



Novel Silica-Based Hybrid Adsorbents: Copper(II) Adsorption Isotherms and Thermodynamics

KEYAN HU, JUNSHENG LIU*, XINGHUA CHEN, MIN XU and KECHUN WANG

Key Laboratory of Membrane Materials & Processes, Department of Chemical and Materials Engineering, Hefei University, 99 Jinxiu Road, Hefei Economic and Technological Development Zone, Hefei 230601, P.R. China

*Corresponding author: Fax: +86 551 62158437; Tel: +86 551 62158439; E-mail: jsliu@hfu.edu.cn

Received: 29 June 2013;

Accepted: 14 August 2013;

Published online: 23 June 2014;

AJC-15358

In this study, copper(II) adsorption isotherms and thermodynamic data have been investigated using a hybrid membrane as an adsorbent. It is found that copper(II) adsorption on sample D followed the Freundlich isotherm model. Moreover, it is found that the adsorption capacity of copper(II) on sample D increases with an increase in solution temperature and the ΔG values are changed from positive to negative as the temperature increased, suggesting that copper(II) adsorption is an endothermic and spontaneous in nature as the solution temperature was elevated to higher level. In addition, based on intraparticle diffusion, it is confirmed that copper(II) adsorption is not governed by intraparticle diffusion and diffusion-controlled adsorption mechanism might be the major control process. This finding is meaningful in the removal of copper(II) from aqueous solution using hybrid membrane as an adsorbent.

Keywords: Hybrid membrane, Adsorption, Isotherms, Thermodynamics, Copper(II) removal.

INTRODUCTION

Water pollution caused by toxic heavy-metal ions, such as Cu^{2+} , Pb^{2+} , etc. has become a major environmental issue¹⁻³. As a typical toxic heavy-metal, copper(II) pollution has captured much attention. To eliminate or reduce copper(II) pollution, various techniques have been developed^{1,2,4,5}. Among which, silica-based hybrid membranes with functionalized ionic groups indicates excellent adsorption performances for heavy-metal ions when they are used as hybrid adsorbents^{5,6}. However, the applications of these hybrid membranes are restricted within a small field. Especially, the relevant engineering data for their applications in industrial processes are deficient. Therefore, these previous researches are insufficient and further study is essential.

To extend the application aspects of hybrid membrane as adsorbents, a series of novel hybrid membranes using as adsorbents are recently developed and some associated engineering data for their applications in industry are calculated⁷⁻⁹. Our continuing interest in these hybrid adsorbents drives us to do further work. Consequently, based on the previous investigation⁹, herein, the adsorption isotherm and thermodynamics of copper(II) ions on silica-based hybrid membranes will be calculated. Its adsorption for copper(II) removal in aqueous solution will be evaluated as a model toxic heavy-metal.

EXPERIMENTAL

The preparation of hybrid membrane sample used in this case was described in a previous article⁹. In the previous study, it is found that the adsorption capacity of copper(II) on sample A-D increased with an increase in TMSPEDA content. Especially, when the volume ratio of GPTMS and TMSPEDA was 1:10 for sample D, the adsorption capacity of copper(II) in 0.01 mol dm⁻³ aqueous $\text{Cu}(\text{NO}_3)_2$ solution for 24 h can arrive at the highest value among the investigated samples A-D. To continue the previous study and the related chemical engineering data, the adsorption isotherm and thermodynamic data of copper(II) ions on sample D will be examined in this job.

Adsorption experiment: To insight into the adsorption properties of these hybrid membranes for copper(II) ions in aqueous solution, adsorption experiment was conducted. The adsorption capacity ($q_{\text{Cu}^{2+}}$) of copper(II) ions can be determined using eq. 1:

$$q_{\text{Cu}^{2+}} = \frac{(C_0 - C_R)V}{W} \quad (1)$$

where V (mL) is the volume of aqueous $\text{Cu}(\text{NO}_3)_2$ solution, C_0 (mol dm⁻³) and C_R (mol dm⁻³) are the concentration of initial and remaining $\text{Cu}(\text{NO}_3)_2$, respectively; W (g) is the weight of hybrid membrane.

