

The Effect of Crosslinking on the Adsorption Behavior of Copper (II) onto Poly(2-hydroxy-4-acryloyloxybenzophenone)

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ABSTRACT: The adsorption behavior of Cu(II) ions onto poly(2-hydroxy-4-acryloyloxybenzophenone), polymer I, and onto poly(2-hydroxy-4-acryloyloxybenzophenone) crosslinked with different amounts of divinylbenzene (DVB), polymers II, III, and IV, in aqueous solutions was investigated using batch adsorption experiments as a function of contact time, pH, and temperature. The amount of metal ion uptake of the polymers was determined by using atomic absorption spectrometry (AAS) and the highest uptake was achieved at pH 7.0 and by using perchlorate as an ionic strength adjuster for polymers I, II, III, and IV. Results revealed that the adsorption capacity (q_e and Q_m) of Cu(II) ions decreases with increasing crosslinking due to the decrease of chelation sites. In addition, the rate

of adsorption (k_2) of Cu(II) ions decreases with the increase of crosslinking because it becomes more difficult for Cu(II) ions to diffuse into the chelation sites. The isothermal behavior and the kinetics of adsorption of Cu(II) ions on these polymers with respect to the initial mass of the polymer and temperature were also investigated. The experimental data of the adsorption process was found to correlate well with the Langmuir isotherm model. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: poly(2-hydroxy-4-acryloyloxybenzophenone); crosslinking; adsorption isotherms; kinetics; thermodynamics; copper(II); ions; atomic absorption spectrophotometry

INTRODUCTION

The presence of heavy metals in the environment is of great concern because of their increased discharge, toxic nature, and other natural water adverse effects on receiving water.¹ Heavy metal contamination of various water resources is also of great concern because of the toxic effect to the human beings and other animals and plants in the environment.² The major sources of heavy metal pollutants are usually from many industries, including mining, metal plating, and electric device manufacturing among others. The potential sources of copper in industrial effluents include the electrical industry, metal cleaning and plating baths, bulb, paper and paper board mills, wood pulp production and the manufacture of fungicides, and antifouling paints.³

The role played by toxic heavy metals in the aquatic environment^{4–6} has stimulated considerable activity and interest^{4,7–16} in the development of metal chelating polymers that found widespread use in the separation and monitoring of trace heavy metal ions from aqueous solutions.^{7,15,16} Addition-

ally, interest in chelating polymers also stems from the need to separate precious metals from aqueous solutions.^{7,8,13,15}

Copper(II) is a potentially toxic trace metal ion and is present at elevated concentrations in coastal waters due to anthropogenic inputs.⁵ Considerable efforts have been made recently to study the chemical speciation of copper in natural waters.^{17,18}

Chelate-forming polymers are produced by incorporating chelating groups into a polymeric matrix; such chelating groups may be covalently bound to a polymer matrix as pendent groups or incorporate into the repeating units of the polymer backbone by polymerization of a suitable monomer containing the required chelating group.^{7,19}

A number of materials, including activated carbon (AC),^{20,21} fly ash,^{22,23} peat,²⁴ sewage sludge ash,²⁵ zeolites,²⁶ biomaterials,^{27,28} recycled alum sludge,²⁹ manganese oxides,³⁰ peanut hulls,³¹ kaolinite,³² and resins,³³ have been reported to be capable of adsorbing heavy metal ions from aqueous solutions. However, these adsorbents suffer from two disadvantages; the first is that these adsorbents are not well characterized. The second is that the species that may leach from these adsorbents may be toxic and the leaching process is not well understood.^{34,35} Therefore, the research for new and more effective materials to be used as adsorbents is a continuous effort for many researchers.

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Recently,³⁶ we have reported on the synthesis and chelation properties of poly(2-hydroxy-4-acryloyloxybenzophenone) toward the divalent metal ions [Cu(II), Zn(II), Ni(II), and Pb(II)] in aqueous solution under different experimental conditions of contact time and pH. The effect of crosslinking with various amounts of divinylbenzene (DVB) on the sorption properties of the polymer was also investigated. The aim of this work was to study the effect of crosslinking on the adsorption properties of the polymers to optimize the crosslinking process to achieve the highest Cu(II) ions removal from wastewater. In this article, we report on the Cu(II) ions adsorption behavior of these previously prepared polymers in addition to the kinetics of the adsorption process. A series of batch adsorption experiments under various experimental conditions of contact time, pH, initial Cu concentrations, and temperature were conducted and the results of the investigation are discussed.

