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Copper Adsorption on Chitosan-Derived Schiff Bases

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The adsorption of Cu(II) ions onto the chitosan derived Schiff bases obtained from the condensation of chitosan with salicyaldehyde (polymer I), 2,4-dihydroxybenzaldehyde (polymer II) and with 4-(diethylamino) salicyaldehyde (polymer III) in aqueous solutions was investigated. Batch adsorption experiments were carried out as a function of contact time, pH, and polymer mass. The amount of metal-ion uptake of the polymers was determined by using atomic absorption spectrometry (AAS) and the highest Cu(II) ions uptake was achieved at pH 7.0 and by using sodium perchlorate as an ionic strength adjuster for polymers I, II, and III. 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; adsorption isothermal equilibrium data could be clearly explained by the Langmuir equation. The experimental data of the adsorption equilibrium from Cu(II) solution correlates well with the Langmuir isotherm equation.

Keywords: Chitosan, Schiff bases, adsorption isotherms, copper(II) ions, atomic absorbtion spectrometry

1 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 anti-fouling paints (3).

Biosorption or sorption to materials of biological origin is recognized as an emerging technique for the treatment of wastewater containing heavy metals (1). Many materials of biological origins have been studied as adsorbents to remove various heavy metal ions from water and industrial effluents (2, 4). Chitosan, which is a poly(D-glucosamine), is prepared from chitin, which is the second, most naturally abundant biopolymer (next to cellulose) and is readily available from seafood processing waste (2), by deacetylating its acetoamide. This polymer has excellent properties for the chemical or physical adsorption of various metal ions including lead, vanadium, platinum, silver, cadmium, chromium, and copper (5, 6) mainly due to the presence of amino groups in the polymer matrix (7, 8); the amine groups and hydroxyl groups on the chitosan chain serve as the binding sites for metal ions (8-10). It has many good properties of natural polymers, such as biocompatibility, biodegradability, non-toxicity, etc., which make it an environmental friendly material (11). However, its capacity to adsorb or chelate metal ions is dependent on the degree of deacetylation, the nature of the metal ion and the pH of the solution (12).

Copper adsorption on chitosan and modified chitosan has been investigated by a number of research groups. Ngah and coworkers (1) studied the adsorption of Cu(II) ions onto chitosan and crosslinked chitosan beads and concluded that Cu(II) ions can be removed from the chitosan and crosslinked chitosan beads rapidly by treatment with an aqueous EDTA. Wan and colleagues (13) investigated copper (II) ion adsorption capacity of chitosan immobilized on sand as compared to chitosan or sand used alone. Copper adsorption on chitosan–cellulose hydrogel beads has recently been undertaken by Li and Bai who found that Cu adsorption on the beads mainly involved the nitrogen atoms in chitosan to form surface complexes (2).

The presence of free amino groups at C-2 position allows chitosan to react with several substituents resulting in a wide series of modified chitosan (modified biopolymer)

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with a wide spectrum of applications (14). Moreover, the insertion of functional groups in the chitosan matrix may improve its capacity of interaction with metallic ions by complexation. Among these substituted biopolymers are the Schiff bases obtained through the reaction of the free amino groups of chitosan with active carbonyl compounds such as aldehydes and ketones (15). In this sense, the modification of chitosan with aldehydes to produce Schiff bases may result in metal complexing polymers with potential analytical and environmental applications (16). Wang and coworkers have prepared a number of copper complexes of Schiff bases, derived from chitosan and substituted salicylaldehydes and utilized them as catalysts to promote the cyclopropanation of olefins with alkyl diazoacetates (11). Tirkistani has synthesized a number of Schiff base polymers from the reaction of chitosan with aromatic aldehydes (17) and found, through thermal analyses, that the polymers were less stable than chitosan itself. Quite recently (14), Cavalheiro and others, prepared Schiff bases from salicylaldehyde and chitosan and discovered that the degree of substitution is dependent on the aldehyde-chitosan mole ratio and other experimental conditions.

In this paper, we report on the synthesis of three chitosan–derived Schiff bases and the adsorption performance of these resins for Cu removal. A series of batch adsorption experiments under various experimental conditions of contact time, pH, initial Cu concentrations, polymer mass, and temperature were conducted and the results of the investigation are discussed.

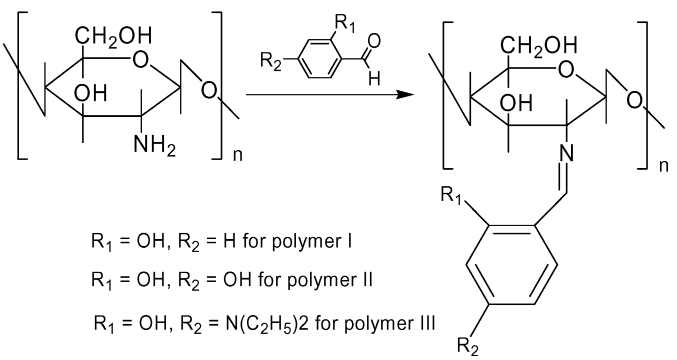
2 Experimental

2.1 Materials

Unless otherwise indicated, all chemicals were obtained from commercial sources and were used as received. Salicylaldehyde (99%) was obtained from Riedel-deHaen, (Seelze, Germany); 2,4-dihydroxybenzaldehyde (98%) from Acros (Geel, Belgium), 4-(diethylamino)salicylaldehyde (98%) from Aldrich (Milwaukee, WI). The copper(II) acetate metal salt (98%), $(CH_3COO)_2Cu.2H_2O$, (Fluka) was also used as received without further purification. Chitosan (2-amino-2-deoxy-β-D-glucan or glucosamine) was obtained from Xiamen Xing Import and Export Trading Co. Ltd., (China), with not less than 85% deacetylation (not less than 85% glucosamine) and a molecular weight of 8000–12000.

2.2 Instrumentation

Infrared spectra of the polymers were recorded with a Nicolet Impact 400 FTIR-Spectrophotometer (4000–400 cm^{-1}) using KBr pellets. Atomic absorption data were obtained with the aid of a Varian Atomic Absorption Spectrophotometer (AAS). Samples were shaken and thermostated using GFL-1083 shaker. A Metrohm pH meter model 525A was used for pH measurements.



Sch. 1. Synthesis of chitosan Schiff bases.

