REMOVAL OF Fe(III) AND Cr(VI) ONTO CHITOSAN OBTAINED FROM SHRIMP WASTES: EVALUATION OF PROCESS FACTORS, KINETICS AND INTERACTIONS

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ABSTRACT

Chitosan was obtained from shrimp wastes, characterized and employed to removal Fe(III) and Cr(VI) from aqueous solutions. The effects of pH (4.0 and 4.5), chitosan dosage (1.5 and 3.0 mg mL^{-1}), particle size (150 and 260 µm) and contact time (4 and 7 h) on the percentage of cation removal were investigated by a factorial design. In the more adequate condition, the kinetic was evaluated using four models and the possible interactions between chitosan and metals were identified by infrared analysis. For both cations, the more adequate condition was at pH 4, chitosan dosage of 3.0 mg mL^{-1}, particle size of 260 µm and contact time of 7 h. Under these conditions, the percentages of cation removal were 85% and 42% to Fe(III) and Cr(VI), respectively. The Avrami model was the more suitable to represent the kinetic data ($R^2 \geq 0.98$ and ARE<4.0%), and the maximum adsorption capacity values were 1.151×10^{-3} and 1.264×10^{-3} mol g^{-1} to Fe(III) and Cr(VI), respectively. Chitosan hydroxyl and amino groups were responsible for the cations binding.

KEYWORDS: CHITOSAN. IONS ADSORPTION. KINETICS ADSORPTION. SHRIMP WASTE.

REMOÇÃO DE Fe (III) E Cr (VI) EM QUITOSANA OBTIDA A PARTIR DE RESÍDUOS DO CAMARÃO: AVALIAÇÃO DOS FATORES DE PROCESSO, CINÉTICA E INTERAÇÕES

RESUMO

A quitosana foi obtida a partir de resíduos de camarão, caracterizada e utilizada para a remoção de Fe(III) e Cr(VI) em soluções aquosas. Os efeitos do pH (4,0 e 4,5), da dosagem de quitosana (1,5 e 3,0 mg mL^{-1}), do tamanho de partícula (150 e 260 µm) e do tempo de contacto (4 e 7 h), sobre a percentagem de remoção dos íos foram investigadas por um delineamento experimental fatorial. Na condição mais adequada, a cinética foi avaliada utilizando quatro modelos, e as interações possíveis entre a quitosana e os íons metálicos foram identificados por análise de infravermelhos. Para ambos os íons, a condição mais adequada foi em pH 4, dosagem de quitosana de 3,0 mg mL-1, tamanho de partícula de 260 µm e tempo de 7 h. Sob estas condições, as percentagens de remoção dos íons foram de 85% e 42% para Fe(III) e Cr(VI), respectivamente. O modelo Avrami foi o mais adequado para representar os dados cinéticos ($R^2 \geq 0.98$; EMR<4,0%), e as

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capacidades máximas de adsorção foram de $1{,}151\times10^{-3}$ e de $1{,}264\times10^{-3}$ mol g^{-1} para Fe(III) e Cr(VI), respectivamente. Os grupos hidroxila e amino da quitosana foram responsáveis pelas ligações dos íons.

PALAVRAS-CHAVES: ADSORÇÃO DE ÍONS. CINÉTICA DE ADSORÇÃO. QUITOSANA. RESÍDUOS DE CAMARÃO.

1. INTRODUCTION

The metallic ions cause adverse effects on ecosystem where are discharged, mainly due its bioaccumulation. Iron and chromium are commonly found in liquid effluents from several industries, such as, paints, fertilizers, paper, leather and pesticides. Moreover, they are extremely toxic to human health, causing irritations, allergies, cancer, or even death [13]. An effective method to metals removal from wastewater is the adsorption, due to its simplicity, high efficiency and availability of a wide range of adsorbents. A suitable adsorbent to removal metals must include features such as, low cost, availability, high capacity and adsorption rate, high selectivity and efficiency for several metals [15,26]. Many adsorbents have been employed to removal metals from aqueous solutions, such as, chestnut shell [25], activated carbon [1], cow dung powder [5], magnetite [27], bentonite [21], chitosan [4], and others materials [9].

