Original Article

Removal Of Copper Ion From Aqueous Solutions Using Chitosan Modified

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Received: 11/04/2023; Accepted: 20/09/2023
DOI: 10.47750/pnr.2023.14.04.93

Abstract

Actually, water pollution by heavy metals has become one of the most important environmental problems. The presence of these toxic metals in the environment can be harmful to humans and living species even at low concentration .The removal of heavy metals from wastewater is significant in the protection of the environment.
In this study, natural clay modified with chitosan, was evaluated for removal of heavy metal ions such as Cu (II) from aqueous solutions. The composite (modified natural clay with chitosan) was characterized with Fourier transform infrared (FT-IR) , X-R-ray diffraction (XRD), and X-ray fluorescence analysis. The influences of the analytical parameters (contact time ,initial metal ion concentration, solution pH , and temperature)were investigated in order to estimate their impact on adsorption process. The experiment's results show that maximum adsorption capacity occurred at pH=5.The adsorption yield of Cu (II) increased from 15 to 90 % when the material dosage was increased from 0.05 to 0.5 g/l . Kinetic data were tested using pseudo-first-order and pseudo –second order kinetic models. The best fit was obtained with the pseudo –second order kinetic model. The adsorption maximum metal increases with the increase of initial concentration .Equilibrium data were correlated to Languimir, Freundlich isotherm models .It was best correlated with the Langmuir model. The thermodynamic data showed the adsorption of Cu(II) on this material was exothermic. From this study , it can be concluded that this clay modified with chitosan is an efficacious material for heavy metal removal from wastewater.

Keywords: Chitosan- natural clay- heavy metal -kinetics-.

1. Introduction

Water pollution, largely caused by human activities and industrial chemical waste, represents a significant environmental challenge. Heavy metals, inorganic compounds extensively used in various industries such as cosmetics, agriculture, textiles, pharmaceuticals, and medical diagnostics [1], pose a major concern for wastewater treatment due to their toxicity, carcinogenicity, mutagenicity, and poor biodegradability [2-3]. Over the past few decades, several wastewater treatment methods have been selectively employed based on the industry and effluent characteristics, including adsorption [4,5], coagulation-flocculation, biological treatments, membrane separation, and extraction [6,7]. Adsorption has proven to be highly effective in treating inorganic pollutants. Recently, considerable attention has been given to the study of chitosan and its derivatives, particularly due to their economic attractiveness. Chitosan exhibits interactions with suspended solid particles possessing surface charges in an aqueous medium[8-10]. Among such solids meeting these conditions, clays hold a prominent position as their dispersion in water often results in persistent turbidity, which can only be effectively resolved using a powerful coagulant-flocculant agent like chitosan[11-13]. This study focuses on the preparation of chitosan beads and a clay-based composite (using natural Maghnia clay modified with chitosan) and their application in the adsorption of Cu(II) ions in aqueous media.

2. Experimental

2.1. Materials All chemicals with a purity of greater than 99.9% were purchased as follow:

copper sulfate ($CuSO_4$), chitosan (Low molecular weight) was supplied from Sigma-Aldrich, naturel clay and glacial acetic acid (HAC, 99%) was supplied from Sigma- Aldrich.NaOH was supplied from Fluka. The aqueous solutions used in this work were prepared with distilled water.

2.2. Methods

Chitosan beads were prepared using the following procedure; Chitosan was dissolved in slightly acidified distilled water containing acetic acid under magnetic stirring to prevent agglomeration. The stirring process was carried out for one to two hours. The resulting chitosan aqueous solution was drawn into a syringe and then dropped, in a gelling manner, into an alkaline solution of NaOH (0.5 - 4 M). The gelation in this solution was instantaneous, and the chitosan beads were formed through chain crosslinking. After a maturation period of two hours, the beads were collected, filtered, and washed before being transferred to distilled water. These obtained beads were referred to as hydrogels. After than The chitosan beads are then added drop by drop to the clay suspension. After decantation and filtration, the solid phase is collected. This process is repeated three times. Finally, the collected solid phase is dried in an oven for 24 hours.The schematic representation of the procedure for the preparation of this biopolymer is depicted in the following figures 1 ;

Figure1: The preparation of composite(clay/chitosanebead).

