SORPTION OF CADMIUM FROM AQUEOUS SOLUTIONS BY CHEMICALLY PRE -TREATED CHITIN

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ABSTRACT:

Chitin was chemically pre-treated in order to improve its sorption performance to metallic ions in wastewater. The pre-treated chitin was evaluated as sorbent material for cadmium ions in aqueous solutions by using equilibrium isotherms and kinetics of adsorption. Except the pre-treatment I, the sorption rates of cadmium are higher on the pre-treated chitin than of the untreated ones. The maximum cadmium uptake of pre-treated chitin was quantitatively evaluated using sorption isotherms. Langmuir model gave a good fit to the experimental equilibrium data. Before the pre-treatment, chitin exhibited relatively low sorption to cadmium ions. The pre-treated chitin showed an increased sorption, due to the partial transformation of amide to amine groups. The maximum sorption capacities of cadmium on the pretreated chitin were 20.68 mg/g and 16.27 mg/g at pH 8 (pretreatments III and II respectively), 18.39 mg/g with NaOH 0.1M, which were higher than that of the untreated chitin 14.21 mg/g.

Key words: cadmium, sorption; chitin; pre-treatment.

INTRODUCTION

Industrial wastewater effluents bearing heavy metals, pose a serious problem for the environment. Cadmium has been well recognized for its negative effect on the environment where it accumulates readily in living systems (Hutton & Symon [1], Nriagu [2]). Various studies have shown that a variety of biological natural origin materials such as chitin has the aptitude to remove important quantities of metallic cations from simple solutions (Muzzarelli and Tubertini [3], Eiden et al. [4], Maruca et al. [5], Tsezos & Volesky [6,7], Tsezos [8], Billie & Wightman [9], Bell et al. [10], Kim et al. [11], Gonzalez-Davila at al. [12], Yang and Zall [13], Santana-Casklano & Gonzalez-Davilla [14], Chui and al. [15], Muzzarelli [16,17], Benguella [18], Benguella & Benaissa [19-22]). Chitin is one of the most abundant organic materials that can be easily obtained in nature. The nature source of chitin is the shell of crustaceans or the broth from industrial fungal process (Aly et al. [23]) Compared with other polysaccharides, chitin is unreactive. One of the main reactions carried out on chitin is deacetylation. Complete deacetylation is rarely achieved nor is it normally necessary since solubility in dilute aqueous acids is obtained at an extent of deacetylation of 60% or above. Its deacetylation process in production of chitosan, therefore, generally requires quite vigorous conditions. Moreover, chitosan is soluble in most of the weak acid solutions. These conditions are not favourable to the use of chitosan as sorbent for removing metal ions due to chitosan dissolution tendency in the effluent (Martel et al. [24]) To reduce such a problem, chitosan has been stabilized by using various crosslinking agents. This approach, however, could considerably increase the application cost (Bell et al. [10], Kim et al. [11], Aly et al. [23]). An alternative approach is to find a certain pre-treatment of chitin which could produce an optimal balance between its maximum sorption and stability in vigorous conditions.

In our earlier studies, chitin has shown a certain potential for removal cadmium from aqueous solutions. In the present work, we examine the cadmium sorption properties of chitin pre-treated chemically by different ways. Batch experiments were conducted to determine the sorption properties of the chitin pre-treated: kinetics and equilibrium of cadmium sorption. This chemical pre-treatment of chitin may improve the sorption capacity of chitin and the stability of this material which is an important aspect of the commercial development of sorbent materials.

MATERIALS AND METHODS

Chitin from crushed crab shells (Sigma Chemicals Co.) in the form of large flakes, was used throughout this work. It was pre-treated chemically by different ways by immersing:

- 2 g of chitin in 1 L of various solutions: distilled water; drinking water, NaOH (0.1M), and HNO_3 (0.1M): pre-treatment called I.

- 2 g of chitin in 1L of distilled water with initial pH adjusted to different values in the interval 2-12: pre-treatment called II.

- 2 g of chitin in 1L of distilled water: pH of the mixture obtained was maintained constant at different values in the interval 2-10: pre-treatment called III.

In all these treatments, the mixture chitin-solution was stirred at a speed of 400 rpm/min for 4 hours at room temperature 25°C. The product was separated from the solution by filtration, and then intensively washed with distilled water for many times up to the final pH of filtrate became near neutral pH. All batch sorption experiments reported here were made with pre-treated chitin having a 0.2 – 6.3 mm particle size.

Cadmium solutions of desired concentration were prepared from $Cd(NO_3)_2.4H_2O$ (Windor Laboratories Limited), by dissolving the exact quantities of cadmium salts in distilled water. All chemicals were commercial products used without purification.

