REMOVAL OF COPPER(II) IONS FROM AQUEOUS SOLUTIONS USING ALGINIC ACID: KINETICS AND ISOTHERM STUDIES

KHỬ ION ĐỒNG (II) TRONG DUNG DỊCH NƯỚC VỚI ACID ALGIN: NGHIÊN CỨU ĐỘNG LỰC HỌC VÀ ĐẲNG NHIỆT

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ABSTRACT

The adsorption of Cu(II) ions from aqueous solution onto alginic acid has been investigated based on the establishment of a relationship among pH, conductivity and the concentration of metal ion. It was shown that the adsorption of this metal ion onto alginic acid followed the pseudo-second-order reaction and was conducted by ion exchange mechanism. Adsorption isotherm was analyzed by using Langmuir, Freundlich, Tempkin and Redlich-Peterson isotherm models. The Langmuir model was found to be the best fitting with the data of copper(II) ion sorption onto alginic acid. From the study on the effect of temperature, thermodynamic parameters were evaluated.

1. INTRODUCTION

Heavy metals have been released to the hydrosphere by both natural and man-made sources in many ways such as weathering and erosion of minerals and metals from certain geological formations, saltwater intrusion, de-icing road salt, sewage disposal systems, animal wastes, petroleum products, industrial effuent, landfills, pesticides, and underground toxic waste disposal, ect. [1,2]. Many researches have been conducted for removal and the recovery of heavy metals from wastewater and some methods have been proposed in recent years. Each method has its own advantage as well as disadvantage in terms of efficiency and cost. Precipitation yields high levels of removal; however, it is inefficient for the removal of metals at low concentrations. Electrokinetic methods may be very effective at removal of low concentrations of heavy metals, but they are not cost-effective. Apart from the techniques mentioned, it is known that adsorption plays an important role in controlling the fate and transport of metal pollutants in ecosystem. Adsorption processes for water treatment with large-scale demand inexpensive, nontoxic, available sorbents of known kinetic parameters and sorption characteristics. Many efforts have been made to develop cheap materials for effective adsorption of heavy metals based on various natural inorganic and organic resources on metal sorption, such as bentonite [3], pyrite [4], zeolite [5], flyash [6,7], red mud [8]. Recent researches have shown that adsorption using biological materials or the materials derived from living organisms as adsorbents has been widely investigated due to their cost efficiency, as well as their high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional nutrient requirement, regeneration of biosorbent and the possibility of metal recovery [9-12].

Alginic acid, which is mainly obtained from brown algae, is a biopolymer composed of varying compositions of β-1, 4 D-mannuronic (M) and α-1, 4 L-guluronic (G) acids. Alginate has great affinity to divalent cations and its viscous solution forms gelation when it contacts with a divalent cation. Various results were reported for the binding mechanism of metals to alginates [13]. However, almost all comparative studies were conducted at equilibrium conditions and they were reported that the equilibrium was reached

within 20 minutes [14]. Therefore, sampling at shorter periods (e.g. 30 seconds) for study on the adsorption kinetics and some characteristics using traditional batch experiments has been a problem. In this work, a new experimental method was used to investigate the removal kinetics, isotherm and thermodynamics of some metal ions starting from very early stages (e.g. 30 seconds) to the equilibrium based on the establishment of relationship among pH, conductivity and metal ion concentration of aqueous solution.

2. EXPERIMENTAL

Sodium alginate was prepared according to our previous paper [15]. The adsorbent alginic acid beads were prepared by allowing drops of 2% sodium alginate solution to fall into a beaker filled with 0.5 N HCl solution. The beads were ellipsoid and approximately 2 to 3 mm in size with soft texture, which were taken out of the beaker and washed thoroughly with deionized water until the conductivity of the washed water reduced below 11 µS/cm (the conductivity of deionized water).

Analytical grades of $CuCl_2 \cdot 2H_2O$ (Merck) were used to prepare stock Cu(II) solutions.

Cu(II) was analyzed using an Atomic Absorption Spectrometer (AAS) (Shimadzu, AA6800).

Prepared alginic acid beads were added into a beaker containing 100 mL of Cu(II) solution with predetermined concentration. Both pH and conductivity of mixed solutions were directly recorded at every 30 seconds. All experiments were conducted at or below pH 5.0. pH of each solution was adjusted to predetermined value using only dilute HCl solution.