2.3 Preparation of Chitosan-Schiff Bases; Polymers I-III

These polymers were synthesized according to a procedure outlined by Wang, Sun, and Xia (11) by refluxing 5.7 g of chitosan with 90 mmol of the corresponding salicylaldehyde derivative for each polymer; (9.5 mL of salicylaldehyde for polymer I, 12.4 g of 2,4-dihydroxybenzaldehyde for polymer II, and 17.40 g of 4-(diethylamino)-salicylaldehyde for polymer III) in 90 mL of methanol and 9 mL of glacial acetic acid for 10 h as shown in Scheme 1. The Chitosan-Schiff bases were then collected by filtration and washed with ethanol and acetone, respectively. After soxhlet extraction with acetone and ethanol for 24 h, the resulting solid polymers (yellow for polymer I, red for polymer II, and brown for polymer III) were dried at 70°C for 24 h and sieved through mesh size 250–500 μm.

2.4 Sorption of Copper(II) Ions on the Polymers

The copper(II) 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 15.0 mg of Cu(II) ions was then added and the mixtures were shaken at 30°C for a specific period of time (0.08–48 h). The samples were filtered out and the amount of metal ions remaining in solution was determined by atomic absorption spectrophotometry (AAS) using standard solutions for calibration.

The extent of Cu(II) ions uptake was studied under similar experimental conditions, where the contact time was varied from 0.08 to 48 h at 30°C after it was equilibrated with distilled water. 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. The effect of polymer mass was also studied by suspending different masses (0.1, 0.2, 0.4, 0.6, 0.8, and 1 g) of the dry resins in 25.0 mL of the acetate buffer solution at pH 6.0 for 2 h to equilibrate. A 25.0 mL solution containing 15.0 mg 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 ions remaining in solution was determined by atomic absorption spectrophotometry (AAS).

2.5 Adsorption Isotherms

The adsorption of copper(II) ions was carried out by suspending 0.1000 g of dry resin in 25.0 mL of 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 20–1000 ppm were added to produce a total of 50 mL solutions containing 0.5–25.0 mg of Cu(II) ions. 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.

2.6 Water Regain (α)

Samples of dry polymers I, II and III were suspended in water, and were left for a period of 2 and 24 h. The polymers were centrifuged, water decanted, and weighed, then were dried at 80°C and re-weighed. Water regain (α) was calculated using the following equation:

$$\alpha = \frac{\text{mass of polymer bound water (g)}}{\text{mass of dry polymer (g)}}$$

2.7 Mathematical Treatment

2.7.1. *Mass balance equations*

In the isotherm experiments, the amount of Cu^{+2} adsorbed at equilibrium, Q_e (mg Cu^{+2}/g chitosan), is calculated using the following mass balance equation:

$$Q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where C_0 and C_e are the initial and liquid phase concentrations of Cu^{+2} (mg/L), after 24 h, respectively, V is the volume of solution (L) and M is the mass of dry resin used (g).

In the kinetic experiments the amount of Cu^{+2} adsorbed, Q_t (mg/g), at any time t, is obtained from the following equation:

$$Q_t = \frac{(C_o - C_t)V}{W} \tag{2}$$

Where C_t (mg/L) is Cu^{+2} concentration in solution at any time t.

2.8 Isotherm Models

The most common sorption models used to fit the experimental data are the Langmuir and Freundlich isotherms (18). The Langmuir isotherm model assumes that equilibrium is attained when a monolayer of the adsorbate molecules saturate the adsorbent. The analogous form of Equation 1 for the liquid phase sorption system is as follows:

$$Q_e = \frac{bQ_oC_e}{1 + bC_e} \tag{3}$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), Q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_0 is Langmuir constant related to adsorption capacity (mg/g) and b (L/mg) is a constant related to the affinity between the adsorbent and the adsorbate. The values of Q_0 and b can be determined by plotting C_e/Q_e vs. C_e.

The linear form of Langmuir model is given as:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_o} + \frac{1}{Q_o}C_e \tag{4}$$

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) (19), which is defined as:

$$R_L = \frac{1}{1 + bC_o} \tag{5}$$

where b is the Langmuir constant and C_0 is the highest ion concentration (mg/L). The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$).

The widely used empirical Freundlich model is the most important multi-site adsorption isotherm for heterogeneous surfaces. It assumes an initial surface adsorption followed by a condensation effect resulting from extremely strong solute-solute interaction. The general form of Freundlich model is as follows:

$$Q_e = K_F(C_e)^{1/n} \tag{6}$$

where, K_F ($(L/mg)^{1/n}$) is Freundlich isotherm constant and n is the Freundlich isotherm exponent constant. K_F is correlated to the maximum adsorption capacity and n gives an indication of how favorable the adsorption process is (20). The linear form of this model is expressed as given in the following equation:

$$\log Q_e = \log K_F + (1/n)\log C_e \tag{7}$$

The values of K_F and n can be obtained by plotting $\log Q_e$ vs. log C_e.

2.9 Kinetic Models

Four kinetic models, pseudo-first-order, pseudo-second-order, Elovich equation and intraparticle diffusion model are used to fit the experimental data. The mathematical description of theses models is given below. The conformity between data predicted by any of these models and the experimental data is indicated by the correlation coefficient R^2. The model of higher values of R^2 means that it more successfully describes the adsorption kinetics.

The differential form of the pseudo-first-order kinetic model could be expressed by the following equation (21):

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \tag{8}$$

Where t is the time (min) and k_1 is the equilibrium rate constant of the pseudo first order adsorption (min^{-1}). Integration of Equation 8 by applying the boundary conditions, $t = 0$ to $t = t$ and $Q_t = 0$ to $Q_t = Q_e$, yields the following integral equation:

$$\log Q_e/(Q_e - Q_t) = 0.4342 k_1 t \tag{9}$$

The value of the model parameters k_1 can be determined by plotting log ($Q_e - Q_t$) vs. t to give a straight line of slope $-0.4342\ k_1$ and intercept of log Q_e.

The differential form of the pseudo-second-order kinetic model is expressed by the following equation (22):

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t)^2 \tag{10}$$

Where k_2 is the equilibrium rate constant of the pseudo-second-order kinetic model (g/mg h). Integration of Equation 10 between the boundary conditions of Equation 8 yields the following equation:

$$t/Q_t = 1/k_2(Q_e)^2 + t/Q_e \tag{11}$$

The value of k_2 can be determined by plotting t/Q_t vs. t to obtain a straight line of slope $1/Q_e$ and intercept of $1/(k_2 Q_e^2)$.