RESULTS AND DISCUSSION

It is well known that both Langmuir and Freundlich isotherm equations are two typical theoretical models to evaluate the adsorption properties of metal ions on the interface of a solid material. Generally speaking, Langmuir isotherm equation can be expressed as eqn. 2^{10,11}, which is mainly based on the monolayer adsorption on the active reaction sites of the adsorbent.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \quad (2)$$

where q_e (mmol g⁻¹) and C_e (mol dm⁻³) are the equilibrium concentrations of metal ion in the adsorbed and liquid phases, respectively. Q_m (mmol g⁻¹) and b (dm³ mol⁻¹) are the Langmuir constants, which can be calculated from the intercept and slope of the linear plot based on C_e/q_e versus C_e .

Differentiating from the Langmuir isotherm model, Freundlich isotherm equation can be expressed as eqns. (3a) and (3b)^{10,11}. Usually, it is considered as the adsorption occurred on a heterogeneous surface with uniform energy.

$$q_e = k_F C_e^{1/n} \quad (3a)$$

$$\log(q_e) = \log k_F + \frac{1}{n} \log(C_e) \quad (3b)$$

where q_e (mmol g⁻¹) and C_e (mol dm⁻³) are the equilibrium concentrations of metal ion in the adsorbed and liquid phases, respectively. k_F [(mmol g⁻¹) (mol dm⁻³)^{-1/n}] and n are the Freundlich constants, which can be calculated from the slope and intercept of the linear plot according to $\log(q_e)$ vs. $\log(C_e)$.

The relationship of adsorption capacity of copper(II) ions with initial solution concentration (*i.e.*, adsorption isotherm of copper(II) ions) is illustrated in Fig. 1. It can be noted in Fig. 1 that the adsorption capacity of copper(II) ions increases when the concentration of initial solution increases.

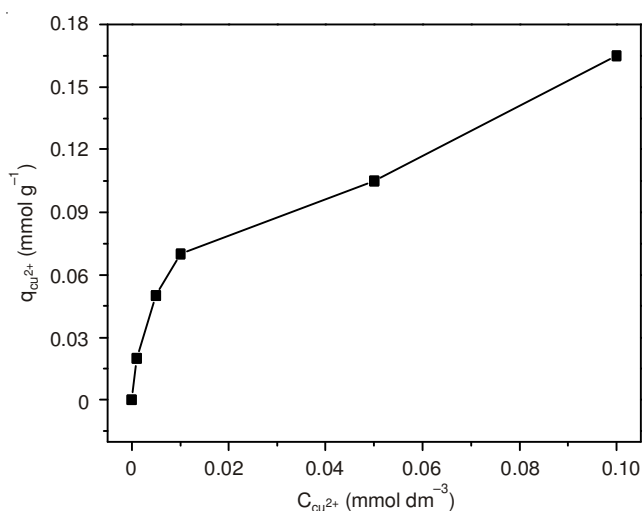


Fig. 1. Copper(II) adsorption capacity versus initial concentration; the sample was immersed in different concentration aqueous Cu(NO₃)₂ solutions for 9 h, respectively

Based on the relationship of copper(II) adsorption capacity with initial solution concentration, Langmuir and Freundlich adsorption isotherms can be calculated. Fig. 2 (a) and (b) presents the Langmuir and Freundlich adsorption isotherm of copper(II) ions. According to these isotherm curves, the Langmuir and Freundlich isotherm parameters are calculated and listed in Table-1. From Table-1, it can be found that the experimental data fitted well with Freundlich isotherm equation ($R^2 > 0.98$). In contrast, these data fitted worse with Langmuir isotherm equation ($R^2 < 0.94$). This finding evidences that copper(II) adsorption on the prepared hybrid membrane is heterogeneous surface adsorption rather than Langmuir monolayer one. Such result will be very meaningful in the removal of copper(II) from aqueous solution using hybrid adsorbents.

