

Sorption characteristics of Cu(II) ions onto silica gel-immobilized calix[4]arene polymer in aqueous solutions: Batch and column studies

Mustafa Tabakci^{a,*}, Mustafa Yilmaz^b

^a Selçuk University, Department of Chemical Engineering, 42075 Konya, Turkey

^b Selçuk University, Department of Chemistry, 42031 Konya, Turkey

Received 18 October 2006; received in revised form 25 May 2007; accepted 29 May 2007

Available online 2 June 2007

Abstract

In the present study, Cu(II) removal from aqueous solutions by sorption was investigated. Aminopropyl silica gel-immobilized calix[4]arene polymer (APSiC[4]P) was used in sorption as sorbent. During the experimental part of this study, the effect of parameters, such as pH, initial Cu(II) concentration, temperature on Cu(II) removal was observed. In addition, sorption isotherm studies and column studies were made. Maximum Cu(II) removal was obtained at pH 6 and 25 °C. In the isotherm studies, Langmuir and Freundlich isotherm models were applied and it was determined that the experimental data confirmed to Langmuir isotherm model. Batch sorption capacity (q_0) was calculated as 5.08 mg/g. The capacity value for column study was obtained by graphical integration as 1.14 mg/g. The Thomas and the Yoon–Nelson models were applied to experimental data to predict the breakthrough curves and to determine the characteristics parameters of the column useful for process design.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Cu(II) removal; Calix[4]arene polymer; Sorption; Batch study; Column study

1. Introduction

Heavy metal contamination to various surface waters or groundwater is great a concern because of the toxic effect of heavy metal ions to plants, animals and human beings [1–6]. Therefore, effective removal of heavy metal ions from water or various industrial effluents is very important and has attracted considerable research and practical interest. Many methods, such as chemical precipitation, ion exchange, reverse osmosis and sorption, etc., have been used to remove heavy metal ions from various aqueous solutions [3–5,7,8]. Among these methods, sorption has increasingly received more attention in recent years because the method is simple, relatively low-cost and effective in removing heavy metal ions, especially at medium to low metal ion concentrations and from wastewaters [3–6,8,9].

Macromolecules are widely used in host–guest chemistry for the construction of various receptors for charged or neutral molecules. Calixarenes are such cyclic oligomers composed of phenol units and are very well known as attractive and excellent

ionophores because they provide a unique three-dimensional structure with almost unlimited derivatization possibilities [10,11]. Generally two strategies have been adopted by the different groups in order to enhance the affinity of calixarenes toward metal ions; either there have been incorporated different ionophoric groups including carbonyl, amide, nitrile and other suitable functionalities onto the calix-platform, or the calixarene units were fixed in a polymeric matrix. Various studies have been carried out in this regard, for instance, calix[4]arene tetraethyl ester and calix[6]arene hexaethyl ester were incorporated onto the surface of silica particles after hydrosilylation of the *p*-allyl calixarenes and were used as selective adsorbents for Na⁺ ions [12,13]. Chelating calix[4]arene hydroxamates supported onto silica particles have been studied for their uptake of different transition metal ions [14]. A chelating resin has been synthesized by linking calix[4]arene-semicarbazone derivatives on chloromethylated polystyrene divinyl benzene copolymer for the separation of La³⁺, Ce³⁺, Th⁴⁺ and U⁶⁺ [15]. In our previous work, we have also synthesized several polymeric calixarenes and it has been investigated their cation extraction properties [16].

The importance of favorable amide (O=C–NH), nitrile (C=N) and amine (NH₂) functionalities for cation binding