2.3. The adsorption experiments

The adsorption experiments were carried out in batch at room temperature and were carried out by introducing a precisely weighed quantity of adsorbent into a volume of 25 ml of pure solution of Cu(II) at 4.10^{-4}M.and pH = 5.5. The samples were taken at equilibrium time. The colored solution was separated from the adsorbent by centrifugation at 3000 rpm for 3 min. UV measures absorption was measured using a UV/visible spectrophotometer at the wavelength which corresponds to the maximum absorbance of the sample, i.e. λ 820 nm. the residual copper concentration in the reaction mixture was deduced using the calibration curve whose equation is given by:

$$A_{820}=163.\,[Cu^{2+}] \qquad (1)$$

Where A_{820} is the absorbance of the sample at wavelength 820nm.

The amount of adsorption of copper ion was calculated using the following formula:

$$\%\ \text{adsorption} = \frac{(C_i - Ct)100}{C_i} \qquad (2)$$

and

$$q_t = \frac{X}{m} = \frac{(C_i - C_t)V}{m} \qquad (3)$$

Where q_t is the quantity of copper ion adsorbed (mg/g), C_i is the initial concentration (mol/L), C_t is the concentration (mol/L) at t , V is the volume (L) of the aqueous phase, m is the adsorbent mass (g), and X the dye adsorption rate.

3. Results and Discussion

3.1. Characterization of material (clay/chitosane bead)

a) X-ray diffraction analysis:

In the X-raydiffraction analysis of the clay/bead chitosan composite, specific reflections at 2θ = 5.828 and d = 15.15 Å corresponding to the basal spacing d001 were observed, this is higher than that of bentonite clay (14.525 Å) which indicates that chitosan was intercalated into the layer of clay,and the interlayer spaces of the modified clay are likely occupied by chitosan species. This suggests successful intercalation of chitosan into the clay structure. The presence of these specific reflections confirms the incorporation of chitosan and the resulting structural changes in the clay material as shown in figure 2.

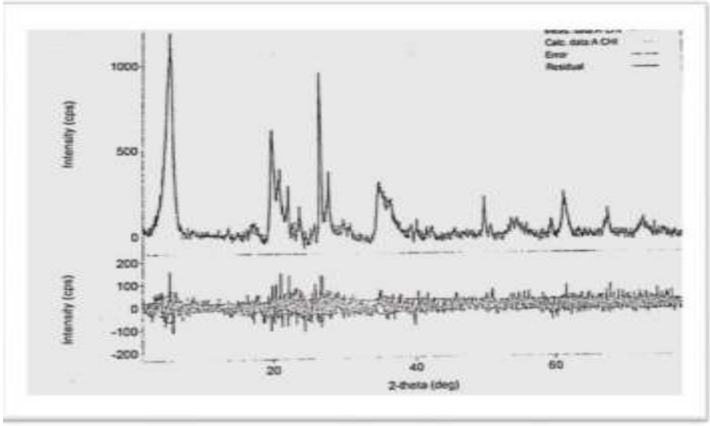

Figure 2: XRD Pattern of Clay-Bead of Chitosan Composite

b) Infrared Spectroscopic Analysis:

FTIR was used to characterize the chemical interactions with Chitosan bead and clay in the composite. The FTIR spectrumin (figure N°3) of the composite shows the characteristic bands of clay at, 1008 and 1130 cm^{-1} due to Si-O vibration modes, and showed additional peaks, including 1635 cm^{-1} NH bending). The absorption band of the carbonyl(C=O) stretching for the secondary amide (amide first band) was observed at 1500 cm^{-1}.