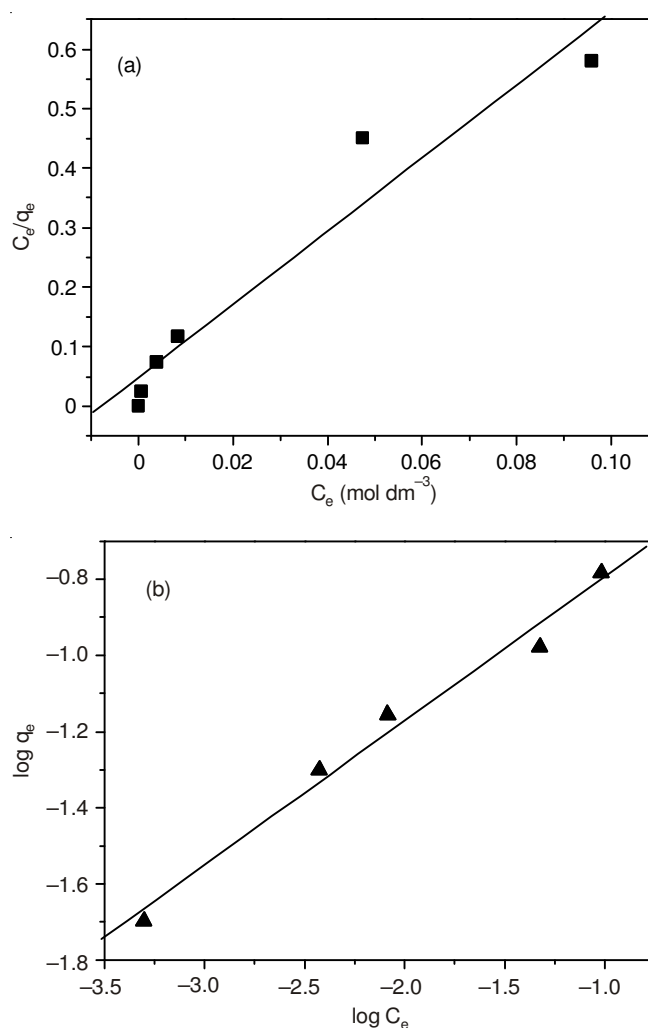


Fig. 2. Plot of adsorption isotherm for copper(II) adsorption, (a) Langmuir model, (b) Freundlich model

TABLE-1
LANGMUIR AND FREUNDLICH ISOTHERM
PARAMETERS FOR COPPER(II) ADSORPTION

Sample	Langmuir			Freundlich		
	Q_m	b	R^2	k_F	n	R^2
D	0.162	125.371	0.936	0.386	2.636	0.981

Thermodynamic study: Thermodynamic parameter calculation is vital importance for the removal of heavy-metal ions *via* adsorption technique. The adsorption experiments at different temperatures for copper(II) removal are thus performed and illustrated in Fig. 3.

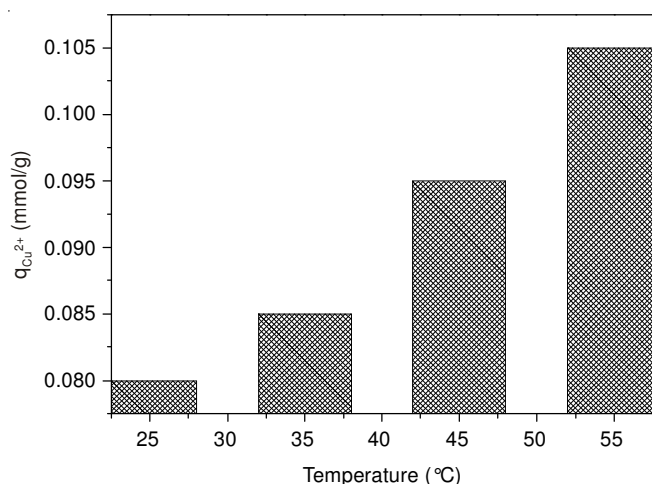


Fig. 3. Copper(II) adsorption capacity *versus* solution temperature, the concentration of aqueous Cu(NO₃)₂ solution was 0.01 mol dm⁻³

As shown in Fig. 3, it can be seen that the adsorption capacity of copper(II) increases with an increase in solution temperature [the linear regression coefficient (R²) values are in the range of 0.91-0.96]. This result indicates that adsorption of copper(II) ions is endothermic in nature¹⁰, which can be confirmed by some thermodynamic parameters such as free energy (ΔG) and enthalpy (ΔH), *etc.*

Furthermore, thermodynamic parameters, free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), can be calculated from eqns. (4) and (5)¹⁰:

$$\Delta G = -RT \ln(K_c) \quad (4)$$

$$\ln(K_c) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

in which, K_c is the equilibrium partition coefficient and can be calculated from eq. (6)¹⁰:

$$K_c = \frac{C_s}{C_e} \quad (6)$$

where R is the gas constant (8.314 J/mol K), C_s and C_e (mol dm⁻³) are the equilibrium concentrations of metal ions in the adsorbent and solution, respectively and T is the solution temperature (K). ΔH and ΔS can thus be calculated from the slope and intercept of the linear plot according to ln(K_c) *versus* 1/T (cf. Fig. 4). The calculated results are presented in Table-2.

