Asian Journal of Chemistry; Vol. 23, No. 8 (2011), 3387-3392

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Adsorption of Pb(II) in Aqueous Solution on SQD-85 Resin

XUEPENG LI, CAIPING YAO, CHUNHUA XIONG* and JIANRONG LI

School of Food and Biotechnolgy, Zhejiang Gongshang University, Hangzhou Zhejiang 310012, P.R. China

*Corresponding author: E-mail: xiongch@163.com

(*Received*: 3 August 2010; *Accepted*: 15 April 2011) AJC-9808

The adsorption and desorption behaviours of Pb(II) on SQD-85 resin were investigated using batch and column methods. Batch adsorption studies were carried out with different pH, contact time and temperature. In the batch system, the SQD-85 resin exhibited the highest Pb(II) uptake as 476 mg/g at 298 K, at an initial pH value of 6.00. The process was very fast initially and equilibrium time was observed within 50 h. And the adsorption data gave better fits with Langmuir isotherms. The thermodynamic parameters such as ΔG, which were all negative, indicated that the adsorption of Pb(II) ions onto SQD-85 resin was spontaneous and the positive value of ΔH showed that the adsorption was endothermic in nature. Pb(II) adsorbed on SQD-85 resin can be completely eluted by 0.1 mol/L HCl. Thomas model was applied to experimental column data to determine the characteristic parameters of column useful for process design. Finally, the SQD-85 resin can be regenerated and reused. The sorption of Pb(II) on SQD-85 resin from simulated seawater is also studied.

Key Words: SQD-85 resin, Pb(II), Adsorption, Thermodynamic.

INTRODUCTION

In many industries such as mining, metal plating, tanning and nuclear power plant operations, there are always serious heavy metal contaminations existing in the discharged wastewater[1]. Most of them are well-known toxic and carcinogenic agents and represent a serious threat to human populations as well as the fauna and flora of receiving water bodies as discharged in wastewater[2]. In addition, heavy metals are not biodegradable and they tend to accumulate in living organisms, causing various diseases and disorders[3]. Thus, to remove the hazardous heavy metals from industrial wastewater is the major course that cannot be ignored.

For years, many methods have been developed to remove heavy metals from the effluents including chemical precipitation, ion exchange, reverse osmosis, electrodialysis and adsorption on several low-cost adsorbents such as activated carbons[4-9]. However, many problems still remain unsolved, for example, the low durability and unsatisfactory selectivity of the electrodialysis membrane[10]. From the standpoints of environmental protection and resource recycling, it is urgent to develop an effective technique to reduce the concentration of Pb(II) in the industrial wastewater and recover lead.

Alternatively, ion exchange adsorption was chose as one of the most effective and common methods for this purpose because of its simplicity, facility and the characteristic that can be easily recovered and reused by regeneration operation[11,12]. Ion exchange resins with specific functional groups like iminodiacetic acid (IDA), aminophosphonic acid and amidoxime, have been widely used to recover heavy metals from wastewaters[13]. They are very powerful because the functional groups can form coordination bonds with many heavy metals. It is often the particular kind of heavy metal, that is selectively removed from wastewater[14,15].

In this work, the removal of Pb(II) from aqueous solutions using batch and column adsorption methods has been investigated by using SQD-85 resins. SQD-85 resin, as a typical ion exchange resin, possesses the advantages of polymeric adsorbent such as the relatively low-cost and effective in removing heavy metal ions[16-18]. SQD-85 resin is a polymeric material containing a functional group (-COOH). It not only has proton which can exchange with cation, but also oxygen atom that can coordinate directly with metal ions. Its principal characteristics are great chemical and physical stability, high exchange capacity and good ability of regeneration so it can be very suitable to remove heavy metals from water and industrial wastewater. Some factors affecting adsorption, such as contact time, initial pH of solution, initial concentration of Pb(II) and temperature have been examined. Kinetics and isotherm adsorption experiments were carried out. Thermodynamic parameters of adsorption for Pb(II) were calculated. The experimental results afford a new possibility to the removal and recovery of Pb(II) from aqueous solutions in hydrometallurgical systems and fit in with the environmental protection.

