Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(4):1274-1282

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Copper adsorption onto starch as biopolymer: Isothermal equilibrium and kinetic studies

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ABSTRACT

The removal of copper from aqueous solutions by adsorption has been studied deeply with a full kinetic study. Native starch has been used as an adsorbent. The selected parameters are temperature (25°C), pH = 7 and the mass of adsorbent (2g/L) with a solution of 100 mL contain different concentrations of copper which are determined at equilibrium by UV-visible spectrophotometer. The results showed that the temperature, pH, the mass of adsorbent and the metal concentration are factors involved for copper removal by starch. The adsorption of copper increases with pH (2-6) and the adsorbent dosage increasingly, but decreases with increasing temperature. Adsorption isotherm studies were also conducted. The maximum adsorption capacity (q_m) was calculated as 106.38 mg / g for the copper concentrations studied. FTIR-ATR analysis was used for the characterization of the complex starch-copper.

Keywords: starch, copper, adsorption, biopolymer, water, heavy metals.

INTRODUCTION

The contamination of soil and water by heavy metals continues around the world to present a serious threat to the environment and human health [1]. The development of innovative technologies for cleaning metal remains a challenge because the current processes have many limitations, such as being expensive, disruptive, and only effective in certain concentrations. Polymers and copolymers contain amino or carboxyl groups that could use for coordinating of heavy metals are studied in literature [2]. The polymers provide an excellent material for chelation of metals with high molecular weight and repetitive functional groups [3]. Heavy metals such as copper, lead and cadmium are environmental concerns because of the widespread use and toxicity to human and wildlife [4-5]. Although a greater understanding of the extent of their toxicity and cycling environment is slowly being made. Native starch granules are insoluble in water containing two major polymers: amylose which is essentially a linear polymer of α- (4.1-bound D-glucopyranosyl) units, with little α- (1-6) linkages having a number average degree of polymerization (DP_n) of 800 to 900, and which is composed of branched chains of amylopectin α-(1,4-linked D-glucose) and is highly branched with α- (6.1 -linked D-glucose) bonds, having a DP_n of 4700-12800. Amylose representing 5 to 30% and amylopectin which represents from 70 to 95% of starch. Pollution by heavy metals is increasingly recognized and their attachments to natural polymers seems to be an effective way in waste water treatment containers of metal ions that plug into OH can allow ion trapping metallic individuals [6]. The objectives of this work were to study the ability of the starch powder on copper adsorption, the effect of different parameters on adsorption process and evaluated the adsorption isotherms.

EXPERIMENTAL SECTION

2.1. Materials

Starch powder, Copper (II) sulphate-pentahydrate ($Cu(SO_4).5H_2O$, hydrochloric acid (HCl, ACS reagent, 37%), and sodium hydroxide (NaOH, reagent grade, ≥ 98%, pellets (anhydrous)) were all purchased from Sigma-Aldrich.

2.2. The experiments of copper ions adsorption

A copper solution (1000 mg/L) was prepared by dissolving 3.93 g of copper sulphate in 1L of demineralised water. For the realization of the adsorption isotherm, copper solutions of different concentrations are prepared with the appropriate dilution of the stock solution with deionized water to obtain different concentrations 735, 635, 535 and 435 mg/L [7]. Adsorption experiments were performed at room temperature with stirring a different concentration of copper and 0.2 g of starch during equilibrium time equal 90 minutes. The concentration of Cu^{2+} ions remaining in each solution was determined using a UV-visible spectrophotometry (Aquarious CECIL CE 7400) at wavelength equal 810 nm and the concentration calculated from the calibration curve of copper. The capacity adsorption of Cu^{2+} at equilibrium and removal were then calculated using the equation (1) and (2) [8].

$$q_e = \frac{C_0 - C_e}{m} \times V \qquad (1)$$

$$\%\ \text{removal} = \frac{C_0 - C_e}{C_e} \times 100 \qquad (2)$$

Where: q_e: amount of copper adsorbed on the starch at equilibrium (mg/g) C_0, C_e initial concentration of copper in solution and at equilibrium (mg/L) respectively, m: mass of starch (g) and V: volume of the solution (L).