The adsorption capacity in mg/g at time t was computed by using the following equation:

$$q_t = \frac{(C_0 - C_t)MV}{m} \qquad (1)$$

The percentage of Cu(II) ions removed ($R\%$) fror the aqueous solution was calculated using Eq. (2):

$$R(\%) = \frac{100(C_0 - C_t)}{C_0} \qquad (2)$$

where C_0, and C_t are the initial metal io concentration and concentration at a given time (mol/L), respectively; V is the volume of the metal io solutions (mL), M is the molecular weight of met (g/mol) and m is the mass of algnic acid in grams.

3. RESULTS AND DISCUSSION

3.1. Relationship among pH, conductivity, an metal concentrations

In the adsorption onto alginic acid proces the metal ions interact with protons attache to the surface groups of the alginic acid and as a result, exchange may occur. Hydrogen ions diffuse into the solution as metal ions are adsorbed onto the beads. The concentrations of anions can be assumed to be constant throughout the sorption process. Thus, it does not change the conductivity, since the mobility of metal ions and hydrogen ions are different, the conductivity of the solution changes as following equation:

$$\Delta\kappa = \Lambda^0_{m,H^+}\Delta C_{H^+} + \Lambda^0_{m,M^{n+}}\Delta C_{M^{n+}} \qquad (3)$$

where, Λ^0_m is the molar conductivity (S.cm²/ mol), which is tabulated in reference books [16]. $\Delta\kappa$ represents the change in conductivity ($\Delta\kappa = \kappa_o - \kappa_t$); κ_o is the initial conductivity and κ_t is the conductivity at any time t (S/cm). ΔC represents the change in concentration ($\Delta C = C_0 - C_t$). An experimental result obtained for initial Cu(II) concentration of 200 mg/L and at pH 4.5 is presented in Fig. 1 a. As a result of hydrogen ion diffusion to the solution, the pH value decreased and the conductivity increased with time. The increase in conductivity can be explained by the fact that the ionic mobility of H^+ is much greater than that of Cu^{2+}.

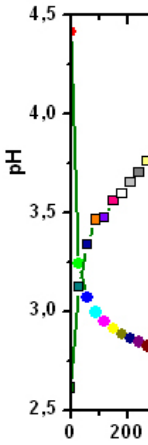

Fig. 1. a.
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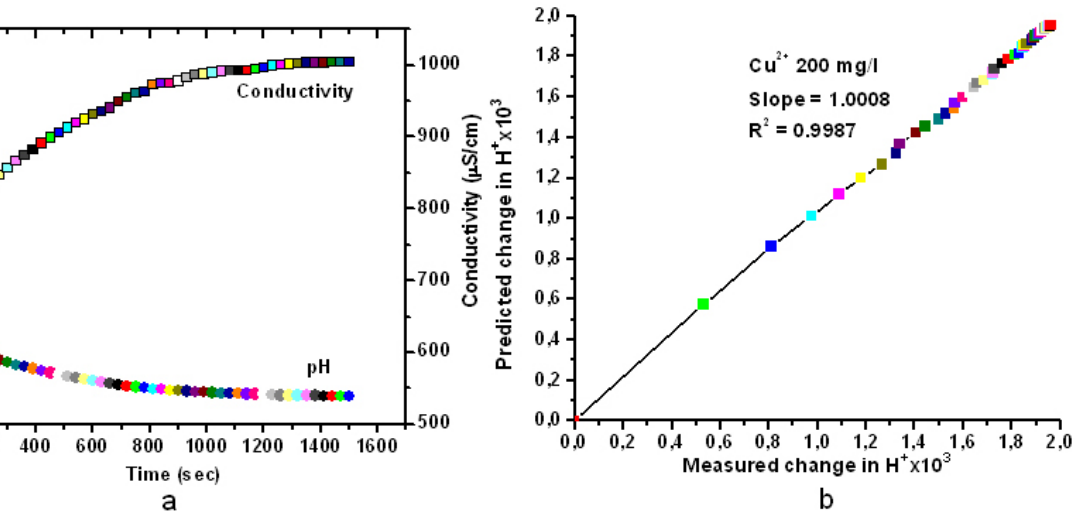

The variation of pH and conductivity with time over the course of experiment;
b. Correlation between measured and predicted changes in H^+ (initial pH = 4.5; initial Cu^{2+} = 200 mg/L; 0.5 g of alginic acid)

