Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.898000

54 (2015) 2307–2313
May

Taylor & Francis
Taylor & Francis Group

Kinetic model investigation on lead(II) adsorption using silica-based hybrid membranes

Junsheng Liu*, Linlin Wu, Xinghua Chen

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, China, Tel. +86 551 62158439; email: jsliu@hfuu.edu.cn

Received 27 August 2013; Accepted 16 February 2014

ABSTRACT

With the rapid development of lead refineries and the wide application of leaded work in electrical industry, lead(II) pollution has deserved much attention. In this study, the kinetic models of lead(II) adsorption onto silica-based hybrid membranes as solid adsorbents were studied. To study the adsorption mechanism of heavy metal ions on these hybrid adsorbents, the experimental data were linearly fitted using six typical two-parameter kinetic equations (i.e. Lagergren pseudo-first-order and pseudo-second-order, Ritchie second-order and modified second-order, Elovich, as well as intraparticle diffusion models). It was found that the experimental results fitted well with Lagergren pseudo-second-order model, Elovich, and intraparticle diffusion models. These findings are very useful in the design and optimization of silica-based hybrid membranes for lead(II) removal from water by adsorption.

Keywords: Adsorption; Kinetic model; Hybrid membrane; Lead(II) removal; Wastewater treatment

1. Introduction

Water contamination caused by toxic heavy metals, such as lead(II), copper(II), and cadmium(II), has deserved increasing attention [1–3]. Particularly, lead has been widely used in some industrial processes and household appliances; its pollution in water threatens not only the human body but also the drinking water resources. This is because toxic lead(II) cannot be biodegraded completely in nature and is easily accumulated in human body and other organisms, which will induce various diseases. Consequently, the removal of toxic lead(II) from water has turned into significantly important and highly needed.

To eliminate or reduce the pollution caused by lead(II), various effective techniques have been newly developed [4,5]. Among them, adsorption using some functionalized hybrid materials or polymers as adsorbents has been considered as one of the most efficient methods because of its high removal efficiency and low operation cost [5,6]. However, these hybrid materials or polymers also disclosed some limitations, such as large-scale production and regeneration problems. These demerits have blocked their further applications in the removal of heavy metals from water. As a result, the development of new substitutes for hybrid materials as adsorbents has become more attractive.

---

*Corresponding author.

Recently, much effort was made to develop new hybrid adsorbents for the removal of lead(II) and copper(II) from water in our laboratory. In the previous articles [7–9], it was found that the prepared hybrid adsorbents revealed excellent adsorption properties for heavy metals lead(II) and copper(II) in aqueous solutions. Meanwhile, to well understand the adsorption mechanism of heavy metal ions on these hybrid adsorbents produced, two-parameter empirical models, such as the Lagergren kinetic pseudo-first-order model and pseudo-second-order model, the Langmuir and Freundlich isotherm models, were used to correlate the experimental data. On the basis of the above-mentioned empirical models, the adsorption behaviors of the hybrid adsorbents produced were reasoned out. Our continuing interest in such investigations has stimulated us to make further effort. Therefore, to continue the previous job and examine the adsorption properties of hybrid adsorbents for divalent heavy metal ions, herein, the kinetics of silica- based hybrid membranes for lead(II) adsorption were correlated using six typical two-parameter kinetic equations (i.e. Lagergren pseudo-first-order model and pseudo-second-order model, Ritchie second-order model and modified second-order model, Elovich model, and intraparticle diffusion model). The linear regression analysis was used to evaluate the applicability of the fitted theoretical models.

2. Materials and methods

2.1. Materials

3-Aminopropyl trimethoxysilane (APTMS, purity ≥ 95.0%) was purchased from Jiangsu Chenguang Coincident Dose Co., Ltd (Danyang City, China) and used without further purification. Poly(vinyl alcohol) (PVA, MW: 10,000) was purchased from Shanghai Chemical Reagent Co., Ltd (Shanghai city, China) and used as received. Other reagents were of analytical grade and used as received.

