STUDIES ON THE PREPARATION MODIFIED CHITOSAN AND ITS APPLICATIONS

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Abstract

Chitosan, as a natural polysaccharide, has reactive amino and hydroxyl groups in its linear polyglucosamine chains, can be used to functionalize and modify. However, conventional modification method using single chitosan crosslinking with glutaraldehyde generally leads to decrease of functional groups ($-NH_2-$) and loading capacity, it's interested to prepare multifunctional chitosan-X which used in many applications such as water treatment by using diethylenetriamine pentaacetic acid (DTPA) with sufficient number of carboxyl groups on the backbones, is a commonly used as chelating agent for heavy metal. The preparation of modified chitosan investigated by IR, XRD, SEM and also mechanical properties which determined the comparative and competitive adsorption of some metal ions from aqueous solutions. Kinetic and thermodynamics of single system were studied.

Keywords: Chitosan, crosslinking, DTPA, mechanical properties, application, Resine (modified crosslinked chitosan).

Introduction

Contamination of water by heavy metals has become an increasing problem to the environment and health once they are very toxic and non-biodegradable, even at low concentrations (Rapsomanikis.S). Heavy metals contamination in wastewater is mainly contributed by anthropogenic sources like electronics assembly and fabrication, battery manufacturing (Sari, A etal). while Fe(II) Cu(II) are essential nutrients needed by the body in trace amounts but increasing in the intake of Fe(II) Cu(II) can cause health problems like gastrointestinal disturbance, and liver and kidney failure. In addition, the presence of heavy metals at elevated levels in surface water and groundwater environment also prevents any beneficial use of the water bodies. Therefore, it is essential to control the concentration of heavy metals in wastewaters before its disposal into the environment. Common removal technologies of heavy metals are membrane separation, ion exchange, electro deposition, and chemical precipitation. These methods proved to be costly and inept, especially in removing trace amounts of heavy metals. Use of natural adsorbents like peat, rice hull and chitosan prove to be economical and effective in removing a variety of contaminants(Popuri, S. R.et al). Due to the reactivity of amine groups and stable chelation, chitosan can be functionalized to improve its adsorption

properties. Chemical modification of chitosan with chelating agents such as diethylenetriaminepentaacetic acid (DTPA), which forms very strong chelates with metal ions, may produce adsorbents with excellent metal binding properties. Chemical modifications also offer a wide spectrum of tools to enhance the sorption properties of chitosan for metals. They may increase the chemical stability of the sorbent in acid media and especially, decrease the solubility in organic acids (Guibal et al.),. The environmental fate of these chelating agents has received attention, but, when immobilized DTPA is not expected to be environmentally critical compound (K. Pirkanniemi et al). In this work, crosslinked DTPA-chitosan were used to adsorb Fe(II) and Cu(II) from aqueous solutions. The effects of variables including the metal concentration, and pH on the adsorption capacity, temperature, The adsorption capacity was determined using the Langmuir and Freundlich isotherm equation models. The kinetics adsorption was evaluated by the pseudo-first order and pseudo-second order models. This information will be useful for further applications of system design in the treatment of practical waste effluents.

Experimental
Materials:

   Chitosan (Aldrich Company), glutaraldehyde (El-Nasr company) , acetic acid and Diethelene triamine penta acetic acid (DTPA) (Mollin Ckrodt Company) of purity 99%. The other chemicals, such as inorganic salts as (ferrous sulphate and cuprous chloride) were used without further purification.

Modification of crosslinked modified chitosan-glutaraldehyde by Diethylene tri-amine penta-Acetic acid (DTPA)

   1- Chitosan solution was prepared by dissolving 5gm chitosan in 200 ml of acetic acid aqueous solution (2%).
   2- Dissolve 2.5g DTPA in 25 ml of acetic acid aqueous solution (2%).
   3- Add step 2 to 1 and still to stir over night then add 2.5gm glutaraldehyde.
   4- Adjust PH 4.7 by using 1N NaOH.
   5- Let the product dry at 40C^o till stable weight.
   6- Washing with distilled water and dry.
   7- The resulted beads were immersed in 0.5M HCl for 12 hrs. to remove the protective group. After filtration and washing with water, the beads were immersed in 5% NaOH aqueous solution for 5 hrs.
   8- Dry again at 40C^o till stable weight.

- Adsorption experiments

   Adsorption experiments were carried out by shaking a 0.1 g of dried chitosan, modified crosslinked chitosan with 25 ml aqueous metal ion solutions of various

concentrations (200, 400, 600, 800 and 1000) ppm, pH values and time intervals, where the ratio of solid phase to solution phase is (0.4:100). The concentration of metal ions was detected by Atomic Absorption Spectrophotometer, Unicam model Solaar 929. The amount of metal ions adsorbed was calculated by the difference of the concentration of metal ions in solution before and after adsorption.