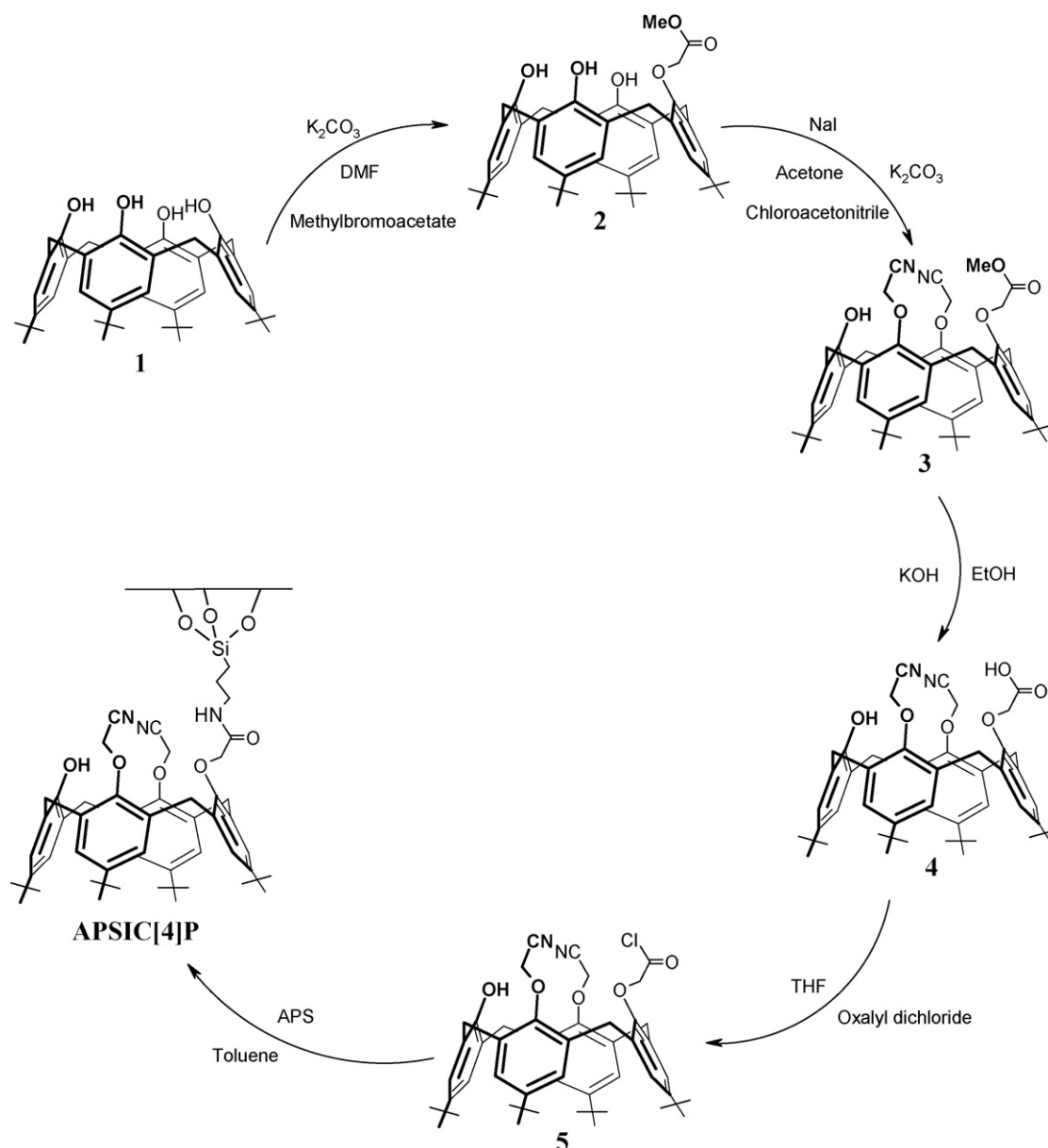
* Corresponding author. Tel.: +90 332 2232142; fax: +90 332 2410635.
E-mail address: mtabakci@selcuk.edu.tr (M. Tabakci).

has recently been explored by various groups in the design of calix[4]arene cation sorbents, which are still relatively rare [16]. In this study to contribute to this area we used an aminopropyl silica gel-immobilized calix[4]arene polymer (APSIC[4]P) bearing amide, nitrile and amine functionalities and previously prepared [17] in Cu(II) sorption as a sorbent.

2. Experimental

An aminopropyl silica gel-immobilized calix[4]arene polymer (APSIC[4]P) used in this study was previously [17] obtained according to synthetic method given in Scheme 1. The APSIC[4]P samples were dried at 105 °C for 2 h before each set of experiments. The aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was prepared by using the analytical grade Merck product. The solution was prepared in such a manner that the initial Cu(II)

concentration in sorption experiments was generally held at 6.35 mg/L. The pH values were measured with pH meter (Orion, 420A+). In batch sorption experiments, known weights of sorbents (0.025 g) were added to capped volumetric flasks each of which containing 10 mL solution (6.35 mg/L Cu(II)) and shaken at 175 rpm in a temperature-controlled shaker (BINDER) for 1 h. After sorption, samples were centrifuged and Cu(II) in supernatants was analyzed by using Atomic Absorption Spectrophotometer (AAS, Unicam 929) at 324.8 nm of wavelength. All of the tests were duplicated. The effect of pH was studied by adjusting the pH of Cu(II) solutions using diluted HCl and NaOH solutions at 25 °C. The effect of temperature was carried out by APSIC[4]P at 25 °C at pH 6. Effect of initial Cu(II) concentration was investigated at pH 6. Langmuir, and Freundlich isotherms were employed to study the sorption properties of the sorbent.



Scheme 1. The synthetic route of preparation of APSIC[4]P.

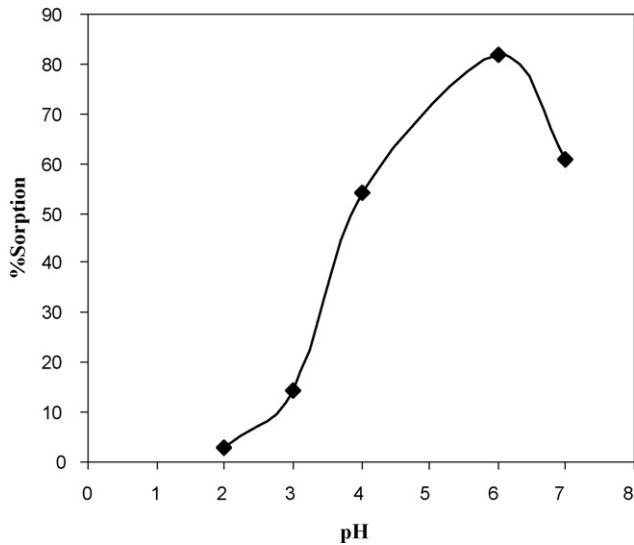


Fig. 1. Effect of pH on the removal of Cu(II).