RESULTS AND DISCUSSION

3.1. Effect of contact time and the initial concentration of copper

The time it takes for the metal ions and the adsorbent to reach equilibrium is a considerable importance in the adsorption tests, because it depends on the type of system used. Therefore, it is necessary to establish the time of such a system which depends on various processing conditions [9]. The adsorption of copper ions on starch was studied as a function of time at different initial concentrations of copper (435-735 mg/L) and the contact time of 1 to 90 minutes selected as a time of equilibrium (Fig. 1). This observation is due to the fact that the adsorption sites are available during this time interval to equilibrium. This implies an increase in adsorption capacity and decreasing concentrations of the ions of Cu^{2+}. The higher adsorption rates at the beginning (20 min) then a small change in the adsorption capacity.

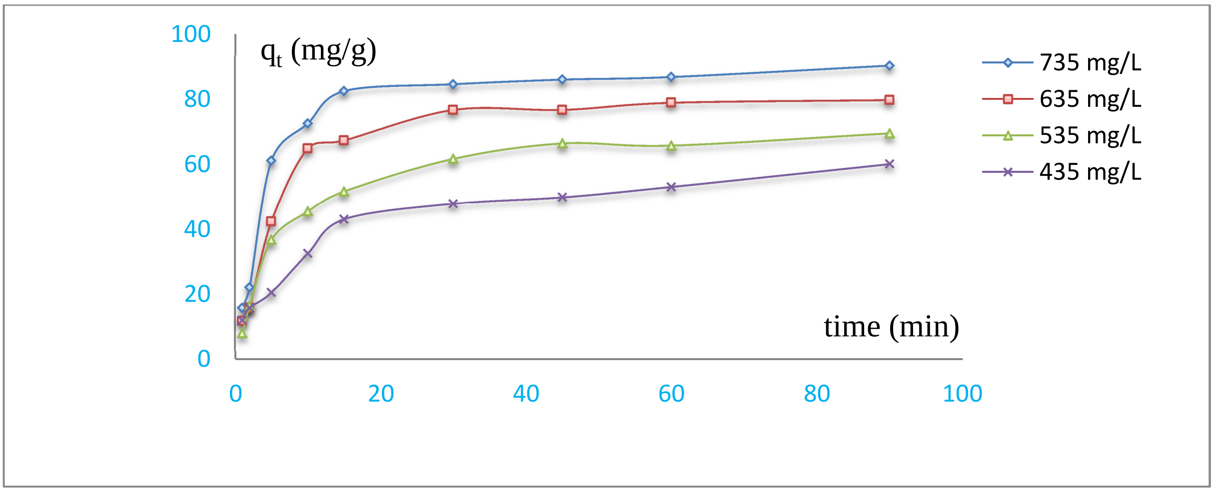

Fig. 1- Effect of the contact time and the initial concentration of Cu^{2+} for the adsorption of copper onto starch

3.2. Kinetics and mechanism of copper adsorption:

The adsorption kinetics of copper by the biopolymer (starch) was evaluated by two kinetic models: pseudo-first-order or pseudo-second-order. The kinetic pseudo-first-order (Lagergren) model is expressed by the following equations (3) and (4) [10]:

$$\frac{dq}{dt} = K_1(q_e - q_t) \qquad \text{(non-linear form)} \qquad (3)$$

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2{,}203} \quad \text{(linear form)} \qquad (4)$$

Where qe and qt are adsorption capacity of Cu^{2+} (mg/g) at equilibrium and at any time (t) (min), respectively, and k_1 is the constant of pseudo-first-order adsorption (l/min). The slope of the linear plot of log (qe - qt) versus (t) is used to determine the constant k_1 (Fig. 2).

