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Biosorption of heavy metals by chitin and the chitosan

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ABSTRACT

In the present work, the usefulness of chitin and chitosan has been investigated for the removal of Zn²⁺, Cd²⁺ and Cu²⁺. Kinetic data and equilibrium sorption isotherm were measured in batch conditions. The influence of different experimental parameters such as time contact, initial concentration of zinc, chitin mass, initial pH of solution and temperature on the kinetics of zinc removal was studied. The main parameters that play an important part in removal phenomenon were initial zinc concentration, chitin mass and initial pH of solution. The process follows a pseudo second-order kinetics. The zinc uptake of chitin was quantitatively evaluated using sorption isotherms. In order to describe the isotherm mathematically, the experimental data of the removal equilibrium were correlated by either the Langmuir or Freundlich equations. Results indicated that the Langmuir model gave a better fit to the experimental data than the Freundlich equation. Scanning electron microscopy dispersed analysis for zinc-equilibrated chitin, demonstrated that zinc existed on its surface. The biosorption of the metals studied by chitin and the chitosane varies in the same order : Cu (II) > Cd (II) > Zn (II) and the quantities biosorbed in equilibrium by the chitosan are higher than that of chitin.

Keywords: Biosorption, Kinetic, heavy metals, chitin, chitosan.

INTRODUCTION

Aqueous effluents emanating from many industries, contain dissolved heavy metals. If these discharges are emitted without treatment, they may have an adverse impact on the environment [1]. Higher awareness of the ecological effects of toxic metals and their accumulation through food chains has prompted a demand for purification of industrial waste waters prior to their discharge into the natural water bodies and increasing interest has been shown in the removal of heavy metals. The search for inexpensive, but cost effective technologies, for heavy metal removal from industrial wastewaters loaded with heavy metal ions normally leads to the use of materials of biological origin as sorbents. Many technologies can eliminate or reduce the presence of these metals in industrial effluents, being the most practical of them precipitation and coprecipitation, electrodeposition and electrocoagulation, cementation, membrane separation, solvent extraction, ion-exchange, sorption and biosorption [2]. Nowadays, biosorption is a strongly explored technique; it is defined as passive, not involving metabolically mediated processes, with the property to bind metals by living or dead biomass [3]. Considerable attention has been paid to the recovery and removal of valuable heavy metal ions from industrial and municipal wastewater by using various biosubstances or natural products, particularly because of the low cost and high availability of these materials, without needing arduous regeneration process for reuse, being capable of binding heavy metals by sorption, chelation and ion exchange processes [4,5]. These low-cost abundant natural materials such as chitin, chitosan, alginate, cellulose, peat and biomass require little processing and are abundant in nature, mainly when obtained as by-products and waste from industry [6]. Chitin, a natural product consisting of N-acetyl glucosamine units linked by β (1→4)

bonds, is one of the most abundant polysaccharides in the world, synthesized by an enormous number of living organisms and found as a structural component of the exoskeletons of crustaceans, the cuticles of insects, and the cell walls of fungi and yeast [7]. Chitin carries one linear amino group per glucose ring, thus making electron pairs available for coordination. It behaves as a Lewis base [8].

Chitosan, a partially N-deacetylated product of chitin, is an important natural biopolymer due to its biocompatibility and biodegradability, with broad applications in wastewater treatment

in chemical, biomedical and pharmaceutical applications and in agriculture and biotechnology [9]. Its high nitrogen atom contents allows uptake of several metal ions through various mechanisms such as chelation, electrostatic attraction or ion-exchange, since both amine and hydroxyl groups act as chelating sites for metal ions [10].

The objective of this paper is to obtain the basic information for the design of sorption equipment, kinetic data and equilibrium in batch systems. During this investigation, the effect of different experimental parameters such as as time contact, initial concentration of zinc, chitin mass, initial pH of solution, agitation speed and temperature, on the removal kinetics was also studied. In order to describe the isotherm mathematically, the experimental data of the removal equilibrium were correlated by either the Langmuir or Freundlich equations. Spectroscopic techniques SEM (scanning electron microscopy) were used to characterize chitin, before and after equilibration with the zinc ion, in an attempt to better understand the mechanism of the removal. The results obtained may contribute to a better understanding or application of the sorption phenomena at the liquid/solid interface.

We also determined the affinity of chitin and the chitosan according to three metals studied separately.