The Elovich model was initially used to describe the adsorption of gases on solids (23), however, the application of this model in liquid phase adsorption is gaining popularity (24). The differential form of this model is given below:

$$\frac{dQ_t}{dt} = \alpha \exp(-\beta Q_t) \tag{12}$$

Where α is the chemisorption rate at zero coverage (mg g^{-1} min^{-1}) and β is the desorption rate constant (mg g^{-1} min^{-1}) during each experiment. Integrating Equation 12 between the same boundary conditions will give the following equation:

$$Q_t = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{13}$$

The values of α and β are obtained by plotting Q_t vs. ln t which gives a straight line of slope $1/\beta$ and an intercept of $1/\beta$ ln ($\alpha\beta$).

Since the above three models cannot give definite mechanisms for the adsorption process, another simplified model that represents the intra-particle diffusion model is tested (25). This model, which is based on the theory proposed by Weber and Morris assumes that the intraparticle mass transfer resistance is the rate determining step which means that the adsorption process is pore diffusion controlled (26). According to this Theory, the initial rates of interaparticle diffusion can be obtained from the following equation:

$$Q_t = x_i + k_p t^{1/2} \tag{14}$$

Where x_i is a constant proportional to the boundary layer thickness, mg/g, k_p is the intraparticle diffusion rate constant (mg/g $t^{1/2}$) (27). For pore diffusion controlled sorption, a plot of Q_t versus $t^{1/2}$ gives a straight line of slope k_p and an intercept of x_i.

The adsorption kinetics of Cu^{+2} onto the chitosan was verified at different initial concentrations. The validity of each model was determined by the sum of squared errors (SSE, %) given by:

$$\text{SSE} = \sqrt{\frac{\sum (Q_{e,\text{exp.}} - Q_{e,cal.})^2}{N}} \tag{15}$$

Where N is the number of data points. The lower the value of SSE, the better the fit.

The thermodynamic parameters for the adsorption process, the standard free energy ΔG^o, the standard enthalpy ΔH^o and the standard entropy ΔS° were calculated using the following equations (22):

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{16}$$

Where R (8.314 J/mol.K) is the universal gas constant, T (K) is the absolute solution temperature and K_d is the distribution coefficient which can be calculated as shown below:

$$K_d = \frac{C_{Ae}}{C_e} \tag{17}$$

Where C_{Ae} (mg/L) is the amount adsorbed on the resin at equilibrium and C_e (mg/L) is the equilibrium concentration.

The values of ΔH° and ΔS° were calculated from the slope and intercept of the plot between ln K_d versus 1/T. ΔG° can be calculated using the relationship below:

$$\Delta G^o = -RT \ln K_d \tag{18}$$

3 Results and Discussion

3.1 Characterization of the Polymers

The Schiff bases formed are intensely colored and are insoluble in common organic solvents. The IR spectra of the prepared polymers are in agreement with the structures assigned to them. The intense broad bands in the 3200–3500 cm^{-1} region in the spectra are attributed to the intramolecular hydrogen bonded O-H stretching vibration and to the N—H group. The strong absorption bands in the 1620–1640 cm^{-1} region are attributed to the (C=N) vibrations characteristic of imines which are not observed in chitosan (28). In addition, there was no evidence of bands characteristic of the free aromatic aldehydes near 1665 cm^{-1} (14). The absorption bands in the 1540–1590 cm^{-1} region, which are not present in the original chitosan sample, are attributed to the C=C stretching in the aromatic ring of the aldehyde. Moreover, bands at 1155 and 895 cm^{-1} are assigned to the polysaccharide structure of chitosan (29). The IR spectra of the prepared Schiff bases are similar to what other researchers found (11, 17).

The IR spectra of the three polymers loaded with copper(II) ions show that the imine and the hydroxyl bands become sharper, less intense, and shifted to lower frequencies, indicating that the coordination with copper(II) ions occur through these groups.

The water regain (some times referred to as the swelling degree) parameter, α, provides an indirect measurement of the hydrophilic character of the resins (30). A high α may indicate the presence of microporous hydrophilic sites, which provide the water-transport channels required for the effective sorption of metal ions from aqueous solutions. The experimental water regain values for the prepared Schiff bases were 1.633, 1.593, and 1.512 gg^{-1} at 2 h for polymers I, II, and III, respectively, and 1.672, 1.632, and 1.523 at 24 h for polymers I, II, and III, respectively. From these values, it is obvious that polymer I has the highest water regain.

3.2 Rate of Metal-Ion Uptake as a Function of Contact Time

The rate of interaction of Cu(II) ions with polymers I, II and III was investigated by a batch equilibration technique as a function of contact time at a fixed pH of 6.0 and with a total ionic strength of 0.20 M (with sodium perchlorate). Figure 1 shows a typical dependence of metal-ion uptake on contact time for polymers I, II, and III. Results indicate that fast rates of equilibration; about 50% of metal-ion uptake was achieved after 1 h for polymer III and reaches a steady state after 5–6 h. As for polymers I and II, the amount of ion uptake increases with contact time and reaches a steady state after about 48 h. Moreover, polymers I and II have higher uptake capacities than polymer III which could be attributed either to structural effects; the presence of the diethylamino group on the salicyaldehyde may make the polymer's surface more sterically hindered and thus decrease the Cu(II) uptake or to the stability constant of the chelated Cu(II) ions. The loading capacity of copper for the three polymers were 29.2, 27.4, and 15.9 mg/g for polymers I, II, and III, respectively. At pH 6.2, chitosan beads (1) have an uptake capacity of 80.7 mg Cu(II)/ g; this is higher than the loading capacity of any of the prepared chitosan-derived Schiff bases. Apparently, the introduction of Schiff bases seems to reduce the amino group sites which can adsorb copper(II) ions by chelation. This behavior has been observed by other workers (1).