Results and Discussion

Metal Sorption Characteristic

The influence of experimental conditions such as pH, ion concentration, agitation period and temperature on metals sorption will be studied.

1- Effect of pH

The pH of a solution strongly affects the adsorption capacity of the two substances chitosan and the resine. So that the effect of pH on the removal of metal ions after 24 hr. was studied in range 2 - 5, by adjusting pH of the solution using 0.1N HCl or 0.1N NaOH. It is important to mention that, pure chitosan and the resine are not stable at strong acidic medium, so that the adsorption behavior was studied at pH ranges from 2-5, (Sun and Wang) .

Figure (1) shows the effect of pH on the individual adsorption of Fe (II) and Cu (II) by chitosan and modified crosslinked chitosan beads. The adsorption increases with increasing pH of the solution till reaching the maximum adsorption at pH 5 and this depends on the metal ion type.

The low adsorption of metal ions in strong acidic solution (at low pH) could be mainly due to the electrostatic repulsion between the positive metal ions (M^+) in the medium and the positive charges in highly acidic solution (H^+) which accumulate on the surface of chitosan and modified crosslinked chitosan. In the other words, the amino groups in chitosan and modified crosslinked chitosan are protonated and reducing the number of binding sites available for the adsorption of heavy metal ions. This leads to the inducing an electrostatic repulsion of the different heavy metal ions. Such repulsion prevents the approach of the metal ions to the beads surface.

While at higher pH value, the adsorption of heavy metal ions increase due to the weak of electrostatic repulsion, and with the increase of pH value, the amino groups are free from protonation. Such positive charge density decreases allowing the metal ion approach to the different sorbent beads surface which result in higher adsorption values. The adsorption mechanism may be partially replaced by a chelation mechanism on the amino groups of the different chitosan beads (natural chitosan and modified crosslinked chitosan) and cation exchange on the carboxylic groups of modified crosslinked chitosan with DTPA, and so the adsorption capacity increases.

Therefore, at high pH the metal uptake of modified crosslinked chitosan with DTPA is more than that chitosan. Further increase in the pH value more than 5 would transform the dissolved metal into precipitated hydroxide form thus the adsorption capacity is decreased. This is well agreement with the previous works (Ngah et al., and Sun and Wang).
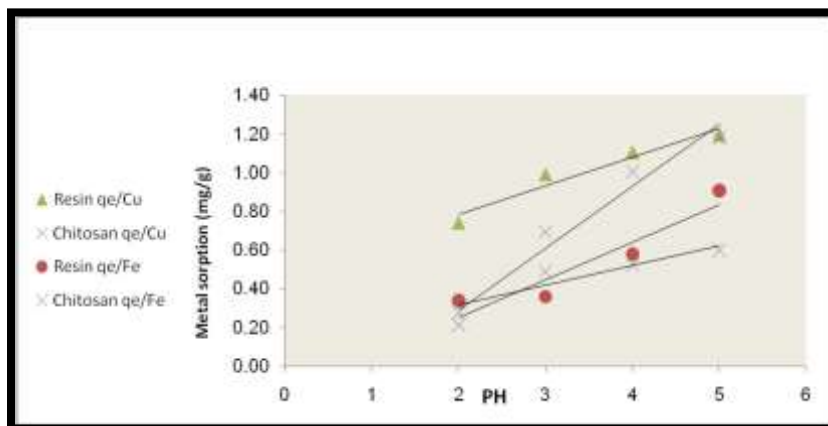

Fig. (1). pH-dependent metal uptake of different metal ions.

Effect of temperature on the adsorption of metal ions.

It is well known that the temperature has a great influence on any chemical process so that it may enhance or retard on the nature of the reactants and/or the products. The effect of temperature on the adsorption of metal ions was studied at 25, 40 and 50°C. From Figure (2) it has been observed that the adsorption of metal ions from aqueous solution increased remarkably with increasing temperature.
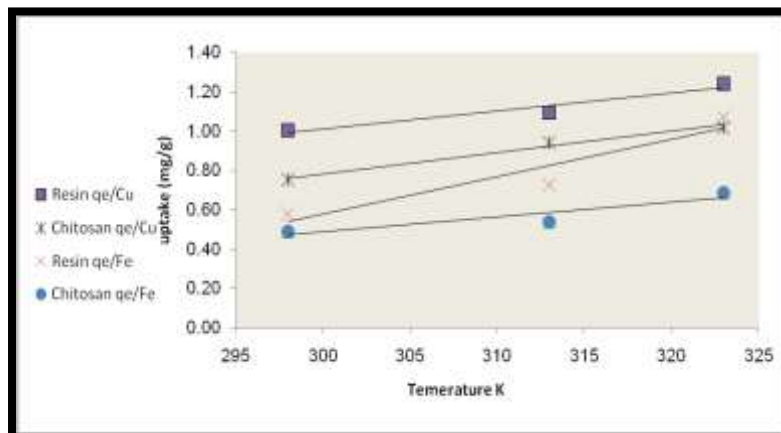