EXPERIMENTAL

Chemicals

Unless otherwise indicated all chemicals were obtained from commercial sources and were used as received. 2,4-dihydroxybenzophenone, triethylamine, and acryloylchloride were obtained from Acros; benzoyl peroxide and hydroquinone from Fluka, DVB from Merck; and acetic acid from GCC. The Cu(II) acetate salt (98%), $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, from Fluka was used as received without further purification.

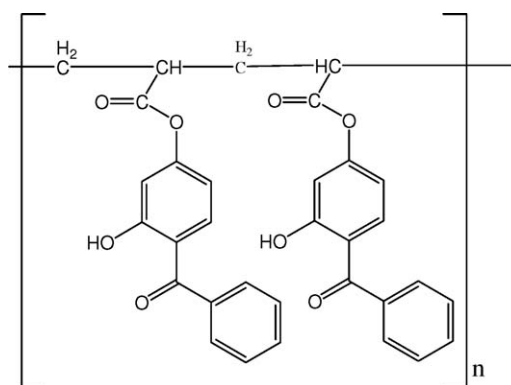
Instrumentation

Infrared spectra of the polymers and their monomers were recorded using a Nicolet Impact 400 FTIR-Spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$) as KBr discs. Atomic absorption data were obtained using a Varian Atomic Absorption Spectrophotometer (AAS) model AA-250 plus. Samples were shaken and thermostated using GFL-1083 shaker. Thermogravimetric analyses were acquired with the aid of a NETZSCH STA 209 PC Thermal Analyzer. A Metrohm pH meter model 525A was used for pH measurements.

Preparation of the polymers

Poly (2-hydroxy-4-acryloyloxybenzophenone), polymer I, was prepared and characterized by following literature procedures³⁶ that involved free-radical polymerization of 2-hydroxy-4-acryloyloxybenzophenone. Polymers II, III, and IV were prepared by following the same general procedure employed for the synthesis of polymer I by the addition of certain amounts of the crosslinker, DVB, to the reaction mix-

ture. The following molar percentages of DVB with respect to monomer were used: 4 mol %, which resulted in a pale yellow solid for polymer II, 8 mol % which resulted in an orange solid for polymer III, and 16 mol % resulted in a dark orange solid for polymer IV.³⁶ After soxhlet extraction with methanol for 24 h, the resulting solid polymers were dried in vacuum oven at 50°C for 24 h and sieved through a mesh size of 35–60 (250–500 μm), as has been described in our earlier publication.³⁶ The structure of Polymer I is shown below.



Adsorption kinetics

The Cu(II) ions sorption characteristics of the resins were investigated by the batch equilibrium method; duplicate experiments involving 0.1000 g of dry, 35–60 mesh size, resin samples were suspended in 25.0 mL of sodium acetate-acetic acid buffer of pH 6.0 for 2 h of continuous shaking to equilibrate. An amount of 25.0 mL solution containing 600 ppm of Cu(II) ions was then added and the mixtures were shaken at 30°C for a specific period of time (0.08–24 h). The samples were filtered out and the amount of metal ion remaining in solution was determined by atomic absorption spectrophotometry (AAS) using standard solutions for calibration.

Effect of pH

Similar experiments were also carried out in buffered solutions, in which the pH was varied between 4.0 and 7.0 for a fixed contact time of 24 h. A 25.0 mL solution containing 600 ppm of Cu(II) ions was then added and the mixtures were shaken at 30°C for an extra 24 h. The samples were filtered out and the amount of metal ion remaining in solution was determined by AAS.