1- **Uptake kinetics of cadmium**

The initial solution cadmium concentration was 100 mg/L for all experiments. For cadmium removal kinetics studies, 0.6 g of pre-treated chitin 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 1ml 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 Perkin Elmer Model 2280 atomic absorption spectrophotometer. The metal uptake q (mg ion metal/g chitin pre-treated) was determined as follows:

$$q = (C_0 - C_t) \times V/m$$

where C_0 and C_t are the initial and final metal ion concentration (mg/L), respectively, V is the volume of solution (mL), and m is the pre-treated chitin weight (g).

Preliminary experiments had shown that cadmium adsorption losses to the container walls and to the filter paper were negligible.

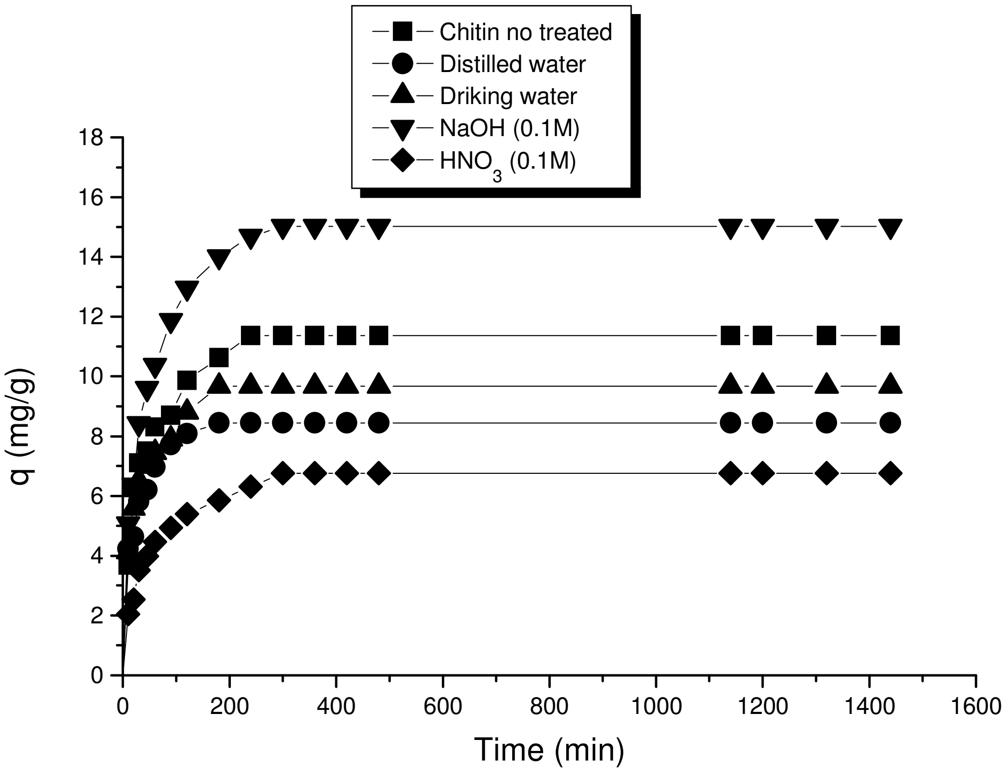
2- Uptake isotherm of cadmium

The equilibrium isotherms were determined by contacting a constant mass (0.2 g) of pre-treated chitin with a range of different concentrations of cadmium solutions. The pre-treated chitin and cadmium solution were agitated in a series of 250 ml conical flasks with equal volumes of solution (100 ml) for a period of 24 hours at room temperature 25°C. The contact time was previously determined by kinetics tests using the same conditions. The reaction mixture pH was not controlled after the initiation of experiments. After shaking the flasks for 24h, the final pH was measured, and a solution sample was removed from the reaction mixtures after decantation. The final concentration of unbound cadmium was determined by AAS and the cadmium loading by the pre-treated chitin calculated.