In column experiment, a glass column (0.1 cm i.d. and 7.5 cm length) was filled with 0.025 g of APSIC[4]P on glass wool support was treated with 25 mL of 1.0 M HCl and repeatedly washed with water until free from acid. Cu(II) solution (6.35 mg/L Cu(II)) at 25 °C and pH 6 was delivered down flow to the column using a peristaltic pump (Heidolph) at 0.2 mL/min flow rate as shown in Fig. 1. To obtain breakthrough curve, the effluent was collected as 2 mL fractions and analyzed with AAS. Column studies were terminated when the column reached exhaustion. The desorption studies carried out after the column sorption studies were conducted at 25 °C and 0.2 mL/min flow rate. The sorbed Cu(II) was desorbed from APSIC[4]P by using 1 M HNO₃ solution.

3. Results and discussion

3.1. Effect of pH

The pH is one of the most important factors affecting the sorption process. The effect of pH on the sorption of Cu(II) was studied as follows: 100 mL of Cu(II) solution was taken in a flask. The pH of solution was adjusted by adding dilute solution of hydrochloric acid or sodium hydroxide. The concentration of Cu(II) in this solution was then determined (initial concentration). Ten milliliters of Cu(II) solution was taken in a conical flask and treated with 0.025 g of sorbent and after equilibrium, the final concentration of Cu(II) was determined by AAS. The sorption of Cu(II) was studied over the pH range 2–7 (Fig. 1). The maximum uptake of Cu(II) takes place at pH 6. The decreasing of sorption at about pH 6.5 may be due to hydrolysis of Cu(II) after this pH.

3.2. Effect of initial Cu(II) concentration

Solutions of different initial Cu(II) concentrations (6.35, 12.7, 25.4, 50.8 mg/L) were used to investigate the effect of concentration on the removal of Cu(II) by 0.025 g sorbent at

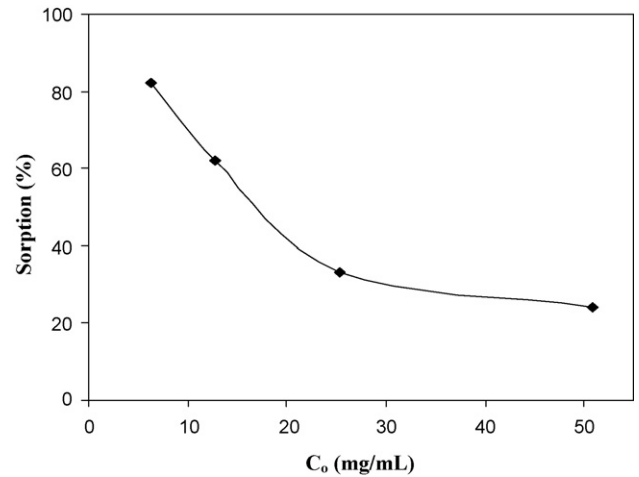


Fig. 2. Effect of initial Cu(II) concentration on the removal of Cu(II) (at pH 6, 25 °C).

pH 6. Sorption yield values were calculated from following equation:

$$\text{Sorption Yield}(\%) = \left[\frac{C_0 - C_e}{C_0} \right] \times 100 \quad (1)$$

where C_0 is the initial Cu(II) concentration (mg/L). As it can be seen from Fig. 2, the sorption yields (%) were decreased by increasing of initial Cu(II) concentration. Although percent of sorption (%) decreased, equilibrium sorption capacity of APSIC[4]P increased with increasing initial Cu(II) ion concentration. The initial concentration provides an important driving force to overcome all mass transfer resistance of Cu(II) ions between the aqueous and solid phases, hence a higher initial concentration of Cu(II) ions may increase the sorption capacity. Ozer et al. [18] indicated that at lower concentrations, all Cu(II) ions present in solution could interact with the binding sites and thus the percentage sorption were higher than those at higher initial Cu(II) ion concentrations. At higher concentrations, lower sorption yield is due to the saturation of sorption sites.

3.3. Sorption isotherms

Several models have been published in the literature to describe experimental data of sorption isotherms. The Langmuir and Freundlich models are the most frequently employed models. In this work, both models were used to describe the relationship between the sorbed amount of Cu(II) and its equilibrium concentration in solution.

Langmuir isotherm is represented by the following equation [19]:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \quad (2)$$

where the constant q_0 signifies the sorption capacity (mg/g) and b is related to the energy of sorption (L/mg).