Adsorption isotherms

The adsorption of Cu(II) ions was carried out by suspending 0.1000 g of dry resin in 25.0 mL of

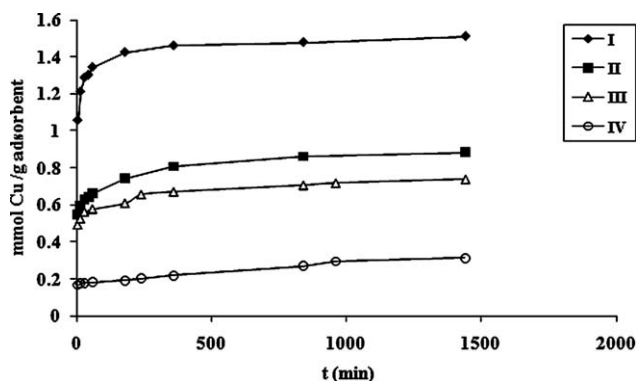


Figure 1 Cu(II) ions uptake by polymers (I, II, III, and IV) as a function of contact time. (Initial concentration of Cu(II) = 300 ppm, 0.1 g polymer, 0.05 L solution, 30°C, and pH = 6.0).

sodium acetate-acetic acid buffer of pH 6.0 for 2 h of continuous shaking. Then 25 mL samples of copper(II) solutions of different concentrations ranging from 20 to 1000 ppm were added to produce a total of 50 mL solutions containing 0.5–25.0 mg of Cu(II) ion. The mixtures were shaken at different temperatures of (30.0, 40.0, and 50.0°C) for a fixed contact time of 24 h. The samples were filtered and the Cu(II) ions concentration remaining in solution was determined with an atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Four polymers of poly (2-hydroxy-4-acryloyloxybenzophenone) with different degrees of crosslinking were used as adsorbents for Cu(II) metal ions. The kinetics, thermodynamics, and effect of pH on the adsorption of Cu(II) ions onto the four adsorbents were investigated. Several parameters of adsorption process were determined, like rate constants, adsorption capacity, equilibrium affinity constants, stoichiometry, enthalpy, and entropy.

Kinetics of adsorption

The amount of Cu(II) ions adsorbed onto polymers I, II, III, and IV as a function of contact time was investigated by a batch equilibration technique. Results for the dependence of the metal ion uptake on contact time are presented in Figure 1. The results indicate fast rates of equilibration; the rates of metal-ion uptake increase in the first 3 h and a steady state is reached within 6 h.

Three kinetic model scan be employed to fit the experimental kinetics data of adsorption of Cu(II) onto the four polymers; pseudo first order, pseudo second order, and intraparticle diffusion model. The model of higher values of R^2 means that the model more successfully describes the adsorption kinetics.

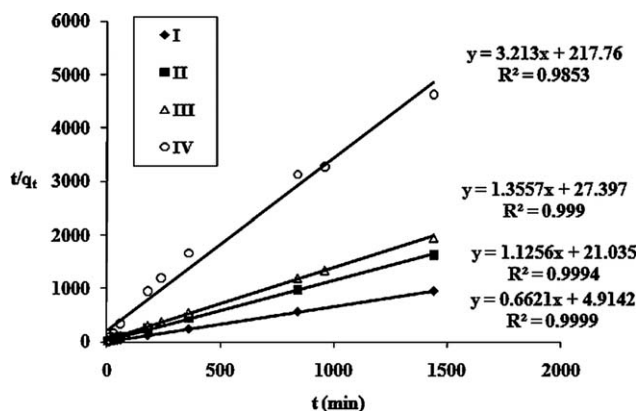


Figure 2 Plots of t/q_t versus t for the pseudo second order model for the adsorption of Cu(II) onto the four polymers. (Initial concentration of Cu(II) = 300 ppm, 0.1 g polymer, 0.05 L solution, 30°C, and pH = 6.0).

The pseudo second order model was selected because it gives the highest correlation coefficients.