MATERIALS AND METHODS

Chitin and chitosan produced from shrimp carapaces, were used throughout this work without any preliminary purification. Metal solutions of desired concentration were prepared from $ZnSO_4 \cdot 7H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and $CuSO_4 \cdot 5H_2O$, by dissolving the exact quantities of metal salts in distilled water.

2.1. Biosorption kinetics

For metal removal kinetics studies, 0.6 g of biosorbent was contacted with 300 ml of metal solutions in a beaker agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature of 25°C. In all cases, the working pH was that of the solution and was not controlled. At appropriate time intervals, stirring was briefly interrupted while 1 ml volumes of supernatant solutions after decantation were pipetted from the reactor and were analyzed to determine the residual metal concentration in the aqueous solution. This was done using a AURORA AI 1200 atomic absorption spectrophotometer. The metal uptake q (mg ion metal/g sorbent) was determined as follows :

$$q = (C_0 - C_t) \cdot v / m \quad (1)$$

where C_0 and C_t are the initial and final metal ion concentrations (mg/l), respectively, v is the volume of solution (ml), and m is the biosorbent weight (g) in dry form.

2.2. Biosorption isotherm

The equilibrium isotherms were determined by contacting a constant mass of biosorbent with a range of different concentrations of metal solutions

RESULTS AND DISCUSSION

3.1. Biosorption kinetics

Different parameters related to the biomaterial, to metal and the medium can influence the kinetics of zinc removal by chitin. In this context, the influence of various experimental parameters such as time of contact, initial concentration of zinc, mass of chitin used, initial pH of solution, temperature and agitation speed, on the kinetics of zinc removal have been studied with a goal of optimization.

3.1.1. Effect of contact time

According to figure 1, the kinetics of zinc removal by chitin presents a shape characterized by a strong increase of the capacity of zinc removal by chitin during the first few minutes of contact between the solution and chitin, follow-up of a slow increase until a state of equilibrium is reached. The necessary time to reach this equilibrium is about 6 h and an increase of removal time to 24 h did not show notable effects. At equilibrium, the amount of zinc

biosorbed by chitin is about 5.35 mg/g. These observations are in agreement with the works of Wightman and coll [11].

During the course of zinc removal by chitin, we noticed an evolution in the value of the initial pH of the solution from 5.5 to 5.98 at the equilibrium. In order to investigate the reason of this pH value change, experiments were performed with the chitin tested in distilled water under the same conditions in absence of metal ions. Initial pH value of solution exhibited an increase from 6 to 6.95 that can be interpreted as a possible fixation of H_3O^+ ions by the negative groups present on the biosorbent surface. Concerning the decrease in its value in the presence of zinc ions, it can be interpreted by a competition between zinc ions and H_3O^+ [12] for binding sites. Similar observations have been made by other researchers [13,14].