2.2. Hybrid membrane preparation

The preparation of silica-based hybrid membranes used in this case could be described briefly as follows: APTMS (ca. 3 g) was mixed with a 5% (weight percentage) aqueous PVA solution (ca. 60 g) and stirred violently for an additional 1 h to produce the coating solution. Subsequently, the previously prepared coating solution was coated on a Teflon plate and was air-dried at room temperature for an additional 12 h to obtain the preproduction substance of hybrid membranes. Finally, such substance of hybrid membrane was cured at different temperatures for 24 h to achieve the final samples (the hybrid membranes cured at 40, 60, 80, and 100℃ were labeled as samples A–D, respectively).

2.3. Adsorption experiments

To examine the adsorption properties of the hybrid membranes for lead(II) ions in an aqueous solution, the adsorption experiments were carried out. In the previous studies [7–9], it was found that the adsorption capacity of lead(II) on hybrid adsorbents can reach the maximal value at pH 4. Meanwhile, the concentration of lead(II) at pH 4 can be preciously measured by titrimetric analysis. For these reasons, the adsorption experiments were conducted under pH 4.

The procedure can be described briefly as follows: about 1.0 g of sample was immersed in a 0.01 mol L^{-1} aqueous $Pb(NO_3)_2$ solution at pH 4 for 24 h. Subsequently, it was taken out and washed with deionized water. An EDTA solution (0.01 mol L^{-1}) was used to determine the concentration of Pb^{2+} ions in the remaining solution by titrimetric analysis.

The adsorption capacity (q^{2+}_{Pb}) of lead(II) ions onto these samples was calculated using Eq. (1):

$$q_{\mathrm{Pb}^{2+}} = \frac{(C_0 - C_R)V}{W} \tag{1}$$

where V is the volume of the aqueous $Pb(NO_3)_2$ solution (L); C_0 and C_R are the concentrations of the initial and remaining $Pb(NO_3)_2$ (mmol g^{-1}), respectively; and W is the weight of the tested sample (g).

3. Results and discussion

3.1. Adsorption properties of hybrid adsorbents

To gain the adsorption properties of hybrid adsorbents for toxic heavy metal ions, a series of hybrid materials and the related membranes [7–9] were prepared and used as solid adsorbents to adsorb heavy metal ions from aqueous solution, in which both Pb^{2+} and Cu^{2+} were used as the models of heavy metal ions. It was observed [7] that the adsorption of Pb^{2+} on the zwitterionic hybrid materials followed the Lagergren second-order kinetic model, in which both the –COOH and –COO^- and $\text{–N}^+\text{–}$ groups located on the hybrid matrix were arrayed in the two sides of the polymer chain and these ionic groups produced a pendant-side molecular structure. In addition, it was also found [8] that the adsorption of Cu^{2+} ions on these zwitterionic hybrid adsorbents also followed the

Lagergren second-order kinetic model, and intraparticle diffusion mechanism was the dominating control process. Moreover, to further investigate the adsorption behaviors of heavy metal ions on the hybrid adsorbents, a new type of substitute of the above-mentioned adsorbents containing –SH groups was prepared and used to adsorb Cu^{2+} ions [9]. It was found that the adsorption of Cu^{2+} ions on this type of hybrid adsorbents fitted well with the Lagergren first-order kinetic model. Such outcome was opposite to those obtained in the previous articles [7,8]. This conclusion demonstrated that the adsorbents containing different ionic groups will produce various adsorption mechanisms of heavy metal ions on them. Consequently, it is essential to study the adsorption mechanism of hybrid adsorbents using different theoretical models as discussed later.

3.2. *Adsorption capacity of lead(II) vs. adsorption time*

To insight into the adsorption properties of hybrid membranes cured at different temperatures for lead(II) ions, the dependency of q_{Pb}^{2+} values on adsorption time was measured. The q_{Pb}^{2+} values on samples A–D vs. adsorption time t (h) is presented in Fig. 1.