The differential form of the pseudo second order kinetic model is³⁷:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{1}$$

where q_e is the amount of Cu(II) adsorbed at equilibrium [mmol Cu(II)/g adsorbent]; t is the time (min); q_t is the amount of Cu(II) adsorbed [mmol Cu(II)/g adsorbent] at time t ; k_2 is the equilibrium rate constant of pseudo second order adsorption [g adsorbent/(mmol Cu(II). min)]. Integration of eq. (1), using the boundary conditions of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, affords the linear form of the equation shown below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2}$$

The values of the slope $1/q_e$ and the intercept $1/(k_2 q_e^2)$ can be obtained by plotting t/q_t versus t , as depicted in Figure 2; these values can be used for the determination of k_2 and q_e as given in Table I.

Results presented in Table I reveal that the amount of Cu(II) ions adsorbed at equilibrium (q_e) decreases with crosslinking. This is due to the

TABLE I
Fitting Parameters Obtained from Pseudo Second Order Model for the Adsorption of Cu(II) Ions Onto Polymers

Adsorbent	q_e (mmol Cu(II)/g adsorbent)	k_2 (g adsorbent/mmol Cu(II). Min)
Polymer I	1.51	0.0892
Polymer II	0.888	0.0602
Polymer III	0.738	0.0671
Polymer IV	0.311	0.0474

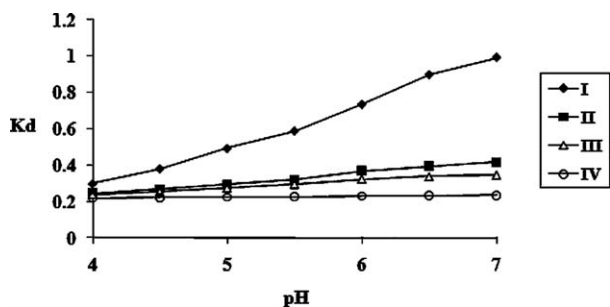


Figure 3 Plots of the distribution coefficient of Cu(II) ions on the four polymers versus pH. (Initial concentration of Cu(II) = 300 ppm, 0.1 g polymer, 0.05 L solution, and 30°C).

decrease of chelation sites in the polymers; these chelation sites are mainly salicyl unites of the polymer. Furthermore, the rate of adsorption (k_2) of Cu(II) ions decreases with an increase of crosslinking. This could be attributed to the fact that crosslinking makes it more difficult for Cu(II) ions to diffuse into the chelation sites.

Effect of pH

The pH dependence of metal ion uptake of the polymers was studied in different acetate buffer solutions in the pH range of 4.0–7.0 under continuous shaking for a fixed contact time of 24 h at 30°C. At higher pH values, hydrolysis of the Cu(II) ions becomes significant and may compete with polymer chelate formation. In addition, the distribution coefficient, K_d , is defined as the amount of metal ion in the adsorbed form on the polymer phase divided by its amount in solution,³⁸ as shown in the following equation:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \quad (3)$$

where C_o and C_e are the initial and equilibrium concentration of metal ions, respectively; V is the volume of the solution and W is the mass of adsorbent (polymer). The distribution coefficient of Cu(II) ions on the four polymers are plotted versus pH as illustrated in Figure 3. The pK_a of chelating sites of the polymer, namely, the salicyl groups could be estimated to be the pK_a of salicylaldehyde is about 8.37.³⁹ So the effect of pH on the dissociation of salicyl group is very small since the pH range used in this investigation was from pH 4 to 7. Furthermore, Cu(II) undergoes its first hydrolysis reaction ($\text{Cu}^{2+} + \text{H}_2\text{O} \rightarrow \text{Cu}(\text{OH})^+ + \text{H}^+$) with pK of reaction equals 8.0, which indicates that the hydrolysis of Cu(II) metal ions is very small in the pH range of study.⁴⁰ EXAFS spectroscopy showed that surface precipitation of Cu(II) is not formed at least up to

pH 6.5.⁴¹ The diversity of pH dependent adsorption curves of the four polymers in Figure 3 is a proof that the pH dependent curves are not due to precipitation but to the adsorption process.