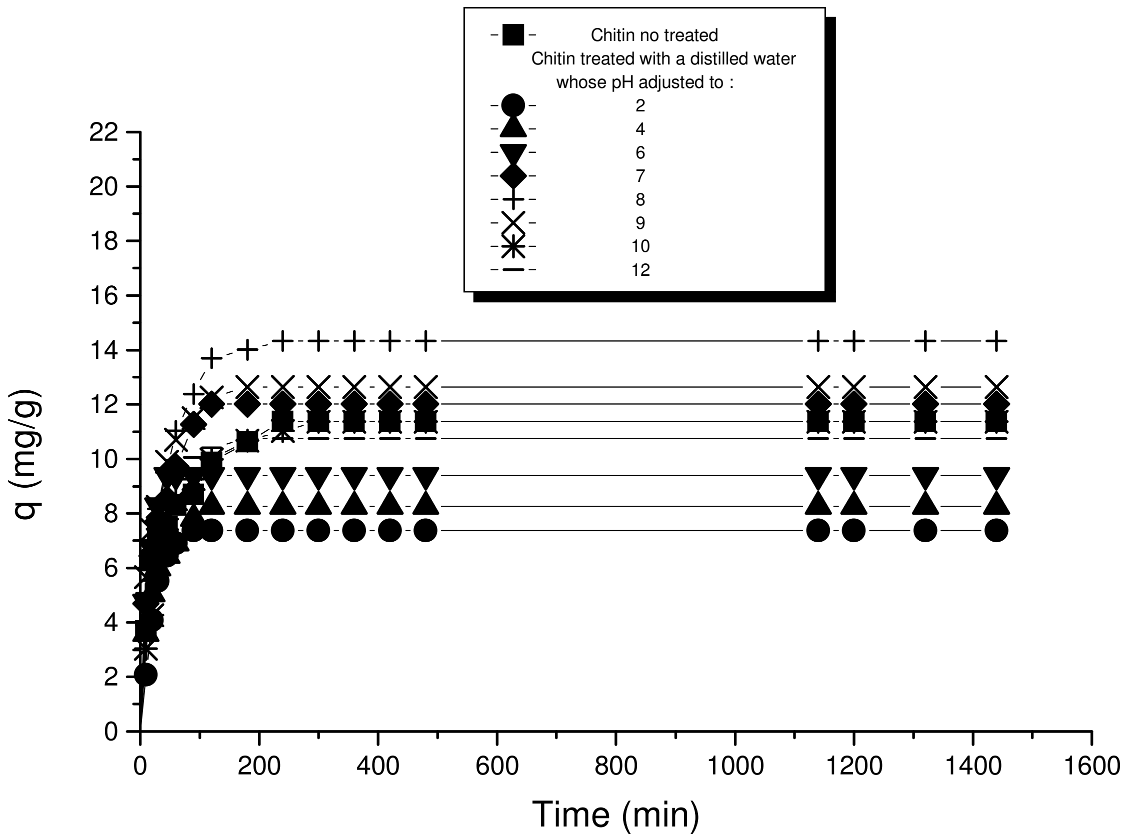
RESULT AND DISCUSSION

1- Kinetics of adsorption

Figures 1a, b, c show the kinetics of cadmium sorption by untreated and pretreated chitin. The obtained curves for any treatment presents a same shape characterized by a strong increase of the capacity of cadmium removal by chitin during the first minutes of contact solution - chitin, follow-up of a slow increase until to reach a state of equilibrium. As an approximation, the removal of cadmium ions can be said to take place in two distincts steps: a relatively fast one followed by a slower one. The necessary time to reach equilibrium is variable according to the type of pre-treatment: about 5-6 for treatment I; about 2-4 hours for treatment II and about 1-5 hours for treatment III. An increase of removal time to 24 hours does not show notable effects in all cases. Except the treatment I, the sorption rates of cadmium are much higher on the pre-treated chitin than of the untreated ones. According to Figure 1a, in treatment I, the maximum capacity of cadmium sorption at equilibrium (about 15.02 mg/g) is obtained with chitin treated with NaOH 0.1M followed by those of drinking water (9.67 mg/g), distilled water (8.45 mg/g), and HNO_3 0.1M (6.76 mg/g). The results presented in Figure 1b, in the pre-treatment II, indicate that an increase of the initial pH of distilled water in the range 2 - 8 deals to an increase in the capacity of cadmium sorption at equilibrium: 7.37 mg/g at pH 2 and about 14.33 mg/g at 8. Thus, a slight difference between untreated and pretreated chitin was obtained on cadmium sorption. Beyond the value of initial pH 8, we notice a reduction in this capacity at equilibrium: 12.64 mg/g for pH 9 and 10.75 mg/g for pH 12. Concerning the pretreatment III of chitin, in Figure 1c, the pH adjustment of chitin-distilled mixture in the interval 2-10 has some effect on the capacity of cadmium sorption at equilibrium. This last increases with increases of pH of mixture from 2 (4.82 mg/g) to 8 (17.95 mg/g). Beyond the value of pH 8, we also observe a reduction in this capacity: pH = 10 (14.02 mg/g). All these results revealed that the pre-treated chitin, in caustic medium or in aqueous solution whose pH is near 8, shows some improvement in the cadmium sorption, due to the partial transformation of amide to amine groups. Their capacities of sorption capacity of cadmium at equilibrium for pH = 8 are higher than that of the untreated chitin (11.37 mg/g without initial pH control of solution) (Benguella [18], Benguella & Benaissa [19]).