EXPERIMENTAL

The Pb(II) was determined with Shimadzu UV-2550 UV-VIS spectrophotometer. Mettler toledo delta 320 pH meter was used for measuring pH of solutions. The sample was shaken in the DSHZ-300A and the THZ-C-1 temperature cons-tant shaking machine. The water used in the present work was purified using Molresearch analysis-type ultra-pure water machine.

SQD-85 resin was supplied by Jiangsu Suqing Water Treatment Engineering Group Co., Ltd. and and the properties were shown in Table-1. AcOH-NaOAc buffer solution with pH 3.50-6.50 were prepared from the NaOAc and AcOH, solutions. All other chemicals were of analytical grade and purified water was used throughout.

TABLE-1
GENERAL DESCRIPTION AND PROPERTIES

Items	Properties
Resin	SQD-85 resin
Functional group	-COOH
Mass capacity (m mol/g)	≥ 10.5
Moisture (%)	50-60
Bulk density (g/mL)	0.7-0.8
Specific density (g/mL)	1.10-1.20
Particle size (≥ 95 %)	0.315-1.25mm
Whole bead after osmotic attrition (%)	≥ 90

Adsorption experiments[19,20]: Experiments were run in a certain range of pH, temperature, contact time as well as adsorption isotherms. The operation for the removal of Pb(II) is usually carried out in batch vessels and glass columns.

Batch experiments were performed under kinetic and equilibrium conditions. A desired amount of treated SQD-85 resin was weighed and added into a conical flask, in which a desired volume of buffer solution with pH 6.00 was added. After 24 h, a required amount of standard solution of Pb(II) was put in. The flask was shaken in a shaker at constant temperature. The upper layer of clear solution was taken for analysis until adsorption equilibrium reached. The procedure of kinetic tests was identical to that of the equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of Pb(II) were similarly measured.

Continuous flow adsorption experiments were conducted in a vertical glass column filled with Pb(II) solution. At the bottom of the column, a stainless sieve was attached followed by a layer of cotton wool. The particles were dropped in from the top of the column. Pb^{2+} solution was fed from the top at a fixed flow rate. The Pb(II) solutions at the outlet of the column were collected periodically and analyzed for the Pb(II) concentration using a UV-visible spectrophotometer at 545 nm. The flow through the column was continued till the outlet and inlet concentrations were equal. All the experiments were carried out at room temperature.

Analytical method[19,20]: A solution containing lower than 75 μg of Pb(II) was accurately added into a 25 mL colorimetric tube and then 2.0 mL visualization reagent and 10 mL hexamethylenetetramine the buffer solution were added, after the addition of deionized water to the mark of colorimetric tube, the absorbency was determined in a 1 cm colorimetric vessel at wavelength of 545 nm and compared with blank test. The adsorption capacity (Q) of Pb(II) ions on SQD-85 resin was calculated with the following formula:

$$Q = \frac{C_o - C_e}{W} V \quad (1)$$

The distribution coefficient (D) of Pb^{2+} between the aqueous phase and the solid phase can be directly obtained using:

$$D = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \quad (2)$$

where C_o (mg/mL) and C_e (mg/mL) are the initial and equilibrium Pb(II) concentrations, respectively, V/W is the ratio of the volume of metal solution (mL) to the amount of SQD-85 resin (g) in a batch.

RESULTS AND DISCUSSION

Influence of pH on the distribution coefficient for Pb(II): The pH of the aqueous solution is an important parameter that controlled the sorption process. The influence of pH on the sorption behaviours of SQD-85 resin for Pb(II) is shown in Fig. 1. For each Pb(II), the highest statically saturated sorption capacity was achieved at pH about 6.0 with AcO-NaOAc. Both with increasing and decreasing pH, the saturated sorption capacity decreased. This sorption trend could likely be ascribed to the effect of competitive binding between Pb(II) and H^+ for the binding sides on the surface of the resins. At low pH, an excess of H^+ compete effectively with Pb(II) for bonding sites, resulting in a lower Pb(II) recovery. The percentage of ion exchange decreased when the pH was increased above 6.0 owing to the formation of Pb(II) precipitation at higher pH values[21]. So the following experiments were performed at pH 6.0 in the AcOH-NaOAc system.

