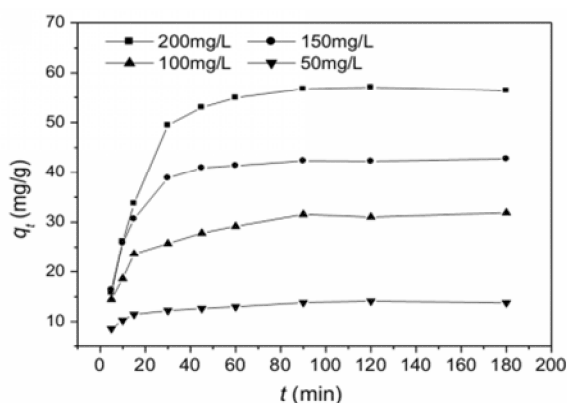


Fig. 3. Effect of contact time and initial Cu(II) ion concentration.

**Adsorption kinetics.** Three models, namely, Lagergren's pseudo-first-order kinetic models, pseudo-second-order kinetic models, were applied to the experimental data to explain the sorption mechanism. The pseudo-first-order rate equation by Lagergren<sup>[12]</sup> is given as Eq. (3). After integrating Eq. (3), the linearized form may be expressed as Eq. (4).

Where  $q_e$  and  $q_t$  are the amounts of metal ion adsorbed (mg/g) at equilibrium and at time  $t$ , respectively,  $k_1$  is the pseudo-first-order rate kinetic constant ( $\text{min}^{-1}$ ).

A straight line could be obtained by plotting  $\log (q_e - q_t)$  versus  $t$ , and the value of  $k_1$  was determined from the slope (Fig. 4A). The pseudo-first-order rate parameter ( $k_1$ ) and the calculated value ( $q_e$ ) are presented in Table 1. Although the correlation coefficient values are quite high ( $R^2 > 0.9$ ) in some cases, the calculated values of  $q_e$  and the experimental values diverge greatly. Therefore, the pseudo-first order model is inappropriate to the adsorption of Cu(II) on AC membranes.

The pseudo-second-order model proposed by Ho and McKay has also been applied widely to many metal ion/sorbent sorption systems, which is based on the assumption that the adsorption follows second-order chemisorptions<sup>[13]</sup>. The equation can be expressed as Eq. (5). After integrating Eq. (5) with boundary conditions  $t=0$  to  $t$  and  $q_t=0$  to  $q_t$ , the linear form can be written as Eq. (6):

Where  $k_2$  is the pseudo-second-order rate constant of adsorption [ $\text{g}/(\text{mg min})$ ].

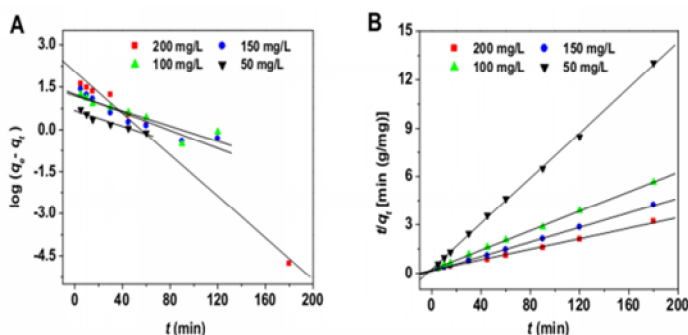


Fig. 4. kinetics model for various initial Cu(II) concentration (A)Pseudo-second-order model (B)Pseudo-second-order model.

Plotting  $t/q_t$  against  $t$  gives an excellent straight line relation with  $R^2 > 0.99$  for all the experimental concentrations (Fig. 4B), confirming the applicability of the pseudo-second-order model. The values of pseudo-second-order rate kinetic constant ( $k_2$ ) and sorption capacity ( $q_e$ ) are calculated from the slope and intercepts, respectively, and present in Table 1. The calculated  $q_e$  values are very close to the experimental values, reinforcing the applicability of this model. It also can be seen in Table 1 that the rate constant ( $k_2$ ) decreases as the initial concentration of Cu(II) ions increases. The confirmation of pseudo-second-order kinetics indicates that the adsorption process may be a chemical adsorption or chemisorptions<sup>[14]</sup>.

Table 1 Pseudo-first-order and pseudo-second-order parameters for the adsorption of Cu(II) on AC membranes with different initial concentrations (adsorbent dosage: 2 g/L; pH: 6.0; 25 °C).

Initial Cu(II) concentratio n (mg/L)	Pseudo-second-order model			Pseudo-second-order model			
	$k_1$	$q_e(\text{cal})$	$R^2$	$k_2$ [g/(mg	$q_e(\text{cal.})$	$q_e(\text{exp.})$	$R^2$
	( $\text{min}^{-1}$ )	(mg/g)		min)]	(mg/g)	(mg/g)	
50	0.0316	4.689	0.9397	0.0176	14.231	13.790	0.9992
100	0.0309	15.720	0.8480	0.00408	33.179	31.871	0.9994
150	0.0367	17.739	0.8857	0.00373	44.524	42.740	0.9992
200	0.0850	112.285	0.9880	0.00137	61.690	56.413	0.9956

$q_e(\text{cal})$  and  $q_e(\text{exp.})$  are the calculated values of  $q_e$  and the experimental values, respectively

## Conclusions

The results of this study show that AC membranes can be successfully used for the adsorption of Cu(II) ions from aqueous solutions. The adsorption extent increased with increasing initial Cu(II) ion concentration and sharply increased between 0 and 15 min. The kinetics of adsorption follows pseudo-second-order model.

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## References

- [1] M. Zhang: Chem. Eng. J. Vol. 172 (2011), p.361-368
- [2] H.K. Hansen, F. Arancibia, C. Gutiérrez: J. Hazard. Mater. Vol. 180 (2010), P. 442-448
- [3] A. Demirbas: J. Hazard. Mater. Vol. 157 (2008), P. 220-229.
- [4] A.A. El-Bayaa, N.A. Badawy, E.A. Alkhalik: J. Hazard. Mater. Vol. 170 (2009), P. 1204-1209
- [5] K. Wilson, H. Yang, C.W. Seo, W.E. Marshall: Biores. Technol. Vol. 97 (2006), P. 2266-2270
- [6] Z. Aksu, I.A. Isoglu: Process Biochem. Vol. 40 (2005), P. 3031-3044
- [7] T. Gotoh, K. Matsushima, K.I. Kikuchi: Chemosphere Vol. 55 (2004), P. 135-140
- [8] W.S. Wan Ngah, S. Fatinathan: Chem. Eng. J. Vol. 143 (2008), P. 62-72
- [9] A. Hiroki, H.T. Tran, N. Nagasawa, T. Yagi, M. Tamada: Radiat: Phys. Chem. Vol. 78 (2009), P. 1076-1080
- [10] K. Hara, M. Iida, K. Yano, T. Nishida: Colloids Surf. B Vol. 38 (2004), P. 227-230
- [11] H. Aydin, Y. Bulut, C. Yerlikaya: J. Environ. Manage. Vol. 87 (2008), p. 37-45
- [12] N. Prakash, S. Latha, P.N. Sudha, N.G. Renganathan: Environ. Sci. Pollut. Res. Vol. 20 (2013), p. 925-938
- [13] Y.S. Ho, G. McKay: Water Res. Vol. 34 (2000), p.735-742.
- [14] M.V. Subbaiah, Y. Vijaya, A.S. Reddy, G. Yuvaraja, A. Krishnaiah, Desalination Vol. 276 (2011), p. 310-316