Chitin no treated
Distilled water
Driking water
NaOH (0.1M)
HNO3 (0.1M)
q (mg/g)
Time (min)
0
2
4
6
8
10
12
14
16
18
200
400
600
800
1000
1200
1400
1600

(a)


Chitin no treated
Chitin treated with a distilled water
whose pH adjusted to :
2
4
6
7
8
9
10
12
q (mg/g)
Time (min)
0
2
4
6
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12
14
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20
22
200
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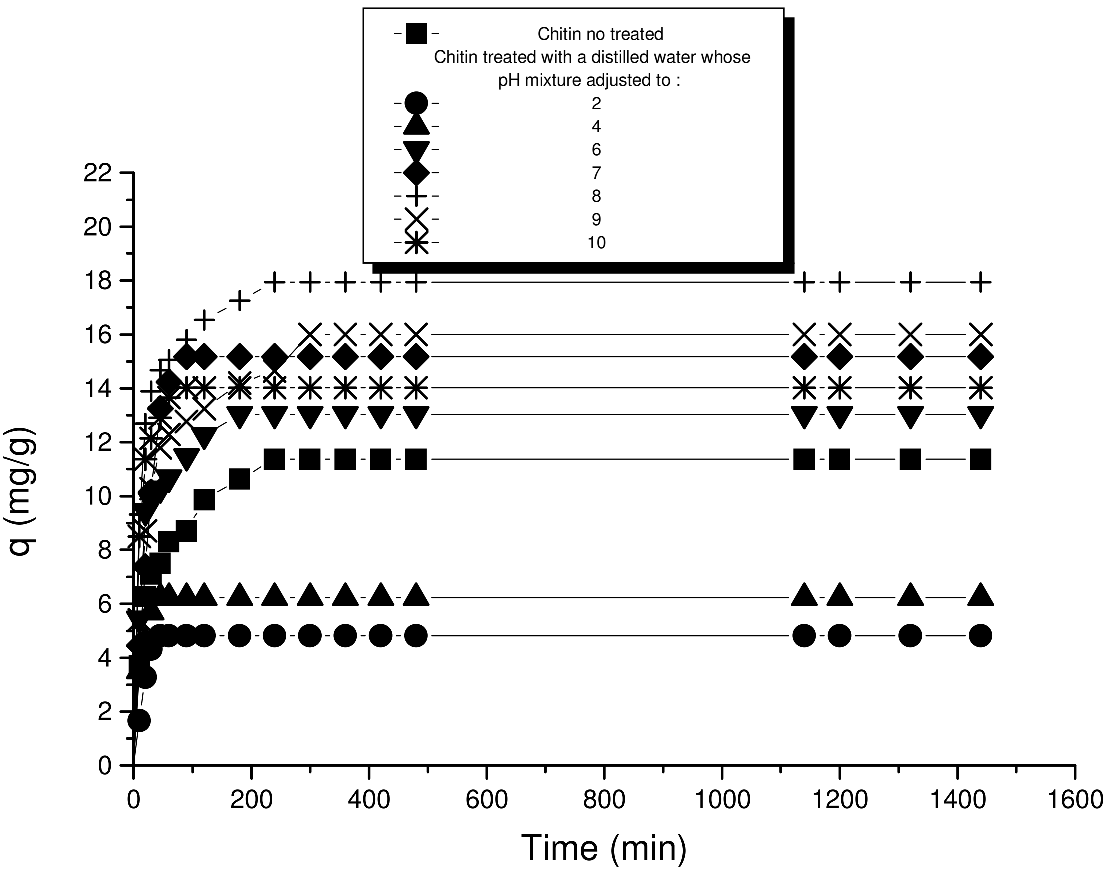
1200
1400
1600

(b)