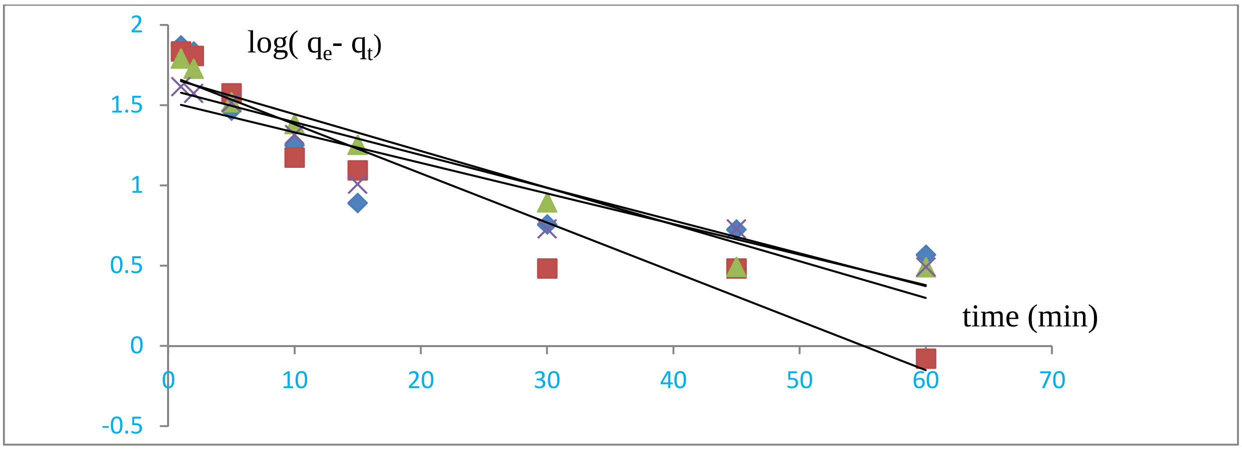

Fig. 2- Pseudo-first-order (Lagergren) for adsorption of copper onto starch at different concentrations of Cu^{2+}

The equation of the kinetic pseudo-second-order (Lagergren) model is expressed by the following equations (5), (6) and (7) [11]:

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \quad \text{(non-linear form)} \qquad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \quad \text{(linear form)} \qquad (6)$$

$$H = k_2 {q_e}^2 \qquad (7)$$

k_2 is the rate constant of pseudo-second-model order (g/mg min). The slopes and intercepts of the t/qt versus t are used to calculate k_2 (Fig. 3).

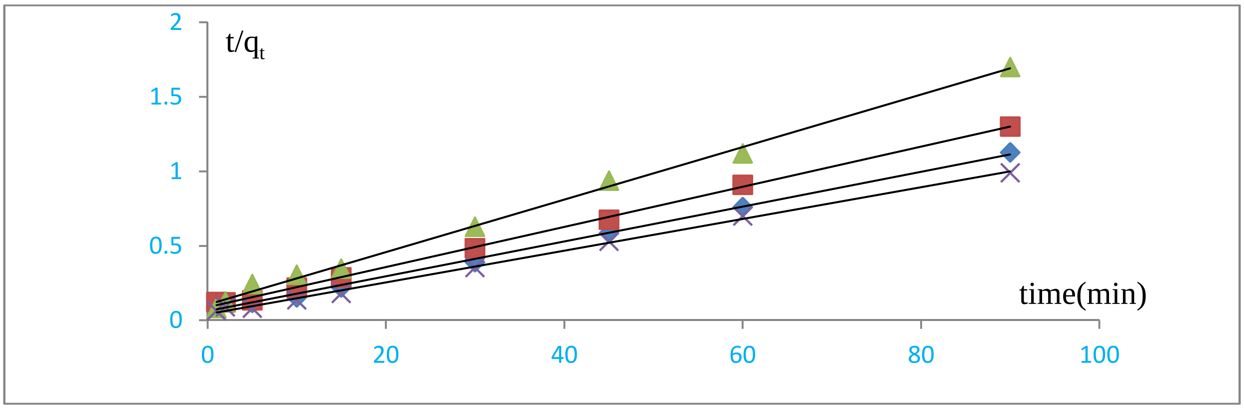

Fig. 3- Pseudo-second-order (Lagergren) for adsorption of copper onto starch at different concentrations of Cu^{2+}

The combination of values Δq (%) and the correlation coefficients even enable the validity of kinetic model with the experimental, for copper adsorption on starch the values of Δq (%) are high and correlation coefficients are less than 0.90 for the kinetic pseudo-first-order model against the kinetic pseudo-second-order model, the values of Δq (%) are low and R^2 values equal to 0.99 (table 1).These values found up the validity of the kinetic model pseudo-second-order for the adsorption of copper onto starch. In another, the experimental values of q_e are close to the values of q_e calculated from the kinetic pseudo-second-order model. Consistency of the experimental data with the pseudo-second-order kinetic model indicates that the adsorption of Cu^{2+} on starch is controlled by chemical adsorption involving valence forces through the sharing or exchange of electrons between the adsorbent and the adsorbate.

