Adsorption Behavior of Cu(II) in Aqueous Solutions by SQD-85 Resin

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ABSTRACT: *The adsorption and desorption properties of SQD-85 resin for Cu(II) had been investigated. A series of experiments were conducted in a batch system to assess the effect of the system variables, i.e. initial pH, contact time and temperature. The results show that the optimal pH for the adsorption was 5.99 in the HAc-NaAc system, and the maximum adsorption capacity was estimated to 324 mg/g at 298 K. The apparent activation energy Ea and adsorption rate constant* k_{298K} *values were 6.19 kJ/mol and* $9.73\times10^{-5}\ s^{-1}$ *, respectively. The isotherms of adsorption data fitted well to Langmuir model. Thermodynamic parameters (ΔG, ΔS, ΔH) suggested that Cu(II) adsorption by SQD-85 resin was endothermic and spontaneous in nature. Thomas model was applied to determine the characteristic parameters of column useful for process design. Desorption studies revealed that Cu(II) ion could be eluted with 1.0 mol/L HCl solution., which indicated that Cu(II) in aqueous solution could be removed and recovered by SQD-85 resin efficiently. Adsorption mechanism was also proposed for the adsorption of Cu(II) onto SQD-85 resin using FT-IR spectrometry technique.*

KEY WORDS: *SQD-85 resin; Adsorption; Cu(II); Kinetics; Thermodynamics; Mechanism.*

INTRODUCTION

Today contamination of a range of heavy metals resulting from the discharge of industrial wastewater is a worldwide environmental problem. Many industries, such as mining, metal plating, tanning and nuclear power plant operations, represent significant sources of heavy metal emissions. Unlike organic compounds, heavy metals are non-biodegradable and toxic even at trace levels [1–4]. Additionally, copper, which is an essential nutrient to humans and other life forms, is biostatic/biocidal to certain organisms. However, copper(II) as one of the heavy metals, causes particular environmental safety problems due to its extreme toxity toward to living organisms [5–7]. The continued intake of copper by humans leads to necrotic changes in the liver and kidney, mucosal irritation; wide spread capillary damage, depression, gastrointestinal irritation, and lung cancer [8-10]. Consequently, there is a considerable need to treat industrial effluents containing such heavy metals prior to discharge to mitigate any impact on plant, animal and human receptors.

The most common treatment processes for metal contaminated wastewater including chemical precipitation [11], ion exchange [12], membrane separation [13], electrochemical deposition [14] and extraction chromatography [15]. Compared with other methods, adsorption via ion exchange mode has increasingly received more attention in environmental treatment applications throughout the world in recent years due to unique advantages including

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simplicity, rapidity, short analysis time, low cost and low consumption of organic solvents, high enrichment factor and easier recovery of analyze and extractant [16–19]. SQD-85 macroporous weak acid 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. Moreover, it is cheaper comparing with imported resins as well widely available as it is commercially produced.

In this work, adsorption behavior of Cu(II) in aqueous solutions by SQD-85 resin using batch and column methods has been investigated. Some factors affecting adsorption, such as initial pH of solution, contact time and temperature were examined. Kinetics and isotherm adsorption experiments were carried out. Thermodynamic parameters of adsorption for Cu(II) ion were calculated. The Thomas model was applied to experimental data obtained from column experiments. The resin was also characterized with FT-IR spectroscopy. The experimental results may provide important information for the removal of Cu(II) ion from aqueous solutions in the environmental protection.

EXPERIMENTAL SECTION

Apparatus

The Cu(II) was determined with Shimadzu UV-2550 ultraviolet–visible spectrophotometer. SQD-85 resin dosage was measured by electronic balance of Sartorius BS 224S. Mettler Toledo delta 320 pH meter was used for measuring pH. The sample was shaken in the DSHZ-300A and THZ-C-1 temperature constant shaking machine. The IR spectrum was detected on Nicolet 380 FT-IR spectrometer. The water used in the present work was purified using Mol research analysis-type ultra-pure water machine.