Chitosan is a biopolymer composed by units of N-acetyl-D-glucosamine and D-glucosamine in different proportions. It is a natural, renewable, biodegradable polysaccharide, being important from economic and environmental viewpoints [16]. In many countries, the fish industries must pay to dispose the shrimp wastes, which present 5-7% (w/w) of chitin. Thus, it is important to find alternatives for the management of these wastes, as example, the chitosan production by alkaline deacetylation of the chitin. Due to its characteristics such as, weak base, polyelectrolyte at acidic pH, chelating agent, the chitosan has advantages in relation other adsorbents [8]. The use of chitosan is considered an alternative to metals removal from aqueous solutions [15,26]. However, most studies use the biopolymer with a commercial grade or modified by several forms [4,19,26]. It is important to cite that the changes in the chitosan, although in some cases, increase its potential for interactions with metals, also it can to increase the its cost of obtainment [4,26].

In the adsorption process to removal metals using chitosan, it is important to check how the experimental factors and characteristics of the biopolymer affect the percentage removal. This process can be affected by many factors, such as stirring rate, contact time, particle size, pH, adsorbent dosage, adsorbate concentration, temperature and intrinsic characteristics of the biopolymer [4,15,19,26]. The experimental design is a good alternative to study the effect of these variables and intervariable interactions on the percentage removal [4,6,17]. Other relevant information in order to evaluate the applicability of chitosan to metals removal is the kinetic behavior [15,26]. The kinetic curves explain how fast the adsorption occurs and also lead to information about the interactions adsorbent/adsorbate [4,8,19]. Finally, it is necessary to know the specific interactions between metals and chitosan [15].

This work aimed to use chitosan obtained from shrimp wastes as adsorbent to remove Fe(III) and Cr(VI) from aqueous solutions. The effects of pH (4.0 and 4.5), chitosan dosage (1.5 and 3.0 mg mL^{-1}), particle size (150 and 260 µm) and contact time (4 and 7 h) on the percentage of cation removal were investigated by a factorial design. In the more appropriate condition for each ion, the models nominated pseudo–first order, pseudo–second order, Elovich and Avrami were employed to elucidate the adsorption kinetic behavior. Infrared analysis (FT-IR) was performed in order to verify the possible interactions between chitosan and metals.

2. MATERIAL AND METHODS

2.1 Preparation and characterization of chitosan

Chitosan was obtained from shrimp (*Penaeus brasiliensis*) wastes as presented in previous works [10,20,22,28]. Firstly, chitin was obtained by demineralization, deproteinization, deodorization and drying steps [20]. Chitosan in paste form was obtained by alkaline deacetylation of chitin followed by purification [20,28]. Chitosan paste was spouted bed dried to obtain a chitosan powder [10]. The samples were sieved and the particle sizes of 150 and 260 µm were used.

The adsorbent particles were characterized according to the deacetylation degree (infrared analysis) (Prestige 21, the 210045, Japan) [7], molecular weight (viscosimetric method) [2], scanning electron microscopy (SEM) (Jeol, JSM-6060, Japan) [19], specific surface area, pore volume and average pore radius (BET method) (Quantachrome, Nova station A, USA) [1].

2.2 Batch experiments

2.2.1 Batch experiments for the experimental design

The batch experiments were carried out in a single solute mode, being the Fe(III) and Cr(VI) removal evaluated separately. The Fe(III) and Cr(VI) solutions were prepared, respectively, by dissolving ferric ammonium sulfate ($NH_4Fe(SO_4)_2.12H_2O$) and potassium dichromate ($K_2Cr_2O_7$) in distilled water. The salts were added to obtain initial ions concentration of 1.8×10^{-3} mol L^{-1} [12,14]. The pH of the solutions was adjusted to 4.0 and 4.5 (Mars, MB–10, Brazil) [11] using buffer solutions of citric acid/sodium diphosphate, which did not present interaction with the metallic ions.

Chitosan dosage (1.5 or 3.0 mg mL^{-1} in dry basis) in powder form with determined particle sizes (150 or 260 µm) was added in 100 mL of Fe(III) and Cr(VI) solutions (1.8×10^{-3} mol L^{-1}) with pH value defined (4.0 or 4.5), according to the factorial design. The solutions were shaken at 50 rpm (Fanem, 315SE, Brazil). Experiments were performed at ambient temperature (298±1 K). Aliquots were removed at 4 and 7 h through filtration with Whatmann Filter Paper no. 40, which did not present interaction with the ions and the ions were quantified by flame atomic absorption spectrometry (FAAS) (GC, AA 7000 SBC, Brazil). All experiments were carried out in replicate (n=3), and blanks were performed. The percentage of ions removal (%R) was determined using the Equation (1):

$$R(\%) = (\frac{C_0 - C_t}{C_0}) \times 100 \qquad (1)$$

where, C_0 is the initial ion concentration in liquid phase (mol L^{-1}) and C_t is the ion concentration in liquid phase at time “t” (mol L^{-1}).