The linear plot of C_e/q_e versus C_e shows that sorption follows a Langmuir isotherm (Fig. 3). Values of q_0 and b were calculated

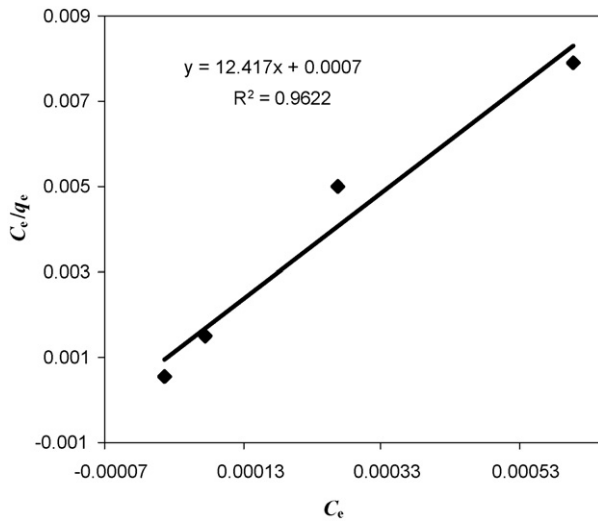


Fig. 3. Langmuir plot for the removal of Cu(II) (at pH 6).

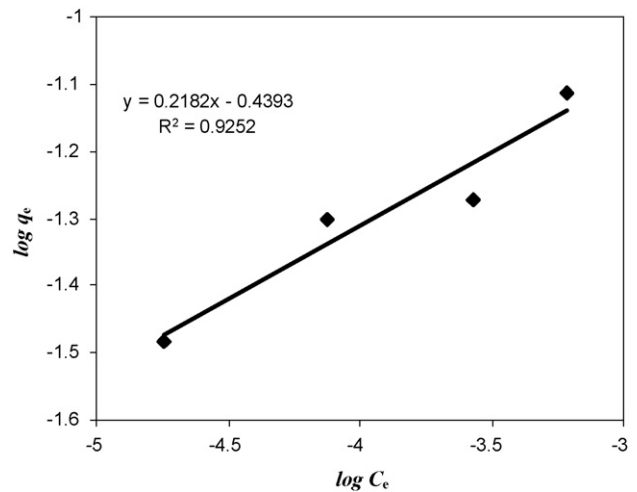


Fig. 4. Freundlich plot for the removal of Cu(II) (at pH 6).

from the slope and intercept of the linear plots and are presented in Table 1. The applicability of the Langmuir isotherm suggests the monolayer coverage of the Cu(II) sorption onto APSIC[4]P [19].

To determine if the Cu(II) sorption process by APSIC[4]P is favorable or unfavorable for the Langmuir type sorption process, the isotherm shape can be classified by a term “ R_L ”, a dimensionless constant separation factor, which is defined below [17]:

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

where R_L is a dimensionless separation factor and b is Langmuir constant (L/mg). The parameter R_L indicates the shape of the isotherm accordingly: $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible.

The calculating of R_L value as 0.08 indicated that sorption of Cu(II) on APSIC[4]P was favorable at 6.35 mg/L initial Cu(II) concentration at 25 °C and pH 6.

The Freundlich isotherm was also applied for the Cu(II) removal by sorption. Freundlich isotherm model is given by the following equation [20]:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

where K_f and n are Freundlich sorption isotherm constants, being indicative of the sorption capacity and intensity of sorption. Values of K_f and n were calculated from the intercept and slope of the plots of $\log q_e$ versus $\log C_e$ (Fig. 4).

In general, as the K_f value increases, the sorption capacity of the sorbent increases. The Freundlich isotherm data are given in Table 1. It has been shown using mathematical calculations that n was between 1 and 10 representing beneficial sorption [21]. So APSIC[4]P sorbent used in the study provide beneficial sorption at 25 °C and pH 6. On the comparison of the R^2 values given in Table 1, we can conclude that in sorption of Cu(II) on APSIC[4]P Langmuir equation represents a slightly better fit to the experimental data than the Freundlich equation.

Although direct comparison of APSIC[4]P with other sorbent materials is difficult, owing to the different applied experimental conditions, it was found, in general, the adsorption capacity of APSIC[4]P for Cu(II), using equilibrium experiments, determined to be around 5.08 mg Cu(II)/g APSIC[4]P, is higher than fly ash + wollastonite [22], fly ash, dead fungal biomass (*Schizophyllum commune*) [23], sawdust [24], baggase fly ash [25], peanut hulls [26], cork bark [27], natural zeolite [28], olive pomace [29] and powder activated carbon [30]. The values of sorption properties of Cu(II) in different sorbents used in the literature with the sorbent of the present study are summarized in Table 2. It may be observed that the uptake of Cu(II) on APSIC[4]P is greater than some other sorbents.