If the process is assumed to be entirely ion exchange, an equivalent amount of hydrogen ions is removed from the solid surface for every metal ion sorbed. Therefore, Eq. (3) can be written as a function of H^+ ion concentration as follows:

$$\Delta\kappa = \Lambda^0_{m,H^+}\Delta C_{H^+} + \Lambda^0_{m,M^{n+}}\frac{\Delta C_{H^+}}{n}$$

$$= \left(\Lambda^0_{m,H^+} - \frac{\Lambda^0_{m,M^{n+}}}{n}\right)\Delta C_{H^+} \qquad (4)$$

Using the Eq. (4), ΔC_{H+} can be determined if Δk is known. Both pH value and conductivity can be measured simultaneously while the experiment is conducted. If ΔC_{H+} value obtained from the pH measurements is the same as the values obtained from conductivity data, then the assumption of pure ion exchange is said to be valid. Therefore, the adsorption process can be performed as equilibrium as follows:

$$nHA + M^{n+} \rightleftharpoons MA_n + nH^+ \qquad (5)$$

where HA represents alginic acid; M represents metal. If M is a Cu(II), Eq. (5) becomes:

$$2HA + Cu^{2+} \rightleftharpoons CuA_2 + 2H^+ \qquad (6)$$

The results ΔC_{H+} obtained from the course of experiment for Cu(II) ions with the same initial concentration of 200 mg/L and initial pH 4.5 onto 0.5 g of alginic acid was performed in Fig. 1 b. As can be seen, the slopes of linear fits were close to 1.00, suggesting that the uptake mechanism of adsorption of Cu(II) by alginic acid was purely ion exchange. Hence, the concentration of metal ion at any time can be determined directly from pH and conductivity measurements.

In order to confirm the findings, five different copper concentrations were equilibrated after the contact time of two hours with 0.45 g of alginic acid beads, initial pH 4.5, the temperature of 25 ^{0}C and the copper concentration at equilibrium predicted by the change of pH and conductivity as well as by the analysis using AAS. Results were performed in Table 1.

Table 1. Comparison between the predicted and analyzed concentration of Cu^{2+} at equilibrium by the pH and conductivity measurements and by AAS.

C_0 (mg/L)	Equilibrated concentration (mg/L)	
	Analyzed (by AAS)	Predicted
20	0.05	0.06
50	3.60	3.70
100	6.40	6.70
200	14.40	14.40
300	17.30	17.20
400	109.50	113.90

It can be seen that the difference between the predicted and analyzed concentration of copper ion at equilibrium was slightly varied (not more than 5 %). These results enabled us to use Eq. (3) to determine the concentration of Cu(II) ion at any time from pH and conductivity data for studying their characteristics of adsorption onto alginic acid.

3.2. Effect of initial pH and initial copper ion concentration

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the heavy metal in solution [17]. Fig. 2 a represents the effect of initial pH of the solution on the adsorption of Cu(II) onto alginic acid under conditions: 100 mL of solution of 200 mg/L initial Cu(II) ion concentration and 0.5 g of adsorbent. It can be seen that the adsorption decreased with the decrease in pH value. The maximum adsorption efficiency was 92% at pH 4.5. It decreased to 72% at pH 3.5, and 48% at pH 2.5. This may be attributed to the competition between the hydrogen and Cu(II) ions on the sorption sites, at low pH values. Furthermore, the equilibrium (6) shift to the left was more favorable at low pH conditions. Consequently, the working pH value for Cu(II) removal onto alginic acid was chosen at 4.5 and the other adsorption experiments were performed at this pH value.

Fig. 2 b represents the experimental results of adsorption of Cu(II) ion onto alginic acid at various initial concentrations (20, 50, 100, 200, 300, 400 mg/L) using 100 mL of Cu(II) solution and 0.5 g of adsorbent. Adsorption capacity increased very quickly at contact time of only a few minutes, then slowly until equilibrium was reached. Such a curved shape was generally observed in most cases of adsorption of heavy metals onto the materials derived from living organisms such as agar, chitosan [18], ect. It can be said that, the copper (II) ion removal process using alginic acid occured in two distinguishable stages: the first stage occured quickly and the next was slow. The required time to reach adsorption equilibrium is about 20 minutes with initial concentration of Cu(II) ion ranging from 20-400 mg/L.