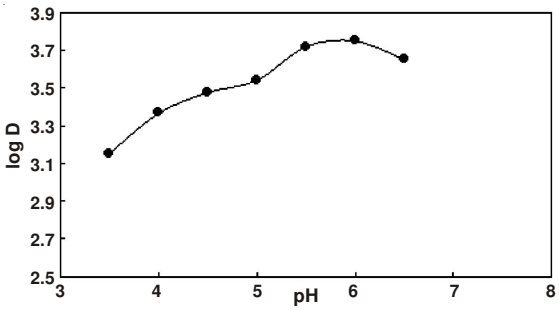

Fig. 1. Influence of pH on adsorption capacity (resin 15.0 mg, 298 K, r = 100 rpm, C_0 = 10 mg/30.0 mL)

Adsorption isotherms: The adsorption data were analyzed to see whether the isotherm obeyed the Langmuir[22] and Freundlich[23] isotherm models. The linear forms of the Langmuir and Freundlich isotherms are represented by the following equations:

Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} K_L} + \frac{C_e}{Q_{max}} \quad (3)$$

Freundlich isotherm:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where Q_e is the equilibrium Pb(II) ions concentration on the adsorbent (mg/g), C_e is the equilibrium Pb(II) ions concentration in solution (mg/mL), Q_{max} is the monolayer capacity of the adsorbent (mg/g) and K_L is the Langmuir constant and related to the free energy of adsorption; K_F is Freundlich constant and n (dimensionless) is the heterogeneity factor. The plots of C_e/Q_e *versus* C_e (Langmuir) for the adsorption of Pb(II) ions onto SQD-85 resin give a straight line of slope $1/Q_{max}$ and intercept $1/Q_{max}K_L$; by plotting log C_e *versus* log Q_e (Freundlich) to generate K_F and n from the intercept and the slope, respectively. One of the Freundlich constants K_F indicates the adsorption capacity of the adsorbent[24]. The other Freundlich constants n is a measure of the deviation from linearity of the adsorption. The numerical values of n at equilibrium lay between 2.30 and 2.57, indicating that Pb^{2+} ions was favourably adsorbed by SQD-85 resin at all the studied temperatures[25].

The Langmuir and Freundlich parameters for the adsorption of Pb^{2+} onto SQD-85 resin are being listed in Table-2. It is evident from these data that the adsorption of Pb^{2+} onto SQD-85 resin is fitted well to the Langmuir isotherm model than that of the Freundlich isotherm models, as indicated by the R^2 values in Table-2. The Langmuir model is the best-known isotherm for describing adsorption from aqueous solution. The Langmuir model assumes that there is no interaction between the adsorbate molecules. The adsorption is localized in a monolayer. The maximum adsorption capacity (Q_{max}) of adsorbent calculated from Langmuir isotherm equation defines the total capacity of the adsorbent for Pb^{2+}. The adsorption capacity increased with an increase in the temperature. The highest value of Q_{max} obtained at 308 K is 476 mg/g. A comparison of the maximum capacity of SQD-85 resin with that of some other adsorbents reported in literatures is given in Table-3. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

TABLE-2
ISOTHERM CONSTANTS

Temp. (K)	Langmuir isotherm		Freundlich isotherm	
	Q_{max} (mg/g)	R^2	n	R^2
288	455	0.9976	2.57	0.9756
298	476	0.9928	2.46	0.9496
308	476	0.9774	2.30	0.9120

TABLE-3
COMPARISON OF THE MAXIMUM ADSORPTION CAPACITIES

Adsorbent	Maximum adsorption capacity of Pb^{2+}/(mg g^{-1})	Ref.
Red mud	64.8	26
Crushed concrete fines	37.0	27
Peat	95.2	28
Palm shell activated carbon	95.2	29
Qafuor tree commercial carbon	27.3	30
Nile rose plant power (water hyacinth)	27.4	30
Bone powder	55.3	30
Phthalic acid functionalized XAD-16 resin	40.0	31
Modified quebracho tannin resin	86.2	32
SQD-85 resin	476.0	Present study

Thermodynamic parameters: In any adsorption procedure, both energy and entropy considerations should be taken into account in order to determine which process will take place spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. The amounts of Pb^{2+} adsorbed at equilibrium at 288, 298 and 308 K have been examined to obtain thermodynamic parameters for the adsorption system.