As for the mathematical treatment of the pH dependant adsorption data (Fig. 3), a model⁴ is adopted, which depends on ion exchange reaction between the Cu(II) ions and the H^+ of the salicyl group of the polymer.



where $[\equiv \text{SH}]$ represents the polymer surface ionizable functional groups which are salicyl or phenolic groups.

$$K = \frac{[\equiv \text{S}_n\text{Cu}^{2-n}][\text{H}^+]^n}{[\text{Cu}^{2+}][\equiv \text{SH}]^n} \quad (5)$$

The distribution coefficient K_d can then be defined as:

$$K_d = \frac{[\equiv \text{S}_n\text{Cu}^{2-n}]}{[\text{Cu}^{2+}]} \times \frac{V}{W} = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \quad (6)$$

where C_o and C_e are the initial and equilibrium concentration of Cu(II) ions, respectively; n is the number of surface salicyl sites bound to the Cu(II) ion, V is the volume of the solution and W is the mass of adsorbent (polymer). Substituting eq. (6) in eq. (5) yields:

$$K = \frac{K_d[\text{H}^+]^n}{[\equiv \text{SH}]^n} \times \frac{W}{V} \quad (7)$$

The mass action relationship can be linearized by taking logarithms of eq. (7) to give:

$$\log K_d = \log K - \log \frac{W}{V} - n \log \frac{[\text{H}^+]}{[\equiv \text{SH}]} \quad (8)$$

The value of $[\equiv \text{SH}]$ can be calculated as follows. The % (w/w) of salicyl group in the polymer unit was estimated from the ratio of salicyl group ($\text{C}_7\text{H}_4\text{O}_2$) divided by the molar mass of polymer unit ($\text{C}_{15}\text{H}_{11}\text{O}_4$) = 120/254 = 47%. Hence, the total salicyl site density ($[\equiv \text{SH}]$) = (47 g salicyl/100 g polymer) \times (0.1 g polymer/0.05 L) \times (1 mol salicyl/120 g salicyl) = 7.8 mmol salicyl sites/L. Note that 0.1 g of polymer and 0.05 L Cu (II) solution were employed in adsorption experiments (Section Preparation of the polymers).

As it is usually handled in the literature,⁴² this model assumes that $[\equiv \text{SH}]$ is independent on pH. However, a correction for the effect of Cu(II) loading on the value of $[\equiv \text{SH}]$ can be made by

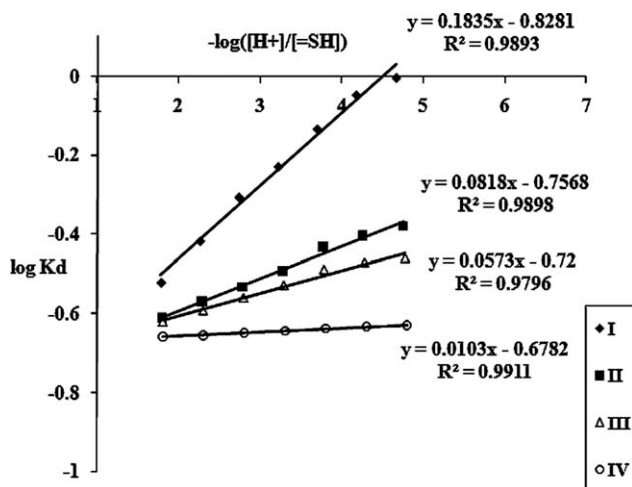


Figure 4 Plots $\log K_d$ versus $\log \frac{[H^+]}{[=SH]}$ for the data of the effect of pH on the adsorption of Cu(II) onto the polymers. (Initial concentration of Cu(II) = 300 ppm, 0.1 g polymer, 0.05 L solution, and 30°C).

multiplication of this value with the correction term: $(1 - \frac{Cu(II)_{adsorbed}(M)}{7.8 \times 10^{-3}(M)})$

By plotting $\log K_d$ versus $\log \frac{[H^+]}{[=SH]}$ (Fig. 4) the values of $\log K$ and n can be calculated (Table II).

The values of n are very strange because they are much lower than 1; this indicates that the H^+ ions of phenol groups (of salicyl groups) of the polymers are not completely displaced upon adsorption. Thus, outer sphere complexation of Cu(II) with the surface of polymers is suggested. An outer sphere complexation between metal ions and surface functional groups occurs when the latter does not replace water of hydration of metal ions and thus the interaction between the surface and metal ions is electrostatic (physical bonding).^{43,44}

Interestingly, the value of n decreases with increasing crosslinking because displacement of H^+ of phenol group becomes more difficult. However, the value of $\log K$ (equilibrium constant) of adsorption increases with increasing crosslinking because of the increasing ability of polymer to encapsulate Cu(II) ions.