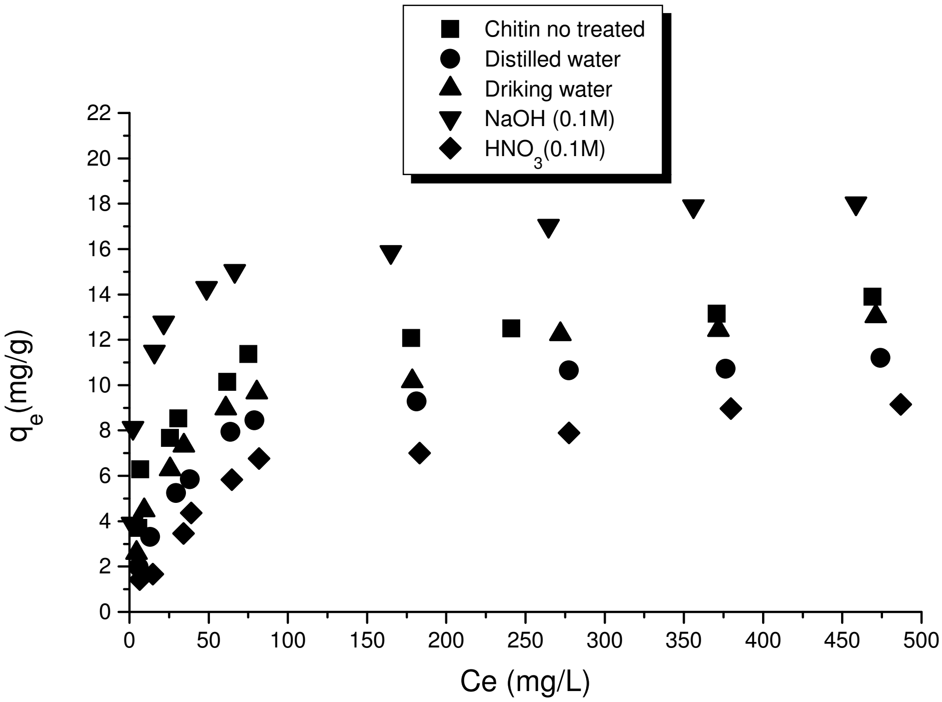
(c)

Figure 1: Kinetics of cadmium sorption by chitin pre-treated.
(a) pre-treatment I
(b) pre-treatment II
(c) pre-treatment III

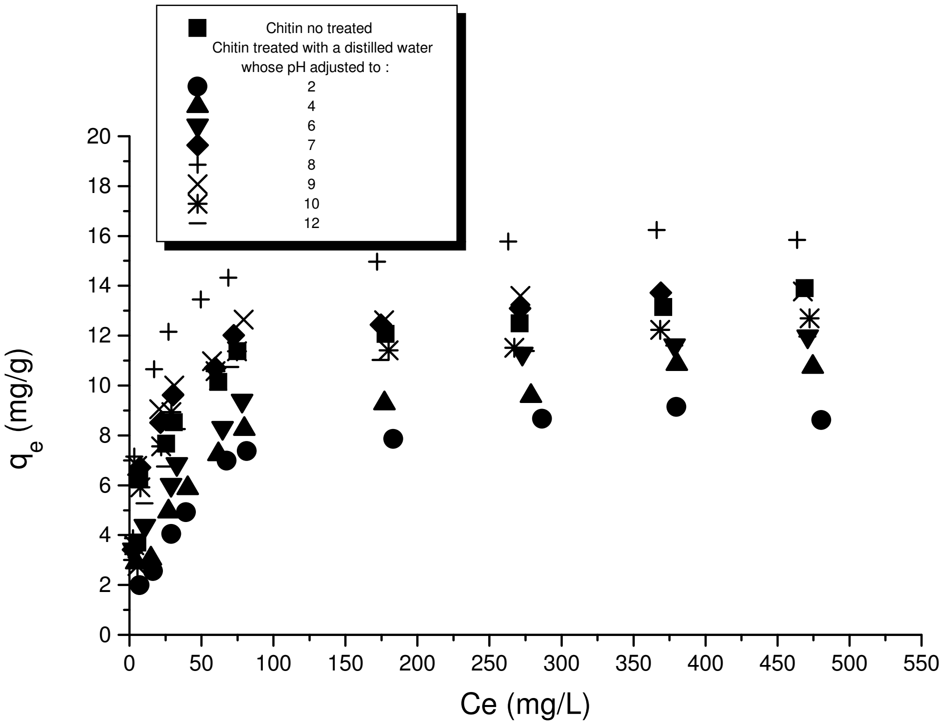
During the course of cadmium sorption by chitin, we noticed an evolution (increase or decrease) in the value of the initial pH of the solution (results no presented here).

2- Equilibrium adsorption

The sorption capacities of cadmium on the pre-treated and untreated chitin were determined by measuring their equilibrium isotherms. Before the chemical treatment, chitin was relatively less effective in removing cadmium (4.21 mg/g with no pH control of solution) (Benguella [18], Benguella & Benaissa [19]). The equilibrium isotherms of cadmium sorption on the treated and untreated chitin at 25 C are shown n Figures 2 a, b, c. Whatever the type of pre-treatment used, the isotherms for cadmium sorption are of Langmuir's type according to the classification of Brunauer et al. [25] and of L type according to the classification of Giles [26]. During experiments of sorption equilibrium, it was observed that the initial H of the solution changed in the same manner as that previously observed in the kinetic study.