Table 1- Parameters of kinetic models for the copper adsorption onto starch

kinetic model	parameters	435 mg/L	535 mg/L	635 mg/L	735 mg/L
Pseudo -first-order	$q_{e,\,cal}$ (mg/g)	33	47.01	48.57	40.2
	K_1 (1 /min)	0.43	0.52	0.07	0.04
	R^2	0.89	0.94	0.93	0.76
	Δq %	37.9	32.38	39.08	54
Pseudo -second-order	$q_{e,\,cal}$ (mg/g)	56.8	74.6	85.4	94.3
	K_2 (g/mg min)	0.0029	0.0020	0.0022	0.0026
	H (mg/g min)	9.46	11.23	16.26	23.47
	R^2	0.99	0.99	0.99	0.99
	q_e (exper)	53.2	69.53	79.73	90.3
	Δq %	6.33	6.79	6.63	4.24

To better understand the mechanism of adsorption, the intraparticle diffusion model is applied and expressed by the following equation (8) [12]:

$$q_t = K_p t^{1/2} + C \qquad (8)$$

K_P (mg/g min$^{1/2}$) is the rate of intraparticle diffusion and C (mg/g) is constant for each step of the adsorption, the values of the constant C (mg/g) provide information on the thickness of the boundary layer, which is plus the intercept, the effect of the boundary layer. The q_t curve according to $t^{1/2}$ is used to terminate the values K_p and C for adsorbing copper on starch at different concentrations of Cu^{2+} (Fig. 4).

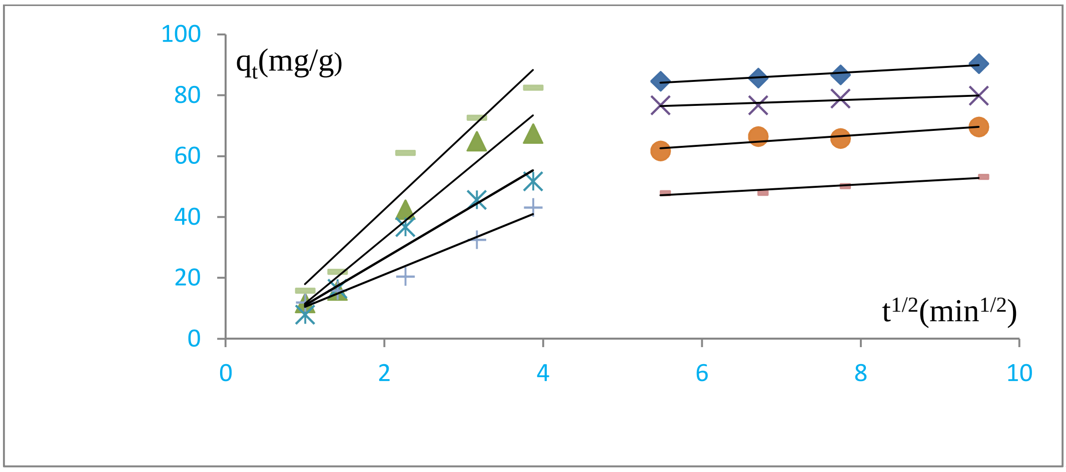

Fig. 4- Intraparticle diffusion model for the adsorption of Cu^{2+} onto starch

Table 2 shows the corresponding model parameters of two parts according to the equation (8) for all initial concentrations the values of kp_1 were higher than kp_2 and C_2 was larger than C_1. This indicates that the metal removal rate is higher at the beginning (20 min) due to a large surface of the adsorbent available for the adsorption of metal ions.