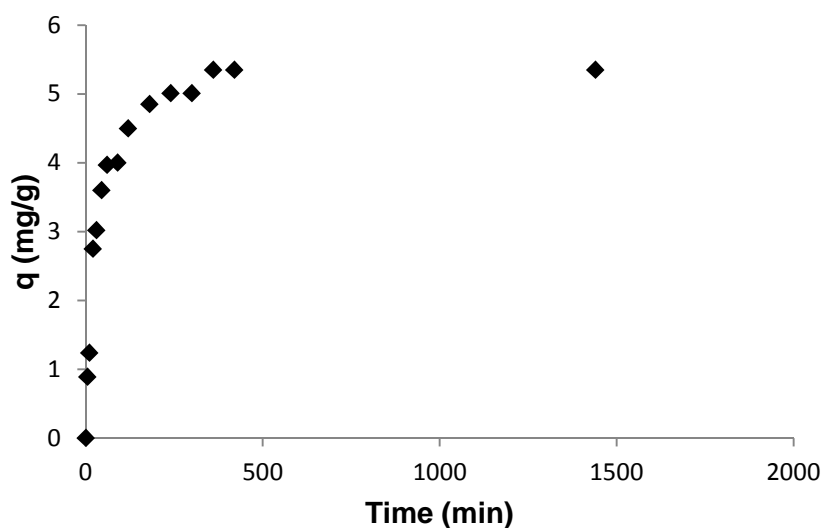


Fig. 1: Kinetics of zinc sorption by chitin

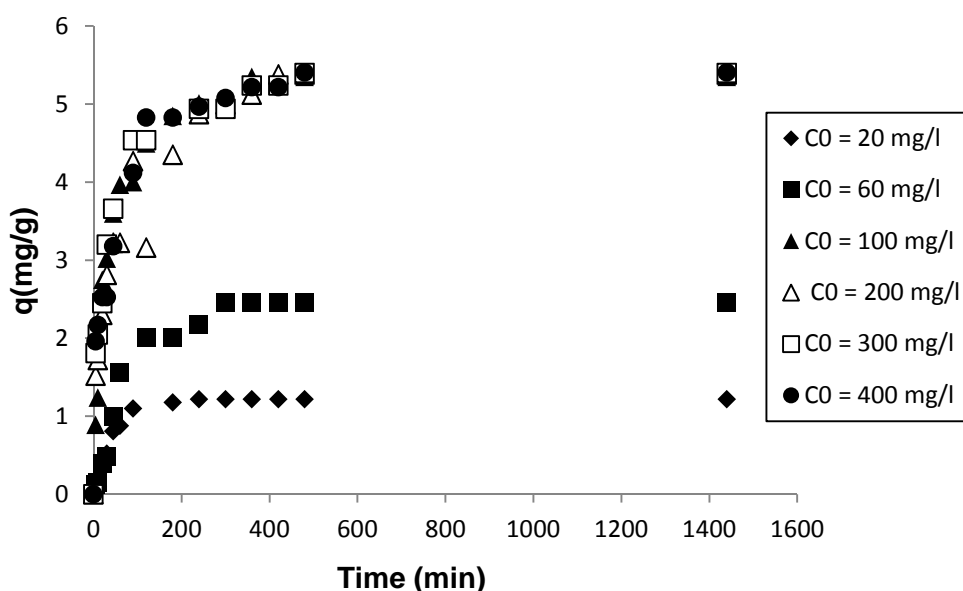


Fig. 2 : Effect of initial zinc concentration on the sorption kinetics of zinc by chitin

3.1.2. Effect of initial zinc concentration

Several experiments were undertaken to study the effect of varying the initial zinc concentration (20, 60, 100, 200, 300 et 400 mg/l), on the zinc biosorption kinetics from solution by chitin. The results obtained are shown in figure 2, and indicate that the obtained curves have the same shape. The necessary time to reach equilibrium is variable according to the initial concentration in zinc : about 4 h ($C_0=20$ and 60 mg/l), 6 h ($C_0=100$ mg/l) and 8 h ($C_0=300$ and 400 mg/l). The amount of zinc biosorbed at the equilibrium increases with the initial zinc concentration from 20

to 100 mg/l, this quantity remains constant when the initial metal concentration passes from 100 mg/l to 400 mg/l. This can be explained that starting from a certain quantity of metal fixed the sites of biosorption of biosorbant material used are saturated. During the phenomenon of zinc removal, we also noticed an increase of the initial pH of the solution for all studied concentrations, without reaching the pH value of zinc precipitation.

3.1.3. Effect of chitin mass

In the goal to determine the necessary chitin quantity for a maximal removal of zinc, the effect of chitin mass on the kinetic of zinc removal was studied. Figure 3 shows that the capacity of zinc sorption at equilibrium by chitin increases with the quantity of chitin introduced (0.1-0.6 g), this can be explained by the fact that more the mass increases, more the surface of contact offered to the sorption of zinc becomes important. Beyond 0.6 g of chitin, this capacity of zinc does not nearly rise, and the maximal quantity at the equilibrium of zinc removal by chitin is about 5.35 mg/g. These observations are in agreement with the works of Benguella [15]. The smallest chitin mass (0.1 g) appears to have reached equilibrium after 2 h, while the higher chitin masses (0.6 g) have achieved equilibrium after 7 h. As above, the same phenomenon in the initial pH variation during the sorption experiment was observed.