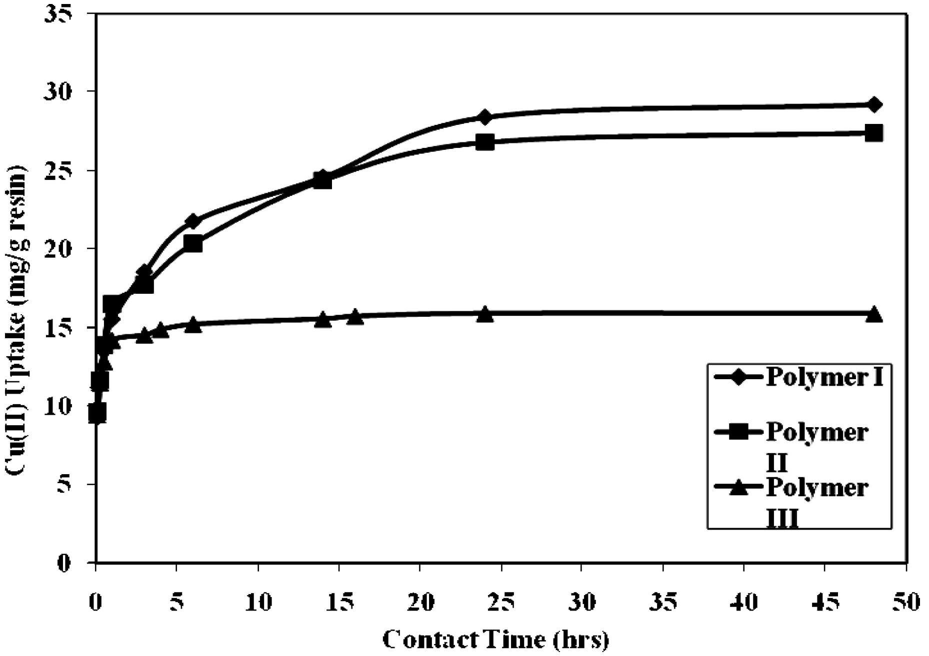


Fig. 1. Cu(II) uptake by polymers I, II and III as a function of contact time.

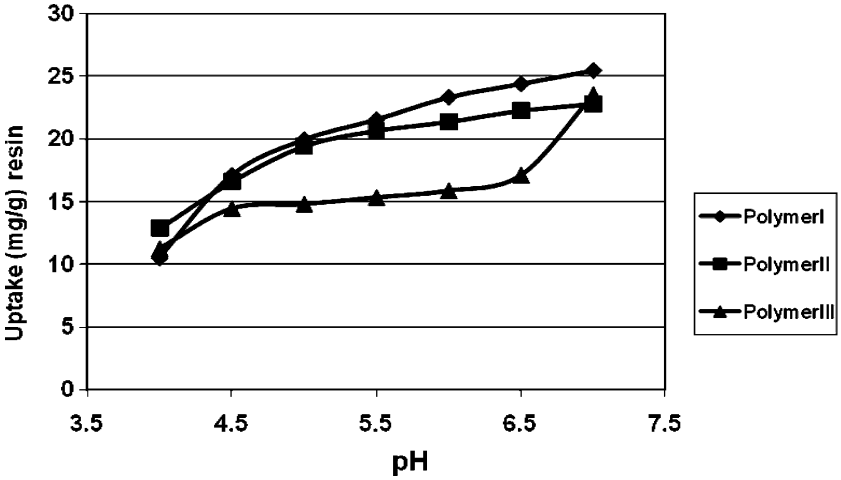


Fig. 2. Effect of pH on Cu(II) ion uptake by polymers I, II and III.

3.3 Effect of pH on Metal-Ion Uptake by the Polymers

The pH dependence of copper(II) uptake for polymers I, II, and III was studied in acetic acid-acetate buffer solutions in the pH range 4.0–7.0 under continuous shaking for a fixed contact time of 24 h at 30°C and at an ionic strength of 0.20 M. At higher pH values, hydrolysis of the Cu(II) ions becomes significant and may compete with polymer chelate formation. The pH-uptake profiles for polymers I, II, and III are displayed in Figure 2. Results reveal that adsorption of Cu(II) ions increases with increasing pH of the solution. The availability of the phenolate oxygen atoms or the lone pairs of electrons on the nitrogen atoms is affected by the pH. As pH increases, the phenol may lose its proton and becomes negatively charged and the amine group lone pair will be more available for binding to metal ions, thus, increasing the attraction of metallic ions onto the surface. On the other hand, at acidic pH, a decrease in the adsorption is attributed to the protonation of complexation sites where a competition between hydrogen and copper ions occurs with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations. These findings are in agreement with the pH profiles of chelating polymers with N, O binding sites (31).

3.4 Effect of the Polymer Mass on the Copper(II) Ion Uptake

Figure 3 shows the dependence of Cu(II) ion uptake on mass of resin for polymers I, II, and III. The results reveal that the percentage of Cu(II) adsorption by the three polymers increases with the increase of the mass of the polymer. This may be explained by the increase of the polymers sites available for adsorption and/or chelation.

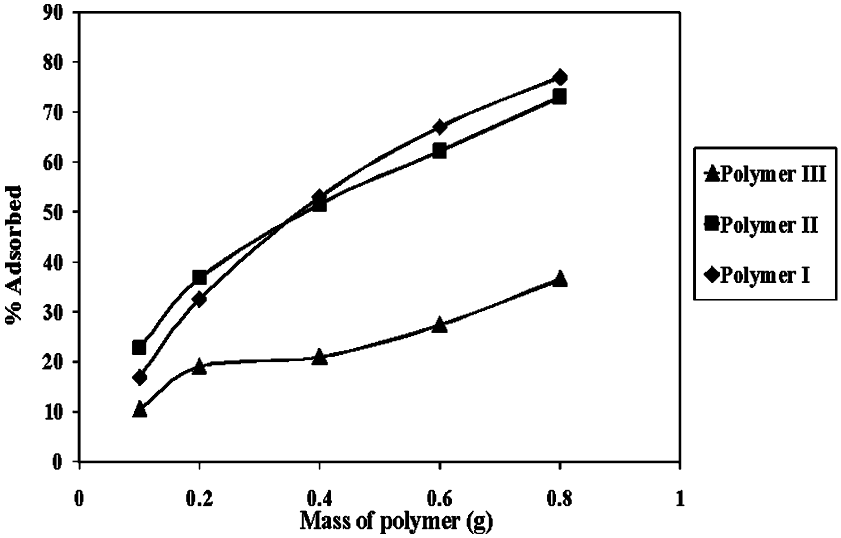


Fig. 3. Effect of the polymer mass on % of Cu(II) adsorbed by polymers I, II and III.