Thermodynamic parameters, such as changes in the Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) associated to the adsorption process and were determined by using following equations:

$$\log D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

where R is the gas constant and T is the absolute temperature. As can be observed in Fig. 2, the correlation coefficient of the straight line $R^2 = 0.9712$ was achieved. ΔH and ΔS values can be estimated from slope and intercept value of this plot log D *vs.* 1/T and the ΔG values at different temperatures were calculated using the eqn. 6, respectively. Table-4 shows the values of thermodynamic parameters of Pb(II) ions adsorption on SQD-85 resin.

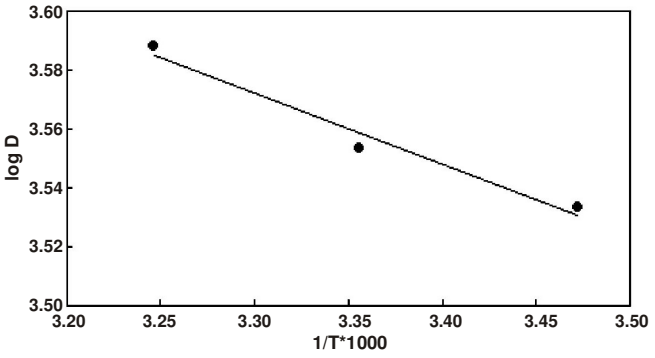

Fig. 2. Influence of tempretures (resin 15.0 mg, C_0 =10 mg/30.0 mL, 288, 298 and 308 K, 100 rpm)

TABLE-4
THERMODYNAMIC PARAMETERS

ΔH (kJ/mol)	ΔS (J/K mol)	ΔG (kJ/mol)		
		288 K	298 K	308 K
7.073	0.0913	-19.23	-20.15	-21.06

The negative value of ΔG confirms the spontaneity of the adsorption process with increasing temperature and the positive value of ΔH suggests that the adsorption is endothermic in nature. Although there are no certain criteria related to the ΔH values that define the adsorption type, the heat of adsorption values, which are heats of chemical reactions, are frequently assumed as the comparable values for the chemical adsorption process. In addition, the values of ΔS were found to be positive due to the exchange of the metal ions with more mobile ions present on the exchanger, which would cause increase in the entropy, during the adsorption process[33].

Determination of adsorption rate constant and apparent activation energy: The influence of contact time on the adsorption of Pb^{2+} onto SQD-85 resins (Fig. 3) was investigated at 288, 298 and 308 K. It is easily seen that the amount of adsorption increased with increasing contact time. Further, the loading half time $t_{1/2}$ was 20 h and the maximum adsorption was observed after 75 h, beyond which there was almost no further increase in the adsorption. Therefore, this interaction time could be very well taken as equivalent to the equilibrium time.

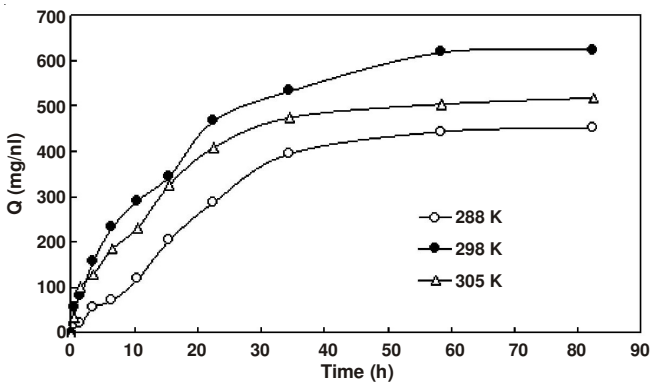

Fig. 3. Adsorption amount of different temperatures (resin 30.0 mg, C_0 = 20.0 mg/60.0 mL, pH = 6.00, 100 rpm)

Adsorption kinetics curves were obtained for Pb^{2+} on SQD-85 resins. The kinetics of adsorption can be described by the liquid film diffusion model[34], using the Brykina method[35]:

$$-\ln(1-F) = kt \quad (7)$$

where F is the fractional attainment of equilibrium ($F = Q_t/Q_e$), where Q_e and Q_t are the amounts of Pb^{2+} adsorbed on the adsorbent at equilibrium at various times, respectively; k is the adsorption rate constant. The experimental results accorded with the equation and a straight line was obtained by plotting -ln (1-F) *vs.* t. Therefore, the adsorption rate constant can be found from the slope of the straight line, which is $k_{298\,K} = 2.50 \times 10^{-7}\ s^{-1}$. The correlation coefficient (R^2 = 0.9923) was obtained *via* linear fitting. The other results were listed in Table-5. According to the Boyd equation, it can be deduced from the linear relationship of-ln (1-F) *vs.* t that the liquid film spreading was the predominating step of the adsorption process[36].