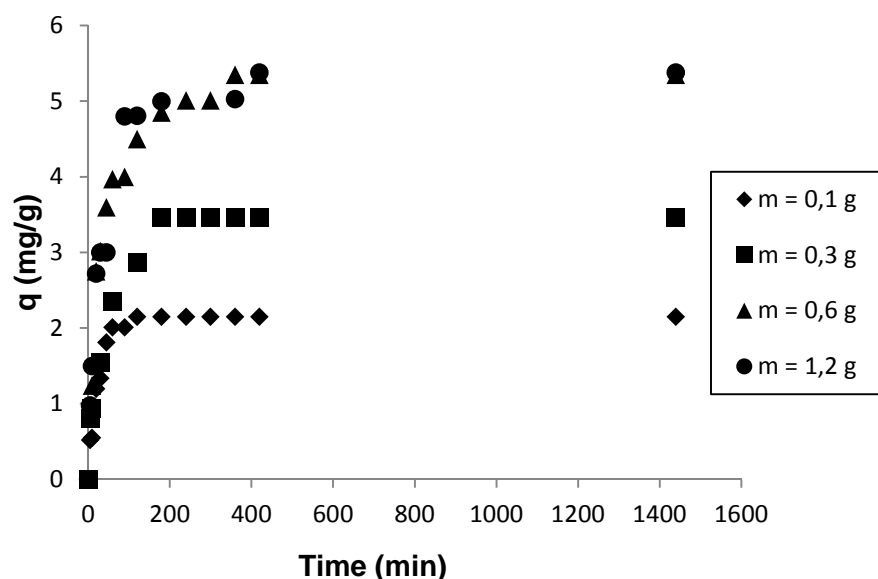


Fig. 3. Effect of chitin mass on the sorption kinetics of zinc by chitin

3.1.4. Effect of initial pH

The effect of pH in the solution on the removal efficiency of Zn (II) by chitin was studied at different pH values in the range 2–7. As shown in figure 4, the initial pH of zinc solution has an influence on the kinetics of zinc biosorption by chitin. The necessary time to reach equilibrium was in the range of 2–4 h depending on initial pH of solution. The amount of zinc biosorbed at the equilibrium increases with the initial pH value. These observations are in agreement with the works of other authors [16]. During the course of zinc removal by chitin, we noticed an increase of the pH of the solution with the initial pH value 2 and 4, thus translating a competition between Zn^{2+} ions and H_3O^+ for binding sites of chitin. Regarding the initial pH of solution equal to 7, the pH decreases in the course of time, that can be explained by a deprotonation of the sites which make more accessible for the biosorption. These same reports were observed by Benguella [15].

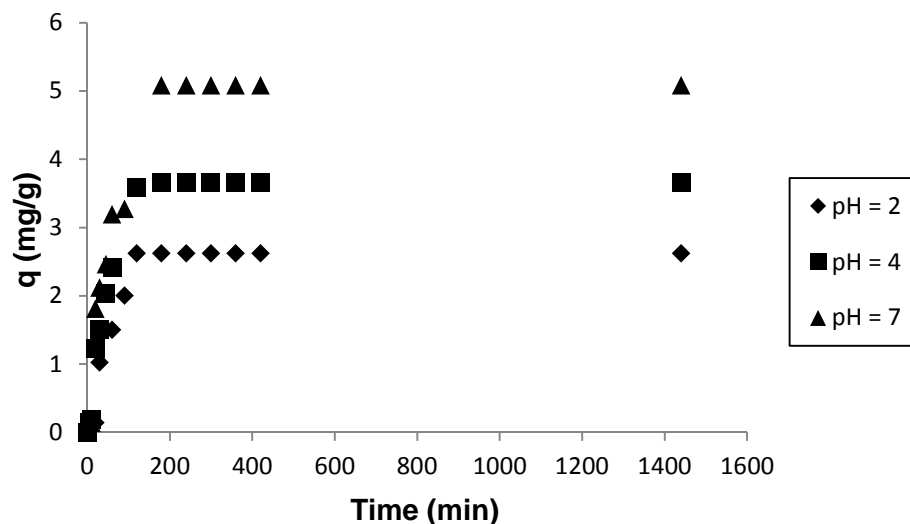


Fig. 4. Effect of initial pH on the sorption kinetics of zinc by chitin

3.1.5. Effect of temperature

To study the effect of this parameter on the kinetics of zinc sorption by chitin, we selected the following temperatures : 10, 20, 25, 30 and 40 °C. The results obtained are presented in figure 5 indicate that an increase of the temperature in the interval 10–30 °C deals with an increase in the capacity of zinc sorption at equilibrium : 3.12 mg/g at 10 °C and a high capacity of sorption about 5.39 mg/g between 20 °C and 30 °C. Beyond 30 °C, we notice a reduction in the capacity of zinc sorption at equilibrium : 3.88 mg/g for 40 °C. The reduction of the removal in the interval of temperature 30–40 °C means that the process of zinc sorption by chitin is exothermic as it is the case for the majority of gas adsorption processes. The time necessary to reach equilibrium of sorption for the different studied temperatures is about 4–7 h. According to the literature, results of study of the effect of the temperature on the phenomenon of sorption for different metal–biomaterials systems are disparate. An increase of the temperature, in the range 5–45 °C, rose the sorption [17], while variations of temperature in the range 5–25 °C did not affect the sorption [18]. As mentioned above, the same phenomenon in the initial pH variation during the sorption experiment was observed.