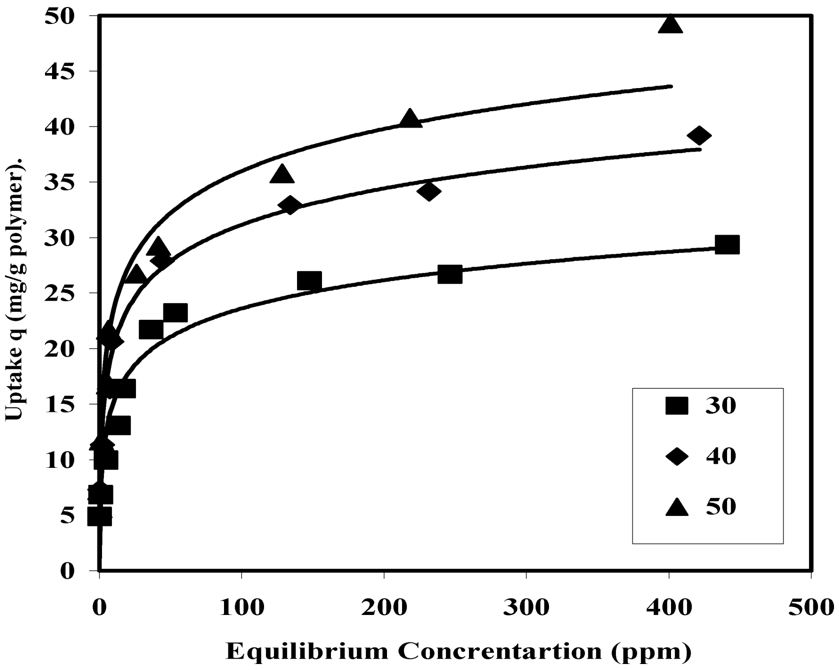


Fig. 4. Adsorption isotherms of Cu(II) ions by polymer I at different temperatures of 30, 40 and 50°C.

3.5 Adsorption Isotherms

The significance of the adsorption isotherms is that they show how the adsorbate molecules are distributed between the solution and the adsorbent at the equilibrium conditions and the effect of equilibrium concentration on the loading capacity of the polymer at different temperatures. Figure 4 shows the adsorption isotherms of Cu(II) ions using polymer I, as an example, at three different temperatures of 30, 40 and 50°C. Results show that for the same equilibrium concentration, the loading capacity of the adsorbent increases as the temperature increases. For example, when the equilibrium concentration, C_e of Cu(II) ions is 150 mg/L the loading capacity, Q_e is 25, 33 and 38 mg/g resin for the temperatures of 30, 40 and 50°C, respectively.

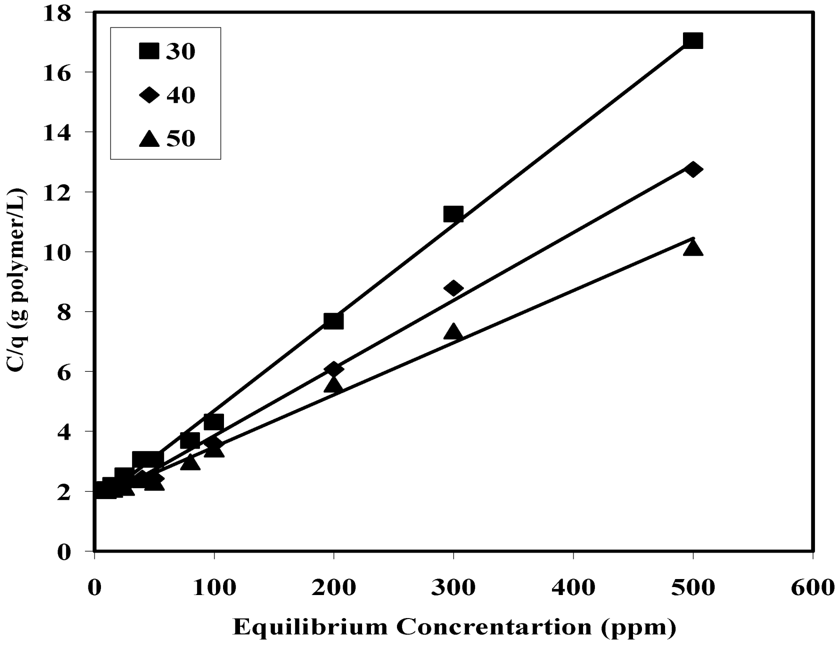


Fig. 5. Linearized Langmuir for Cu(II) ions adsorption by polymer I at different temperatures (30, 40 and 50°C). The lines represent the fitted linear equations for each temperature.

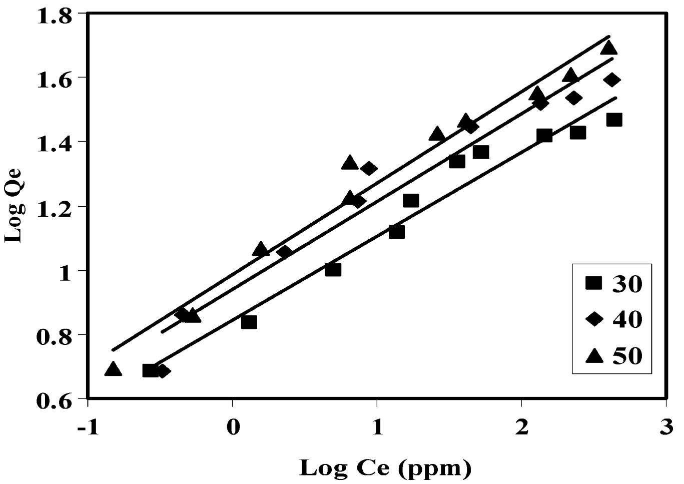


Fig. 6. Linearized Freundlich for Cu(II) ions adsorption by polymer I at different temperatures (30, 40 and 50°C). The lines represent the fitted linear equations for each temperature.

Polymers II and III (Figures are not shown) exhibit the same behavior.

Two isotherm models were used to fit the experimental data; the Langmuir and the Freundlich isotherm models. Displayed in Figures 5 and 6 are the linearized forms of the two models for polymer I.