Fig. (2). Effect of temperature on the adsorption of different metal ions

Metals sorption by functionalized polymer

Total sorption capacity of chitosan and modified crosslinked chitosan are presents evaluating property in determining the amount needed for the removal of certain amount of polluting metal ion. Figure (3) shows the maximum sorption capacity of the chelating natural chitosan and modified crosslinked chitosan towards two different individual metal ions at their respective optimum pH value. The data shows that the affinity of the chelating pure chitosan and modified crosslinked chitosan towards the under investigation metal ions proceeds in the following order $Cu^{2+} > Fe^{2+}$

The mechanism of metal ion removal by chitosan, modified crosslinked chitosan can be suggested in four steps (Shawky *et al*).

1- *Bulk diffusion:* metal ion transfer from the bulk solution to the boundary film bordering the sorbent surface.

2- *Film diffusion:* metal ion transport from the boundary film to the surface of the sorbent.

3- *Intraparticular diffusion:* transfer of the metal ion from the surface to the intraparticular active sites.

4- *Chemical reaction:* uptake of the metal ion on the active sites, via chelating, ion-exchange or complexation.
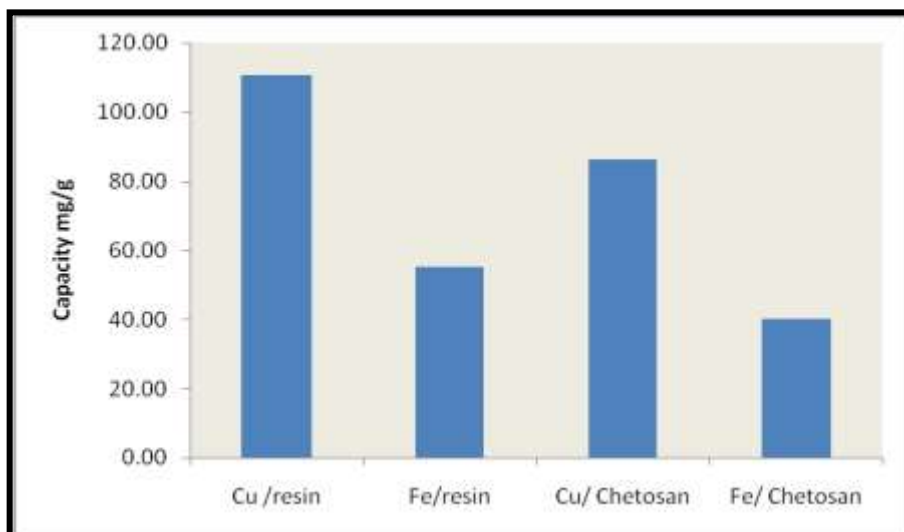

Figure (3) sorption capacity of natural chitosan, modified crosslinked chitosan.

Regarding to the first two steps, it has been demonstrated that they could be neglected if a sufficient speed of stirring was used (>400rpm). For this reason, intraparticular diffusion or chemical reaction (chelating or ion-exchange) would be the rate-limiting step of sorption kinetics.

Sorption isotherm studies

The adsorption data of eight contaminant metal ions were analyezed by a regression analysis to fit the Freundlich and Langmuir isotherms models (Kinniburgh, Hasany et al.). The coefficients of these two models were computed with linear square fitting of the plot of metal ion concentration at equilibrium versus the metal ion concentration at equilibrium. Langmuir model is the best known model to study and determine the chemisorption parameters on well defined localized sorption sites of the same energy independent of surface coverage (Rutheven). Langmuir sorption isotherm was used to fit the experimental sorption data. Langmuir equation can be described by the linearized form:
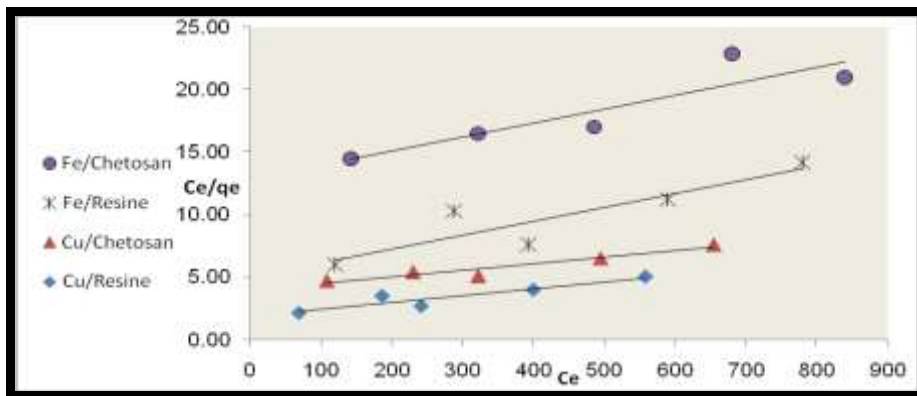
$$C_e/q_e = (1/Q_o.K_L) + (1/Q_o)C_e$$