3.4. Column studies

The performance of packed beds is described through the concept of the breakthrough curve. The breakthrough curve shows the loading behavior of Cu(II) to be removed from solution in a fixed bed and is usually expressed in terms of sorbed Cu(II) concentration ($C_s = \text{inlet Cu(II) concentration } (C_0) - \text{outlet Cu(II) concentration } (C_e)$) or normalized concentration defined as the

Table 1
Langmuir and Freundlich isotherm parameters

Langmuir isotherm parameters				Freundlich isotherm parameters		
q_0 (mg/g)	b (L/mmol)	R^2	R_L	K_f (mmol/g)	n	R^2
5.08	115	0.9622	0.08	23.144	4.58	0.9252

Table 2
Comparison of Cu(II) sorption on APSIC[4]P and other sorbents

Sorbent	q_{\max} (mg g ⁻¹)	Reference
Fly ash + wollastonite	1.18	[22]
Fly ash	1.39	[22]
Dead fungal biomass (<i>Schizophyllum communie</i>)	1.52	[23]
Sawdust	1.79	[24]
Baggase fly ash	2.26	[25]
Peanut hulls	2.95	[26]
Cork bark	3.00	[27]
Natural zeolite	3.4	[28]
Olive pomace	4.26	[29]
Powder activated carbon	4.45	[30]
APSID[4]P	5.08	[Current work]

ratio of effluent Cu(II) concentration to inlet Cu(II) concentration (C_e/C_0) as a function of time or volume of effluent for a given bed height [31]. The area under the breakthrough curve obtained by integrating the sorbed concentration (C_s (mg/L)) versus the throughput volume (V (L)) plot can be used to find the total sorbed Cu(II) quantity (maximum column capacity). Total sorbed Cu(II) quantity (q_0 (mg/g)) in the column for a given feed concentration and flow rate is calculated from Eq. (5):

$$q_0 = \int_0^{V_T} \frac{(C_0 - C_e) dV}{m} \quad (5)$$

where m is the mass of the sorbent (g). The capacity value q_0 was obtained by graphical integration as 1.14 mg/g. From comparison of sorption capacity from batch and column experiments, we can see that the less-stirred property in column mode reduced the Cu(II) sorption capacity on APSIC[4]P.

3.4.1. Application of the Thomas model

Successful design of a column sorption process requires prediction of the concentration–time profile or breakthrough curve for the effluent. The maximum sorption capacity of a sorbent is also needed in design. Traditionally, the Thomas model is used to fulfill the purpose. The model has the following form [32]:

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp[K_T(q_0 m - C_0 V)/\theta]} \quad (6)$$

where K_T is the Thomas rate constant (L/(min mg)) and θ is the volumetric flow rate (L/min). The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_0}{C_e} - 1\right) = \frac{K_T q_0 m}{\theta} - \frac{K_T C_0}{\theta} V \quad (7)$$

The kinetic coefficient K_T and the sorption capacity of the bed q_0 can be determined from a plot of $\ln[(C_0/C_e) - 1]$ against t at a given flow rate (Fig. 5).

The Thomas equation coefficients for Cu(II) sorption were $K_T = 7.57 \times 10^{-3}$ L/(min mg) and $q_0 = 1.13$ mg/g. The value of q_0 is a measure of the sorption capacity at the APSIC[4]P for

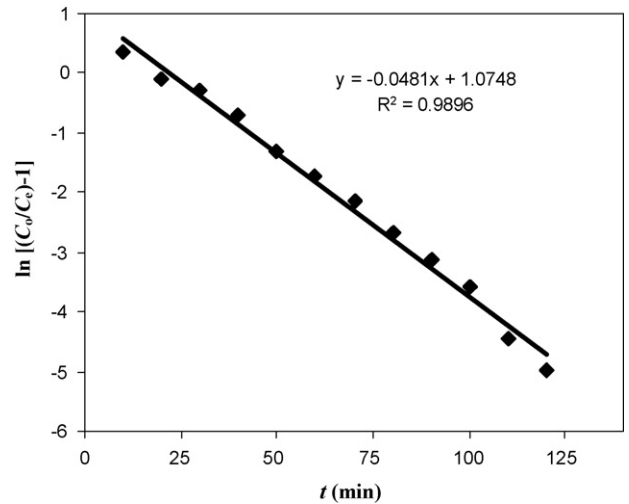


Fig. 5. Plot of t vs. $\ln[(C_0/C_e) - 1]$.

Cu(II). The theoretical predictions based on the model parameters are compared in Fig. 6 with the observed data.

3.4.2. Application of the Yoon and Nelson model

This model is based on the assumption that the rate of decrease in the probability of sorption for each sorbate molecule is proportional to the probability of sorbate sorption and the probability of sorbate breakthrough on the sorbent. The Yoon and Nelson model not only is less complicated than other models, but also requires no detailed data concerning the characteristics of sorbate, the type of sorbent and the physical properties of sorption bed. The Yoon and Nelson equation regarding to a single component system is expressed as [32]:

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp[k(\tau - t)]} \quad (8)$$

where k is the rate constant (min⁻¹), τ the time required for 50% sorbate breakthrough (min) and t is the breakthrough (sampling)

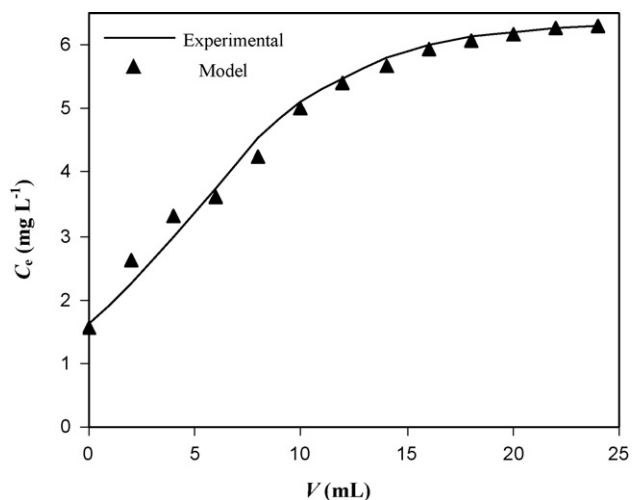


Fig. 6. Comparison of the experimental and predicted breakthrough curves according to Thomas model (at 25 °C, pH 6 and $C_0 = 6.35$ mg/L).