Adsorption isotherms

The significance of the adsorption isotherms is that they show how the adsorbate molecules are distrib-

TABLE II
The Values of $\log K$ and n Calculated from eq. (8) and Figure 4

Adsorbent	n	Log K
Polymer I	0.18	-0.528
Polymer II	0.08	-0.457
Polymer III	0.06	-0.420
Polymer IV	0.01	-0.378

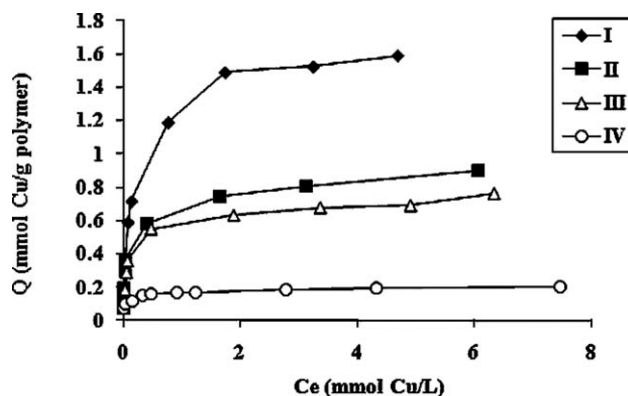


Figure 5 Adsorption isotherms of Cu(II) ions onto polymer I, II, III, and IV (0.1 g polymer, 0.05 L solution, 30°C, and pH = 6.0).

uted between the solution and the adsorbent at the equilibrium conditions and the effect of equilibrium concentration on the loading capacity at different temperatures.⁴⁵ Shown in Figure 5 are the adsorption isotherms of Cu(II) ions for polymers I, II, III, and IV at 30°C and pH = 6.0. Results reveal that the amount of Cu(II) ions adsorbed onto the polymer increases as the equilibrium concentration of the Cu(II) ions in the aqueous phase increases, progressively reaching saturation at higher concentrations.

The Langmuir equation [eq. (9)] is the most commonly used equation for modeling adsorption isotherms⁴⁶:

$$Q = \frac{Q_m K_L C}{1 + K_L C} \tag{9}$$

where, Q is the amount of Cu(II) ions adsorbed (mol Cu(II)/g adsorbent), Q_m is the adsorption capacity (mol Cu(II)/g adsorbent), K_L is the affinity constant [L/mol Cu(II)], and C is the equilibrium

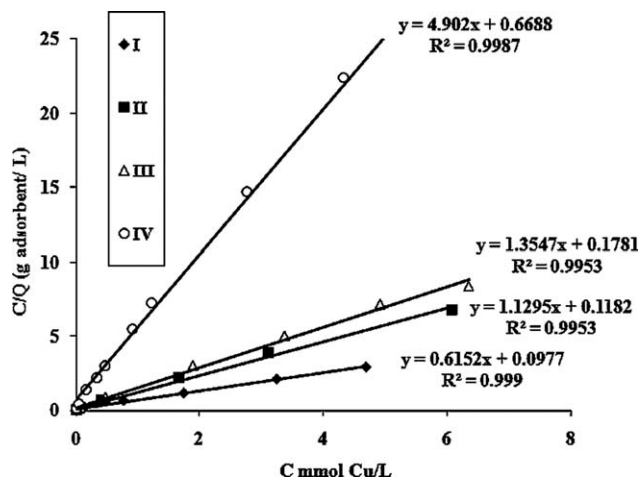


Figure 6 Plots C/Q versus C of adsorption isotherms of Cu(II) ions onto polymers I, II, III, and IV (0.1 g polymer, 0.05 L solution, 30°C, and pH = 6.0).