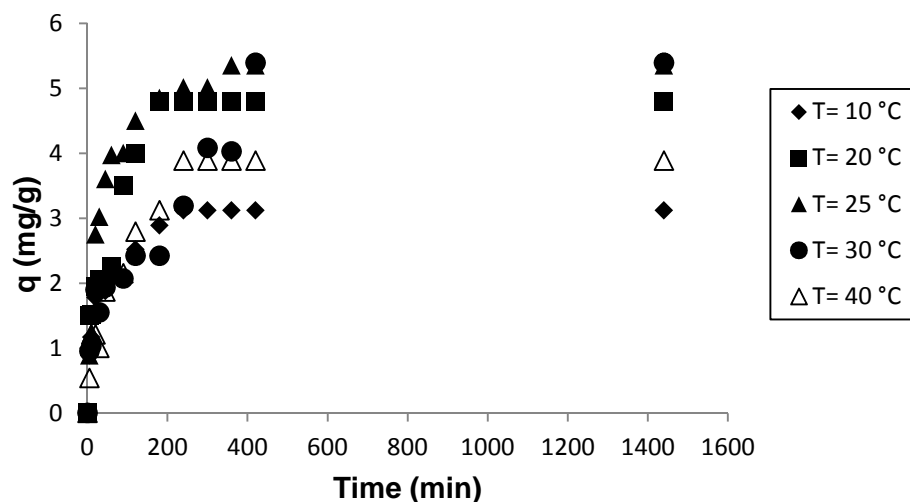


Fig. 5. Effect of temperature on the sorption kinetics of zinc by chitin

3.2. Equilibrium of biosorption

3.2.1. Isotherm of biosorption

To study equilibrium of zinc removal by chitin, the approach more used frequently consists in measuring the isotherm of sorption. It represents the quantity of metal removed (q_e) against the equilibrium concentration of metal ion (C_e) in the solution, and it corresponds to the equilibrium distribution of metal ions between the aqueous and solid phases when the concentration increases.

As shown in figure 6, the isotherm for zinc sorption is of Langmuir's type according to the classification of Brunauer [19] and of L type according to the classification of Giles [20].

From the graph of this isotherm, the maximum capacity of zinc removal by chitin is about 5.40 mg/g.

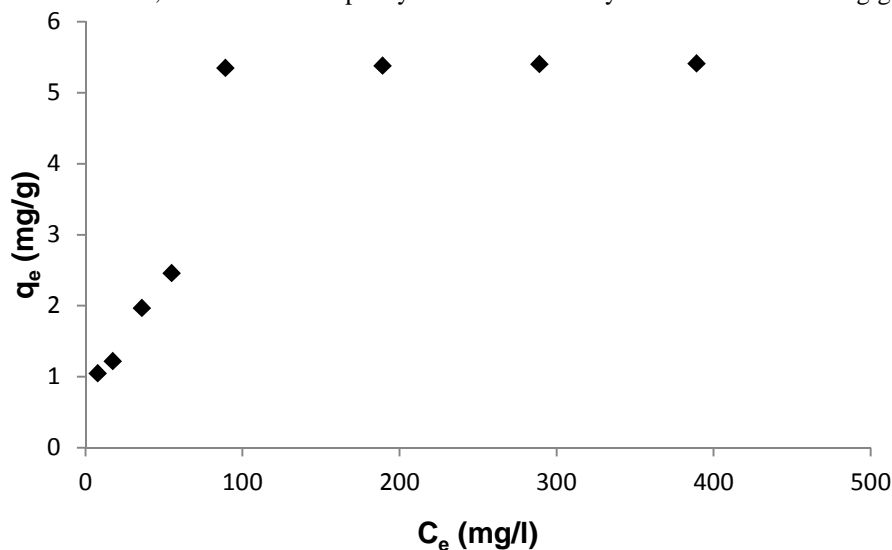


Fig.6. Isotherm of zinc biosorption by chitin at 25 °C

3.2.2. Modelling of isotherm of zinc biosorption

Two isotherm equations have been tested in the present study, namely, Langmuir [21] and Freundlich [22]. This modelling permits us to determine the maximal capacity of biosorption. The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the regression; i.e. the isotherm giving an R^2 value closest to unity is deemed to provide the best fit.