Materials

SQD-85 resin was supplied by Jiangsu Suqing Co., Ltd. and the properties were shown in Table 1. The standard stock solutions were prepared by dissolving an appropriate amount of $CuSO_4.5H_2O$. HAc–NaAc with pH 3.02∼6.76 and KOH–$Na_2B_4O_7$ with pH 10.00 buffer solutions were prepared from the NaAc, HAc, $Na_2B_4O_7$ and KOH solutions. The chromophoric reagent of 0.1% 4-(2-pyridylazo)resorcinol (PAR) solution was obtained by dissolving 0.1000 g PAR powder into 100 mL 95% ethanol solution. All other chemicals were of analytical grade and purified water was used throughout.

Table 1: General description and properties of SQD-85 resin.

Items	Properties
Resin	macroporous weak acid resin
Functional group	−COOH
Structure	Macroporous
Containing moisture (%)	45−50
Wet superficial density (g/mL)	0.70−0.80
True wet density (g/mL)	1.10−1.20

Adsorption experiments

Experiments were run in a certain range of pH, temperature, contact time as well as adsorption isotherms. The operations for the adsorption and desorption of Cu(II) were 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 5.99 was added. After 24 h, a required amount of standard solution of Cu(II) was put. The flask was shaken in a shaker at constant temperature and rotation speed. 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 Cu(II) were similarly measured.

The dynamic adsorption was taken in a glass column. Continuous packed bed studies were performed in a fixed bed mini glass column (Φ3 mm×300 mm) with SQD-85 resin and filled with the Cu(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. Time taken by the particles to travel a distance of resin column in vertical direction was noted. The Cu(II) solutions at the outlet of the column were collected at regular time intervals and the concentrations of Cu(II) were measured. The column

studies were performed at the optimum pH value determined from batch studies and at a constant temperature of 25°C to be representative of environmentally relevant conditions.

Analytical method

A solution containing a required amount of Cu(II) was added into a 25 mL colorimetric tube, and then 1mL colour reagent of 0.1%PAR-ethanol solution and 5mL with KOH–$Na_2B_4O_7$ buffer solutions pH 10.00 were added. After the addition of purified water to the mark of the colorimetric tube, the absorbency was determined in a 1 cm colorimetric vessel at wavelength of 493 nm and compared with blank test. The adsorption capacity (Q, mg/g) and distribution coefficient (D, mL/g) were calculated with the following formulas:

$$Q = \frac{C_0 - C_e}{W} V \quad (1)$$

$$D = \frac{C_0 - C_e}{W \cdot C_e} V \quad (2)$$

where C_0 is initial concentration in solution (mg/mL), C_e is equilibrium concentration in solution (mg/mL), V is solution volume of solution (mL), W is resin dry weight (g).

RESULTS AND DISCUSSION

Influence of pH on the distribution coefficient for Cu(II)

The pH of the metal ion solution is one of the most important factors in the whole adsorption process and particularly on the adsorption capacity [20]. Since it influences the solution chemistry of the heavy metals (i.e. hydrolysis, complexation redox reactions, and precipitation) also strongly influence the speciation and the adsorption availability of the heavy metals.

The Fig. 1 shows the effect of the solution pH on the adsorption of Cu(II) at 298K, for an initial concentration of 10mg/30mL. As seen from Fig. 1, the distribution coefficient for Cu(II) ion was the highest when pH was 5.99 with HAc–NaAc and decreased by either raising or lowering pH under the experimental condition. This can be explained by the fact that at low pH, an excess of H^+ compete effectively with Cu(II) for bonding sites, resulting in a lower Cu(II) recovery. The percentage of ion exchange decreased when the pH was increased above 5.99 owing to the formation of Cu(II) precipitation at higher pH values [21]. Therefore, pH 5.99 was chosen for the adsorption of Cu(II) ions to avoid the formation of Cu(II) hydroxide which will affect the adsorption by the SQD-85 resin.