TABLE III
The Values of Q_m and K_L Calculated from Eq. (10)

Adsorbent	30°C			40°C			50°C		
	Q_m mmolCu/g adsorbent	$\log K_L$	R^2	Q_m mmolCu/g adsorbent	$\log K_L$	R^2	Q_m mmolCu/g adsorbent	$\log K_L$	R^2
Polymer I	1.63	3.80	0.999	1.85	3.70	0.998	1.97	3.70	0.999
Polymer II	0.885	3.98	0.995	1.20	4.04	0.998	1.41	3.93	0.995
Polymer III	0.738	3.88	0.995	0.865	3.91	0.996	1.09	4.01	0.999
Polymer IV	0.204	3.86	0.999	0.316	4.42	0.999	0.560	4.12	0.998

concentration of Cu(II) (mol/L). Plots of Q versus C for the four polymers are shown in Figure 5. The linearized form of the Langmuir equation is given below:

$$\frac{C}{Q} = \frac{C}{Q_m} + \frac{1}{Q_m K_L} \quad (10)$$

Plots C/Q versus C of adsorption isotherms of Cu(II) onto polymers I, II, III, and IV at 30°C and pH = 6.0 are given in Figure 6. The Langmuir parameters Q_m and K_L are determined from the slope and the intercept and are given in Table III.

Results in Table III, demonstrate that at 30°C, the highest loading capacity (Q_m) toward Cu(II) is for polymer I and equals to 1.63 mmol Cu/g polymer. In addition, results indicate that the adsorption capacity of the investigated polymers decreases with increasing crosslinking due to the decrease of chelating sites (salicyl groups). However, the affinity constant K_L showed no trend; K_L is calculated from the intercept, which has more error than the slope [of eq. (7)] from which Q_m is calculated (Table III).

Thermodynamics of adsorption

Adsorption isotherms of Cu(II) ions for polymers I, II, III, and IV were also performed at 40 and 50°C; results are given in Table III. Results presented show that the adsorption capacities of the four poly-

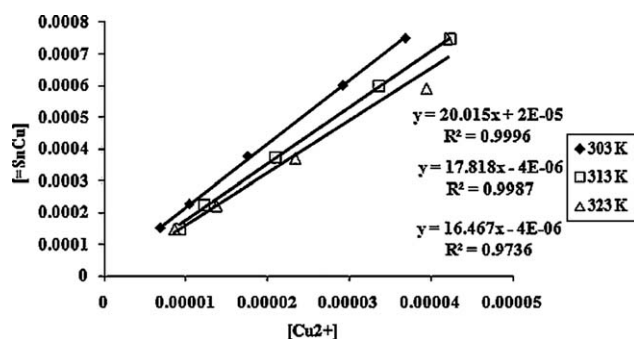


Figure 7 Plot of $[≡S_nCu^{2-n}]$ versus $[Cu(II)]$ according to eq. (12) for adsorption of Cu(II) onto polymer I at 30, 40, and 50°C. (0.1 g polymer, 0.05 L solution, 30°C, and pH = 6.0).

mers increase as the temperature increases. The increase in the adsorption capacity with temperature suggests that the active surface centers available for adsorption have increased with temperature. This increase could be explained by the suggestion that as the temperature increases the pore size could increase and the liquid phase viscosity decreases. This will enhance the rate of intraparticle diffusion of solute. Moreover, results also demonstrate that the adsorption capacity of polymers decreases with increasing crosslinking.

Linear Langmuir equation [eq. (10)] was applied to the isotherms of adsorption of Cu(II) onto the polymers at 30, 40, and 50°C and pH = 6.0. Calculated Langmuir parameters (Q_m and K_L) for the isotherms at 30, 40, and 50°C are given in Table III.

The thermodynamic parameters ΔH and ΔS for the adsorption process can be calculated using eq. (11)⁴⁷:

$$\ln K_L = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (11)$$

where K_L is Langmuir affinity constant. The plot of $\ln K_L$ versus the inverse of temperature $1/T$ should give a straight line where the thermodynamic parameters could be calculated from the slope and intercept. However, since this linear relationship was not obtained, due, probably, to the large error associated with intercept of eq. (10), Table III, an alternative model should be employed for the calculation of thermodynamic parameters.