Fig. (4). The linear plot of *(C_e/q_e)* against *C_e* for different metal ions

Where; C_e is the concentration of metal ions in solution at equilibrium, q_e is the amount of metal ions adsorbed at equilibrium (mg/g), K_L is the equilibrium adsorption constant and Q_o (mg/g) represents the maximum adsorption capacity of the resin towards particular metal ion. The linear plot of *(C_e/q_e)* against *C_e,* Figure (4), of the metal ions under investigation shows that the adsorption obeyed the Langmuir model. The Langmuir constants were evaluated and reported in (Table 1).

TABLE (1). Langmuir and Freundlich adsorption constants associated to adsorption isotherms of different metal ions on natural chitosan, modified crosslinked chitosan

Metal	Langmuir constants (Resin)			Freundlich constants(Resin)		
	Qo (mg/g)	**Binding energy** $(K_{Lx10}{}^{3})$	r^2	Indicator adsorption capacity (K_F)	Indicator adsorption intensity (n)	r^2
Cupper	200	2.67	0.92	0.41	0.87	0.98
Iron	90.91	2.3	0.81	1.63	0.68	0.95
Metal	Langmuir constants(Chitosan)			Freundlich constants(Chitosan)		
	Q_o (mg/g)	**Binding energy** $(K_{Lx10}{}^{3})$	r^2	Indicator adsorption capacity (K_F)	Indicator adsorption intensity(n)	r^2
Cupper	200	1.26	0.87	1.77	0.77	0.93
Iron	90.91	8.6	0.80	1.59	0.58	0.88

Meanwhile, Freundlich isotherm is a characterizing model used to estimate the surface homogeneity and active site distribution empirically using the following equation:

$$\log q_e = \log K_F + (1/n) \log C_e$$

Where; K_F and n are the Freundlich constants characteristics on the system. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. The linear plot of log q_e versus log C_e shows the applicability of the Freundlich model Fig. 5, from which Freundlich constants K_F and n were calculated and reported in Table (1). Values of 1<n<10 show the positive sorption of metal ion (McKay et al.). If n< 1, bond energies increase with the surface density (Doina Humelnicu).
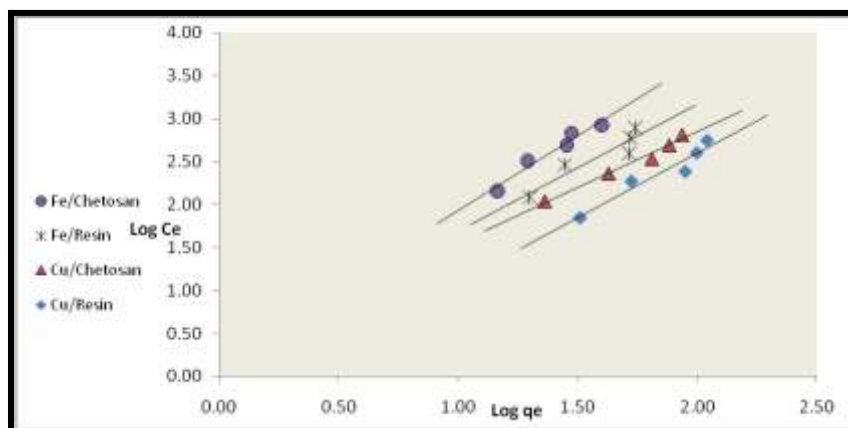
Fig. (5). The linear plot of log q_e versus log C_e for different metal ions

It has been reported that the effect of isotherm shape with a view to predicting if an adsorption system is favourable or unfavourable (Weber and Chakravorti).

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined by (Hall et al. and Zhai et al.)

$$R_L = 1/(1+K_L C_o)$$

Where; C_o is the initial metal ions concentration (mg/l), and K_L is Langmuir adsorption equilibrium constant (L mg^{-1}), the parameter indicates the isotherm shape presented in table (2), (Zhai et al.).

Table (2). Separation factor (R_L, equilibrium parameter) which indicates the isotherm shape.