As shown in Fig. 1, it can be seen that the adsorption capacity of lead(II) increased from sample A to D and arrived at an equilibrium state at around 12 h, which indicated an upward trend as the curing temperature was elevated. Two chief factors might be responsible for such trend. One can be assigned to the cross-linking of –OH groups and methoxysilane in APTMS, which will produce the Si–O–Si bonds in the hybrid precursor and lead to the creation of silica and an increase in the thermal stability of samples [10]. As a result, the functionalized groups in the molecular chains are not easily destroyed with an increase in the curing temperature. Accordingly, more amounts of functionalized groups will participate in the adsorption for heavy metal ions, leading to an increase in the adsorption capacity of lead(II) from sample A to D. The other factor is related to the further formation of hybrid network between the organic and inorganic moieties, resulting in the formation of intimate structure of samples with the elevated curing temperature. In this case, the adsorption effect of particle size cannot be ignored, which will also increase the adsorption capacity of lead(II) from sample A to D as discussed in section 3.6.

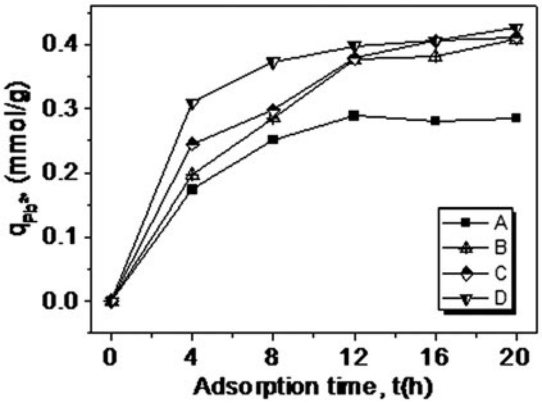

Fig. 1. The adsorption capacity of lead(II) on samples A–D vs. adsorption time, t.

Moreover, it can also be seen that the adsorption capacity of lead(II) elevated rapidly in the range of 0–4 h and then increased slowly with the elapsed time, indicating a rapid adsorption process in short time. The reason can be assigned to the electrostatic attraction effect of $-NH_2$ groups from APTMS on the molecular chains to the lead(II) ions in the aqueous solution, i.e. the electric effect from the functionalized and heavy metal ions has dominated the starting adsorption period. This finding is similar to the result reported in a previous article [8].

Currently, it is well accepted that two-parameter kinetic equations are practical techniques to evaluate the adsorption behaviors of an adsorbent. To acquire the adsorption mechanism of lead(II) on these hybrid adsorbents, the experimental data were analyzed using six typical two-parameter kinetic equations (i.e. the Lagergren pseudo-first-order model and pseudo-second-order model [4,11,12], the Ritchie second-order model and modified second-order model [13,14], the Elovich model [14,15], and the intraparticle diffusion model [16]).

3.3. *Lagergren kinetic model*

Presently, the Lagergren pseudo-first-order and pseudo-second-order models can be linearly expressed as Eqs. (2b) and (3b), respectively [4,11,12]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2a}$$

$$\text{or} \quad \log\,(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2b}$$