Table 2- Intraparticle diffusion model parameters of copper adsorption onto starch

C_0	K_{p1}	K_{P2}	C_1	C_2	R_1^2	R_2^2
735 mg/L	28.49	1.32	12.9	77.1	0.94	0.96
635 mg/L	21.52	0.86	9.9	71.6	0.95	0.87
535 mg/L	15.44	1.6	4.4	52.9	0.95	0.90
435 mg/L	10.59	1.41	0.07	39.3	0.96	0.91

3.3 Adsorption isotherms

3.3.1 Langmuir isotherm

The Langmuir model describes the formation of a monolayer adsorbate on the outer surface of the adsorbent and either adsorption takes place once a saturation value is reached [13]. This model is described in the non-linear and linear form in the following equations (9) and (10):

$$q_e = \frac{q_m}{1 + K_l\, q_m} \qquad \text{(non-linear form)} \qquad (9)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_l\, q_m} \qquad \text{(linear form)} \qquad (10)$$

q_e is the amount of copper on starch at equilibrium (mg /g), C_e is the concentration at equilibrium of the solute in the bulk solution. q_m is the maximum adsorption capacity at equilibrium, and k_l (L/g) a constant related to adsorption. The essential characteristics of the Langmuir isotherm can be expressed in terms of R_l as a dimensionless separation factor, defined by the equation (11).

$$R_l = \frac{1}{1+K_l\, C_0} \qquad (11)$$

K_l (L/g) is the Langmuir constant and C_0 is the initial concentration of metal (mg/L). The R_l indicates whether the adsorption is favourable ($0<R_l<1$) or unfavourable ($R_l>1$) .The Langmuir model parameters were calculated from the slope and intercept of C_e / q_e versus C_e.

3.3.2. Freundlich isotherm

The Freundlich model is based on the mode that the adsorption site is distributed exponentially with respect to the heat of adsorption [14]. However, this multilayer adsorption model described in the non-linear and linear form shown in the equations (12) and (13):

$$q_e = K_f\, C_e^{\frac{1}{n}} \qquad \text{(non-linear form)} \qquad (12)$$

$$log q_e = \frac{1}{n} log C_e + log K_f \qquad \text{(linear form)} \qquad (13)$$

In these equations, K_f and n are dimensionless constant representing the adsorption capacity and adsorption intensity respectively. In normal adsorption condition, the value of 1/n should be in favourable conditions ($0 <1/n <1$). Freundlich model parameters were calculated from the slope and intercept of log q_e versus C_e.

3.3.3. Temkin isotherm

Temkin considered that the effects of indirect interaction of adsorbent-adsorbate on the adsorption isotherm are suggested that the heat of adsorption of all the molecules in the layer linearly decrease with the coverage of the adsorbent [15]. The Temkin isotherm was applied at the following form equations (14) and (15):

$$q_e = \frac{RT}{b} \mathrm{Ln}(AC_e) \qquad \text{(non-linear form)} \qquad (14)$$

$$q_e = B_1 \mathrm{Ln}\, A + B_1 \mathrm{Ln}\, C_e \qquad \text{(linear form)} \qquad (15)$$

$B_1 = RT/b$, T (k) is the absolute temperature, R is gas constant (8.314 J/mol K), A (L/mg) corresponding to the maximum bonding energy balance and B_1 is related to the heat of adsorption. Temkin constants can be determined from the slope and intercept of q_e versus lnCe.

For all the concentrations studied, the Langmuir isotherm shows a better fit to the experimental data as well the Freundlich isotherm. Moreover, Table 3 shows the Langmuir constant, K_l linked to the affinity of adsorption sites and factor R_l indicates that the favourable adsorption and the q_m value which is equal to 106.38 (mg/g) at 25°C at the concentrations of copper and the Coefficient Update of high correlation (0.98). Also Freundlich isotherm is in agreement with the experimental results (R^2 = 0.99), $0 <1/n <1$ indicating adsorbate-adsorbent interaction. The starch used in this study provided a beneficial adsorption at 25°C and pH = 7.