Unlike other studies on the adsorption using activated carbon or other adsorbents of which the metal ion removal processes can be conducted with a high mass of adsorbates [19] but the remained concentration of adsorbate after adsorption is still high (ppm). Whereas, alginic acid cannot adsorb a high mass of adsorbates but the adsorption is very deep. The remained concentration of adsorbate after adsorption is low (ppb). The adsorption increased from 7% to 99% with a decrease in Cu(II) ion concentration from 400 mg/L to 20 mg/L indicating that the lower the concentration of copper ion solution, the higher the degree of adsorption. With the initial concentration of 20 mg/L, the remaining concentration of Cu(II) is only 50 ppb. This advantage of the adsorption using alginic acid allows to remove heavy metals from wastewater at low concentration.

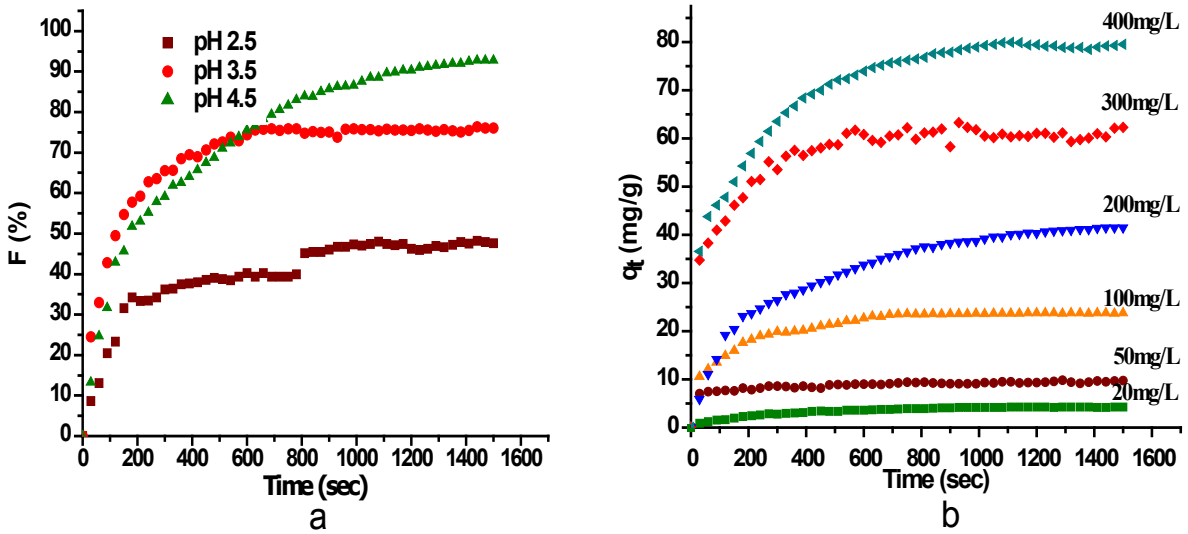

Fig 2. a. Effect of initial pH; b. initial concentration on copper(II) ion adsorption capacity onto alginic acid

3.3. Adsorption kinetic study

From Eq. (6), if the adsorption of Cu(II) ions onto alginic acid is well-fixed to pseudo-second-order kinetic model, the rate equation can be expressed as follows:

$$\frac{d(HA)_t}{dt} = k_2[(HA)_o - (HA)_t]^2 \qquad (7)$$

where $(HA)_o$ and $(HA)_t$ represents the number of active sites on the surface of adsorbent at the equilibrium and at time t, respectively. It was assumed that the adsorption capacity is directly proportional to the number of active sites on the adsorbent, Eq. (7) becomes:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (8)$$

where k_2 is the rate constant of second-order-adsorption (g/mg.sec); q_e, q_t are the adsorption capacity of Cu(II) ion onto alginic acid at equilibrium and at time t, respectively (mg/g). Eq. (8) is the differential form of pseudo-second-order kinetic equation. In order to confirm the above assumption, experimental data on kinetics of Cu(II) ion adsorption onto alginic acid were tested by the pseudo-first-order rate equation, pseudo-second-order rate equation and Elovich equation. The best suitable kinetic model to experimental data will provide informations on characteristics of adsorption processes.

The integrated form of the pseudo-first-order rate equation of Lagergren is generally expressed as follows [19]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (9)$$

where k_1 is the rate constant of first order adsorption (1/sec). The plot of $\ln(q_e - q_t)$ *vs.* t should give a linear relationship from which k_1 and q_e can be determined from the slope and the intercept of the plot, respectively.