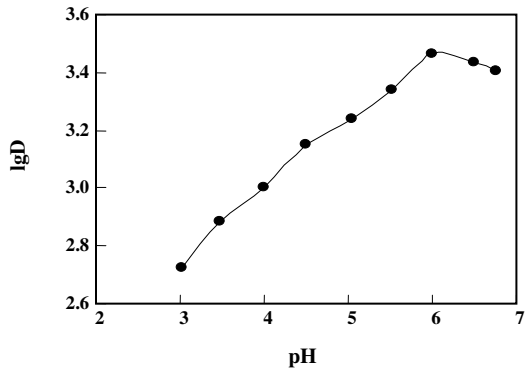

Fig. 1: Influence of pH on the distribution coefficient of Cu(II), resin 15.0 mg, $[Cu^{2+}]_0$=10.0 mg/30.0 mL, T = 298 K, 100 rpm.

Although direct comparison of SQD-85 resin with other sorbent materials is difficult, owing to the different applied experimental conditions, it was found, in general, the adsorption capacity of SQD-85 resin for Cu(II), using equilibrium experiments, determined to be around 324 mg/g, is higher than already reported in literature [22–27]. The values of adsorption 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 SQD-85 resin is greater than some other sorbents.

Determination of adsorption rate constant and apparent activation energy

The adsorption kinetics of Cu(II) ions onto SQD-85 resin has been investigated for a metal ions concentration of 10.0mg/30.0mL with 15.0mg SQD-85 resin at different temperature. At predetermined intervals, aliquots of 0.2mL solution were taken out for analysis and the concentration of metal ion was determined. After the remains kept constant and volume was corrected, a series of data were obtained (Fig. 2)

From Fig. 2 it is clear that the removal amount of metal ions increased rapidly during the few hours, and then increased slowly until the equilibrium state was reached within 15h. A further increase in contact time had a negligible effect on the removal amount. The initial adsorption rate was very fast may be due to the existence of greater number of resin sites available for metal ions adsorption. As the remaining vacant surface sites decreasing, the adsorption rate slowed down due to formation of repulsive forces between the metals on the solid surface and in the liquid phase.

Table 2: Comparison of Cu(II) adsorption on SQD-85 resin and other sorbents.

Sorbent	Qmax(mg/g)	Reference
H-ePAN Fiber Mats	31.3	[22]
Undaria pinnatifida	38.82	[23]
PTFE Selective Resin	39.84	[24]
CT-8HQ	52.9	[25]
Cationic Resin TP 207	68.7	[26]
clay-polymer chelating resin	124.02	[27]
SQD-85	324	[Current work]

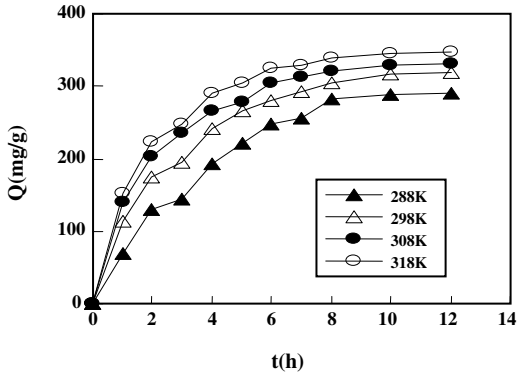

Fig. 2: Adsorption amount of different temperatures , resin 15.0 mg, $[Cu^{2+}]_0$=10.0 mg/30.0 mL, pH = 5.99, 100 rpm.

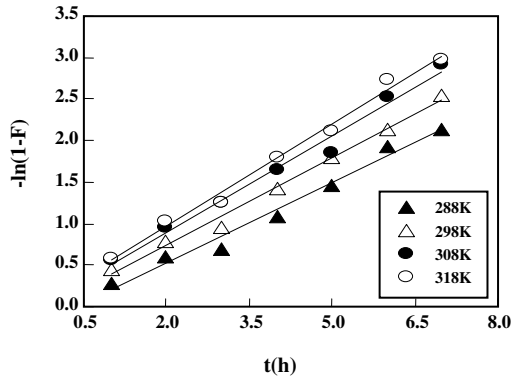

Fig. 3: Linear plots of −ln(1−F) versus t by application of Brykina method.