Table 3- Constants of copper adsorption isotherms onto starch at 25°C

Langmuir				Freundlich			Temkin		
q_m (mg/g)	R_l	k_l (L/g)	R^2	K_f	1/n	R^2	B	A (L/mg)	R^2
106.38	435 mg/L = 0.22 535 mg/L = 0.19 635 mg/L = 0.16 735 mg/L = 0.14	0.0078	0.98	9 .90	0.34	0.99	31.31	0.031	0.98

In order to justify the validity of the adsorption of copper by the starch powder, its adsorption capacity must be compared to other adsorbents. Table 4 shows the maximum adsorption capacity of copper on different adsorbents reported in the literature [16-19]. It shows that starch powder has high adsorption capacity (q_m = 106.38) than the other adsorbents.

Table 4 - Adsorption capacity of copper by different adsorbents reported in other studies

Adsorbents	q_m (mg/g)	Reference
Cellulose-g-acrylic acid copolymer	18.17	[16]
Starch-g-acrylic acid copolymer	5.08	[17]
Crosslinked carboxymethyl KGM	27.57	[18]
Amberlite IR-120 resin	21.22	[19]

3.4 pH effect on copper adsorption

In the aqueous solution, copper is converted to different hydrolyzed products. At low pH, copper ions exist as Cu^{2+}, Cu $(OH)^{+}$ and the neutral compound such as $Cu(OH)_2$. The dominant species of copper in the pH range of 3 to 5 are Cu^{2+} and $Cu(OH)^{+}$, while the copper occurs as insoluble $(Cu\ OH)_2$ above pH 6.3. The experiments were performed with pH values in the range of (1.5 – 8.8) as $Cu(OH)_2$ began to precipitate above pH = 6 . Increasing pH (2 to 5) increase in adsorption efficiency of (20-94%) [20]. Fig. 6 shows the pH influence on the efficiency of the adsorption of copper onto the starch, it is evident that the percentage of adsorbed copper ions increases sharply with increasing pH reach the higher value of pH (4-5). It can be explained by the observation that increasing the pH causes the displacement of oxygen doublet of the surface of the starch to the copper ions [21].

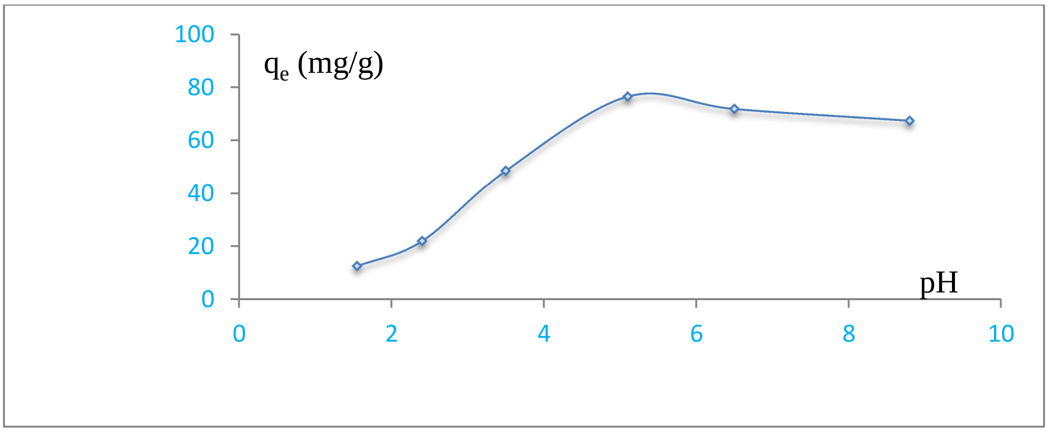

Fig. 5- PH effect on copper adsorption (0.2 g of starch, C_0 = 735 mg/L, contact time = 90 min)

3.5 Effect of the amount of adsorbent in the copper removal

The effect of the amount of adsorbent on the adsorption efficiency is shown in Fig. 6. The increased amount of starch (0.1 to 0.8 g) of the same concentration of copper in the solution leads to a reduction of metal per unit weight of starch. This is particularly evident in the solution with a higher concentration of copper while this influence decreases in solutions with low copper concentrations. The amount of adsorbent does not substantially affect the efficiency of adsorption which remains constant regardless of the concentration of the initial solution [22].