The figures indicate that the Langmuir isotherm model gives the best fit of the experimental data for polymer I with a higher R^2 compared to Freundlich isotherm model. This behavior is the same for polymers II and III as presented in Table 1, which gives the models constants for the three polymers in addition to the correlation coefficient values, R^2. The results demonstrate that the adsorption of Cu(II) ions by chitosan is characterized by monolayer coverage of the Cu(II) ions on the adsorbent outer surface. In addition, the adsorption process has a homogenous nature or equal activation energy for each adsorbed molecule.

These results are in agreement with those obtained by Cheung and coworkers (24) who used a practical grade chitosan supplied by Sigma Chemicals for the adsorption of Cu(II) ions. They reported that the adsorption data fit the Langmuir isotherm with a maximum loading capacity of 35.8 mg/g. Similar results were obtained by Ngah et al., (32) who employed chitosan and chitosan/PVA beads to remove Cu(II) ions from solution with a maximum loading capacity of 33.44 and 47.85 mg/g for chitosan and chitosan/PVA, respectively (PVA = polyvinyl alcohol).

Based on the influence of the separation factor, $R_{L,}$ given by Equation 5 on the isotherm shape, it was found that in the range of Cu(II) ions concentration used in this investigation its values were such that $0 < R_L < 1$; this indicates that the adsorption of Cu(II) ions on the three polymers particles is favorable.

3.6 Adsorption Kinetics

The effect of contact time and the initial Cu(II) ions concentration on the adsorption rate, equilibrium concentration and equilibrium loading capacity of Cu(II) ions on polymers I, II, and III are shown in Figures 1 and 4. Results reveal that the amount of Cu(II) ions adsorbed, Q_t, increases with time for all initial concentrations. However, the time needed to reach equilibrium is not the same for the three polymers. In addition, the uptake rate of the Cu(II) ions decreases with time until it approaches a pseudo steady state value known as the equilibrium loading capacity, Q_e. The contact time needed to reach equilibrium conditions was about 3 h in the case of polymer III. On the other hand, for polymer I and II the rate of adsorptions sharply increases in the first 2 h, then continues to increase but at a lower rate until it reaches a steady state at about 48 h.

The loading capacity in the first two hours, Q_2 for polymer I, II and III were 17, 17.5 and 14.4 mg/g, respectively. However, the loading capacity after 24 h, Q_{24} for the three polymers was 28.39, 27.18 and 15.90 mg/g for polymers I, II, and III, respectively. These results indicate that the mechanism of adsorption in polymers I and II is similar and pore diffusion (intraparticle diffusion could play an important role in the adsorption process). On the other hand, for polymer III, equilibrium was attained in a relatively short time of 3 h; this indicates that intraparticle diffusion resistance is negligible. When equilibrium is established, Cu(II) ions in solutions are in a state of dynamic equilibrium with Cu(II) ions adsorbed by the adsorbent. This behavior indicates that further removal of Cu(II) ions is negligible and is attributed to the continuous decrease in the concentration driving force; this indicates a monolayer formation of Cu(II) ions on the external surface (33).

As previously mentioned, four kinetic models can be used to examine the mechanism of the adsorption process; pseudo first order, pseudo second order, Elovich, and intraparticle diffusion models; fitting results of the experimental data are shown in Figures 7–10 for the four models, respectively.

The models constants, in addition to experimental and predicted values of Q_e, are given in Table 2. Results from the Figures show that the Cu(II) ions adsorption by the different polymers is best described by the pseudo-second order model and by the Elovich model. This is confirmed by the values of R^2 shown in Table 2, which are close to unity for the pseudo-second order and the Elovich models, and less than 0.74, and 0.86 for the pseudo-first order and intraparticle diffusion models, respectively. In addition, the values of predicted Q_e in the case of the second order model are very close to the experimental values for all Cu(II) ions initial concentrations. For example, when the initial concentration of Cu(II) ions was 300 mg/L and the temperature was 30°C, the experimental $Q_{e,\text{exp}}$ values for polymers I, II and III after 24 h were 28.39, 27.18 and 15.9 mg/g, respectively. On the other hand, the predicted

Table 1. Calculated values of Langmuir and Freundlich isothermal constants for the adsorption of Cu(II) ions by polymers I, II, and III at 30, 40 and 50°C

Temp. (°C)	$Q_o (mg/g)$	*b (L/mg)*	R^2	β (−)	*n (−)*	$K_F\ (L/mg)^{1/n}$	R^2
			a. Polymer I				
30	29.452	0.0141	0.9974	0.262	3.813	6.938	0.9733
40	38.679	0.011	0.9963	0.273	3.662	8.704	0.9501
50	48.247	0.009	0.9924	0.286	3.500	9.635	0.9637
			b. Polymer II				
30	32.512	0.068	0.9976	0.285	3.509	6.485	0.9830
40	33.781	0.088	0.9987	0.231	4.337	9.033	0.9952
50	41.232	0.088	0.9945	0.269	3.716	9.490	0.9719
			c. Ploymer III				
30	16.551	0.027	0.9969	0.365	2.738	1.883	0.9657
40	17.581	0.031	0.9957	0.360	2.779	2.182	0.9383
50	17.960	0.051	0.9987	0.258	3.875	4.055	0.964

values for the three polymers, $Q_{e,pre}$ by the pseudo second order were 28.57, 27.4 and 15.92 mg/g, respectively. The validity of the four models was further verified using the sum of squared errors, SSE, %; the values of SSE, % are given in Table 2.

As presented in Table 2, the SSE % values are relatively low for the pseudo second order and Elovich models compared to those of the pseudo first order and intraparticle diffusion models. These results indicate that the adsorption of Cu(II) ions on the chitosan-derived Schiff base polymers is best described by the pseudo-second order model and that the pseudo first-order and intraparticle diffusion models were not suitable for the interpretation of the adsorption mechanism within the concentration range under study; this is in agreement with the results obtained by other researchers (22, 32, 34).

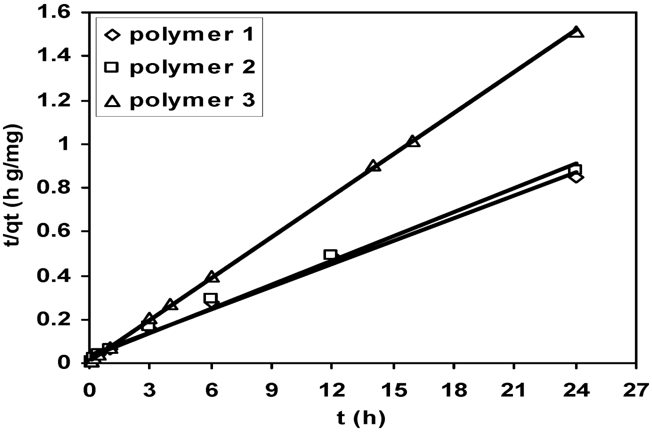


Fig. 8. Pseudo-second-order kinetics for adsorption of Cu(II) ions onto the three polymers at 30°C.