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

$$\text{or} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3b}$$

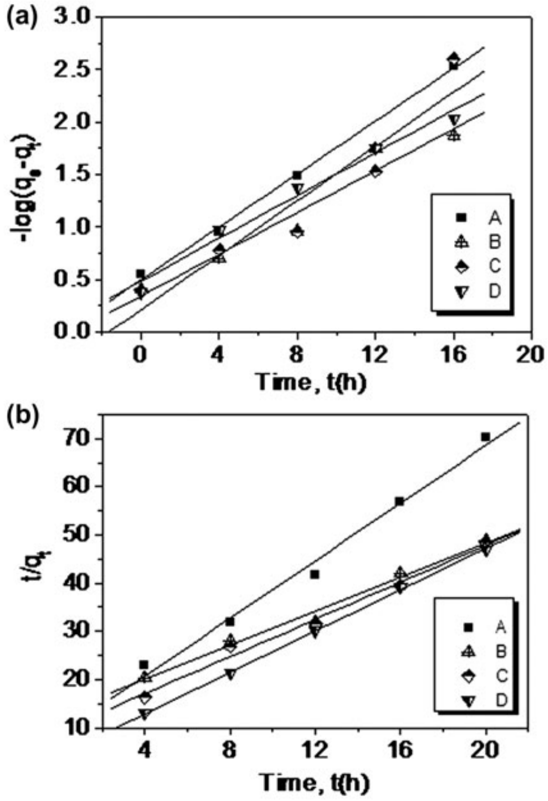

Fig. 2. Lagergren kinetic model for lead(II) adsorption onto samples A–D, (a) the pseudo-first-order model, and (b) the pseudo-second-order model.

where k_1 (h^{-1}) and k_2 ($g\,h^{-1}\,mmol^{-1}$) are the rate constants of the pseudo-first-order and pseudo-second-order models, respectively; and q_t ($mmol\,g^{-1}$) and q_e ($mmol\,g^{-1}$) are the adsorption capacities of the metal ions (Me^{2+}) at time t (h) and in the equilibrium state, respectively.

The Lagergren kinetic model for lead(II) adsorption onto samples A–D is given in Fig. 2(a) and (b). The corresponding kinetic model parameters were calculated and are listed in Table 1.

Table 1
Lagergren kinetic isotherm parameters for lead(II) adsorption onto samples A–D

	Pseudo-first-order model			Pseudo-second-order model		
Sample	k_1	q_{cal}	R^2	k_2	q_e	R^2
A	0.290	0.315	0.997	1.009	0.334	0.987
B	0.229	0.456	0.949	0.243	0.563	0.985
C	0.297	0.606	0.906	0.390	0.520	0.989
D	0.234	0.326	0.981	1.048	0.466	0.999

It can be observed that the linear regression coefficient (R^2) of the Lagergren pseudo-second-order model for lead(II) adsorption fitted better than that of the pseudo-first-order model (cf. Table 1). This outcome demonstrated that lead(II) adsorption onto samples A–D followed the Lagergren pseudo-second-order kinetic model.

3.4. Ritchie second-order model and modified second-order model

The Ritchie second-order and modified second-order models are usually used to measure the initial particle loading, which can be linearly expressed as Eqs. (4b) and (5b), respectively [13,14]:

$$q_t = q_e\left\{1 - \left[\frac{1}{1 + k_2 t}\right]\right\} \tag{4a}$$

$$\text{or}\quad \frac{q_e}{q_e - q_t} - 1 = k_2 t \tag{4b}$$

$$q_t = q_e\left\{1 - \left[\frac{1}{\beta + k_{2m} t}\right]\right\} \tag{5a}$$

$$\text{or}\quad \frac{q_e}{q_e - q_t} = \beta + k_{2m} t \tag{5b}$$

where k_2 (h^{-1}) is the Ritchie second-order rate constant of adsorption. k_{2m} (h^{-1}) is the Ritchie modified second-order rate constant of adsorption, and β is a constant representing the initial particle loading.

Fig. 3(a) and (b) illustrates the Ritchie second-order and modified second-order models for lead(II) adsorption onto samples A–D. As shown in Fig. 3(a) and (b), it can be found that both the Ritchie second-order and Ritchie modified second-order models for lead(II) adsorption onto samples A–D all exhibited a worse fit for lead(II) adsorption onto samples A–D ($R^2 = 0.330$, 0.0122, 0.0106, and 0.0151 for samples A–D, respectively). This result revealed that lead(II) adsorption onto these samples did not follow the Ritchie modified second-order model. Such finding suggests that lead (II) was not adsorbed onto the two surface sites of these samples. Thus, the initial particle loading cannot be determined in this case.