The pseudo second-order adsorption kinetic rate equation can be expressed as the integrated form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (10)$$

The plot of t/q_t and t of Eq. (11) should give a linear relationship from which q_e and k_2 can be determined from the slope and the intercept of the plot, respectively.

The Elovich model [19] equation is generally expressed as

$$\acute{q}\hat{a} = \frac{1}{\hat{a}}\ln(\ t\ ) + \frac{1}{\hat{a}}\ln(\ ) \qquad (11)$$

If Cu(II) adsorption fits the Elovich model, a plot of q_t *vs.* $\ln(t)$ should yield a linear relationship with a slope of $1/\beta$ and an intercept of $(1/\beta)\ln(\alpha\beta)$.

Table 2. The kinetic parameters predicted by using three models mentioned and correlation coefficients (T = 25 ^{0}C, 0.5 g of alginic acid/100 mL Cu^{2+} solution, initial pH 4.5).

Kinetic model	Parameter	Initial concentration of copper (II) ion (mg/L)				
		20	100	200	300	400
Pseudo-first-order ln $(q_e-q_t) = \ln q_e - k_1 t$	k_1	0.004	0.0049	0.003	0.0022	0.0037
	R^2	0.9127	0.9514	0.9809	0.4012	0.9103
Pseudo-second-order $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	k_2	0.00099	0.000545	0.000142	0.000431	0.00014
	R^2	0.9975	0.9981	0.9994	0.9983	0.999
Elovich model $q_t = \frac{1}{\beta}\ln(\alpha\beta t) + \frac{1}{\beta}\ln(\beta)$	α	0.0596	2.9326	0.8546	0.927589	7.35927
	β	1.00301	0.28601	0.11586	0.145688	0.08212
	R^2	0.9790	0.9711	0.9817	0.8682	0.9645

Table 2 shows the calculated values of the kinetic parameters and correlation coefficients by three models mentioned. It was observed that the pseudo-second-order model gives a linear relationship with very high correlation coefficients ($R^2 > 0.99$) for all data examined and the values of q_e predicted by using this model were closer to q_e from experiments comparing with those obtained from other models. Consequently, it can be concluded that the pseudo-second-order model is suitable model for description of Cu(II) ion adsorption onto alginic acid. It was also evidence to prove the adsorption of copper(II) ion onto alginic acid assumed to be entirely ion exchange and Eq. (6) is entirely suitable.

3.4. Adsorption isotherm study

Objective of adsorption isotherm study is to obtain some informations about adsorption process such as maximum adsorption capacity, the most appropriate correlations for equilibrium curves, to optimize the design of a sorption system. In this study, four most popular isotherm models used to describe the adsorption equilibrium are Langmuir, Freundlich, Temkin and Redlich-Peterson [19]. Experimental isotherm data were conducted at an equilibrium time of 25 minutes for different concentrations of adsorbate solution.

The Langmuir adsorption isotherm is based on the assumption that all sites possess equal affinity for the adsorbate. It may be represented as Eq. (12).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (12)$$

where q_m is the maximum Cu(II) adsorption capacity (mg/g); K_L is the Langmuir adsorption constant (L/mg); C_e is the concentration of Cu(II) solution at equilibrium time (mg/L). Values of q_e, C_e were obtained from experiments. Values of the parameters q_m, K_L can be determined from slope and intercept of plot of C_e/q_e vs. C_e. Results

were performed in Table 3. It can be seen that the maximum copper(II) adsorption capacity of alginic acid (q_m) is rather remarkable (90.09 mg/L) [19].

The empirical Freundlich isotherm is based on the equilibrium relationship between heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. It's logarithmic linear form may be represented as Eq. (13).

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (13)$$

where K_F (L/g) and n are the Freundlich constants indicating the sorption capacity and sorption intensity, respectively. They can be determined from the slope and the intercept of plot of $\ln q_e$ vs. $\ln C_e$ and the results were presented in Table 3. The magnitude of K_F showed a high copper (II) adsorptive capacity of alginic acid from aqueous solutions studied. It also indicated that $0 < 1/n < 1$ copper (II) is favorably adsorbed on alginic acid [19].

The Tempkin isotherm has generally been applied in the following linear form [19]:

$$q_e = B\ln A + B\ln C_e \;; \qquad B = \frac{RT}{b} \qquad (14)$$

where A (L/g) is Tempkin isotherm constant; b (cal/mol) is a constant related to heat of sorption; R is the gas constant (1.98 cal/mol.K) and T is the absolute temperature (K). A plot of q_e versus $\ln C_e$ enables to determine the isotherm constants A, b from the slope and intercept. The results were listed in Table 3.