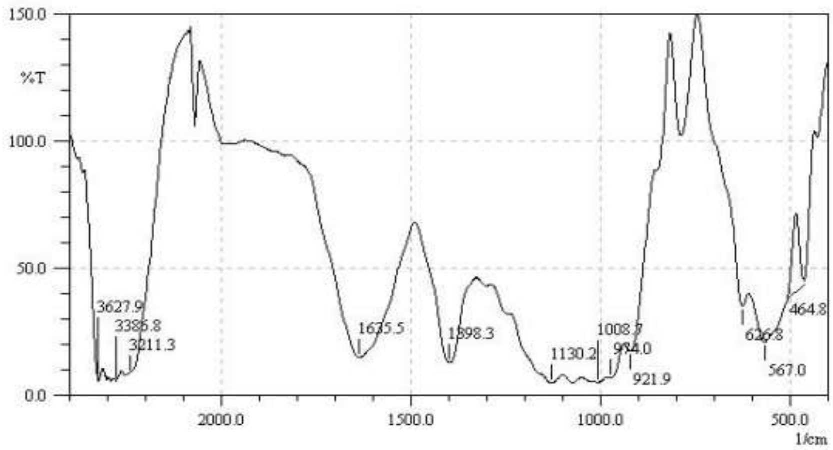

Figure3: Infrared Spectrum of Clay Chitosan.

3.2. Results of the adsorption of Cu (II) ions on the two materials.

In this study, we investigated the influence of several physicochemical parameters such as time of contact, concentration of Cu^{2+},pH and Temperature on the efficiency and adsorption capacity of Cu(II) ions by the two materials, chitosan beads and clay-chitosan composite. The experimental values obtained were modeled using Langmuir and Freundlich isotherm models, as well as pseudo-first-order and pseudo-second-order kinetic models. The results of the parametric study on the adsorption of Cu(II) ions on the two materials showed the following:

1-Contact time:

The results have shown that the adsorption kinetics of Cu(II) is rapid in both cases of study (chitosan beads and chitosan clay), with an eiquilbrium time corresponding to maximum adsorption of 25 minutes as shown in figureN°4below .

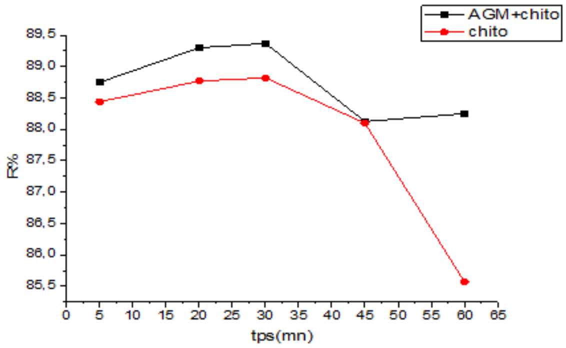

Figure 4: Contact time on the adsorption of Cu (II) ions.
$Ci=4.8.10^{-4}M$ V=20ml .m_{ads}=0.05g,$m_{bille.}$pHi=5 .

2-Effect of concentration:

The study of the effect of Cu (II) ion concentration on the adsorption efficiency was conducted in the range of 8.10^{-5} to $5.6.10^{-4}$ mol/L . The experimental results are presented in the figure N°5 below.

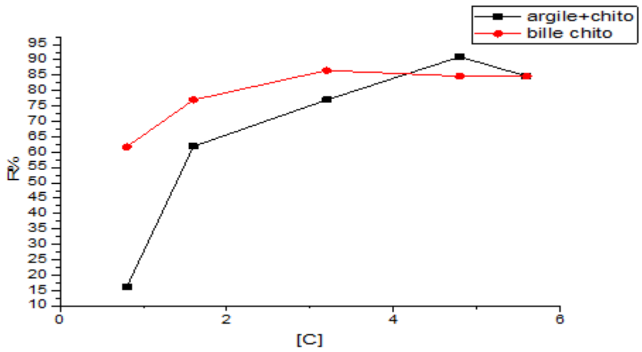

Figure 5: Effect of concentration of Cu (II) ions on the adsorption.
V=20ml .m_{ads}=0.05g,$m_{bille.}$pHi=5 . t=25mn