According to the Brykina method [28], the adsorption rate constant k can be calculated from:

$$-\ln(1-F) = kt \quad (3)$$

Where F =Q_t/Q_e. Q_e and Qt. are the amounts of Cu(II) adsorbed on the adsorbent at equilibrium and at various time (mg/g); The experimental results accord with the equation and a straight line was obtained by plotting −ln(1−F) versus t (Fig. 3). Therefore, the adsorption rate constant (k) can be found from the slope of the straight line, which was k_{298K} = 9.73×10^{-5} s^{-1}. The correlation coefficient (R^2= 0.9923) was obtained via linear fitting. The other results were listed in Table 3. According to Boyd form the linear relationship of −ln(1−F) versus t, it can be deduced that the liquid film spreading was the predominating step of the adsorption process [29].

According to the Arrhenius equation

$$\log k = -\frac{E_a}{2.303RT} + \log A \quad (4)$$

Where E_a is the Arrhenius activation energy for the adsorption process indicating the minimum energy that reactants must have for the reaction to precede, 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 solution temperature.

The slope of straight line was made by plotting–log k versus 1/T, and calculated by linear fitting, yields the apparent activation energy of E_a = 6.19 kJ/mol, which could be considered as a low energy barrier in this study. It can be deduced that the adsorption speed accelerated when the temperature rose within the scope of experimental temperature [30].

Adsorption isotherms

Adsorption isotherms are important to describe how solutes interact with adsorbents and to design adsorption systems for practical or technological use. In this work, The Langmuir and Freundlich isotherms

Table 3: Adsorption rate constants (k) for the adsorption of Cu(II) with SQD-85 resin and its correlation coefficient (R^2).

T (k)	Linearity relation of −ln (1−F) and t	k $\times 10^{-5}$ s^{-1}	R^2
288	y=0.3227x−0.1234	8.96	0.9812
298	y=0.3502x+0.0374	9.72	0.9916
308	y=0.3877x+0.1201	10.76	0.9851
318	y=0.4088x+0.1470	11.35	0.9905

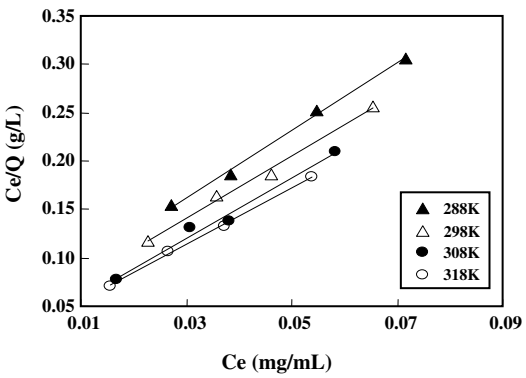

Fig. 4: Langmuir isotherm curve $[Cu^{2+}]_0$=3.0mg/30.0mL ~ 6.0mg/30.0mL, pH=5.99, 100 rpm, resin 15.0 mg

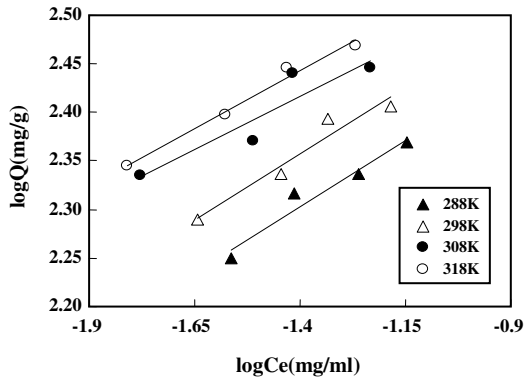

Fig. 5: Freundlich isotherm for Cu(II) on resin10.0mg, 15.0mg, 20.0mg, 25.0mg, $[Cu^{2+}]_0$=10.0 mg/30.0 mL, pH=5.99, 100 rpm

are studied by varying the initial concentrations (4.0mg/30.0mL~6.0mg/30.0mL) of the Cu(II) ion solutions at a fixed pH of 5.99.