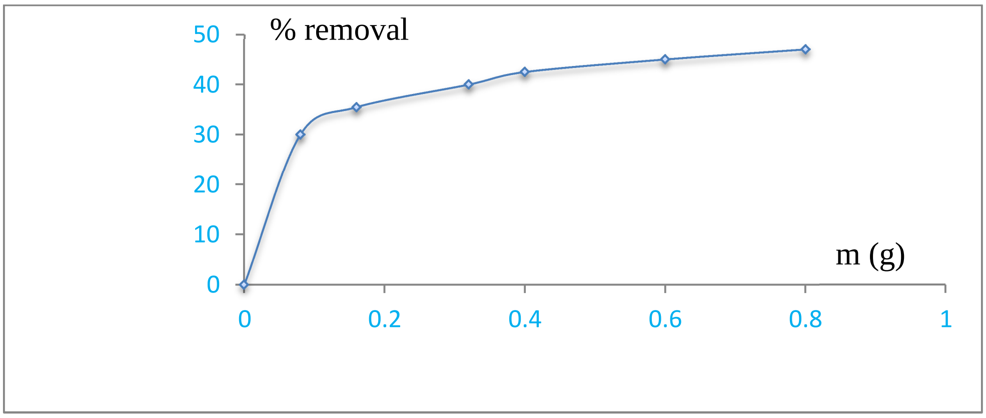

Fig.6- Influence of the mass of adsorbent on copper removal (pH = 7, the contact time = 90 min, C_0 = 735 mg/L)

3.6 Effect of the temperature on copper adsorption

We studied the effect of temperature on the adsorption of copper onto starch in the temperature range of (25-50°C) and pH = 7, as shown in Fig. 7. The adsorption capacity for the adsorption of copper on the starch decreases with the increase of the temperature, which means that the copper complexation by starch is exothermic [23].

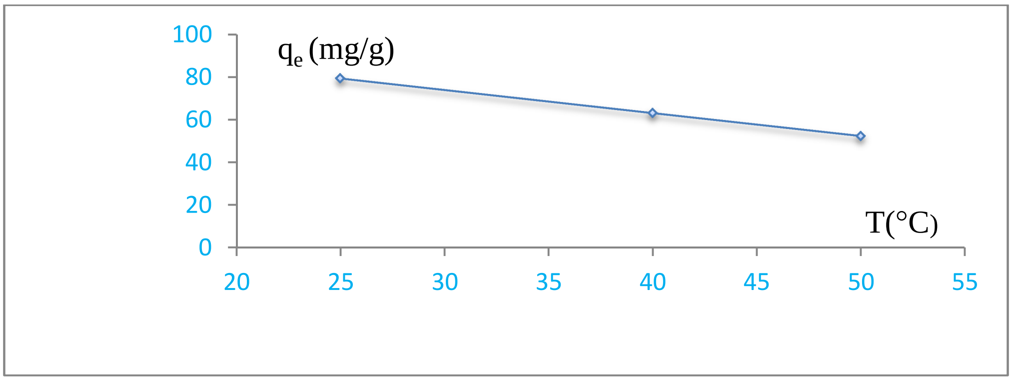

Fig. 7- Effect of temperature on copper adsorption (0.2 g of starch, C_0 = 735 mg/L, contact time = 90 min and pH = 7)

3.7 Mechanism of copper adsorption onto starch

The complexation of copper is confirmed by FTIR-ATR spectroscopy in the wavelength region between 400 and 4000 cm^{-1} The FT-IR spectra of starch/Cu^{2+} reveals adsorptions at O-H (3323-3272 cm^{-1}) stretch, C-H, the skeletal mode vibration of the glycosidic linkage (900-950 cm^{-1}) and the infrared band of water adsorbed in the amorphous parts of starch (1550-1750 cm^{-1}) (Fig. 8) . There is a slight modification of the peaks of hydroxyl groups after the Cu^{2+} adsorption, which highlighted the copper chelation these groups [24-25] and the efficiency of starch for the adsorption of the toxic metal [26].