Rearrangement of eq. (5) yields eq. (12):

$$[≡S_nCu^{2-n}] = \frac{K' [≡SH]^n [Cu^{2+}]}{[H^+]^n} \quad (12)$$

TABLE IV
The Values of Conditional Equilibrium Constant $\log K'$ Depending on Eq. (12) for Adsorption of Cu(II) Ions Onto Polymer I

Adsorbent	$\log K'$
30°C	1.23
40°C	1.18
50°C	1.15

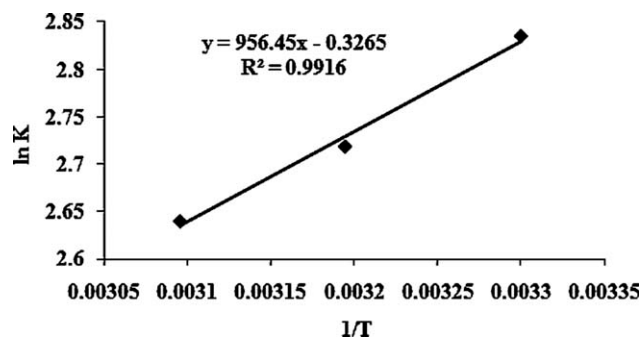


Figure 8 A plot of $\ln K$ versus $1/T$ for the adsorption of Cu(II) ions onto polymer I.

The plot of $[\equiv S_n Cu^{2-n}]$, which is the molar concentration of adsorbed Cu(II) versus $[Cu(II)]$, which is the molar concentration of Cu(II) in solution at constant pH and assuming that $[\equiv SH]$ is constant (7.8×10^{-3} mol), should be linear. The value of the conditional equilibrium constant K' can be calculated from the slope of this plot. The plots $[\equiv S_n Cu^{2-n}]$ versus $[Cu(II)]$ for the adsorption isotherms of polymer I were satisfactory with good correlation coefficients (up to initial concentration of 50 ppm) at 30, 40, and 50°C (Fig. 7). The $\log K'$ values calculated from the slopes of these plots are given in Table IV.

The plot of $\ln K'$ versus $1/T$ is given in Figure 8; the value of ΔH calculated from the slope of the line in Figure 8 equals $-7.952 \text{ kJ mol}^{-1}$ and that of ΔS calculated from the intercept equals $2.71 \text{ J mol}^{-1} \text{ K}^{-1}$. Depending on the plot of $\ln K'$ versus $1/T$ (Fig. 8), the value of ΔH calculated from the slope of the line in Figure 8 equals $-7.952 \text{ kJ mol}^{-1}$ and the value of ΔS calculated from the intercept equals $2.71 \text{ J mol}^{-1} \text{ K}^{-1}$. These results indicate that the adsorption of Cu(II) onto polymer I is an exothermic process with an enthalpy of adsorption in the range of physical adsorption.⁴⁷ Furthermore, the entropy change was very small during adsorption. This supports the assumption of outer sphere adsorption, where the Cu(II) ion and its water sphere is adsorbed physically onto the surface of polymer without direct chemical bonding with the salicyl group.

CONCLUSIONS

In this investigation, the adsorption behavior, isothermal behavior, and the kinetics of adsorption of Cu(II) ions on poly(2-hydroxy-4-acryloyloxybenzophenone), and on poly(2-hydroxy-4-acryloyloxybenzophenone) crosslinked with different amounts of DVB, in aqueous solutions was studied using batch adsorption experiments as a function of contact time, pH, and temperature. The adsorption capacity (q_e and Q_m) of Cu (II) ions decreases with increasing

crosslinking of the polymer due to the decrease of chelating salicyl sites. However, the rate of adsorption (k_2) of Cu (II) decreases with an increase of crosslinking of the polymer because of the increasing difficulty for Cu (II) ions to diffuse into the chelating sites. Based on the thermodynamic parameters, ΔH and ΔS , and the values of the slope of $\log K_d$ versus pH (or $-\log \frac{[H^+]}{[\equiv SH]}$), the mechanism of adsorption of Cu(II) onto poly (2-hydroxy-4-acryloyloxybenzophenone) was suggested as an outer sphere (physical) adsorption.

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