3- Effect of the pH

The figure N°6 shows that the optimal pH value is around 5, which corresponds to an adsorption efficiency of 65% for clay /chitosane and 55% for chitosane beads. Adsorption is unfavorable in alkaline conditions, which can be explained by the precipitation of copper hydroxide at pH values above 6.

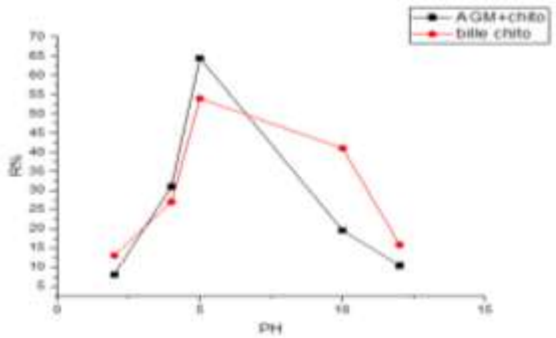

Figure 6: Effect of pH on the adsorption of Cu (II) ions
Ci=4.8.10^{-4}M V=20ml , m_{ads}=0.05g , t=25mn

4- Effect of the temperature.

To investigate the influence of temperature on the adsorption process, experiments were conducted at different temperatures (2, 20, 30, and 50 °C) under the same operating conditions using a water bath and ice for temperature adjustment. The results are compiled and presented in the respective figureN°7 below.

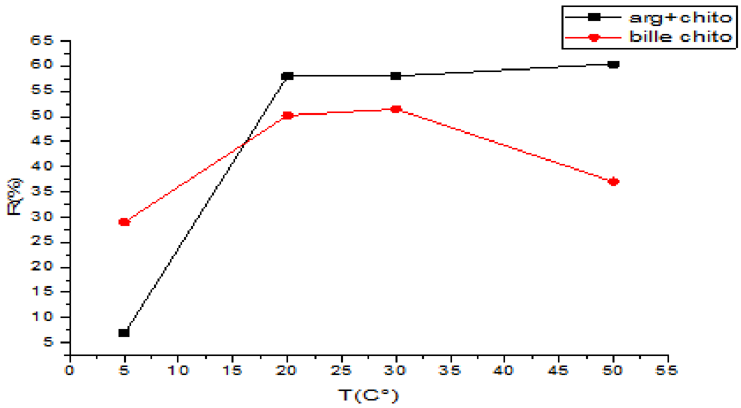

Figure7: Effect of temperature on Cu (II) adsorption by (Beads and ClayCHI)
Ci=4.8.10^{-4}M V=20ml, m_{ads}=0.05g,.pHi=5 . t=25mn

It is observed that the effect of temperature on the adsorbed quantity is significant. In the case of chitosan beads, an increase in temperature leads to a decrease in the adsorbed quantity. However, an increase in adsorption efficiency is observed in the case of chitosan clay. This result can be explained by the increased mobility of Cu(II) ions with increasing temperature, as well as the physical nature of adsorption, which is enhanced at lower temperatures. The decrease in efficiency for the chitosan beads may be attributed to changes in the physical properties of the beads.