3.7 Adsorption Thermodynamics

Results presented earlier showed that the adsorption capacities of the three polymers increase as the temperature increases. For example, $Q_{\max}$ for polymer I increases from 29.45 to 48.25 mg/g as the temperature increases from 30 to 50°C. This result confirms the endothermic nature of the adsorption of Cu(II) ions onto chitosan polymers. The

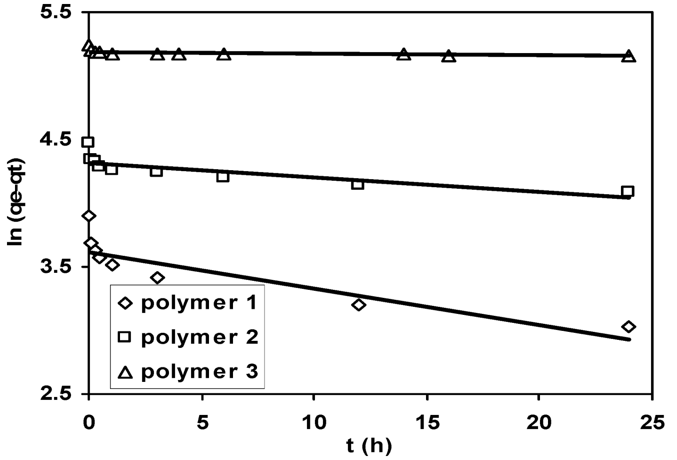


Fig. 7. Pseudo-first-order kinetics for adsorption of Cu(II) ions onto the three polymers at 30°C.

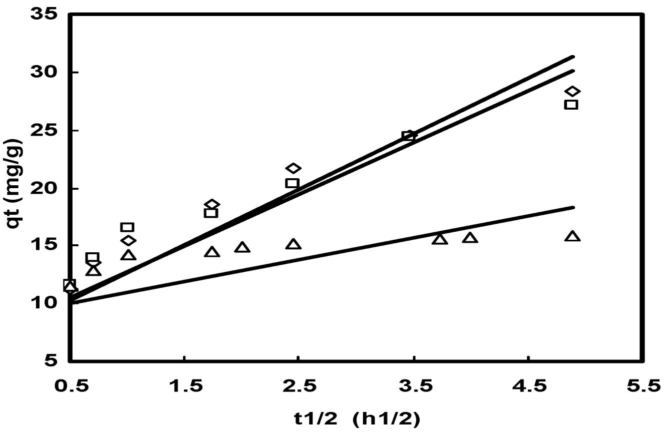


Fig. 9. Intraparticle diffusion model for adsorption of Cu(II) ions onto the three polymers at 30°C.

Table 2. Comparison of the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models for the three polymers when Cu(II) ions initial concentration was 50 mg/L at 30°C

		Pseudo-first-order kinetic model				*Pseudo-second-order kinetic model*			
Polymer	$q_{e,exp}$ *(mg/g)*	$q_{e,pre}$ *(mg/g)*	k_1 (h^{-1})	R^2	*SSE (%)*	$q_{e,prel}$ *(mg/g)*	k_2 *(g/mg h)*	R^2	*SSE (%)*
1	28.4	37.44	0.004	0.56	32.06	28.4	1.75	0.9918	−0.18
2	27.2	44.14	0.01	0.74	57.27	27.4	6.66	0.9921	−0.2
3	15.9	12.3	0.0094	0.64	25.7	15.92	3.58	0.9998	−0.02

			Elovich kinetic model				*Intraparticle diffusion model*				
Polymer	$q_{e,exp}$ *mg/g*	$q_{e,prel}$ *mg/g*	α *mg* g^{-1} *min*$^{-1}$	β *mg* g^{-1} *min*$^{-1}$	R^2	*SSE (%)*	$q_{e,pre}$ *mg/g*	k_p *mg/g* $h^{1/2}$	X_i *mg/g*	R^2	*SSE (%)*
1	28.4	28.1	13135.6	0.4116	0.9208	1.06	161.3	2.93	9.02	0.83	71.2
2	27.2	25.6	652.83	0.3341	0.9664	5.88	98.34	2.8	8.26	0.86	31.3
3	15.9	15.4	820.95	0.2923	0.9809	3.1	50.82	1.26	7.84	0.79	12.8

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 following: 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 molecules.

Calculation of the thermodynamic parameters for the adsorption process was accomplished by using Equations 16 to 18. The variation of the distribution coefficient, K_d, with temperature for the three polymers at two Cu(II) ions initial concentrations of 50 and 100 mg/L are given in Table 3.

As shown in Table 3, K_d values increase for all polymers as the temperature increases. This confirms the endothermic nature of the adsorption process. However, the values of K_d at 100 mg/L are lower than those at 50 mg/L. This indicates the feasibility of the adsorption process if Cu(II) ions initial concentration is not high.

To calculate the standard enthalpy ΔH^o and the standard entropy ΔS°, $\ln K_d$ was plotted against 1/T for the three polymers at two different concentrations as depicted in Figure 11 (a and b).

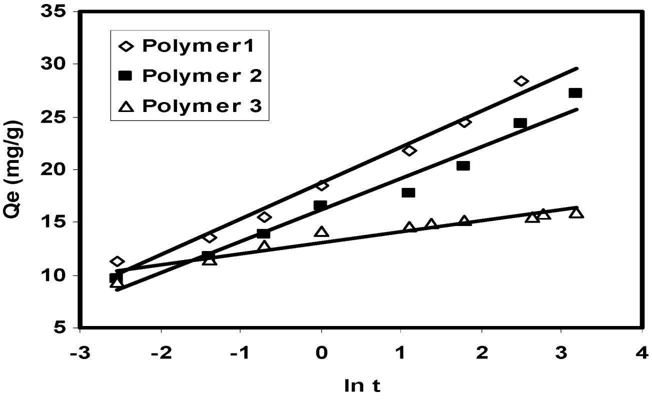


Fig. 10. Elovich model for adsorption of Cu(II) ions adsorption onto the three polymers at 30°C.