3.5. Elovich model

The Elovich equation [14,15] is usually used in the kinetic study of chemisorption of gases on the solid surface. Presently, it was reported that this equation

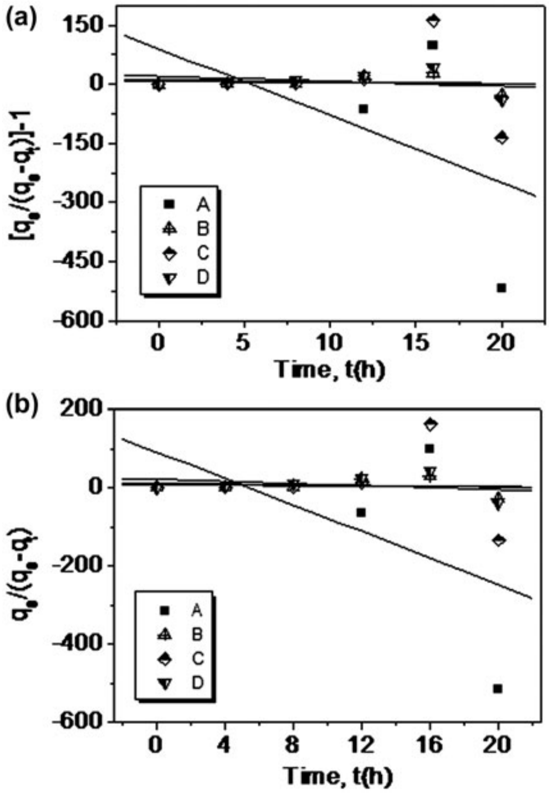

Fig. 3. The Ritchie second-order model (a), and the Ritchie modified second-order model (b) for lead(II) adsorption onto samples A–D.

can also be applied to study the liquid-state sorption and expressed as Eq. (6) [14]:

$$q_t = a + b \ln (t) \tag{6}$$

where a (mmol g^{-1}) and b are the Elovich parameters.

Fig. 4 presents the Elovich model for lead(II) adsorption onto samples A–D. The related model parameters were calculated and are tabulated in Table 2.

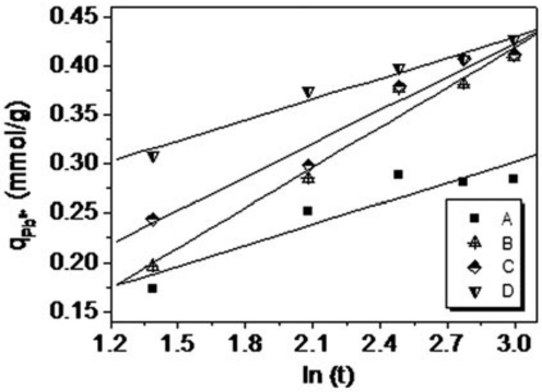

Fig. 4. The Elovich model for lead(II) adsorption onto samples A–D.

Table 2
Elovich isotherm parameters for lead(II) adsorption onto samples A–D

Sample	a	b	R^2
A	0.0903	0.0706	0.864
B	0.0105	0.136	0.968
C	0.0819	0.113	0.960
D	0.217	0.0704	0.975

As showed in Fig. 4, it can be noted that the Elovich model for lead(II) adsorption onto samples A–D gave a better fit with the R^2 values; such result demonstrates that lead(II) adsorption onto these samples could be described using the Elovich model. This finding confirmed the existence of chemical interactions between the active sites on the surface of the samples and lead(II) ions in the solution.

3.6. Intraparticle diffusion model

Intraparticle diffusion [16] usually gives the information of the metal ions transport from the solution through the interface between the solution and the adsorbent into the pores of the particles. To obtain the interface transport properties of the lead(II) ions from the interior to the pores of samples A–D, the intraparticle diffusion model was measured. The intraparticle diffusion on the adsorption rate of the lead(II) ions was determined on the basis of the dependency of adsorption capacity q_t on adsorption time t, which can be expressed as Eq. (7) [16,17]:

$$q_t = x_i + k_p t^{0.5} \tag{7}$$

where k_p is the intraparticle diffusion rate constant (mmol g^{-1} h$^{-1/2}$) and x_i is the intercept, which is related to the boundary layer thickness (mmol g^{-1}).