TABLE-5
ADSORPTION RATE CONSTANTS

Temp. (K)	Linearity relation of -ln (1-F) and t	$k \times 10^{-7}$ (s^{-1})	R^2
288	y = 0.0008x – 0.0627	2.22	0.9893
298	y = 0.0009x + 0.0732	2.50	0.9923
308	y = 0.0012x + 0.0059	3.33	0.9896

According to the Arrhenius equation[37]:

$$\log k = -\frac{E_a}{2.303RT} + \log A \quad (8)$$

where E_a is the Arrhenius activation energy for the adsorption process indicating the minimum energy that reactants must have for the reaction to proceed, A is the Arrhenius factor, R is the gas constant (8.314 J/(mol K)), k is the adsorption rate constant and T is the temperature. As can be observed in Fig. 4, E_a and A values can be estimated from slope and intercept value of this plot log K *vs.* 1/T, respectively. The slope of straight line was k_{slope} = -0.7771. The correlation coefficient of the straight line R^2 = 0.9368 was achieved. The apparent activation energy E_a was 14.88 kJ/mol, which could be considered as a low energy barrier in this study.

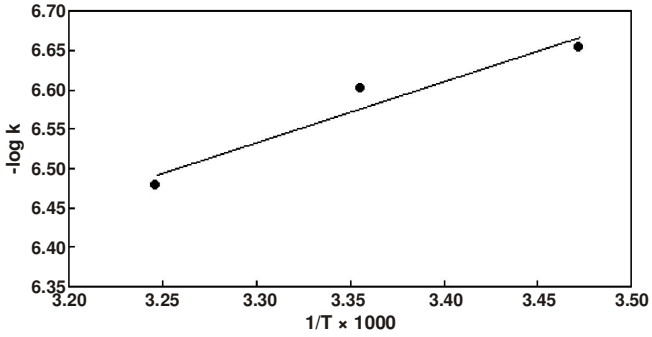

Fig. 4. Relationship between log k and 1/T (C_0 = 20.0 mg/60.0 mL, resin = 30.0 mg, pH = 6.0, 100 rpm)

Elution tests: 15.0 mg SQD-85 resin was added into a mixed solution composed of pH 6.00 buffer solution and desired amount of Pb(II) solution. After equilibrium reached, the concentration of Pb(II) in the aqueous phase was determined and the adsorption capacity of the SQD-85 resin for Pb(II) was obtained.

Then, the SQD-85 resin separated from aqueous phase was washed three times with pH 6.0 buffer solution. The SQD-85 resin adsorbed Pb(II) was shaken with 30.0 mL HCl eluant. After equilibrium reached, the concentration of Pb(II) in aqueous phase was determined and then the percentage of elution for Pb(II) was obtained. It has been showed that the percentage of elution for Pb(II) seems to be weakly influenced by the molarity of HCl varying from 0.1 mol/L to 5.00 mol/L and the maximum recovery can reach *ca.* 100 %. Considering the environmental pollution, the 0.1 mol/L HCl solution was chose as an eluant.

Dynamic adsorption curve: The performance of packed beds is described through the concept of the breakthrough curve. The breakthrough curve shows the loading behaviour of Pb(II) to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed Pb(II) concentration [C_{ad} = inlet Pb(II) concentration (C_o) - outlet Pb(II) concentration (C_e)] or normalized concentration defined as the ratio of effluent Pb(II) concentration to inlet Pb(II) concentration (C_e/C_o) as a function of time or volume of effluent for a given bed height[38]. The area under the breakthrough curve obtained by integrating the adsorbed concentration (C_{ad}; mg/mL) *vs.* the throughput volume (V; mL) plot can be used to find the total adsorbed Pb(II) quantity (maximum column capacity). Total adsorbed Pb(II) quantity (Q; mg/g) in the column for a given feed concentration and flow rate is calculated from eqn. 9 as follows:

$$Q = \int_0^v \frac{(C_o - C_e)}{m} dV \quad (9)$$

where m (g) is the mass of the adsorbent. The capacity value Q was obtained by graphical integration as 540 mg/g. Traditionally,

the Thomas model is used to fulfill the purpose. The model has the following form[39]:

$$\frac{C_e}{C_o} = \frac{1}{1+\exp[K_T(Qm - C_oV)/\theta]} \quad (10)$$

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

$$\ln\left(\frac{C_o}{C_e} - 1\right) = \frac{K_T Qm}{\theta} - \frac{K_T C_o}{\theta} V \quad (11)$$