Values (R)	types of isotherm
R > 1	Unfavorable
R = 1	Linear
0 <R < 1	Favorable
R < 1	Irreversible

The values of R_L calculated for different initial metal ions, Fe(II) and Cu(II) concentration for natural chitosan, modified crosslinked chitosan are given in table (3). The R_L values (0 < L <1) show favourable adsorption of Fe(II) and Cu(II) on natural chitosan, modified crosslinked chitosan(Resin). This indicates the suitability of these resins for the recovery of Fe^{2+} and Cu^{2+}.

Table (3). Separation factor (R_L, equilibrium parameter) values based on Langmuir equation.

Fe(II)		Cu(II)	
Initial concentration C_0(mg/l)	Separation factor (equilibrium parameter) R_L values$_s$	Initial concentration C_0(mg/l)	Separation factor (equilibrium parameter) R_L values
Resin			
200	0.685	200	0.652
400	0.521	400	0.484
600	0.420	600	0.384
800	0.352	800	0.319
1000	0.303	1000	0.272
Chitosan			
200	0.368	200	0.799
400	0.225	400	0.655
600	0.162	600	0.569
800	0.127	800	0.498
1000	0.104	1000	0.442

Sorption kinetics of metal ions

Pseudo first order kinetic model

In 1898, Lagergren suggested a pseudo first order equation for the sorption of liquid / solid system based on solid capacity. It assumes that the rate of change of sorbate uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The Lagergren equation is the most widely used rate equation in liquid phase sorption. The general equation is expressed as:

$$\log (q_e - q_t) = \log (q_e) - k_1 t / 2.303 \qquad (1)$$

Where q_e and q_t are the amounts of metal ions adsorbed onto the adsorbents (mg/g) at equilibrium and at time t, respectively. k_1 is the rate constant of the first order (min^{-1}). By plotting $\log (q_e - q_t)$ versus t, the first-order constant k_1 and equilibrium capacity q_e can be obtained from the slope and intercept, respectively.

The pseudo first order model fitted well for Fe^{+2} and Cu^{+2} where $\log (q_e - q_t)$ is highly significant correlated with time (t), Fig. (6) and table (4). The figure shows the kinetics of metal ions adsorption onto chitosan, modified crosslinked chitosan. It was observed that maximum adsorption of metal ions (Fe^{+2} and Cu^{+2}) obey that calculated from the pseudo-first-order reaction where theoretical values of q_e (mg/g) are equal or nearly close to its practical values, table (4).
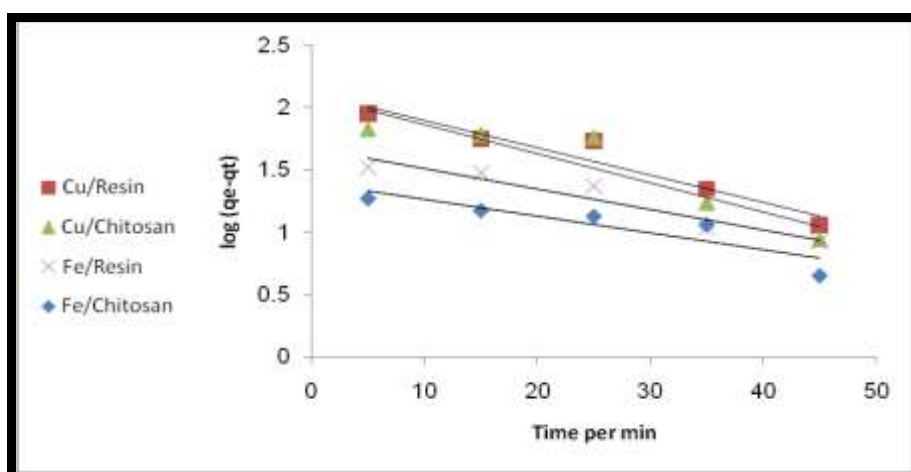

Fig.(6): Plots of $\log(q_e - q_t)$ against time for the exchange of Fe^{+2} and Cu^{+2} ions on chitosan and modified crosslinked chitosan.

Table (4) Kinetic parameters (pseudo first order) for the adsorption of Fe^{+2} and Cu^{+2} ions on chitosan, modified crosslinked chitosan.