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 exhibits multilinear curves, two or more steps influence the adsorption process as stated in some published articles [16,17].

The intraparticle diffusion curves of lead(II) adsorption onto samples A–D are illustrated in Fig. 5, and the model parameters are summarized in Table 3.

As shown in Fig. 5, it can be discovered that the linear regression coefficient (R^2) indicated a better fit for lead(II) adsorption onto samples A–D when the

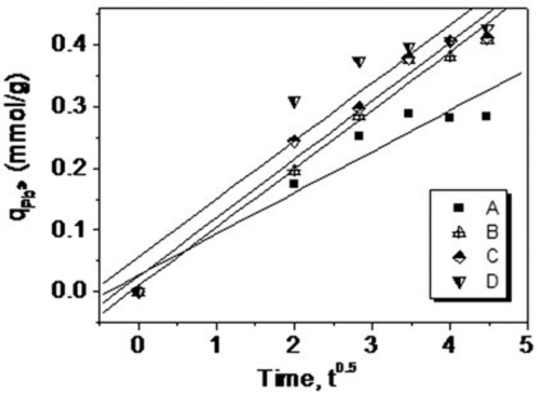

Fig. 5. Intraparticle diffusion curves of lead(II) adsorption onto samples A–D.

Table 3
Intraparticle diffusion parameters for lead(II) adsorption onto samples A–D

Sample	k_p	x_i	R^2
A	0.0669	0.0262	0.922
B	0.0951	0.00878	0.981
C	0.0951	0.0242	0.970
D	0.0942	0.0557	0.896

tested points were linearly fitted. Meanwhile, it can also be discovered that the plot nearly passed through the origin of coordinates because the x_i value was close to the zero for an individual sample (see Table 3). Based on this finding, it can thus be deduced that lead (II) adsorption onto samples A–D was mainly governed by intraparticle diffusion, demonstrating that the effect of boundary layer thickness on lead(II) adsorption could be ignored. This finding was consistent with the result reported by Chung et al. [18].

4. Conclusion

The silica-based hybrid membranes were used to adsorb lead(II) ions from an aqueous solution. To evaluate the adsorption mechanism of lead(II) on these hybrid adsorbents, their adsorption kinetic performances were modeled using six typical two-parameter kinetic equations. It was confirmed that the lead(II) adsorption onto these samples followed the Lagergren pseudo-second-order model, the Elovich model, and the intraparticle diffusion model. The Elovich model evidenced the existence of chemical interactions between the active sites on the surface of the samples and lead(II) ions in the solution. Moreover, the measurement of the intraparticle diffusion demonstrated that lead(II) adsorption onto samples A–D was solely governed by intraparticle diffusion.

Acknowledgements

This project was financially supported in part by the National Natural Science Foundation of China (No. 21076055), the Significant Foundation of the Educational Committee of Anhui Province (No. ZD2008002-1), and the Second National-Level College Students' Innovative Entrepreneurial Training Plan Program (No. 201211059,010).

References

[1] A. Krobba, D. Nibou, S. Amokrane, H. Mekatel, Adsorption of copper(II) onto molecular sieves NaY, Desalin. Water Treat. 37 (2012) 31–37.

[2] J. Li, S.W. Zhang, C.L. Chen, G.X. Zhao, X. Yang, J.X. Li, X.K. Wang, Removal of Cu(II) and fulvic acid by graphene oxide nanosheets decorated with Fe_3O_4 nanoparticles, ACS Appl. Mater. Inter. 4 (2012) 4991–5000.