The kinetic coefficient K_T and the adsorption capacity of the bed Q can be determined from a plot of $\ln[(C_o/C_e)-1]$ *vs.* t at a certain flow rate as shown in Fig. 5. Thomas equation coefficients for Pb(II) adsorption were $K_T = 2.64 \times 10^{-2}$ mL/(min mg) and Q = 502.0 mg/g. The theoretical predictions based on the model parameters were compared with the observed data as shown in Fig. 6.

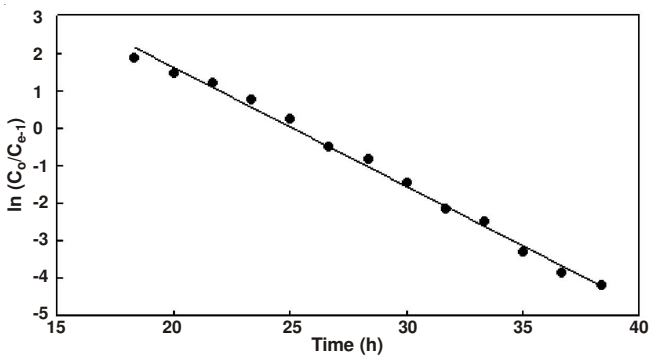

Fig. 5. Plot of ln $[(C_o/C_e)-1]$ *vs.* t (resin 150 mg, pH = 6.0, C_0 = 0.20 mg/mL, flow rate = 0.25 mL/min)

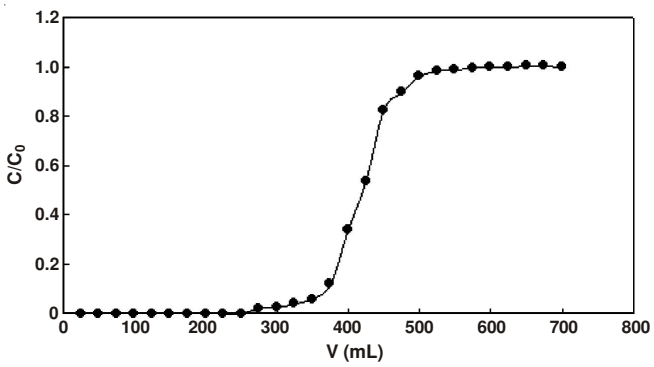

Fig. 6. Breakthrough curve (resin 150 mg, pH = 6.0, C_0 = 0.20 mg/mL, flow rate = 0.25 mL/min)

Dynamic desorption curve: Efficient elution of adsorbed solute from SQD-85 resin in column was essential to ensure the reuse of SQD-85 resin for repeated adsorption/desorption cycles. With respect to the stripping of Pb(II) from SQD-85 resin, the 0.1mol/L HCl eluant was employed. Desorption curve was plotted the effluent concentration (C_e) *vs.* elution volume from the column at a certain flow rate. It can be seen from Fig. 7 that the adsorption flow rate was less so that the volume of elution was less which helped in easy handling and high in concentration for economical recovery of Pb(II). It was observed that the total volume of eluent was 375 mL and the desorption process took 25 h, after which further desorption was negligible. Therefore, the 0.1 mol/L HCl eluant could help in easy handling and removing of Pb(II).