The adsorption data are usually analyzed on the basis of either the Langmuir or the Freundlich isotherm model [31, 32]. The Langmuir model is developed to describe the adsorption of an adsorbate on a homogeneous, flat surface of an adsorbent. The model assumes that each adsorptive site can only be occupied once in a one-on-one manner. The model can be written as follows:

Langmuir isotherm [31]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (5)$$

Where Q_e is the equilibrium Cu(II) ions concentration on the adsorbent (mg/g), C_e is the equilibrium Cu(II) ions concentration in solution (mg/mL), Q_m is the maximal adsorption capacity of the metal ions on the adsorbent (mg/g) and K_L is the adsorption equilibrium constant (mL/mg) which reflects quantitatively the affinity between the SQD-85 and Cu (II) ions. The plots of C_e/Q_e versus C_e for the adsorption of Cu(II) ions onto resin give a straight line of slope $1/Q_m$ and intercept $1/Q_mK_L$. The Freundlich isotherm model, on the other hand, is used to describe the adsorption of an absorbate on a heterogeneous surface of an adsorbent. This model can be written as follows:

Freundlich isotherm [32]:

$$\log Q_e = \frac{1}{n}\log C_e + \log K_F \quad (6)$$

Where K_F ((mg/g)/(mg/mL)1/n) is the Freundlich constant, and n is an empirical constant related to the magnitude of the adsorption driving force; By plotting $\log C_e$ versus $\log Q_e$ to generate K_F and n from the intercept and the slope, respectively. The numerical values of n at equilibrium lay between 1 and 10, indicating that Cu(II) ions is favorably adsorbed by SQD-85 resin at all the studied temperatures [28].

The linearized Langmuir and Freundlich adsorption isotherms are given in Figs. 4 and 5, respectively. The adsorption constants evaluated from the isotherms and their correlation coefficients are shown in Table 4. Evidently, both data sets were fitted particularly well with the Langmuir model, with all R^2 values greater than 0.98 [33]. This suggests that the adsorption of Cu(II) ions by SQD-85 is monolayertype and agrees with the observation that the metal ion adsorption from an

Table 4: Isotherm constants for the adsorption of Cu(II) on SQD-85 at various temperatures.

T (K)	Langmuir isotherm		Freundlich isotherm	
	Q_m (mg/g)	R^2	n	R^2
288	284	0.9965	4.22	0.9822
298	311	0.9928	4.55	0.8503
308	322	0.9856	3.67	0.9426
318	342	0.9984	3.69	0.9487

Table 5: Thermodynamic parameters for Cu(II) on SQD-85 resin.

ΔH (kJ/mol)	ΔS (J/(K·mol))	ΔG (kJ/mol)			
		T = 288K	T = 298K	T = 308K	T = 318K
10.1	103.4	−19.6	−20.7	−21.7	−22.7

aqueous solution usually forms a layer on the adsorbent surface. The increase of Q_m value with the temperature rise signifies that the process needs thermal energy (endothermic) and there was a chemical interaction between adsorbent and adsorbate [34].

Thermodynamic parameters

In any adsorption procedure, both energy and entropy considerations should be considered in order to determine what process will take place spontaneously. Values of thermodynamic parameters have the great significance for practical application of a process [35]. The amounts of Cu(II) ions adsorbed at equilibrium at different temperatures have been examined to obtain thermodynamic parameters for the adsorption system.

Thermodynamic parameters such as the Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the adsorption process can be determined by using following equations [12] and reported in Table 5.

$$\log D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

Where R is the gas constant (8.314 J/ (mol K)), T is the absolute temperature (K), D is the distribution coefficient of the adsorbate. From the slope and intercept of the plot logD versus $1/T\times10^3$, the values of ΔH and ΔS had been computed, while ΔG was calculated using Eq. (8). As seen from Table 5, Gibb's free energy (ΔG) is negative, as expected for a spontaneous process under the conditions applied and the decreasing of ΔG with increasing temperature that indicated a better adsorption was occurred at higher temperatures. The positive value of entropy (ΔS) indicates the increasing randomness at the solid/liquid interface during the adsorption of Cu^{2+} ions on SQD-85. The positive value of enthalpy (ΔH) indicates the endothermic nature of adsorption process. [12, 36].