2.2.2 Batch kinetic experiments

The kinetic experiments were carried out in the best conditions for each ion, which were determined by the experimental design. The same procedure presented in the section 2.2.1 was employed, but, aliquots were removed from the liquid at preset time intervals (2, 4, 6, 8, 10, 15, 20, 25, 30, 40, 50, 60, 80, 100, 120, 180, 240, 300, 360 min). The adsorption capacity at time t (q_t) was determined using the Equation (2):

$$q_t = (\frac{C_0 - C_t}{m})V \qquad (2)$$

where, C_0 is the initial ion concentration in liquid phase (mol L^{-1}), C_t is the ion concentration in liquid phase at time “t” (mol L^{-1}), m is chitosan amount (g) and V is the volume of solution (L).

2.3 Experimental design

The pH, chitosan dosage, particle size and contact time are relevant factors which can affect the metals removal from aqueous solutions onto chitosan. In this work, a 2^4 experimental factorial design [6] was employed to investigate the effects of pH (4.0 and 4.5), chitosan dosage (1.5 and 3.0 mg mL^{-1}), particle size (150 and 260 µm) and contact time (4 and 7 h) on the percentage of ions removal (%R). The factors and respective levels were selected from preliminary tests and the literature [4,12,14,15,19,26]. In addition, experimental design was used to determine the more appropriate process condition for removal of each ion. For the statistical analysis, the significance level was 95% ($p<0.05$). The results were analyzed using the software Statistic 7.0 (Statsoft, USA).

2.4 Kinetic models

Adsorption kinetics is an important design parameter that describes how the adsorbate interacts with the adsorbent [11]. In the more suitable condition (determined from experimental design) the models nominated pseudo–first order, pseudo–second order, Elovich and Avrami were fitted to the experimental data in order to investigate the adsorption kinetics of Fe(III) and Cr(VI) onto chitosan.

The kinetic models of pseudo-first order and pseudo-second order assume that adsorption is a pseudo-chemical reaction, and the adsorption rate can be determined, respectively, for equations of pseudo-first (Equation (3)) and pseudo-second order (Equation (4)) [23]:

$$q_t = q_1(1-\exp(-k_1 t)) \tag{3}$$

$$q_t = \frac{t}{(1/k_2 q_2^{\,2}) + (t/q_2)} \tag{4}$$

where q_t is the adsorbate amount adsorbed at time “t” (mol g^{-1}), k_1 and k_2 are the rate constants of pseudo-first and pseudo-second order models, respectively, in (min^{-1}) and (g mol^{-1} min^{-1}), q_1 and q_2 are the theoretical values for the adsorption capacity (mol g^{-1}) and “t” is the time (min).

When the adsorption processes occurs through chemisorption in solid surface, and the adsorption rate decreases with time due to covering of the superficial layer, the Elovich model is most used [29]. The Elovich kinetic model can be described according to the Equation (5):

$$q_t = \frac{1}{a}\ln(1+abt) \tag{5}$$

where “a” is the initial sorption rate due to dq/dt with q_t=0 (mol g^{-1} min^{-1}) and “b” is the desorption constant of the Elovich model (g mol^{-1}).

An alternative fractionary Avrami kinetic equation was proposed, based in the thermal decomposition modeling [3], as presented in Equation (6):

$$q_t = q_{AV}(1-\exp(-k_{AV}t)^n) \tag{6}$$

where, k_{AV} is the Avrami kinetic constant (min^{-1}), q_{AV} is the Avrami theoretical values for the adsorption capacity (mol g^{-1}) and “n” is a fractionary reaction order which can be related, to the adsorption mechanism.

The kinetic parameters were determined from fit of the models to the experimental data by nonlinear regression, using Statistic 7.0 software (Statsoft, USA) through Quasi-Newton estimation method. The fit quality was measured through coefficient of determination (R^2) and average relative error (ARE).

2.5 FT–IR analysis

To verify the possible interactions of chitosan with Fe(III) and Cr(VI), FT–IR analysis was carried out in the more suitable conditions of the adsorption process. Chitosan samples before and after the adsorption were dried (105°C) until constant weight. After this, the samples were macerated and carried out in the spectroscopic determination in the region of the infrared ray (Prestige 21, the 210045, Japan), using the technique of diffuse reflectance in potassium bromide [25].