Sample	Temp. (K)	ΔG (kJ/mol)	ΔS (J/mol K)	ΔH (kJ/mol)	R ²
D	298.15	1.005	43.043	13.922	0.973
	308.15	0.774			
	318.15	0.265			
	328.15	-0.273			

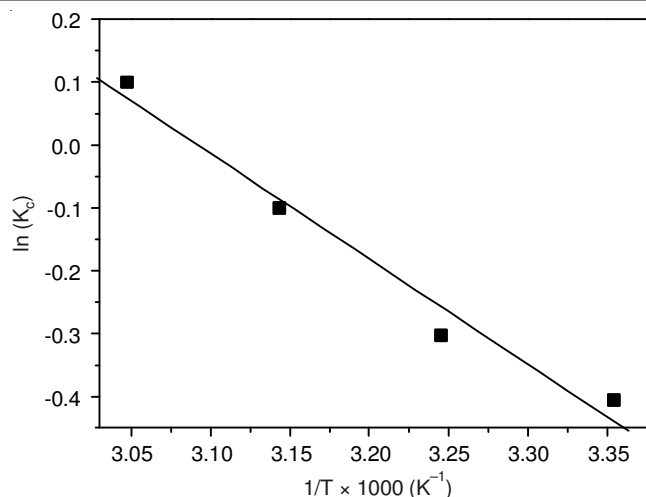


Fig. 4. van't Hoff plot of copper(II) adsorption, the concentration of aqueous Cu(NO₃)₂ solution was 0.01 mol dm⁻³ at 25, 35, 45 and 55 °C for 24 h, respectively

As shown in Table-2, the ΔG values are changed from positive to negative with the elevated solution temperature. Meanwhile, the ΔH values are all positive in the tested temperature range. These observations imply that copper(II) adsorption on the prepared hybrid membrane is spontaneous and endothermic process when the solution temperature is elevated to higher level. Moreover, it can be seen that the ΔS values are all positive, demonstrating that the randomness increased during copper(II) adsorption on sample D. These findings evidence that temperature has a larger impact on copper(II) adsorption on the investigated hybrid membrane.

Intraparticle diffusion mechanism: It is reported that when metal ions are adsorbed by an adsorbent, the metal ions transport from the solution through the interface between the solution and the adsorbent into the pores of the particles. Such transport property of metal ions can be modeled *via* intraparticle diffusion¹¹. To gain the interface transport property of copper(II) ions from the interior of the prepared sample D, intraparticle diffusion model was determined. The intraparticle diffusion on the adsorption rate of copper(II) ions can be calculated according to the dependency of adsorption capacity q_t on contact time t, which can be expressed as eq. (4)¹².

$$q_t = x_i + k_p t^{0.5} \quad (4)$$

where q_t (mmol g⁻¹) is the adsorbed amount at time t (h), k_p (mmol g⁻¹ h^{-1/2}) is the intraparticle diffusion rate constant and x_i (mmol g⁻¹) is the intercept of straight line, which is related to the boundary layer thickness.

Presently, it is well accepted that if the plot of q_t vs. t^{0.5} gives a straight line, the adsorption process is solely controlled by intraparticle diffusion. In contrast, if the linear fitting exhibit multi-linear curves, two or more steps will influence the adsorption process^{11,12}.

Fig. 5 gives the intraparticle diffusion curve of copper(II) adsorption on sample D. From Fig. 5, it can be noted that the graph doesn't exhibit the straight line and the linear regression coefficient (R²) fitted worse for copper(II) adsorption as the tested data are linearly fitted. This result copper(II) adsorption on the prepared hybrid membrane is not governed by intra-