Metal Ions	$q_{e\ (mg/g)}$ Theoretical.	$q_{e\ (mg/g)}$ practical	$K_1(min^{-1})$ $\times 10^{-3}$	R
Cu^{2+} /Resin	131.5	110.5	51	0.93
Fe^{2+} /Resin	47.32	55	37	0.84
Cu^{2+} /Chitosan	123.9	86.25	53	0.92
Fe^{2+} / Chitosan	24.95	40	30	0.80

Pseudo second order kinetic model

Ho and Mackay developed a pseudo second order equation based on the amount of sorbed sorbate on the sorbent. If the rate of sorption is a second-order mechanism, the pseudo second order chemisorption kinetics rate equation is expressed as:

$$dq_t/dt = k_2(q_e-q_t)^2 \qquad (2)$$

For the boundary conditions t = 0 to t, and q_t =0 to q_t, the integrated form of equation (2) becomes:

$$1/ (q_e-q_t) = 1/q_e +k_2t \qquad (3)$$

which is the integrated rate law for a pseudo second order reaction. Equation (3) can be rearranged to obtain a linear form:

$$t/q_t = 1/k_2q_e^2 + t/q_e \qquad (4)$$

The constants can be determined by plotting t/q_t versus t. The second-order sorption rate constant k_2 (g/mg min) and q_e (mg/g) can be determined from the intercept and   the slope (positive values) of the plot. This model is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate (Taty).

By applying the pseudo-second order model, it was found that the kinetic data can be more fitted as shown in Fig. (7) for Fe^{+2} and Cu^{+2}ions in the studied sorption system. The pseudo-second order model fitted well for Fe^{+2} and Cu^{+2} where t/q_t is highly significant positively correlated with time (t), Fig. (7) and table (5). This indicates that chemisorption occurs involving valence forces through sharing or exchange of electrons between the exchanger and adsorbed heavy metal ions as covalent forces. The pseudo-second-order equation has the following advantages: it does not have the problem of assigning an effective adsorption capacity, i.e., the adsorption capacity, the rate constant of pseudo-second-order, and the initial

adsorption rate all can be determined from the equation without knowing any parameter beforehand. The corresponding parameters of the different kinetic models are determined by linear regression (Hoshan).
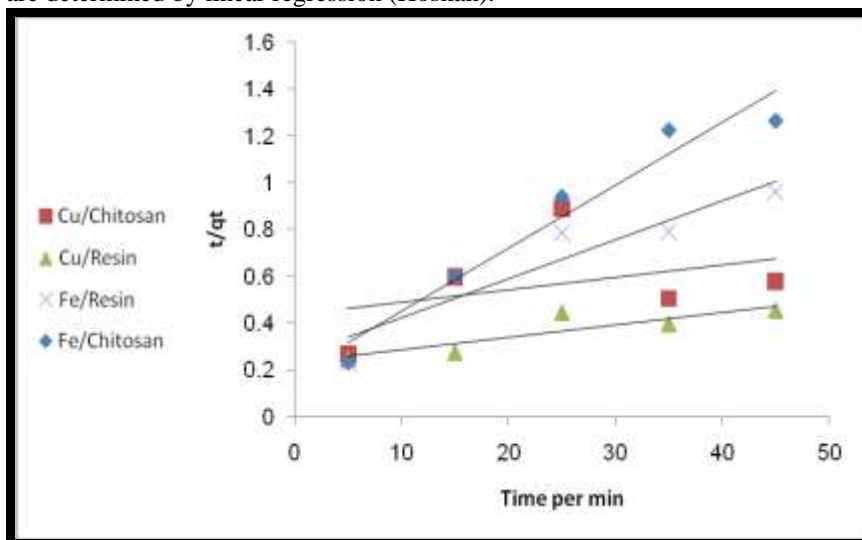

Fig. (7): Pseudo second order model for the exchange of of Fe^{+2} and Cu^{+2} ions on chitosan, modified crosslinked chitosan.

From table (5) it is clear that the theoretical q_e values do not obey that calculated from the pseudo second order reaction where theoretical values of qe (mg/g) are not equal or close to its practical values well with their experimental values. This implies that sorption of Fe^{+2} and Cu^{+2} ions on chitosan and modified crosslinked chitosan do not follows the pseudo-second order kinetics but the pseudo first order because the theoretical q_e values agree with experimental values.

Table (5): Kinetic parameters (pseudo second order) for the adsorption of of Fe^{+2} and Cu^{+2} ions on chitosan, modified crosslinked chitosan.

Metal Ions	$q_{e\ (mg/g)}$ Theoretical.	$q_{e\ (mg/g)}$ practical	$K_2(min^{-1})$	R
Cu^{2+} /Resin	200	110.5	$1.07*10^{-4}$	0.77
Fe^{2+} /Resin	62.5	55	$9.96*10^{-4}$	0.88
Cu^{2+} /Chitosan	200	86.25	$5.747*10^{-5}$	0.14
Fe^{2+} / Chitosan	38.5	40	$3.67*10^{-3}$	0.95