3. RESULTS AND DISCUSSION

3.1 Chitosan characterization

Chitosan obtained from shrimp wastes showed deacetylation degree of 85 ± 1% and molecular weight of 150 ± 3 kDa. Chitosan with these characteristics is suitable to removal pollutants from aqueous solutions [11,12,14]. The surface characteristics of chitosan particles are shown in FIGURE 1(a, b).

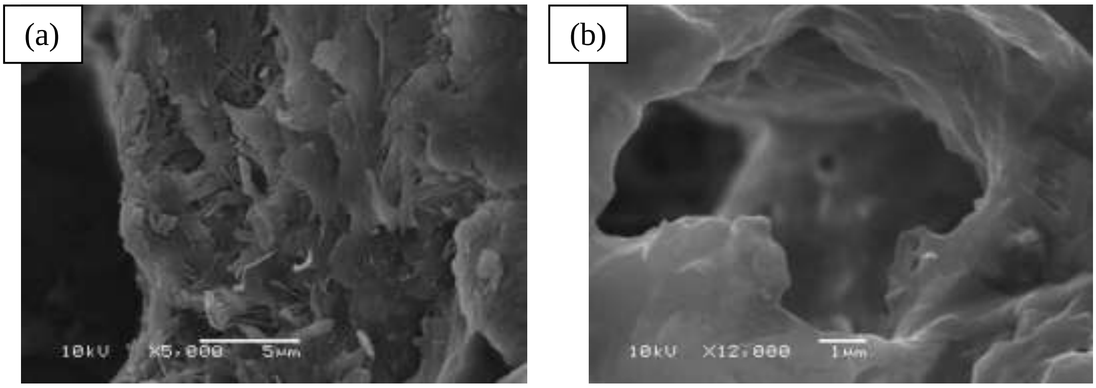


Figure 1: Surface characteristics of chitosan particles: (a) × 5,000; (b) × 12,000.

It can be observed in FIGURE 1(a) chitosan presented heterogeneous and rough, surface with some protuberances. In FIGURE 1(b) can be observed that chitosan has a pore structure. These surface characteristics are important to facilitate possible interactions between chitosan and metallic ions [4,15,26]. The specific surface area, pore volume and average pore radius of chitosan particles are shown in TABLE 1.

Table 1: Surface area, pore volume and average pore radius of chitosan with different particle sizes.

Characteristics	Particle size (μm)	
	150	260
Surface area* (m^2 g^{-1})	3.8±0,1	1.6±0.1
Average pore radius* (nm)	1.5±0.3	2.5±0.3
Pore volume* (mm^3 g^{-1})	1.1±0.1	2.1±0.1

*mean ± standard deviation, in replicate (n=2).

Chitosan particles with size of 150 µm presented higher specific surface area than chitosan particles with size of 260 µm (TABLE 1). However, higher values of average pore radius and pore volume were observed in the particles of 260 µm. These characteristics of the particles are essential to understand the adsorption process [1].

3.2 Evaluation of process factors

TABLE 2 shows the experimental results of removal percentage (%R) of Fe(III) and Cr(VI) in all conditions, according to the factorial experimental design. These results show that the potential of chitosan as adsorbent is strongly dependent of the experimental conditions and the characteristics of the biopolymer. Thus, it is important verify the influence of these factors and the characteristics of chitosan on the removal percentage in order to maximize the application of this biopolymer.

Analysis of variance (ANOVA) was used to verify the significance of pH, chitosan dosage, particle size and contact time on removal percentage of Fe(III) and Cr(VI). Analysis of variance is shown in TABLE 3. The values of models regression coefficients for the removal of Fe(III) and Cr(VI) onto chitosan are shown in TABLE 4.

It can be observed in TABLE 3, that all main effects were significant on the removal percentage of Fe(III) and Cr(VI) ($p<0.05$). Only the interaction effect of chitosan dosage with particle size not influenced the removal percentage of Fe(III) ($p> 0.05$). For Cr(VI) removal, the interaction effect of pH with particle size was not significant ($p>0.05$).

Table 2: Experimental design results of removal percentage of Fe(III) and Cr(VI)onto chitosan.