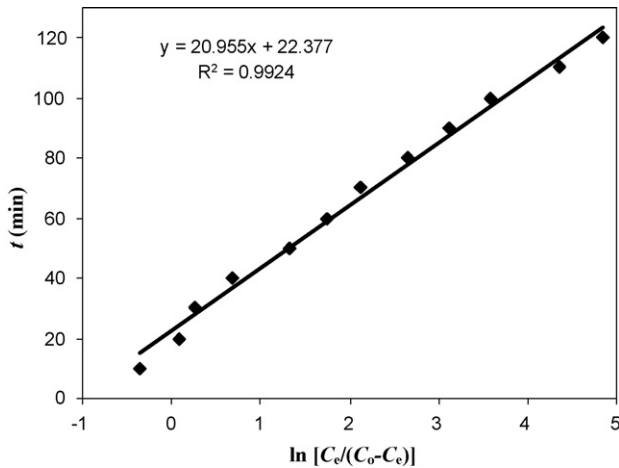


Fig. 7. Plot of $\ln [C_e / (C_0 - C_e)]$ vs. t .

time (min). The linearized form of the Yoon and Nelson model is as follows:

$$t = \tau + \frac{1}{k} \ln \frac{C_e}{C_0 - C_e} \quad (9)$$

The calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters k and τ for the sorbate of interest. These values may be determined from available experimental data.

The approach involves a plot of sampling time (t) versus $\ln [C_e / (C_0 - C_e)]$ according to Eq. (9) (Fig. 7). The model parameters for Cu(II) sorption by APSIC[4]P were $k = 0.048$ L/min and $\tau = 22.377$ min. Alternatively, τ can also be obtained at the sorption time when $\ln [C_e / (C_0 - C_e)]$ is zero because of the fact that by definition τ is the sorption time when C_e is one-half of C_0 . These values were used to calculate the breakthrough curve. The theoretical curves were compared with the corresponding experimental data in Fig. 8.

The derivation for Eq. (8) was based on the definition that 50% breakthrough of the sorption process occurs at τ . Accord-

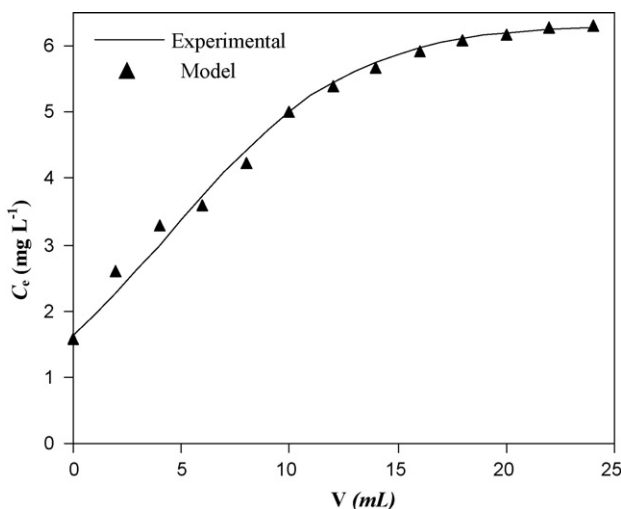


Fig. 8. Comparison of the experimental and predicted breakthrough curves according to Yoon–Nelson model (at 25 °C, pH 6 and $C_0 = 6.35$ mg/L).

ingly the bed should be completely saturated at 2τ . Due to the symmetrical nature of breakthrough curve, the amount of Cu(II) sorbed by the APSIC[4]P is one half of the total Cu(II) entering the sorption column within the 2τ period. Hence, the following equation can be written [33]:

$$q_0 = \frac{1}{2} C_0 \theta (2\tau) = C_0 \theta \tau \quad (10)$$

The above equation establishes the relation among the sorption capacity of the column (q_0), inlet concentration (C_0), liquid flow rate (θ) and the 50% breakthrough time (τ). The sorption capacity, q_0 , was calculated as 1.14 mg/g using Yoon and Nelson model.