The rapid adsorption of metal ions by the adsorbent is an important characteristic for practical use which indicates shortening the time needed for water purification. Figure (8) shows the result of kinetic experiments conducted to determine the

equilibrium time required for the uptake of metal ions by the natural chitosan, modified crosslinked chitosan. A two-stage kinetic behavior is evident: a very rapid initial sorption over a few minutes, followed by a long period of much slower uptake. The equilibrium time needed for the different metals ranged from about 5-45 min. The result suggested that, at the beginning of the process, the adsorption occurs on the natural chitosan, modified crosslinked chitosan surface, so, a fast adsorption rate was found (Fritz et al., Lee et al.). After that; the adsorption takes place at the functional groups located in inner structure of the polymer, so, the adsorption rate was slow due to the pore diffusion of metal ions into the polymer matrix. The metal adsorption by functionalized polymer is a reversible sorption-desorption process which can be described by Langmuir according to the following equation:

$$-\ln (1-F_{(t)}) = Kt + C$$

Where; $F_{(t)} = C_o - C_t / C_o - C_e$, K is the equilibrium constant and C_o, C_t, C_e are the concentrations of metal ions at the beginning and at time (t) and equilibrium concentration, respectively.
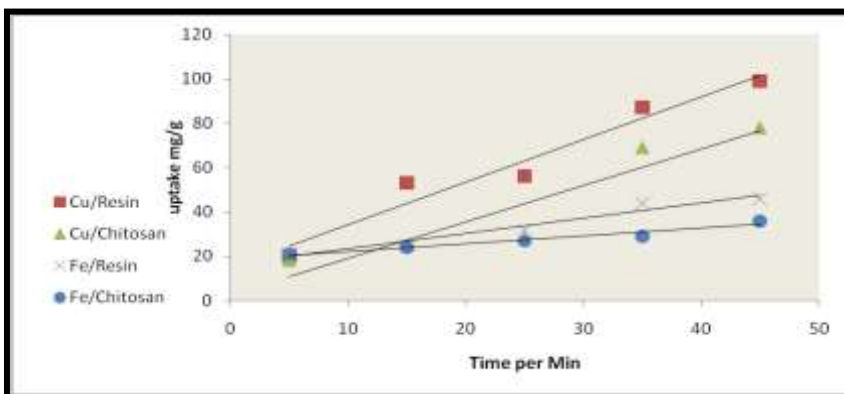

Fig. (8). The change in amount of adsorbed metal ions with time for natural chitosan, modified crosslinked chitosan.

(Fig. 9) shows a plot of $-\ln (1-F_{(t)})$ against t as conducted from the experimental results. Where; $F_{(t)} = C_o - C_t / C_o - C_e$ and C_o, C_t, C_e are the concentrations of metal ions at the beginning and at time (t) and equilibrium concentration, respectively. The reaction rate of sorption (K_s) and rate of desorption (K_d) of natural chitosan and modified crosslinked chitosan can be determined from the slope and intercept as follow and its values in(Table 6):
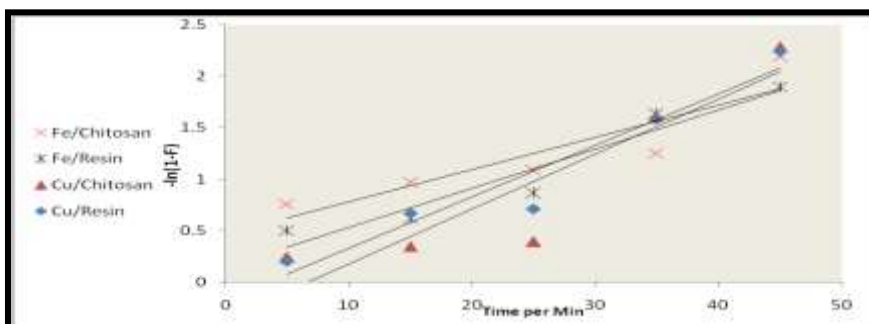
$$K_d = k(C_e / C_o) \text{ and } K_s = K - K_d$$

Fig. (9) Plots of *-ln* (1-F (t)) versus time for different metal ions.

Table (6) shows the value of K_d, from which it can be seen that the Iron/Chitosan has much low kd, and Cupper/ Chitosan has the highest

K_d, which explain the high affinity of the copolymer towards Cu^{2+} and its low affinity towards Fe^{2+}.

TABLE (6). Adsorption rate constant for different metals on the resin.

Metal ions	Equilibrium constant $K(s^{-1}) \times 10^{-3}$	$\left(C_e / C_o\right)$	Rate of desorption $K_d (s^{-1}) \times 10^{-3}$	Rate of sorption $K_s (s^{-1}) \times 10^{-3}$	r^2
Iron/Resin	38	0.78	30	8	0.92
Iron/Chitosan	31	0.84	26	5	0.80
Cupper/ Resin	50	0.56	28	22	0.93
Cupper/ Chitosan	53	0.66	35	18	0.84

Thermodynamic studies

The effect of temperature on the adsorption process can be explained by calculating the thermodynamic parameters such as changes in free energy ΔG, enthalpy (ΔH) and entropy (ΔS) according to the following equations:

D = qe/Ce

Log D = - (ΔH/2.303 RT) + (ΔS /R)

ΔG = ΔH –TΔS

Where D is the distribution ratio between metal ions and the adsorbent in aqueous solution and R is the gas constant (8.314 j/mol k).