3.3 Adsorption Kinetic Model of copper ion

In order to better understand the adsorption mechanism of copper ion Cu^{2+} onto the mixtures (clay) and (clay - chitosan beads), the linear forms of the pseudo-first-order and pseudo-second-order kinetic models were used, considering the equations given in [14]. The values of the adsorbed quantities qe, kinetic constants k_1 and k_2, and the regression coefficients R^2 are reported in Table 2.
The pseudo-first-order kinetic model (Lagergren's equation) differential equation that describes the pseudo-first-order kinetic model is given as:

$$\frac{d_{qt}}{dt} = k_1(q_e - q_t) \quad \textbf{(4)}$$

This equation may be rearranged into a linear form:

$$\ln(q_e - q_t) = \ln(q_t) - k_1 t \quad \textbf{(5)}$$

Similarly:

$$\frac{d_{qt}}{dt} = k_2(qe - qt)^2 \quad (6)$$

This equation can also be rearranged to obtain the linear form given below:

$$\frac{1}{q_t} = \frac{1}{q_e^2 K_2} + \frac{t}{q_e} \quad (7)$$

Table 2: Kinetic parameters for the adsorption of Cu^{2+} onto Clay and Clay-bead chitosan
Pseudo-first-order kinetic model

	Qe(mg/g)	k_1	R^2
Bead of Chitosane	**35.71**	**0.046**	**0.469**
Clay-Chitosane	**37.18**	**0.042**	**0.467**

Pseudo-second-order kinetic model;

	Qe(mg/g)	**k_2**	R^2
Bead of Chitosane	35.71	0.0052	0.998
Clay-chitosane	37.18	0.0035	0.998

According to Table 2, the experimental data are better described by the pseudo-second-order kinetic model. Consequently, based on the obtained experimental data, one may assert that the pseudo-second-order kinetic model is more appropriate for the evaluation of the adsorptive removal of copper ion from aqueous solutions by both adsorbents.

3.4 Modeling of copper ion adsorption isotherm

The amount of copper ion adsorbed at a state of equilibrium (qe) (mg/g) was calculated using the following equation[15]:

$$qe = V\,(C_0 – Ce)/m \quad (8)$$

where C_0 (mg/L) is the initial copper ion concentration, C_e (mg/L) the equilibrium concentration of copper ion in solution, V (L) the volume of solution, and m (g) is the mass of adsorbent.

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites [16] .

If copper ion adsorption conforms to the Langmuir model, the adsorption process can be expressed as:

$$\frac{1}{Q_e} = \frac{1}{qm} + \frac{1}{k_l Q_m} * \frac{1}{C_e} \quad (9)$$

Where Q_m(mg/g) is the maximum adsorption capacity and k_L(L/g) is the Langmuir constant related to the adsorption equilibrium.

The Freundlich model is usually adopted for heterogeneous adsorption [16]. One of its limitations is that the amount of adsorbed solute increases indefinitely with the concentration of solute in the solution. This isotherm can be described as:

$$\ln Q_e = \ln kf + \frac{1}{n}\ln C_e \quad (10)$$

Where K_f and n are the physical constants of the Freundlich isotherm,

Experimental values of n are usually greater than unity and this means that the forces between the adsorbed molecules are repulsive. In addition, the closer the n value of the Freundlich sorption equations is to zero, the more heterogeneous is the system [16].

The isotherm parameters for the adsorption of copper ion onto materials obtained are listed in Table N°3. The results show the Langmuir isotherm to be most appropriate for copper ions indicating that the monolayer of copper molecules covers the clay/beadchitosane surface.

Table N°3 : Isotherm constants and correlation coefficients for the adsorption of copper ions Cu^{2+} on clay-chi and bead of chitosane.

Material/model of isotherm	Freundlich : $\ln Q_e = \ln kf + \frac{1}{n}\ln C_e$			Langmuir : $\frac{1}{Q_e} = \frac{1}{qm} + \frac{1}{klQ_m} * \frac{1}{C_e}$		
Constantes	n	$k_f\,(\frac{1}{g})$	R^2	q_m(mg/g)	kl($^1/_g$)	R^2
Clay- chitosane	2.15	1.41	89	45	0.97	94
Bead of chitosane	2.33	3.23	91	67	1.56	97