[3] S. Bekkouche, S. Baup, M. Bouhelassa, S. Molina-Boisseau, C. Petrier, Competitive adsorption of phenol and heavy metal ions onto titanium dioxide (Dugussa P25), Desalin. Water Treat. 37 (2012) 364–372.

[4] H.A. Hadar, V. Bulatov, B. Dolgin, I. Schechter, Detection of heavy metals in water using dye nano-complexants and a polymeric film, J. Hazard. Mater. 260 (2013) 652–659.

[5] S.M. Maliyekkal, K.P. Lisha, T. Pradeep, A novel cellulose–manganese oxide hybrid material by *in situ* soft chemical synthesis and its application for the removal of Pb(II) from water, J. Hazard. Mater. 181 (2010) 986–995.

[6] X.J. Zhang, T.Y. Ma, Z.Y. Yuan, Titania–phosphonate hybrid porous materials: Preparation, photocatalytic activity and heavy metal ion adsorption, J. Mater. Chem. 18 (2008) 2003–2010.

[7] J.S. Liu, L. Song, G.Q. Shao, Novel zwitterionic inorganic−organic hybrids: Kinetic and equilibrium model studies on Pb^{2+} removal from aqueous solution, J. Chem. Eng. Data 56 (2011) 2119–2127.

[8] Q. Dong, J.S. Liu, L. Song, G.Q. Shao, Novel zwitterionic inorganic–organic hybrids: Synthesis of hybrid adsorbents and their applications for Cu^{2+} removal, J. Hazard. Mater. 186 (2011) 1335–1342.

[9] Y.P. Zhang, X. Wang, J.S. Liu, L.L. Wu, Removal of copper (Cu^{2+}) from water using novel hybrid adsorbents: Kinetics and isotherms, J. Chem. Eng. Data 58 (2013) 1141–1150.

[10] S.-S. Hou, P.-L. Kuo, Function and performance of silicone copolymers, 3a. Synthesis and properties of a novel siliconized acrylic monomer containing three reactive sites, Macromol. Chem. Phys. 200 (1999) 2501–2507.

[11] B. Singha, S.K. Das, Adsorptive removal of Cu(II) from aqueous solution and industrial effluent using natural/agricultural wastes, Colloids Surf. B 107 (2013) 97–106.

[12] M.A. Ashraf, M.A. Rehman, Y. Alias, I. Yusoff, Removal of Cd(II) onto *Raphanus sativus* peels biomass: Equilibrium, kinetics, and thermodynamics, Desalin. Water Treat. 51 (2013) 4402–4412.

[13] T.S. Anirudhan, P.G. Radhakrishnan, Kinetic and equilibrium modelling of cadmium(II) ions sorption onto polymerized tamarind fruit shell, Desalination 249 (2009) 1298–1307.

[14] X.S. Wang, Z.P. Lu, H.H. Miao, W. He, H.L. Shen, Kinetics of Pb (II) adsorption on black carbon derived from wheat residue, Chem. Eng. J. 166 (2011) 986–993.

[15] S.H. Chien, W.R. Clayton, Application of Elovich equation to the kinetics of phosphate release and sorption in soils, Soil Sci. Soc. Am. J. 44 (1980) 265–268.

[16] A.A. Atia, Ahmed M. Donia, A.M. Yousif, Removal of some hazardous heavy metals from aqueous solution using magnetic chelating resin with iminodiacetate functionality, Sep. Purifi. Technol. 61 (2008) 348–357.

[17] E. Guibal, C. Milot, J.M. Tobin, Metal-anion sorption by chitosan beads: Equilibrium and kinetic studies, Ind. Eng. Chem. Res. 37 (1998) 1454–1463.

[18] J. Chung, J. Chun, J. Lee, S.H. Lee, Y.J. Lee, S.W. Hong, Sorption of Pb(II) and Cu(II) onto multi-amine grafted mesoporous silica embedded with nano-magnetite: Effects of steric factors, J. Hazard. Mater. 239-240 (2012) 183–191.