(a) The Langmuir model has the following form :

$$q_e = q_m b C_e / (1 + b C_e) \quad (2)$$

where q_e is the amount of metal ion sorbed at equilibrium per gram of adsorbent (mg/g), q_m is the maximal metal sorption capacity of sorbent material (mg/g), C_e the equilibrium concentration of metal ion in the solution (mg/l) and b is the constant of equilibrium (l/mg) depending on temperature and the applied conditions. This equation can be linearised under the following shape :

$$C_e/q_e = 1/b q_m + C_e/q_m \quad (3)$$

If the equation of Langmuir is valid to describe the experimental results, it must verify the linearised shape of the basis equation, in system of coordinates $C_e/q_e = f(C_e)$, that will permit to obtain the constants q_m and b from the intercepts and slopes.

(b) The Freundlich model has the form:

$$q_e = K C_e^n \quad (4)$$

where q_e and C_e are as described before, K and n are the positive constants depending on the nature of system solute-sorbent and temperature, $n < 1$. This equation can be linearised under the following form :

$$\ln q_e = \ln K + n \ln C_e \quad (5)$$

If this equation is verified with data of sorption equilibrium, we must obtain a straight line in the system of coordinates $\ln q_e = f(\ln C_e)$, the slope and the intercept to the origin give the values of constants n and K respectively.

Results of the modelling of the isotherm of zinc sorption by the chitin, according to either Langmuir and Freundlich models, are represented in Figures 7 and 8 respectively, hence the Table 1 summarizes the model parameters determined by least squares fit of the experimental sorption data, along with correlation coefficients.

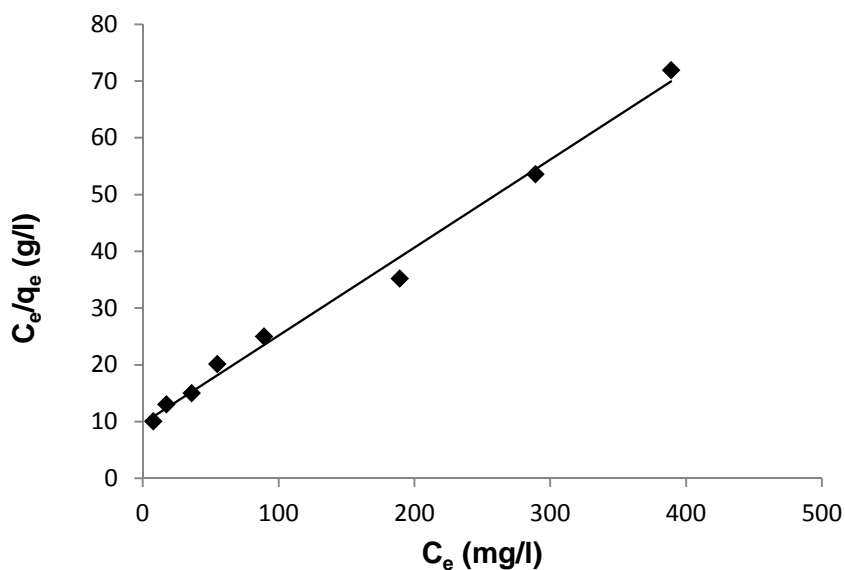


Fig.7. Modelling of isotherm of zinc biosorption by chitin according to Langmuir model

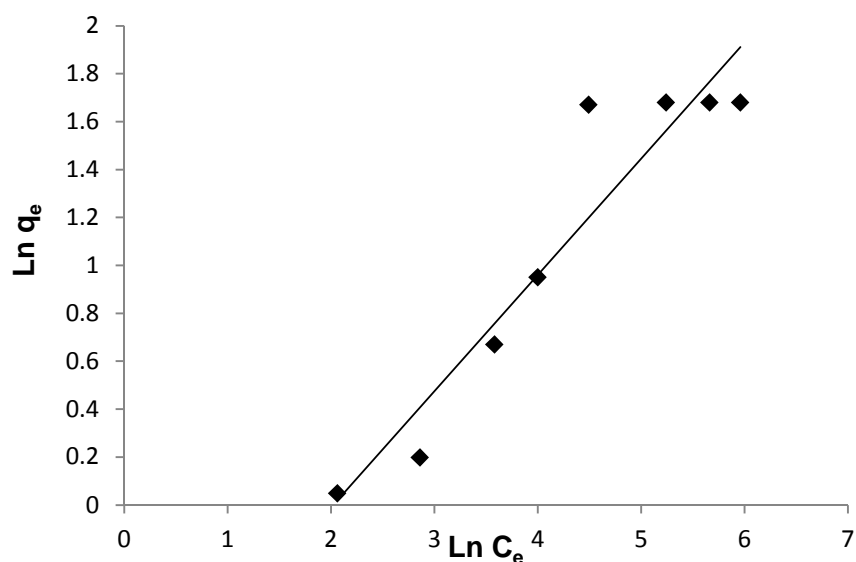


Fig.8. Modelling of isotherm of zinc biosorption by chitin according to Freundlich model