Redlich- Peterson isotherm (R-P) contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms into a single equation. The general isotherm equation can be described as follows [19].

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{b_R}} \qquad (15)$$

where K_R (L/g) and a_R (L/mg) are R-P isotherm constants and b_R is the exponent between 0 and 1. There are two limiting behaviors; Langmuir form for $b_R = 1$ and Henry's law for $b_R = 0$. Unlike three refered models with two parameters that can be determined by linearizing the experimental data, the Redlich- Peterson isotherm contains three unknown parameters, it cannot be solved using linearization techniques. Instead, parameter estimation was only determined using spreadsheet optimization. In this work, we used a method for parameter estimation using "the Solver Add-In of Microsoft Excel". The experimental data used to evaluate this model is the same to that used for the above isotherms evaluation. The values of three parameters were presented in Table 3. To evaluate the fit of isotherm equations to the experimental data, different error functions of non-linear regression basin were used: the residual root mean square error (*RMSE*) and the chi-square test (X^2). *RMSE* and the chi-square test can be defined as [20]:

$$RMSE = \sqrt{\frac{1}{n-2}\sum_{i=1}^{n}(q_{e,\exp} - q_{e,calc})^2} \qquad (16)$$

$$X^2 = \sum_{i=1}^{n}\frac{(q_{e,\exp} - q_{e,calc})^2}{q_{e,\exp}} \qquad (17)$$

The subscripts "*exp*" and '*calc*" show the experimental and calculated values and n is the number of observations in the experimental isotherm. The small the *RMSE* and the X^2 value, the better the curve fitting [20].

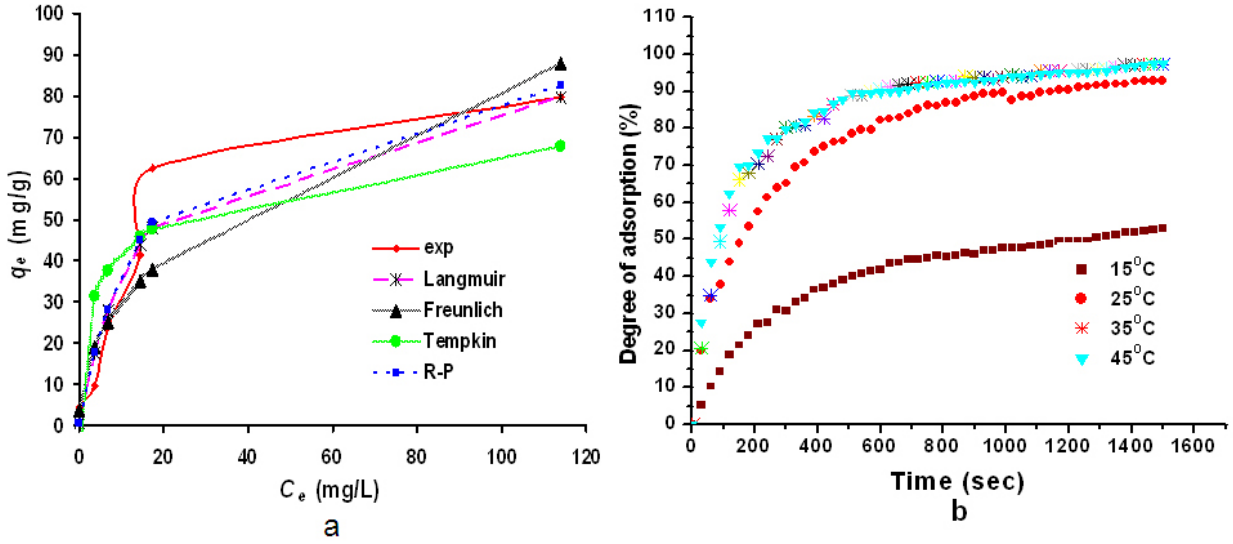

Fig. 3. a. The adsorption isotherms of the copper(II) adsorption onto alginic acid; b. Effect of temperature on the adsorption of copper(II) onto alginic acid.

Table 3. Isotherm parameters for the adsorption of copper(II) ion onto alginic acid.