The relationship between log D versus 1/T for the prepared resin is shown in Fig. (10). Thermodynamic parameters were then calculated, table (7).
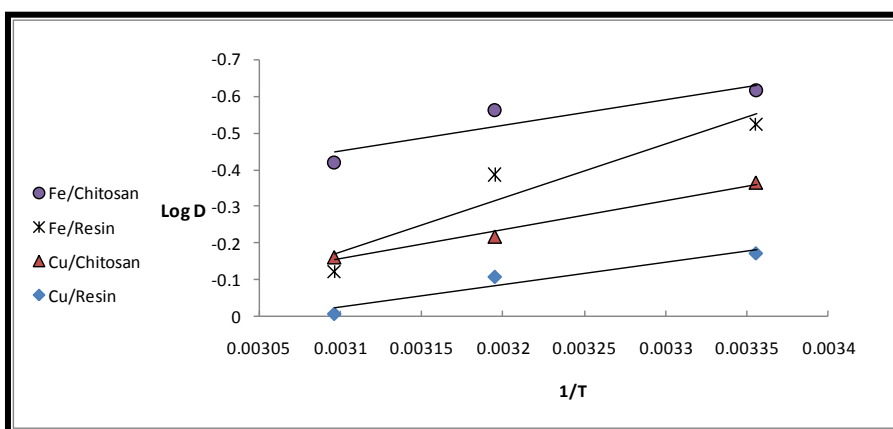
Fig. (10) The relationship between *log D* and *1/T* for the prepared copolymer resin for different metal ions

The positive values of (ΔH) were found as 11.762,15.3, 28.07, and 13.397Kj/mol for Cupper / Resin (modified crosslinked chitosan), Cupper/Chitosan, Iron/ Resin (modified crosslinked chitosan) and Iron/ Chitosan, respectively. These values indicate that adsorption is an endothermic process   and is responsible for the increasing in adsorption rate as the temperature increased.

The negative values of ΔS indicate a more orderly structure of Fe^{+2} and Cu^{+2} on the surface of chitosan, modified crosslinked chitosan, since the entropy of the system is related to the way of arrangements that can assume a higher degree of order for Fe^{+2} and Cu^{+2} which, in turn, is attributed to their greater proximity to the surface of chitosan, modified crosslinked chitosan, this restricts the freedom of Fe^{+2} and Cu^{+2} ions close to the surface.

The values of ΔG decrease with increasing temperature, demonstrating increase in the feasibility of adsorption at higher temperatures (El-sayed et al.). Also the most striking feature in such values of   ΔG is the +ve sign which suggests stronger binding of Fe^{+2} and Cu^{+2} but this is not conclusive as the free energy is determined by enthalpy and entropy while the binding strength is normally defined in terms of enthalpy alone (El Sayed).

This is confirmed from Langmuir constant (k_L, is the equilibrium adsorption constant) which indicated that the effect of binding energy for Fe^{+2} is more than that of Cu^{+2}.

Table (7). Thermodynamics parameters of adsorption of three metal ions, Fe(II) and Cu(II) by natural chitosan, Resin.

Adsorbents	Temperature K^0	Thermodynamics		
		ΔG (KJ/mol)	$\Delta Hads$ (KJ/mol)	$\Delta Sads$ (J/mol K)
Cupper/Resin	298	0.984	11.762	-15.66
	313	0.649		
	323	0.043		
Cupper/Chitosan	298	2.087	15.3	-19.3
	313	1.307		
	323	1.00		
Iron/ Resin	298	2.980	28.07	-36.3
	313	2.317		
	323	0.768		
Iron/ Chitosan	298	3.497	13.397	-14.28
	313	3.355		
	323	2.603		

Notes:

$\Delta G_{ads} = -RT \ln K_c$ and $K_c = C_{Ae}/ C_e$ where C_{Ae} is the adsorbed amount of metal and C_e is the equilibrium concentration, R is an ideal gas constant (8.314 j/mol k) and T is the absolute temperature in (K).

plotting log Kc against 1/T gives a straight line, with slope and intercept equal -$\Delta H_{ads}/2.303R$ and $\Delta S_{ads}/2.303R$ were calculated and reported in table (7).

$\Delta H_{ads} = \Delta G + T \Delta S_{ads}$

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