Chitin no treated
Distilled water
Driking water
NaOH (0.1M)
HNO3(0.1M)
qe(mg/g)
Ce (mg/L)

(a)


Chitin no treated
Chitin treated with a distilled water
whose pH adjusted to :
2
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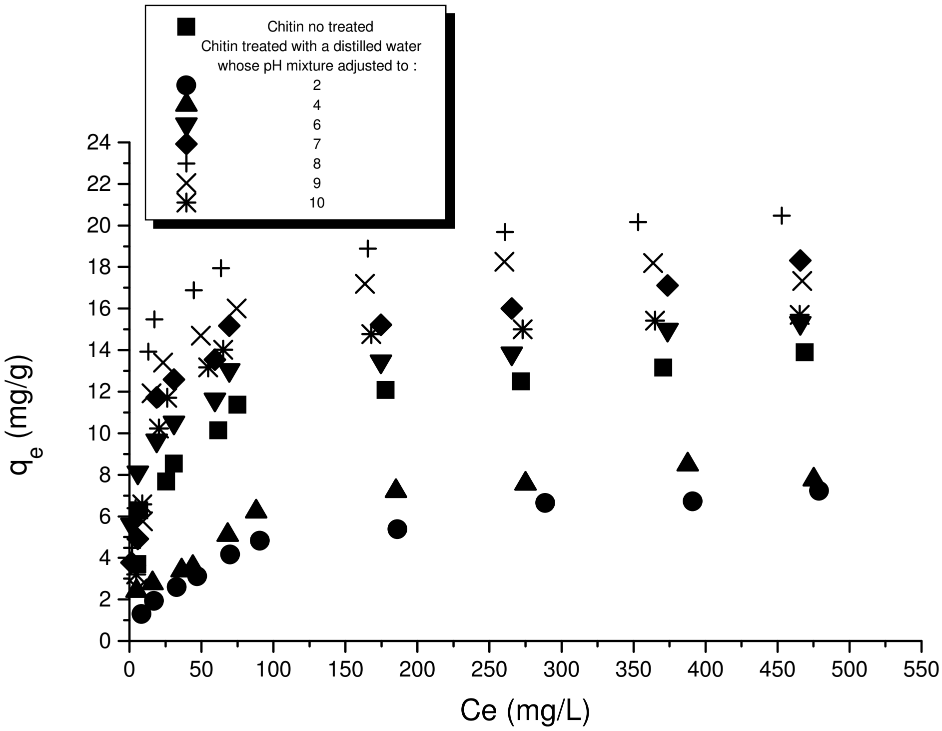
12
qe (mg/g)
Ce (mg/L)

(b)



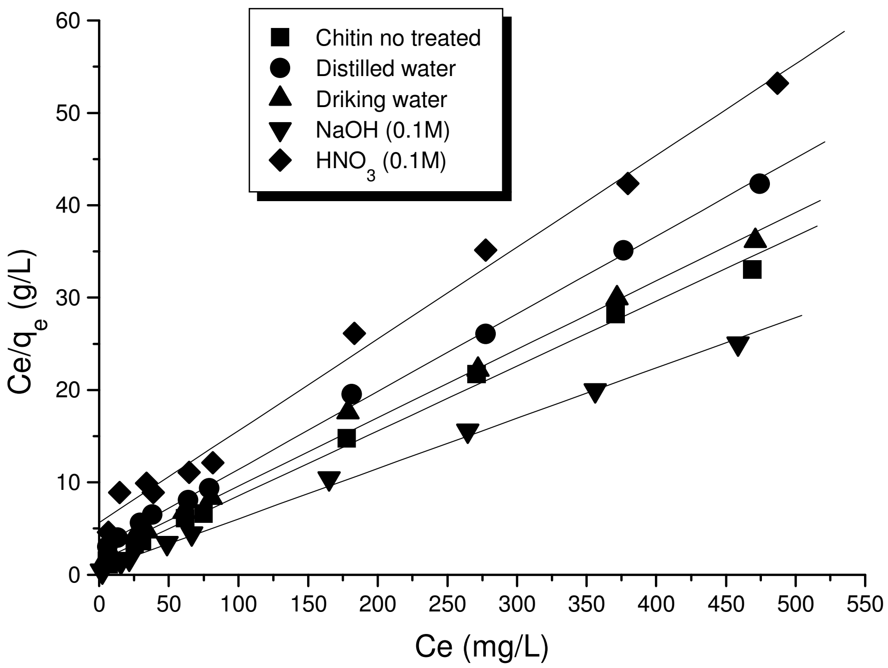
(c)