Exp.	pH	Chitosan dosage (mg mL^{-1})	Particle size (µm)	Contact time (h)	Fe (III) removal (%)*	Cr (VI) removal (%)*
1	4 (–1)	1.5 (–1)	260 (+1)	4 (–1)	48.3±0.8	18.2±0.3
2	4 (–1)	3.0 (+1)	260 (+1)	4 (–1)	82.0±0.4	26.8±0.5
3	4 (–1)	1.5 (–1)	150 (–1)	4 (–1)	45.3±0.7	20.4±0.8
4	4 (–1)	3.0 (+1)	150 (–1)	4 (–1)	77.1±0.3	19.3±0.7
5	4.5 (+1)	1.5 (–1)	260 (+1)	4 (–1)	38.3±0.2	10.9±0.2
6	4.5 (+1)	3.0 (+1)	260 (+1)	4 (–1)	72.8±0.5	29.2±0.1
7	4.5 (+1)	1.5 (–1)	150 (–1)	4 (–1)	34.1±0.6	19.3±0.2
8	4.5 (+1)	3.0 (+1)	150 (–1)	4 (–1)	71.3±0.1	22.8±0.1
9	4 (–1)	1.5 (–1)	260 (+1)	7 (+1)	54.8±0.4	26.2±0.3
10	4 (–1)	3.0 (+1)	260 (+1)	7 (+1)	85.1±0.5	42.1±0.2

11	4 (–1)	1.5 (–1)	150 (–1)	7 (+1)	51.4±0.7	24.1±0.5
12	4 (–1)	3.0 (+1)	150 (–1)	7 (+1)	81.1±0.4	26.2±0.5
13	4.5 (+1)	1.5 (–1)	260 (+1)	7 (+1)	41.2±0.7	31.7±0.1
14	4.5 (+1)	3.0 (+1)	260 (+1)	7 (+1)	75.3±0.3	20.9±0.6
15	4.5 (+1)	1.5 (–1)	150 (–1)	7 (+1)	39.0±0.5	13.1±0.3
16	4.5 (+1)	3.0 (+1)	150 (–1)	7 (+1)	73.1±0.6	13.6±0.4

* mean ± standard deviation (n=3)

Table 3: Analysis of variance (ANOVA) for the removal percentage of Fe(III) and Cr(VI) onto chitosan.

Factors	Fe(III)*			Cr(VI)**		
	Mean Square	F test	P	Mean Square	F test	P
pH (A)	790.0	22982.7	<0.0001	226.3	519.1	<0.0001
Dosage (B)	8831.2	256907.8	<0.0001	176.2	404.3	<0.0001
Size (C)	80.6	2346.0	<0.0001	289.8	664.7	<0.0001
Time (D)	130.4	3793.8	<0.0001	125.2	287.2	<0.0001
AB	22.7	662.7	<0.0001	23.9	55.0	<0.0001
AC	2.5	73.6	<0.0001	0.1	0.3	0.5817
AD	5.7	168.1	<0.0001	199.5	457.6	<0.0001
BC	0.0	0.0	1.0000	102.6	235.3	<0.0001
BD	9.4	275.2	0.0051	57.5	131.9	<0.0001
CD	0.4	10.5	<0.0001	207.5	476.1	<0.0001
Error	0.03			0.43		

* R^2=0.999; ** R^2=0.752; Significance level = 95%.

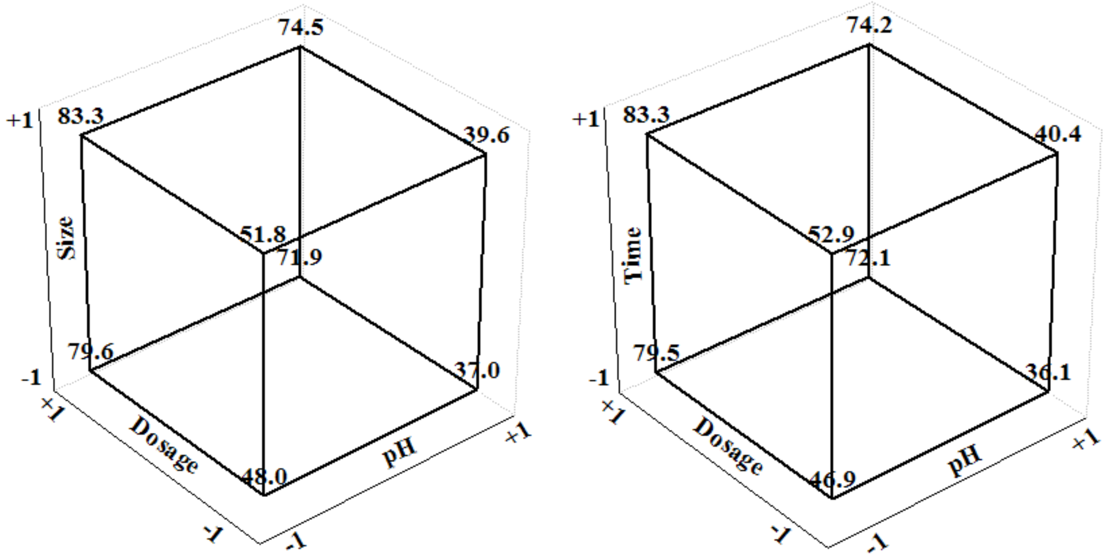
Table 4: Models regression coefficients for the removal percentage of Fe(III) and Cr(VI) onto by chitosan.