Figure 11(a) reveals that the relationship between $\ln K_d$ and 1/T is linear with high correlation coefficient R^2 of about 0.9987. On the other hand, R^2 in 11-b was about 0.45 only.

Table 4 lists values of the thermodynamic parameters of the adsorption process for Cu(II) ions at two initial concentrations, 50 and 100 mg/L. When $C_o = 50$ mg/L, the standard free energies, ΔG^o for polymers I and II are negative and decrease from −1604.4 to −5020.6 J/mol and from −971.0 to −3614.8 J/mol as the temperature increases from 30 to 50°C, respectively, whereas ΔG^o, of polymer III

Table 3. Variation of K_d with temperature for the adsorption of Cu(II) ions onto the three polymers

Polymer	*Temperature (K)*	C_{Ae} *(mg/L)*	C_e *(mg/L)*	K_d
		a. $C_o = 50$ mg/L.		
I	303.15	32.632	17.268	1.89
	313.15	41.253	8.747	4.72
	323.15	43.315	6.685	6.48
II	303.15	29.785	20.215	1.47
	313.15	33.679	16.321	2.06
	323.15	39.671	10.329	3.84
III	303.15	13.961	36.039	0.39
	313.15	15.774	34.226	0.46
	323.15	21.916	28.084	0.78
		b. $C_o = 100$ mg/L.		
I	303.15	46.392	53.608	0.8654
	313.15	55.798	44.202	1.2623
	323.15	58.632	41.368	1.417
II	303.15	43.695	56.305	0.7760
	313.15	44.145	55.855	0.7903
	323.15	61.038	39.962	1.5274
III	303.15	20.678	79.322	0.2607
	313.15	25.805	74.195	0.3478
	323.15	27.246	72.754	0.3744

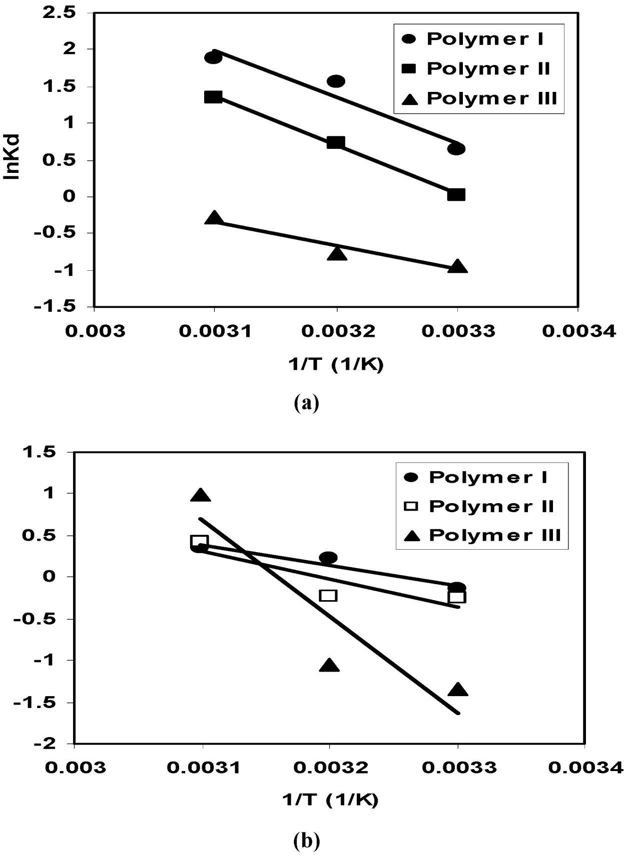


Fig. 11. Variation of thermodynamic parameters with temperature for the adsorption of Cu(II) ions on polymers I, II, and III, a- $C_o = 50$ mg/L, b- $C_o = 100$ mg/L.

is positive but decreases from 2373.2 to 667.5 J/mol as the temperature increases from 30 to 50°C, respectively. These results indicate the spontaneous nature and feasibility of the process in the case of polymers I and II when the initial concentration of Cu(II) ions is 50 mg/L. On the other hand, if the initial concentration increases to 100 mg/L, ΔG^o is positive for each of the three polymers when calculated at 30 °C and starts to decrease as the temperature increases.

Table 4. Thermodynamic parameters for the adsorption of Cu(II) ions onto the three polymers

	ΔG^o (J/mol)			ΔH^o	ΔS^o
Polymer	*T = 30°C*	*T = 40°C*	*T = 50°C*	*(kJ/mol)*	*(J/K mol)*
		a- $C_o = 50$ mg/L.			
1	−1604.4	−4040.2	−5020.6	51.634	176.5
2	−971.0	−1881.6	−3614.8	54.864	181.1
3	2373.2	2021.7	667.5	27.316	81.9
		b- $C_o = 100$ mg/L.			
1	364.38	−606.54	−937.04	18.282	66.8
2	639.04	612.55	−1127.99	20.349	90.0
3	3388.52	2749.66	2638.78	25.899	305.6

In addition, Table 4 shows positive values of ΔH^o and the standard entropy of activation ΔS^o for the three polymers at the two initial concentrations. This was previously confirmed by the isotherm experiments at different temperatures. The positive values of standard entropy of activation, ΔS° indicate the affinity of the chitosan polymers for adsorbates such as Cu(II) ions as a result of the increased randomness at the interface between the solid liquid phases although the values of ΔS° were found to decrease as the initial concentration increases. These results could represent a strategy for heavy metals adsorption such as Cu(II) on polymeric materials such as chitosan. Best results could be obtained when the ion concentration is relatively low and the temperature is relatively high.

4 Conclusions

Three chitosan Schiff bases were synthesized and characterized by IR spectroscopy. The sorption properties of these polymers toward Cu(II) ions were investigated by the batch equilibration technique under experimental conditions of contact time, pH, and mass of polymer. The effect of temperature was studied by performing the adsorption at different temperatures. Results of this investigation revealed that modified chitosan derived Schiff bases can be used as sorbents for Cu(II) ions removal from aqueous solutions. The adsorption isotherm which best fits the experimental data was the Langmuir monolayer model. Moreover, kinetic studies adsorption of Cu(II) ions on the chitosan derived Schiff bases is best described by the pseudo-second order model.

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