Influence of concentration of eluant solution on the desorption ratio

Efficient elution of adsorbed solute from resin is essential to ensure the reuse of resin for repeated adsorption-desorption cycles. Therefore, different concentrations of HCl solutions were used to perform desorption tests in order to choose proper desorption solution. The results listed in Table 6. showed that the percentage of elution for Cu(II) was different when the concentration of HCl was in the range of 0.25mol/L～3.0mol/L. At first, with the increasing of HCl concentration the percentage of elution for Cu(II) increased accordingly and the percentage can achieve 100 % at the concentration of 1.0 mol/L HCl, then descended to 78.24% at the concentration of 3.0 mol/L HCl. Generally, the tendency of Cu forming the coordination anion enhances, and the eluting effect is better as the acidity increases. However, the results showed that the eluting rate was 100% with 1.0 mol/L HCl while it was 78.24% with 3.0 mol/L HCl. This is probably because as the HCl concentration increased, the cation $[OH]^+$ formed by resin function group (CO) and H^+, which led to the

Table 6: The elution test of Cu(II) from loaded SQD-85 resin.

Eluents	0.25mol/LHCl	0.5mol/LHCl	1.0mol/LHCl	2.0mol/LHCl	3.0mol/LHCl
Eluention percentage	85.83%	89.46%	100%	83.24%	78.24%

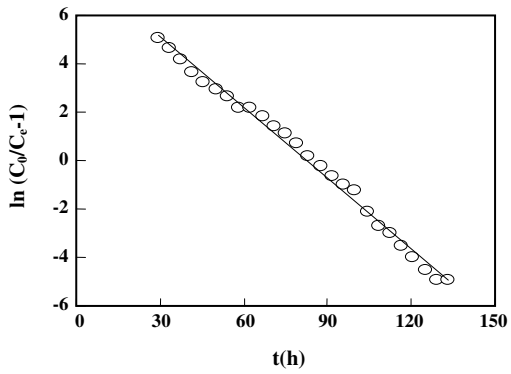

Fig. 6: Linear Plot of ln [(C_o/C_e) − 1] versus t (resin 150.0 mg, pH = 5.99, C_0 = 0.20 mg/mL, flow rate = 0.25 mL/min).

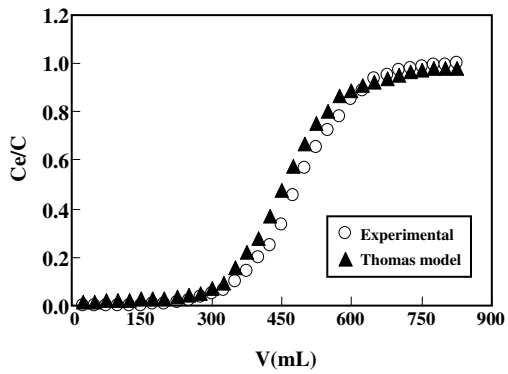

Fig. 7: Breakthrough curves (resin 150.0 mg, pH = 5.99, C_0 = 0.20 mg/mL, flow rate = 0.25 mL/min).

decline of the elution rate. It was evident from data that the maximum percentages of elution for Cu(II) were obtained by using 1.0mol/L HCl solution as an eluant.

Dynamic adsorption and desorption

Dynamic adsorption curve

Batch experimental data are often difficult to apply directly to the fixed-bed sorption because isotherms are unable to give accurate data for a dynamically operated column. The fixed-bed column operation allows more efficient utilization of the adsorptive capacity than the batch process. One of the main tools used in the investigation of the efficiency in adsorption columns is the breakthrough analysis. Total adsorbed Cu(II) quantity (Q; mg/g) in the column for a given feed concentration and flow rate can be calculated from [4]:

$$Q = \int_0^v \frac{(C_0 - C_e)}{m} dV \tag{9}$$

Where C_0 and C_e are metal ion concentrations in the influent and effluent, respectively, m is the total weight of the sorbent loaded in the column and V is the volume of metal solution passed through the column. The capacity value Q was obtained by graphical integration as 349 mg/g. 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 [22]:

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp\left[K_T (Qm - C_0) / \theta\right]} \tag{10}$$

Where K_T is the Thomas rate constant (mL/(min mg) and θ is the volumetric flow rate (mL/min), m is the mass of the resin (g), The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_0}{C_e} - 1\right) = \frac{K_T Qm}{\theta} - \frac{K_T C_0}{\theta} V \tag{11}$$