Factors	Fe(III)*		Cr(VI)**	
	Regression coefficients	Standard error	Regression coefficients	Standard error
Mean	73.291	3.4779	-121.071	12.3856
pH (A)	-19.578	0.8010	37.349	2.8527
Dosage (B)	0.0571	0.0077	0.204	0.0277
Size (C)	0.122	0.0105	-0.192	0.0375
Time (D)	7.517	0.3865	25.969	1.3764

AB	0.041	0.0017	-0.046	0.0062
AC	-0.021	0.0024	-0.005	0.0085
AD	-1.132	0.0874	-6.658	0.3112
BC	0.000	<0.0001	0.000	<0.0001
BD	-0.005	0.0003	-0.012	0.0010
CD	-0.001	0.0004	0.031	0.0014

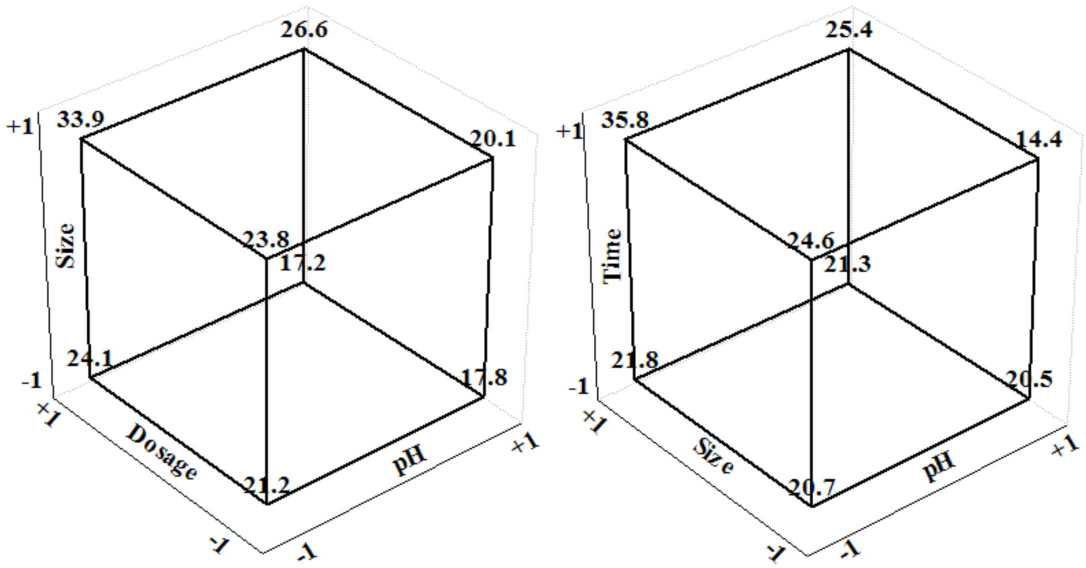
* R^2=0.999; ** R^2=0.752.

In order to evaluate the effects of pH, chitosan dosage, particle size and contact time on the percentage of ions removal (%R), response cubes were plotted. The response cubes obtained from the statistical analysis are shown in FIGURE 2(a, b) and FIGURE 3(a, b), respectively.



(a) (b)

Figure 2: Response cubes for the % of Fe(III) removal onto chitosan.



(a) (b)

Figure 3: Response cubes for the % of Cr(VI) removal onto chitosan.

FIGURES 2 and 3 show that the pH decrease and the chitosan dosage increase, particle size increase and contact time increase caused an increase in the removal percentage of Fe(III) and Cr(VI).