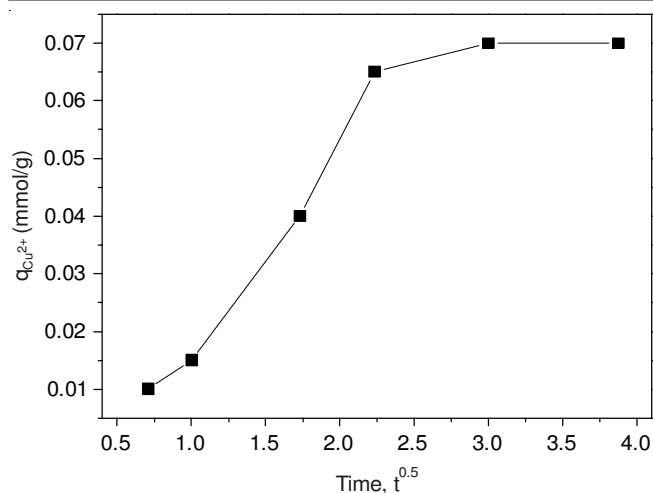


Fig. 5. Intraparticle diffusion curve of copper(II) adsorption on sample D

particle diffusion and diffusion-controlled adsorption mechanism might be the major control process.

Desorption experiment: Currently, for the removal of heavy metal ions from aqueous solution, the significance consists in both desorption and reuse of metal ion in industrial processes rather than the simple adsorption and disposal^{6,13}. To regenerate and recycle the adsorbent spent, desorption experiment was performed using 0.1 mol dm^{-3} HCl, H_2SO_4 and HNO_3 as typical desorbents, respectively. The obtained data are listed in Table-3. Clearly, for copper(II) desorption, the desorption efficiency (%) can be elevated to 100 % demonstrating an effective regeneration cycle.

TABLE-3
DESORPTION EFFICIENCY OF SAMPLE D FOR
COPPER(II) IN VARIOUS DESORBENTS

Desorbent	Desorption time (h)	Efficiency (%)
HCl	9	99.3
H_2SO_4	9	100
HNO_3	9	100

Based on the above obtained desorption data, it can be concluded that this type of hybrid membrane is a promising adsorbent for removal of copper(II) from copper(II)-bearing water in industry.

Conclusion

Copper (II) adsorption isotherms and thermodynamic data are examined. It demonstrates that copper(II) adsorption on sample D followed the Freundlich isotherm model. The calculation of thermodynamic parameters indicates solution temperature has an important impact on copper(II) adsorption and such adsorption is an endothermic in nature. In addition, the measurement of intraparticle diffusion suggests that copper(II) adsorption is not governed by intraparticle diffusion and diffusion-controlled adsorption mechanism might be the major control step.

ACKNOWLEDGEMENTS

This project was financially supported by the National Natural Science Foundation of China (No. 21076055), the Significant Foundation of Educational Committee of Anhui Province (No. ZD2008002-1), the 2th National-level College Students' Innovative Entrepreneurial Training Plan Program (No. 201211059010).

REFERENCES

- J. Li, S.W. Zhang, C.L. Chen, G.X. Zhao, X. Yang, J.X. Li and X.K. Wang, *ACS Appl. Mater. Interfaces*, **4**, 4991 (2012).
- S.A. Ali, O.C.S. Al Hamouz and N.M. Hassan, *J. Hazard. Mater.*, **248**, 47 (2013).
- M. Karatas, *J. Hazard. Mater.*, **199**, 383 (2012).
- J.-J. Guo and W.-B. Chen, *Asian J. Chem.*, **25**, 3609 (2013).
- E. Repo, J.K. Warchol, A. Bhatnagar and M. Sillanpää, *J. Colloid Interf. Sci.*, **358**, 261 (2011).
- G.P. Kumar, P.A. Kumar, S. Chakraborty and M. Ray, *Sep. Purif. Technol.*, **57**, 47 (2007).
- Q. Dong, J.S. Liu, L. Song and G.Q. Shao, *J. Hazard. Mater.*, **186**, 1335 (2011).
- X. Wang, W.X. Zhang, J.S. Liu and L.L. Wu, *Asian J. Chem.*, **25**, 6575 (2013).
- K.Y. Hu, J.S. Liu and K.C. Wang, *Asian J. Chem.*, **26**, 2571 (2014).
- A. Ramesh, H. Hasegawa, T. Maki and K. Ueda, *Sep. Purif. Technol.*, **56**, 90 (2007).
- A.A. Atia, A.M. Donia and A.M. Yousif, *Sep. Purif. Technol.*, **61**, 348 (2008).
- E. Guibal, C. Milot and J.M. Tobin, *Ind. Eng. Chem. Res.*, **37**, 1454 (1998).
- P.K. Chatterjee and A.K. Sengupta, *AIChE J.*, **55**, 2997 (2009).