The kinetics coefficient K_T and the adsorption capacity Q of the column can be determined from a plot of ln[(C_0/C_e) − 1] versus t at a certain flow rate as shown in Fig. 6. The Thomas equation coefficient for Cu(II) adsorption was K_T=1.42×10^{-2} mL/(min mg) and Q=337 mg/g. The theoretical predictions based on the model parameters were compared with the observed data as shown in Fig. 7. It was shown that the experimental data were well fitted by the model of Thomas model with the high R^2 value (0.9927) and the calculated Q value was very close to the experimental data. The successful simulation of the experimental result demonstrates the validity of applying Thomas model for the design and simulation of column adsorption.

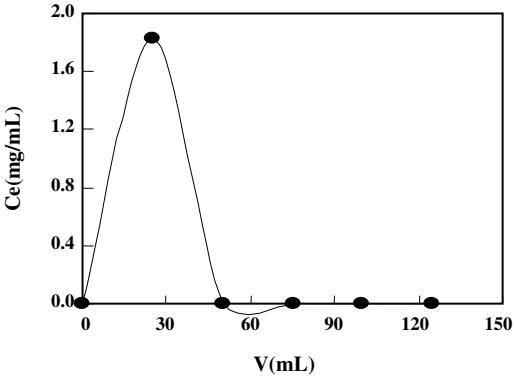

Fig. 8: Dynamic desorption curve (resin 150.0 mg, pH = 5.99, flow rate =0.25 mL/min).

Dynamic desorption curve

With respect to the dynamic desorption of Cu(II) from SQD-85 resin, the 1.0 mol/L HCl eluant was employed. Desorption curve was plotted with the effluent concentration (C_e) versus elution volume (V) from the column at a certain flow rate. As shown in Fig. 8, the total volume of eluent was 100 mL and the desorption process took 6.5 h, after which further desorption was negligible.

The volume of elution was significantly less than saturation volume, which was beneficial to the easy handling and it can obtain a relatively high concentration for economical recovery of Cu(II).

IR Spectra

IR analysis is an important analytical tool for determination of adsorption mechanism. The information about structural changes caused by the SQD-85 resin loading with Cu (II) was given by FT-IR spectra. It was found that the characteristic peak of hydroxyl groups stretching vibrations shift to lower frequency (from 3436.04 cm^{-1} to 3423.49 cm^{-1}), the characteristic peak of the bond CO shifts from 1629.32 cm^{-1} to 1608.41 cm^{-1} and the characteristic peak of the bond C–OH shifts from 1385.86 cm^{-1} to 1401.81 cm^{-1}. These results showed that there are coordination bonds between oxygen atoms and Cu(II) and that H of C–OH had been exchanged with the formation of a complex compound.

CONCLUSIONS

Cu(II) can be optimally adsorbed on SQD-85 resin in HAc–NaAc medium at pH 5.99. The statically saturated adsorption capacity of Cu(II) was 324 mg/g at 298 K. It is evident from the experimental data that the adsorption of Cu(II) onto SQD-85 resin obeys the Langmuir isotherm model. The adsorption coefficients agree well with the conditions supporting favourable adsorption. The adsorption rate constant k_{298K} was 9.73×10^{-5} s^{-1} and the apparent activation energy E_a was 6.19 kJ/mol, indicating that the adsorption had a low potentialbarrier. Thermodynamic parameters, ΔS, ΔH and ΔG, on the adsorption for Cu(II) indicated that the adsorption process was spontaneous and endothermic. The Cu(II) adsorbed on SQD-85 resin can be eluted by using 1.0 mol/L HCl solution as an eluant indicating that the resin can be regenerated and reused. Thomas model was reasonably accurate in predicting experimental column results for this work. Column experiments showed that it is possible to removal and recovery Cu(II) from aqueous medium dynamically. The FT-IR spectra of SQD-85 resin before and after the adsorption of Cu(II) showed that hydrogen and oxygen atoms in the –OH and C=O groups were involved in Cu(II) adsorption.

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