3.5. Desorption studies

The column with a bed depth of 4.5 cm was selected for this study, for which the sorption breakthrough curves. It was observed that at about 2 h, the column was exhausted. The extra Cu(II) solution inside the column was pumped out leaving only APSIC[4]P loaded with Cu(II). Desorption was carried out by 1 M HNO₃ solution through the bed in the downward direction at a flow rate of 0.2 mL/min, slightly less than the sorption flow rate 0.2 mL/min so that volume of regenerant is less which helps in easy handling and high in concentration so that economical metal recovery is possible. The regenerations were carried in the counter-current mode, that is, in the down flow mode. Counter-current operation generally reduces regeneration costs and regenerant volume and increases effluent quality [34]. The concentration of Cu(II) was monitored after different time interval as shown in Fig. 9. It was observed that desorption cycle took 1 h, after which further desorption was negligible. The total volume of this eluent at 1 h was 12 mL. The maximum concentration of Cu(II) was obtained at a contact time of 10 min and recorded as 7.63 mg/L, which is 1.2 times higher than influent Cu(II) concentration. The eluting solution was low in volume and high in concentration, which could help in easy handling and recovery and reuse of Cu(II). Furthermore, the reuse of sorbent was carried out three times and the results showed that the

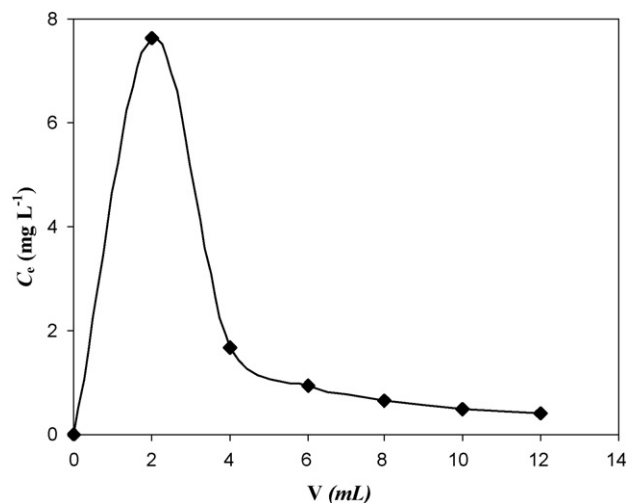


Fig. 9. Desorption profile of Cu(II).

sorption efficiency of sorbent was decreased about 2% at per reuse. This can be attributed to decomposition effect of HNO₃ used as stripping agent on sorbent.

4. Conclusions

- APSIC[4]P containing amide, nitrile and amine functionalities is an effective sorbent for the removal of Cu(II).
- Maximum Cu(II) removal was obtained at 25 °C and pH 6 for APSIC[4]P.
- The sorption yield was decreased by increasing of initial Cu(II) concentration.
- Equilibrium sorption data followed Langmuir isotherm for APSIC[4]P.
- The batch sorption capacity was found as 5.08 mg/g.
- The column capacity value was obtained by graphical integration as 1.14 mg/g, which indicates that practically sorption capacity of APSIC[4]P is far less than batch mode results. This may be due to the potential irreversibility of the sorption process and the different approaches to sorption equilibrium in different systems, i.e. the solution phase concentration is continuously decreasing in the sorption.
- The Thomas and the Yoon–Nelson models were applied to data obtained from experimental studies performed on fixed column to predict the breakthrough curves and to determine the column kinetic parameters. The capacity values were obtained as 1.13 and 1.14 mg/g using Thomas and Yoon–Nelson models, respectively, for APSIC[4]P.
- The column studies data has shown good agreement with the predicted results obtained by application of these models.

Acknowledgement

We thank the Scientific Research Projects Foundation of Selçuk University (SUBAP-Grant Number 2003-187) for financial support of this work.