3.5 Thermodynamic study

The thermodynamic adsorption of copper ion was measured by the formula:

$$K_d = V/m\left[(C_0 - C_{eq})/C_{eq}\right] \quad \textbf{(11)}$$

$$\Delta G^{\circ} = -\mathrm{RT} \ln K_d \quad \textbf{(12)}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^0 \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^0 \quad \textbf{(13)}$$

$$ln\ \mathrm{K_d} = (-\Delta H^{\circ}/\mathrm{R})\ 1/\mathrm{T} + \Delta S^{\circ}/\mathrm{R} \quad \textbf{(14)}$$

Where:
K_d : the adsorption distribution coefficient; C_{eq} and C_0 : sample concentration at the equilibrium and initial phase (mg/L); R and T ; the gas constants and absolute temperature (K).
The values of the thermodynamic parameters are presented in the tableN°4.

TableN°4: Thermodynamic parameters of Cu (II) adsorption on clay-chitosane and beads of chitosane.

Thermodynamic parameters	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° kJ mol^{-1} 278/293/323 K°			
Bead of Chitosane	**-5.82**	**10.56**	**-2.8**	**-2.7**	**-2.4**	
Clay/chitosane	**-4.1**	**8.73**	**-1.6**	**-1.5**	**-1.2**	

As seen in Table N°4, the ΔG°values are negative for all the experimental temperatures indicating that copper ion adsorbed onto bead of chitosane and clay/chitosane was spontaneous and that the system did not gain energy from an external source.

In adsorption processes, a ΔG°value in the range -20 to 0 kJ/mol correspond to spontaneous physical processes, while with a value in the range of -80 to -40 kJ/mol corresponds to chemisorption [17].

The recorded results in the table show negative values of ΔH, confirming that the adsorption of Cu(II) on the tested materials, chitosan beads and clay/chitosan, is an exothermic process. The positive values of entropy indicate that the adsorption of Cu(II) on both materials is accompanied by an increase in disorder in the system. Furthermore, the negative values of the free energy ΔG demonstrate that the adsorption process of copper ions is spontaneous.

Conclusion

The main objective of this study was to investigate the application of chitosan beads and chitosan-modified clay in the adsorption of **Cu(II)** ions. The key findings demonstrated a strong affinity of Cu(II) ions towards the materials (beads, chitosan-modified clay). Through **IR** and **XRD** analysis, it was confirmed that chitosan particles were successfully modified, and that the chitosan beads exhibited homogeneous spherical shapes.

The results of the parametric study on the adsorption of Cu(II) ions on the two materials showed the following:

- The contact time was 25 minutes for both materials, with an adsorption rate of 90%.
- Intense agitation had a detrimental effect on the adsorption of Cu(II) ions by the beads.
- The optimal pH for both cases was pH 5.
- The kinetics of adsorption was found to follow the pseudo-second-order kinetic model for both types of materials.
- The effect of temperature showed that an increase in temperature influenced the adsorption phenomenon. The removal efficiency of Cu (II) ions slightly decreased, suggesting an exothermic process. (ΔH°<0).
- The thermodynamic study revealed that the retention process is spontaneous (negative free energy).
- The results show the Langmuir isotherm to be most appropriate for copper ions indicating that the monolayer of copper molecules covers the clay/bead chitosane surface.
- In both cases, it can be concluded that the adsorption is of a physical nature.
- From this study, it can be concluded that chitosan-modified clay and chitosan beads can be used for the adsorption of heavy metals.

In conclusion, the findings from this study highlight the efficacy of clay-chitosan modification as an effective means for removing heavy metals, particularly Cu(II), from wastewater. The utilization of this composite material holds promise for addressing water pollution issues associated with heavy metal contamination, thereby contributing to the protection and preservation of the environment.

From this study, it can be concluded that this clay modified with chitosan is an efficacious material for heavy metal removal from wastewater.

Acknowledgements

The authors gratefully acknowledge the editor and reviewers for their extensive revision and comments on earlier drafts of this paper.

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