Table 1 : Summary of isotherm parameters for zinc sorption by chitin

Parameters of the Langmuir model	q_m (mg/g)	b (l/mg)	R^2
	5.86	0.027	0.992
Parameters of the Freundlich model	n	K	R^2
	0.418	0.374	0.935

Whatever be the linearized shape of the Langmuir equation used, it appears that the Langmuir model best fits the experimental results over the experimental range with good coefficients of correlation. According to the values obtained from parameters q_m and b , presented in Table 1, we notice that they are nearly identical ($q_m = 5.86$ mg/g). According to the coefficients of correlation obtained, we deduct that the model of Freundlich is not adequate for modelling the isotherm of removal of zinc by chitin in all the studied concentration domain, which is beyond our objective.

3. Scanning electron microscopy (SEM)

Electron microscopic examination of chitin, before and after metal removal, was undertaken in order to locate the active sorptive sites of the chitin. The scanning electron microscopic (SEM) micrographs of chitin, before and after equilibration with a metal solution, are shown in Figure 9.

The SEM micrograph in Figure 9a shows the presence of " holes " on surface which correspond to the pores present on chitin.

Figure 9b shows the presence of white nodules indicating the presence of heavy elements such as : zinc.

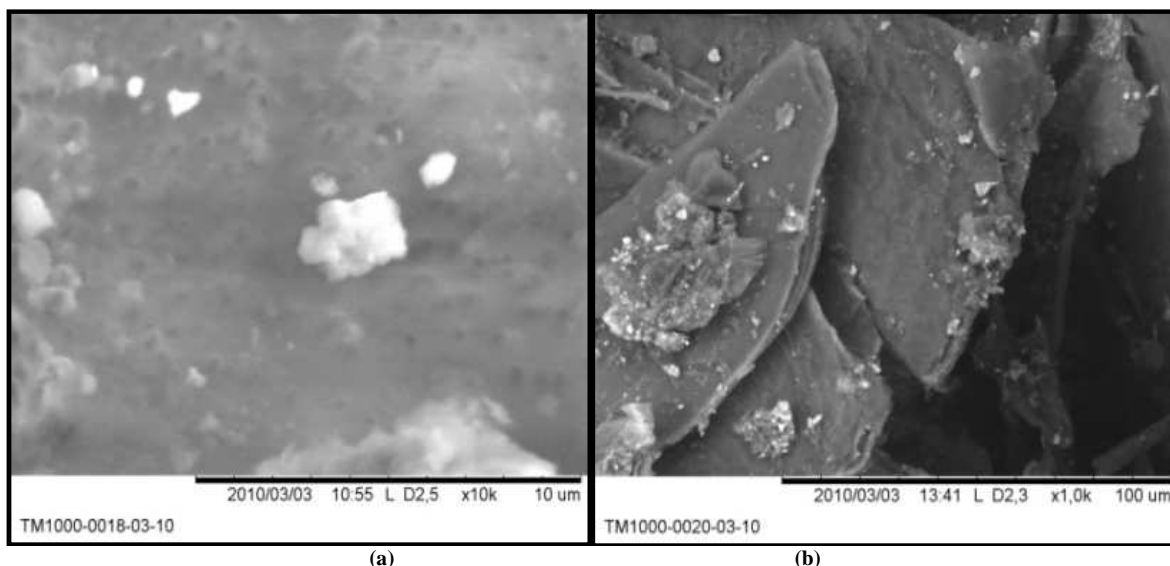


Fig. 9. SEM micrographs of chitin: (a) in the absence of zinc, (b) after zinc sorption

4. Biosorption kinetics of zinc, cadmium and copper by chitin

Figure 10, shows the kinetics of zinc, cadmium and copper biosorption by chitin. They take similar forms characterized by a strong increase of the quantity of metal removal by chitin during the first few minutes of contact between the solution and chitin, follow-up of a slow increase until a state of equilibrium is reached. The necessary time to reach this equilibrium is about 6 h (5.35 mg/g) for zinc, 4 h (13.27 mg/g) for cadmium and 3 h (20.5 mg/g) for copper. The biosorption of the metals studied by chitin varies in the same order : Cu (II) > Cd (II) > Zn (II).