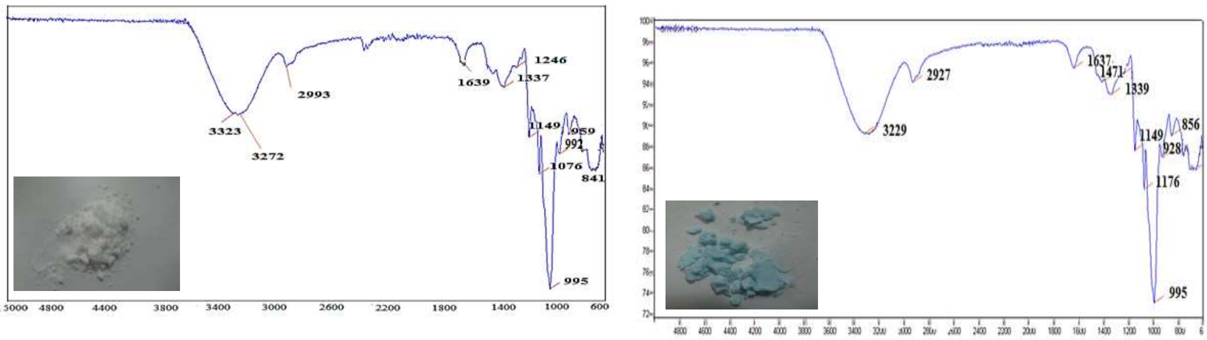

Fig. 8- FTIR spectra and pictures of starch and starch-copper

We proposed a coordinated form of the copper–starch complex (fig. 9), it was also concluded that the most probable retention of Cu^{2+} ions by its association with the functional groups (OH, CO) that act as ligands complexant in chains of polymer [27-28]. The experimental results show the metal ion can be captured from aqueous solutions by starch, which may have practical importance for the precious metal recovery and can help protect lakes and rivers against spills or pollution.

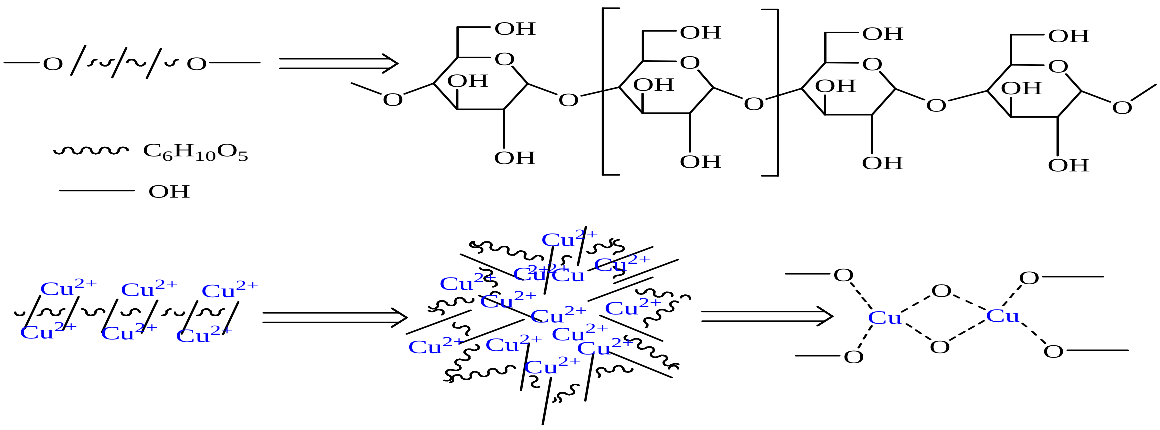

Fig. 9- Proposed mechanism of complex formed between hydroxyl groups of starch and Cu^{2+} ions

CONCLUSION

In summary, the adsorption of copper ions in aqueous solution onto starch as biopolymer was studied. A preliminary mechanism explaining the metal ions with starch was also proposed. Spherical assemblies were obtained through a complexation and/or bridging effect between the hydroxyl groups of starch and the Cu^{2+} ions. The adsorption system is dependent on the Cu^{2+} concentration and follows a pseudo -second-order model. The adsorption equilibrium is reached soon and isotherms are simulated well by the Langmuir model, Freundlich and Temkin.

Acknowledgments
The authors would like to thank the director of laboratory of materials, molecules and applications (IPEST), Professor Manef Abderrabba for the financial support to carry out this research work.

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