References

- [1] A. Benhammou, A. Yaacoubi, L. Nibou, B. Tanouti, Adsorption of metal ions onto moroccan stevensite: kinetic and isotherm studies, *J. Colloid Interface Sci.* 282 (2005) 320–326.
- [2] D.C.K. Ko, J.F. Porter, G. McKay, Mass transport model for the fixed bed sorption of metal ions on bone char, *Ind. Eng. Chem. Res.* 42 (2003) 3458–3469.
- [3] M. Prasad, S. Saxena, Sorption mechanism of some divalent metal ions onto low-cost mineral adsorbent, *Ind. Eng. Chem. Res.* 43 (2004) 1512–1522.
- [4] C.C. Liu, M.K. Wang, Y.S. Li, Removal of nickel from aqueous solution using wine processing waste sludge, *Ind. Eng. Chem. Res.* 44 (2005) 1438–1445.
- [5] A. Özcan, A.S. Özcan, S. Tunali, T. Akar, I. Kiran, Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of *Capsicum annum*, *J. Hazard. Mater. B* 124 (2005) 200–208.
- [6] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, *J. Hazard. Mater. B* 122 (2005) 161–170.
- [7] A. Mellah, S. Chegrouche, M. Barkat, The removal of uranium(VI) from aqueous solutions onto activated carbon: kinetic and thermodynamic investigations, *J. Colloid Interface Sci.* 296 (2006) 434–441.
- [8] M. Kobya, Adsorption, kinetic and equilibrium studies of Cr(VI) by hazelnut shell activated carbon, *Adsorpt. Sci. Technol.* 22 (2004) 51–64.
- [9] Z. Aksu, İ.A. İšoğlu, Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, *Process Biochem.* 40 (2005) 3031–3044.
- [10] C.D. Gutsche, *Calixarenes Revisited*, The Royal Society of Chemistry, Cambridge, 1998.
- [11] Z. Asfari, V. Böhmer, M.McB. Harrowfield, J. Vicens, *Calixarenes 2001*, Kluwer Academic Publishers, Dordrecht, 2001.
- [12] S. Memon, M. Yilmaz, Synthesis and complexation studies of 1,3-dialkylated *p-tert-butylcalix[4]arene* telomers, *React. Funct. Polym.* 44 (2000) 227–233.
- [13] J.D. Glennon, K. O'Connor, S. Srijaranal, K. Manley, S.J. Harris, M.A. McKervey, Enhanced chromatographic selectivity for Na⁺ ions on a calixarene-bonded silica phase, *Anal. Lett.* 26 (1993) 153–162.
- [14] J.D. Glennon, E. Horne, K. O'Connor, G. Kearney, S.J. Harris, M.A. McKervey, Chromatographic selectivity of amino acid esters and alkali metal ions on a silica bonded calix[4]arene tetraester stationary phase, *Anal. Proc.* 31 (1994) 33–35.
- [15] V.K. Jain, H.R. Pandya, P. Shrivastav, Y.K. Agrawal, Polymer supported calix[4]arene-semicarbazone derivative for separation and preconcentration of La(III), Ce(III), Th(IV) and U(VI), *React. Funct. Polym.* 51 (2002) 101–110.
- [16] M. Yilmaz, S. Memon, M. Tabakci, R.A. Bartsch, in: R.K. Bregg (Ed.), *New Frontiers in Polymer Research: "Design of Polymer Appended Calixarenes as Ion Carriers"*, Nova Science Publishers, Hauppauge, NY, 2006, pp. 125–171.
- [17] O. Gezici, M. Tabakci, H. Kara, M. Yilmaz, Synthesis of *p-tert-butylcalix[4]arene* dinitrile bonded aminopropyl silica and investigating its usability as a stationary phase in HPLC, *J. Macromol. Sci. Pure Appl. Chem.* 43 (2006) 221–231.
- [18] A. Ozer, D. Ozer, A. Ozer, The adsorption of copper(II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters, *Process Biochem.* 39 (2004) 2183–2191.
- [19] W.J. Weber, *Physicochemical Processes for Water Quality Control*, John Wiley and Sons Inc., New York, 1972.
- [20] M. Rao, A.V. Parwate, A.G. Bhole, Removal of Cr and Ni from aqueous solution using bagasse and fly ash, *Waste Manage.* 22 (2002) 821–830.
- [21] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of Acid Violet 17 (acid dye) from aqueous solutions, *Waste Manage.* 21 (2001) 105–110.
- [22] K.K. Panday, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solutions by fly ash, *Water Res.* 19 (1985) 869–873.
- [23] M.T. Veit, C.R.G. Tavares, S.M. Gomes-da-Costa, T.A. Guedes, Adsorption isotherms of copper(II) for two species of dead fungi biomasses, *Process Biochem.* 40 (2005) 3303–3308.
- [24] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, The removal of heavy metal from aqueous solutions by sawdust adsorption—removal of copper, *J. Hazard. Mater. B* 80 (2000) 33–42.
- [25] V.K. Gupta, I. Ali, Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater, *Sep. Purif. Technol.* 18 (2000) 131–140.
- [26] H.D. Ozsoy, H. Kumbur, Z. Ozer, Adsorption of copper(II) ions to peanut hulls and *Pinus brutia* sawdust, *Int. J. Environ. Pollut.*, in press.
- [27] I. Villaescusa, N. Fiol, M. Martinez, N. Miralles, J. Poch, J. Serarols, Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, *Water Res.* 38 (2004) 992–1002.
- [28] S. Wang, L. Li, Z.H. Zhu, Solid-state conversion of fly ash to effective adsorbents for Cu removal from wastewater, *J. Hazard. Mater. B* 139 (2007) 254–259.
- [29] F. Pagnanelli, S. Mainelli, F. Veglio, L. Toro, Heavy metal removal by olive pomace: biosorbent characterisation and equilibrium modelling, *Chem. Eng. Sci.* 58 (2003) 4709–4717.

- [30] K.H. An, Y.B. Park, S.D. Kim, Crab shell for the removal of heavy metals from aqueous solution, *Water Res.* 35 (2001) 3551–3556.
- [31] Z. Aksu, F. Gönen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, *Process Biochem.* 39 (2004) 599–613.
- [32] T. Mathialagan, T. Viraraghavan, Adsorption of cadmium from aqueous solutions by perlite, *J. Hazard. Mater.* 94 (2002) 291–303.
- [33] S.H. Lin, C.S. Wang, Treatment of high-strength phenolic wastewater by a new two-step method, *J. Hazard. Mater.* 90 (2002) 205–216.
- [34] C.R. Fox, D.C. Kennedy, in: F.L. Slejko (Ed.), *Conceptual Design of Adsorption Systems, Adsorption Technology: A Step-by-step Approach to Process Evaluation and Application*, Marcel Dekker, Inc., New York, 1985, pp. 91–165, Tall Oaks publishing Inc., Voorhees, New Jersey.