The pH of the solution has considerable influence on metal ions adsorption onto chitosan. The adsorbent charge and the metal species in solution are strongly dependent of this parameter [15]. In this work the pH decrease from 4.5 to 4.0 caused an increase in removal of Fe(III) (FIGURE 2(a,b)) and Cr(VI) (FIGURE 3(a,b)). In acidic mean, the chitosan amine groups are protonated in the form of $(NH_3)^+$, and with pH decrease, the $(NH_3)^+$ groups are increased [8,15]. Coupled to this, in diluted solutions at pH range from 1.0 to 6.0, Cr(VI) coexists in the form of $HCrO^{-4}$, $Cr_2O_7^{-2}$, $Cr_3O_{10}^{-1}$ and $Cr_4O_{13}^{-1}$ [4]. Thus, electrostatic interactions occur between chitosan protonated amine groups and chromium in the anionic form. Similar behavior was obtained by Aydin and Aksoy [4] in chromium removal using commercial chitosan. In the case of Fe(III), its presence in cationic form at lower pH values makes it more able to coordinate the amine groups present in chitosan structure. In addition, the pH increasing lead to a formation of iron hydroxide, decreasing the capacity of complexation [14]. Similar behavior was obtained by other researchers [24] in Fe(III) removal from aqueous solutions.

The chitosan dosage is particularly important because determines the extent of decontamination and can be used to predict the cost of chitosan per unit of solution to be treated [8,15,26]. From FIGURES 2(a) and 3(a), it was observed that the removal percentage (%R) of Fe(III) and Cr(VI) were increased with the increase of chitosan dosage. This behavior may be explained due to an increase in the adsorbent surface and presence of more available sites to interactions with ions. This same relation between adsorbent dosage and removal percentage was observed by others researches [4,13].

It can be seen in FIGURE 2(a) to Fe(III) and FIGURE 3(a) to Cr(VI) that the particle size increase caused an increase in the percentage of ions removal. This fact can be explained by the results of specific surface area, pore volume and average pore radius (TABLE 1). The particles of 150 µm presented higher values of specific surface area, on the other hand, higher values of pore volume and average pore radius were observed for the particles of 260 µm. Although, its lower specific surface area, the higher values of pore volume and average pore radius of particles with 260 µm favored the percentage of both ions removal.

In the studied range, the contact time increase caused an increase in the removal percentage of Fe(III)) and Cr(VI). This occurred because, during the process, the metal ions migrate from the solution to the adsorbent surface, increasing its fraction in solid phase and thus decreasing the concentration in liquid phase. The surface of chitosan was progressively blocked by the ions, increasing the percentage of ions removal over time. Similar behavior was reported by other authors [4,15,26].

Based on statistical analysis, under the studied range, the more suitable conditions to removal Fe(III) and Cr(VI) by chitosan was at pH = 4 (−1), chitosan dosage of 3.0 mg mL^{-1} (+1), particle size of 260 µm (+1) and contact time of 7 h (+1). Under these conditions, the percentages of ions removal were 85.1% and 42.1% to Fe(III) and Cr(VI), respectively. The predicted values by the statistical model were 85.1 and 39.5% for the removal of Fe(III) and Cr(VI), respectively. These results can be compared with other published studies [4,12–15,26] showing that chitosan produced from shrimp wastes is a potential adsorbent for the removal Fe(III) and Cr(VI) from aqueous solutions.

3.3 Kinetic analysis

In the more appropriate condition to removal Fe(III) and Cr(VI), a kinetic analysis was realized. FIGURE 4 shows the adsorption kinetic curves of Fe(III) and Cr(VI) onto chitosan. It was observed in FIGURE 4 that for Fe(III), about 90% of saturation was attained at 60 min, indicating a very fast process. On the opposite, for Cr(VI), a gradual increase of the adsorption capacity was observed until 350 min, suggesting a slow process.

In order to obtain more information about the adsorption process, pseudo–first order, pseudo–second order, Elovich and Avrami models were fitted to the experimental data. TABLE 5 shows the kinetic parameters, the coefficient of determination (R^2) and the average relative error values (ARE), for Fe(III) and Cr(VI) adsorption onto chitosan in the more suitable conditions.