Isotherm model	Equation	Parameters		R^2	*RMSE*	X^2
Langmuir	$\frac{C_e}{q_e}=\frac{C_e}{q_m}+\frac{1}{K_L q_m}$	q_m K_L	90.09 0.066	0.9513	8.7189	13.792
Freundlich	$\ln q_e=\ln K_F+\frac{1}{n}\ln C_e$	K_F n	10.7575 2.2558	0.8806	14.056	20.564
Temkin	$q_e=B\ln A+B\ln C_e$	A B	5.093 10.644	0.7317	17.296	100.645
Redlich - Peterson	$q_e=\frac{K_R C_e}{1+a_R C_e^{b_R}}$	K_R a_R b_R	5.9765 0.0638 1	*	8.566	14.019

* *not determined*

Fig. 3 a shows plot comparing different isotherm equations with experimental data. From Fig. 3 a and values of R^2, *RMSE*, X^2 of the isotherm models represented in Table 3, it can be seen that, the degree of fit with experimental data is expressed as order: Redlich-Peterson ~ Langmuir, Freundlich, Temkin. where the Redlich- Peterson model and the Langmuir model described very well the adsorption of Cu(II) ion onto alginic acid.

Particularly, results from calculation refered that value of b_R parameter of Redlich- Peterson equation is 1. As mentioned earlier, with this value, Redlich-Peterson equation becomes Langmuir equation. The value of the *RMSE*, X^2 of the two models are very close. Thus, the Langmuir model best described the adsorption Cu(II) ion onto alginic acid, or in other words

almost adsorption process leads to the formation of a single layer on absorbent surfaces. This conclusion once more again confirms that the nature of the adsorption is chemical adsorption.

3.5. Effect of temperature

Fig. 3 b represents effect of temperature on the adsorption of Cu(II) onto alginic acid. It shows that the adsorption increases with increasing temperature. This is the evidence of an endothermic process in the range of studied temperature (15-45 ^{0}C) accompanied by the adsorption.

In range of 35 – 45 ^{0}C, the removal efficiency of Cu(II) changed insignificantly, indicating that the removal efficiency has reached maximum. This is the other advantage of the removal of heavy metal using alginic acid because it can be carried out at room temperature. When temperature reached 45 ^{0}C, the adsorption almost remains unchanged. This can be due to the fact that at higher temperature the adsorption was limited by the intra-particle diffusion process and as a result the rate of adsorption was decreased and the rate of desorption was increased.

Thermodynamic parameters used to confirm one more time the nature of adsorption in this study including Gibbs's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated using the following expressions:

$$K_c = \frac{C_{ae}}{C_e} = \frac{C_0 - C_e}{C_e} \qquad \Delta G = -RT \ln K_C ,$$

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (18)$$

where K_C is the equilibrium constant of adsorption process; C_{ae} and C_e (mg/L) are the concentration of copper ions in the solid and the liquid phase, respectively. Equation (18) was used to construct Van't Hoff plots and the value of ΔH and ΔS were calculated from the slope and intercept of the Van't Hoff plot, respectively. Results were represented in Table 4.

Table 4. Thermodynamic parameters for the adsorption of copper (II) ion on alginic acid.

T (K)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
288	-0.063		
298	-1.508	30.52	106.62
308	-2.178		

The ΔG values obtained for adsorption were negative at all three observed temperatures indicating that the adsorption is highly favorable for copper(II) ion and the adsorption is spontaneous. The positive value of ΔH demonstrates again the endothermic and chemisorption nature of adsorption process. Remarkably, the positive value of ΔS suggests increased randomness at the solid-liquid interface during the adsorption of copper(II) ion. Furthermore, before the adsorption process takes place the adsorbate ions are heavily solvated (the system is more ordered) and this order is lost when the ions are adsorbed on the surface, due to the release of solvated water molecules.

4. CONCLUSIONS

Studies on the adsorption of Cu(II) ions from aqueous solutions onto alginic acid using pH and conductivity data were conducted. It was shown that the adsorption of these metal ions onto alginic acid followed the pseudo-second-order reaction and was conducted by ion exchange mechanism. The Langmuir model was found to be the best model for describing the adsorption process of Cu(II) ion onto alginic acid. Effect of temperature on the removal efficiency of adsorption showed that the removal efficiency of Cu(II) ion by alginic acid reach to maximum value in the temperature range of 30-35 ^{0}C. The values of ΔG, ΔH and ΔS obtained show that alginic acid is a remarkable type of adsorbent from aqueous solutions.

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