Figure 2: Isotherms of cadmium sorption by pretreated chitin at 25°C
(a) pre-treatment I
(b) pre-treatment II
(c) pre-treatment III

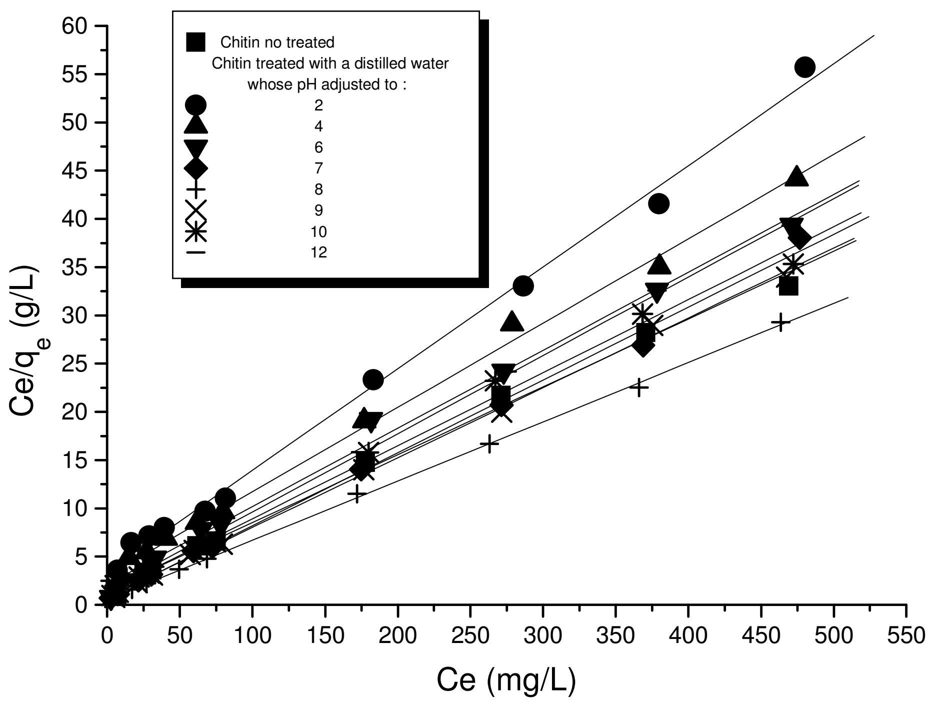
The sorption data can be interpreted using several relationships which describe the distribution of metal ion between the biomaterial and the liquid phase. Such predictive models have value in comparing different biomaterials under different operating conditions. Furthermore, these models can be used to design and optimize an operating procedure (Yang & Zall [13]). Among these last, the Langmuir sorption model [27] is commonly used to fit experimental data when solute uptake occurs by a monolayer sorption. This model was tested in the present work. This modelling permits us to determine the maximal capacity of removal. 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. The Langmuir model has the following form:

$$q = q_m \, b \, Ce / (1+bCe)$$

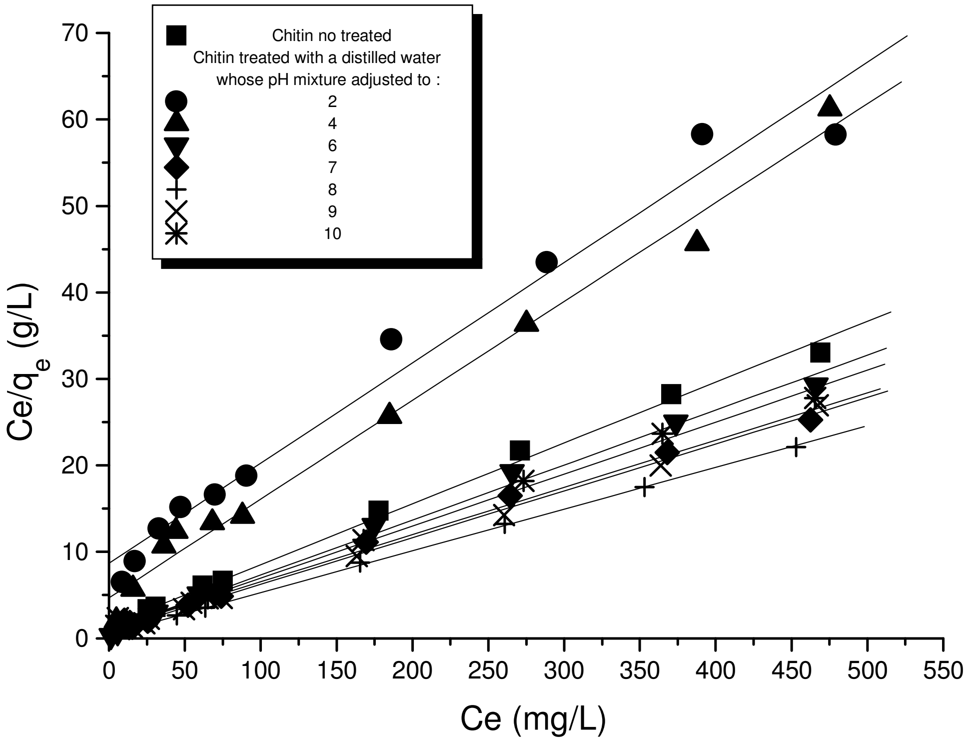
where: q is the amount of metal ion adsorbed at equilibrium per g of adsorbent (mg/g); Ce the equilibrium concentration of metal ion in the solution (mg/L); q_m , b are the Langmuir model constants. If the equation of Langmuir is valid to describe our experimental results, it must verify the linearized shape of the basis equation, in system of coordinates Ce/qe vs. Ce. What will permit us to obtain the constants qm and b from the intercepts and slopes. Results of the modelling of the isotherm of cadmium sorption by untreated and pre-treated chitin, according to model of Langmuir, are represented in Figures 3 a, b, c; hence the Table 1 summarizes the model parameters determined by least squares fit of the experimental sorption data, along with correlation coefficients.