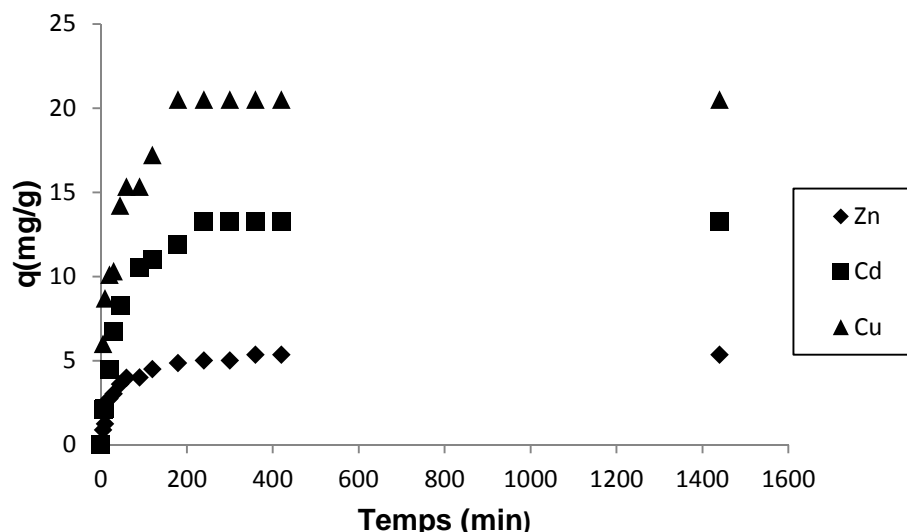


Fig. 10. Kinetics of zinc, cadmium and copper biosorption by chitin

5. Biosorption kinetics of zinc, cadmium and copper by chitosan

The results obtained are represented in Figure 11, shows that the three curves obtained take the same form characterized by a strong increase of the quantity of metal removal by chitosan during the first few minutes of

contact between the solution and chitosan, follow-up of a slow increase until a state of equilibrium is reached. The necessary time to reach this equilibrium is about 5 h (19.31 mg/g) for zinc, 4 h (37.5 mg/g) for cadmium and 2 h (44.7 mg/g) for copper. The biosorption of the metals studied by chitosan varies in the same order : Cu (II) > Cd (II) > Zn (II).

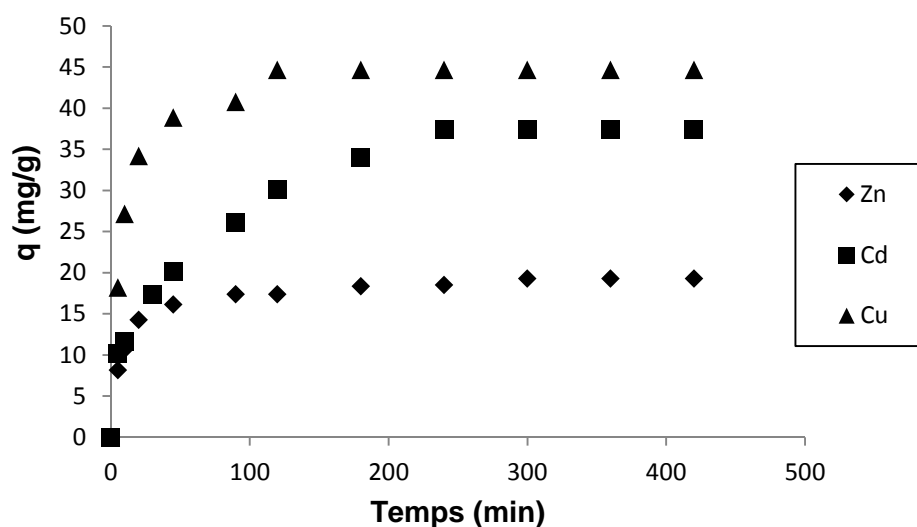


Fig. 11. Kinetics of zinc, cadmium and copper biosorption by chitosan

CONCLUSION

The biosorption of zinc in solution by chitin is influenced by various parameters, such as initial concentration of zinc and chitin mass. Thus for acid pH, the competition between the protons and the metal ion reduced the performances of biosorption of chitin, whereas an increase in its value up to 7, improves considerably the capacity of biosorption of zinc.

The biosorption of the metals studied by chitin and chitosan varies in the same order : Cu (II) > Cd (II) > Zn (II) and the quantities biosorbed in equilibrium by the chitosan are higher than that of chitin.

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