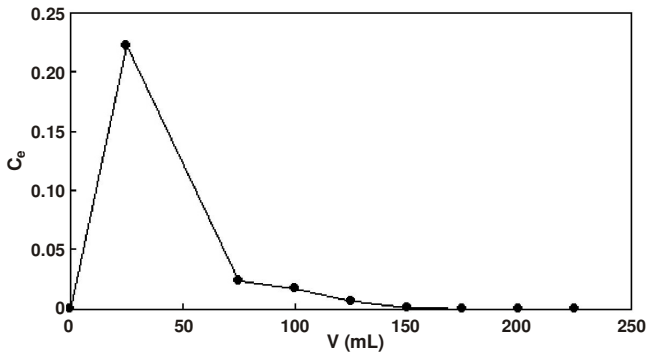

Fig. 7. Dynamic desorption curve (resin 150 mg, pH = 6.0, flow rate = 0.25 mL/min)

Reusability: Reusability (*i.e.*, repeated usability or regenerability) is an important factor for an effective absorption material. As such, the desorption of the adsorbed Pb(II) from the SQD-85 resin was also studied by static experiment. When the 0.1 mol/L HCl solution with a pH value of 6.0 was used as an eluent, the hydrogen bond between Pb(II) and SQD-85 resin was disrupted and subsequently, Pb(II) was released into the eluent. In order to show the reusability of the SQD-85 resin, the adsorption-desorption cycle was repeated several times using the same material. The results (Table-6) clearly show that the the SQD-85 resin could be used repeatedly without significantly losing its adsorption capacity.

TABLE-6
ADSORPTION-DESORPTION CYCLE OF Pb(II) ION

Repeat time	1	2	3	4
Adsorption capacity (mg/g)	476.3	482.2	482.0	479.1

Sorption from simulated seawater: Here the sorption equilibria of Pb^{2+} are investigated in a simulated seawater, in which the concentration of Pb^{2+} is 0.2 μg/mL, which is the highest concentration in heavy polluted seawater. The simulated seawater is also obtained according to literature, containing NaCl with the concentration of 3.5 %. Results show that the removal rate of Pb^{2+} in the simulated seawater can reach *ca.* 100 %, which is of great interest in the case of natural waters.

Conclusion

From the results, it is obtained that Pb(II) can be optimally adsorbed on SQD-85 resin in AcOH-NaOAc medium at pH value of 6.0. It is evident from the experimental data that the adsorption of Pb^{2+} onto SQD-85 resin obeys both the Langmuir isotherm and Freundlich isotherm and fitted better to the Langmuir isotherm model. The adsorption coefficients agree well with the conditions supporting favourable adsorption. Then the statically saturated adsorption capacity of Pb(II) was 476 mg/g on SQD-85 resin at 298 K, calculated from the Langmuir isotherm model. The adsorption rate constant $k_{298\,K}$ was 2.50×10^{-5} s^{-1} and the apparent activation energy E_a was 14.88 kJ/mol, indicating that the adsorption had a low potential

barrier. Thermodynamic parameters, ΔS, ΔH and ΔG, on the adsorption for Pb(II) indicated that the adsorption process was spontaneous and endothermic. The Pb(II) adsorbed on SQD-85 resin can be eluted by using 0.1 mol/L HCl solution as an eluant indicating that the resin can be regenerated and reused. The Thomas model was applied to predict the breakthrough curves and to determine the column kinetic parameters. The capacity values were obtained as 475 mg/g resin using this model. The results also indicated that the Thomas model is reasonably accurate in predicting experimental column results for this work.

In conclusion, SQD-85 resin has a very good potential for utilization as an adsorbent for Pb(II) from aqueous medium because of its comparatively high sorption capacity, easy regeneration, convenient operation and advantages to preconcentrate, concentrate, purify and recover Pb(II) in the AcOH-NaOAc system. The experimental results develop the theory of heavy metal removal chemistry, that may be used for understanding and optimizing the recovery, purification and refining of Pb(II) hydrometallurgical systems and fit in with the environmental protection.

ACKNOWLEDGEMENTS

This research was funded by the grants from the National Key Technologies Research and Development Program of China (No 2008BAD94B09),and was supported by the Key Grant of Education Department of Zhejiang Province, China (Project Z200907459).