(a)



(b)



(c)

Figure 3: Linearized plot of Langmuir isotherms for cadmium sorption by untreated and pretreated chitin.
(a) pre-treatment I
(b) pre-treatment II
(c) pre-treatment III

Whatever the nature of chitin pretreatment, it appears that the Langmuir model best fits the experimental results over the experimental range with good coefficients of correlation. According to values obtained of parameters q_m and b, listed in the Table 1, the maximum sorption (q_{max}) of cadmium ions by the pretreated chitin is highest than that of the untreated ones. We notice that the results obtained in this equilibrium study and the Langmuir isotherm analysis are in agreement with those observed previously in the kinetic study. Chitin with pretreatment III, presents the highest maximum capacity of cadmium sorption: (20.68 mg/g at pH = 8), followed by NaOH 0.1 M (18.39 mg/g) and pretreatment II (16.27 mg/g at pH 8). In the pretreatments II and III, we observe an increase in the maximum capacity of cadmium sorption with initial pH of solution from the value 2 (8.62 mg/g in pretreatment III and 9.49 mg/g in pretreatment II) to 8 (20.68 mg/g in pretreatment III and 16.27 mg/g in pretreatment II). This improvement observed in the capacity of cadmium sorption by chitin can be due to the partial transformation of amide to amine groups. This suggested that in chitin sorbent, degree of deacetylation, a proportion between amine and acetylamino groups could be a key parameter in controlling sorption and desorption of metal ions (Kim et al. [11]).

Table 1: Langmuir parameters of cadmium sorption by untreated and pre-treated chitin

Nature of pretreatment	q_m (mg/g)	b (L/g)	R^2
Chitin untreated	14.21	0.048	0.996
Pretreatment I			
Distilled water	11.88	0.028	0.998
Drinking water	13.50	0.034	0.995
NaOH (0.1M)	18.39	0.086	0.998
HNO_3 (0.1M)	10.07	0.018	0.992
Pretreatment II			
pH = 2	9.49	0.031	0.996
pH = 4	11.45	0.029	0.995
pH = 6	12.37	0.038	0.994
pH = 7	13.24	0.116	0.997
pH = 8	16.27	0.115	0.999
pH = 9	13.80	0.095	0.998
pH = 10	13.21	0.056	0.994
pH = 12	12.32	0.054	0.999
Pretreatment III			
pH = 2	8.62	0.013	0.975
pH = 4	8.75	0.025	0.988
pH = 6	15.71	0.068	0.994
pH = 7	18.29	0.052	0.995
pH = 8	20.68	0.111	0.999
pH = 9	18.48	0.066	0.996
pH = 10	16.65	0.062	0.997

CONCLUSION

- The pre-treated chitin, though no longer inexpensive after the chemical pre-treatments, exhibited a certain enhanced sorption to cadmium ion.
- In general, both equilibrium isothermic and kinetic studies showed that pre-treatment of chitin could improve their cadmium ion adsorption. The chemical pretreatment will increase the cost of the sorbent materials. However, the increased sorptive capacities and efficiencies may compensate the added cost and make the pre-treated chitin more acceptable to the wastewater treatment facilities.
- As perspectives in the future, we will optimize the different experimental parameters of each pre-treatment in order to improve these results encouraging obtained.

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