REFERENCES

1. C.H. Xiong, C.P. Yao, L. Wang and J.J. Ke, *Hydrometallurgy*, **98**, 318 (2009).
2. D. Zhou, L.N. Zhang, J.P. Zhou and S.L. Guo, *Water Res.*, **38**, 2643 (2004).
3. M. Ucurum, *Fuel*, **88**, 1460 (2009).
4. Z. Djedidi, B. Médard, R.B. Cheikh, G. Mercier, R.D. Tyagi and J. Blais, *Hydrometallurgy*, **98**, 247 (2009).
5. A. Dabrowski, Z. Hubicki, P. Podkoscielny and E. Robens, *Chemosphere*, **56**, 91 (2004).
6. H. Eccles and H. Greenwood, *Solv. Extract. Ion Exch.*, **10**, 713 (1992).
7. Z. Ujang and G.K. Anderson, *Water Sci. Technol.*, **38**, 521 (1998).
8. T. Mohammadi, A. Moheb, M. Sadrzadeh and A. Razmi, *Sep. Sci. Technol.*, **41**, 73 (2005).
9. H.J. Wang, A.L. Zhou, F. Peng, H. Yu and L.F. Chen, *Mater. Sci. Eng.*, **A466**, 201 (2007).
10. M. Kul and Ü. Çetinkaya, *Hydrometallurgy*, **98**, 86 (2009).
11. R. Navarro, V. Gallardo, I. Saucedo and E. Guibal, *Hydrometallurgy*, **98**, 257 (2009).
12. C.H. Xiong, C.P. Yao and X.M. Wu, *Hydrometallurgy*, **90**, 221 (2008).
13. Z. Zainol and M.J. Nicol, *Hydrometallurgy*, **96**, 283 (2009).
14. M.E. Malla, M.B. Alvarez and D.A. Batistoni, *Talanta*, **57**, 277 (2002).
15. R.K. Sharma, N. Bhojak, S. Mittal and B.S. Garg, *Microchem. J.*, **61**, 94 (1999).
16. I.A.W. Tan, A.L. Ahmad and B.H. Hameed, *Desalination*, **225**, 13 (2008).
17. X.M. Wu, C.H. Xiong and C.P. Yao, *J. Rare Earths*, **22**, 785 (2004).
18. A.M. El-Kamash, *J. Hazard. Mater.*, **151**, 432 (2008).
19. C.H. Xiong and C.P. Yao, *J. Hazard. Mater.*, **166**, 815 (2009).
20. C.H. Xiong and C.P. Yao, *J. Hazard. Mater.*, **170**, 1125 (2009).
21. F. Gode and E. Pehlivan, *J. Hazard. Mater. B*, **100**, 231 (2003).
22. I. Langmuir, *J. Franklin Institute*, **183**, 102 (1917).
23. H.M.F. Freundlich, *Z. Physik. Chem.*, **57**, 385 (1906).
24. N. Öztürk and D. Kavak, *J. Hazard. Mater. B*, **127**, 81 (2005).
25. F.Gode and E. Pehlivan, *J. Hazard. Mater. B*, **136**, 330 (2006).
26. V.K. Gupta, M. Gupta and S. Sharma, *Water Res.*, **35**, 1125 (2001).
27. N.J. Coleman, W.E. Lee and I.J. Slipper, *J. Hazard. Mater.*, **121**, 203 (2005).
28. Y.S. Ho and G. Mckay, *Water Res.*, **33**, 578 (1999).
29. G. Issabayeya, M.K. Aroua and N.M.N. Sulaiman, *Bioresour. Technol.*, **97**, 2350 (2006).
30. S.H. Abdel-halim, A.M.A. Shehata and M.F. El-Shahat, *Water Res.*, **37**, 1678 (2003).
31. S.Q. Memon, S.M. Hasany, M.I. Bhanger and M.Y. Khuhawar, *J. Colloid Interf. Sci.*, **291**, 84 (2005).
32. M. Yurtsever and I.A. Sengil, *J. Hazard. Mater.*, **163**, 58 (2009).
33. N. Ünlü and M. Ersoz, *J. Hazard. Mater. B*, **136**, 272 (2006).
34. C.H. Xiong, *Asian J. Chem.*, **21**, 6005 (2009).
35. G.D. Brykina, T.V. Marchak, L.S. Krysina and T.A. Belyavskaya,, *Zh. Anal. Khim.*, **35**, 2294 (1980).
36. G.E. Boyd, A.W. Adamson and L.S. Myers, *J. Am. Chem. Soc.*, **69**, 2836 (1947).
37. A. Kandelbauer, G. Wuzella, A. Mahendran, I. Taudes and P. Widsten, *Chem. Eng. J.*, **152**, 556 (2009).
38. Z. Aksu and F. Gönen, *Process Biochem.*, **39**, 599 (2004).
39. T. Mathialagan and T. Viraraghavan, *J. Hazard. Mater.*, **94**, 291 (2002).