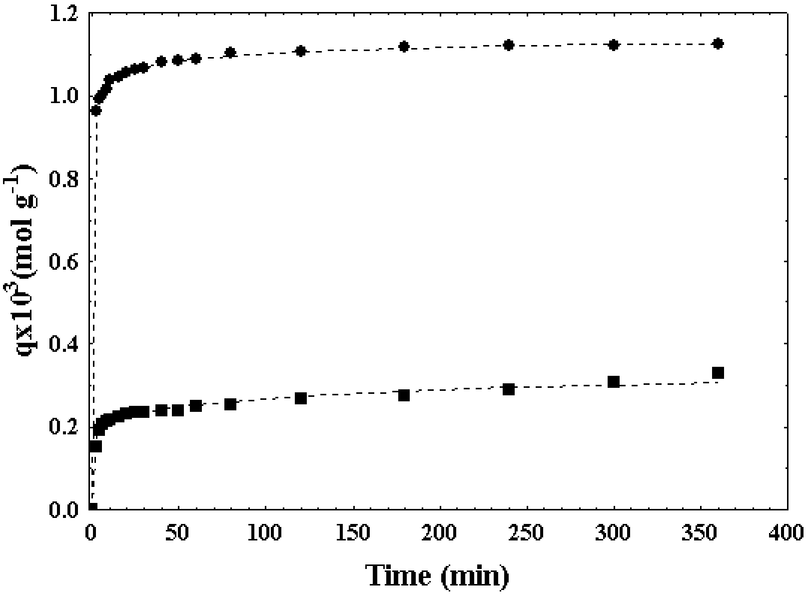


Figure 4: Adsorption kinetics of Fe(III) and Cr(VI) onto chitosan (pH=4, chitosan dosage=3.0 mg mL^{-1}, particle size=260 μm). ●, Fe(III), ■, Cr(VI), -----, Avrami model.

Table 5: Kinetic parameters of Fe(III) and Cr(VI) adsorption onto chitosan

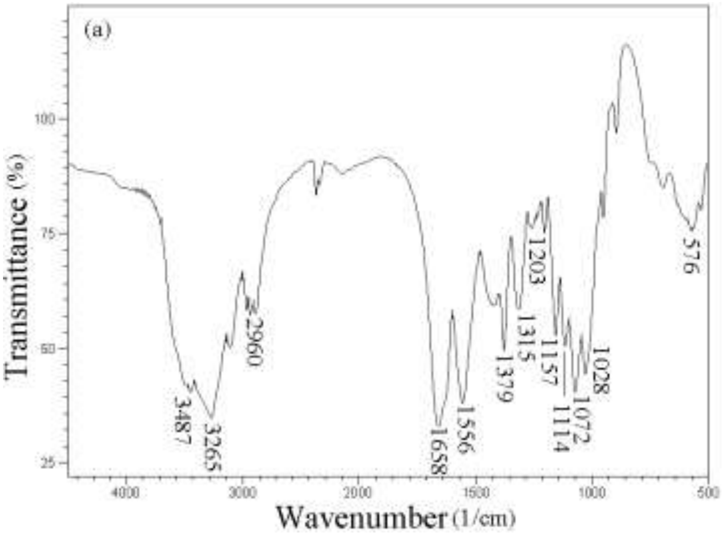
Model	Fe(III)	Cr(VI)
Pseudo–first order		
q_1×10^3 (mol g^{-1})	1.074	0.256
k_1(min^{-1})	1.046	0.312
R^2	0.977	0.828
ARE (%)	2.93	12.57
Pseudo–second order		
q_2×10^3 (mol g^{-1})	1.096	0.272
k_2×10^{-3}(g mol^{-1}min^{-1})	2.408	1.720
R^2	0.993	0.908
ARE (%)	1.68	6.37

Elovich		
a×10^3(mol g^{-1} min^{-1})	14.64	37.95
b×10^3(g mol^{-1})	10784.14	7.17
R^2	0.948	0.938
ARE (%)	4.31	5.72
Avrami		
q_{AV}×10^3 (mol g^{-1})	1.151	1.264
k_{AV} (min^{-1})	1.614	0.135
N	0.145	0.123
R^2	0.999	0.980
ARE (%)	0.233	3.51

As can be seen in TABLE 5, the Avrami kinetic model was the more appropriate to represent the experimental data for both ions (R^2≥0.980 and ARE<4.00%). The k_{AV} values for Fe(III) were about twelve times higher than k_{AV} values of Cr(VI). This confirm that the Fe(III) adsorption was very faster than Cr(VI) adsorption. The “n” parameter of the Avrami model showed that both, Fe(III) and Cr(VI), followed a multiple kinetic order [3,24]. The adsorption capacity (q_{AV}) values of Fe(III) and Cr(VI) onto chitosan are comparable with the literature values [4,9,12,14,26].

3.4 Interaction analysis

Figure 5 shows the FT-IR analysis of the chitosan before and after ions adsorption process.



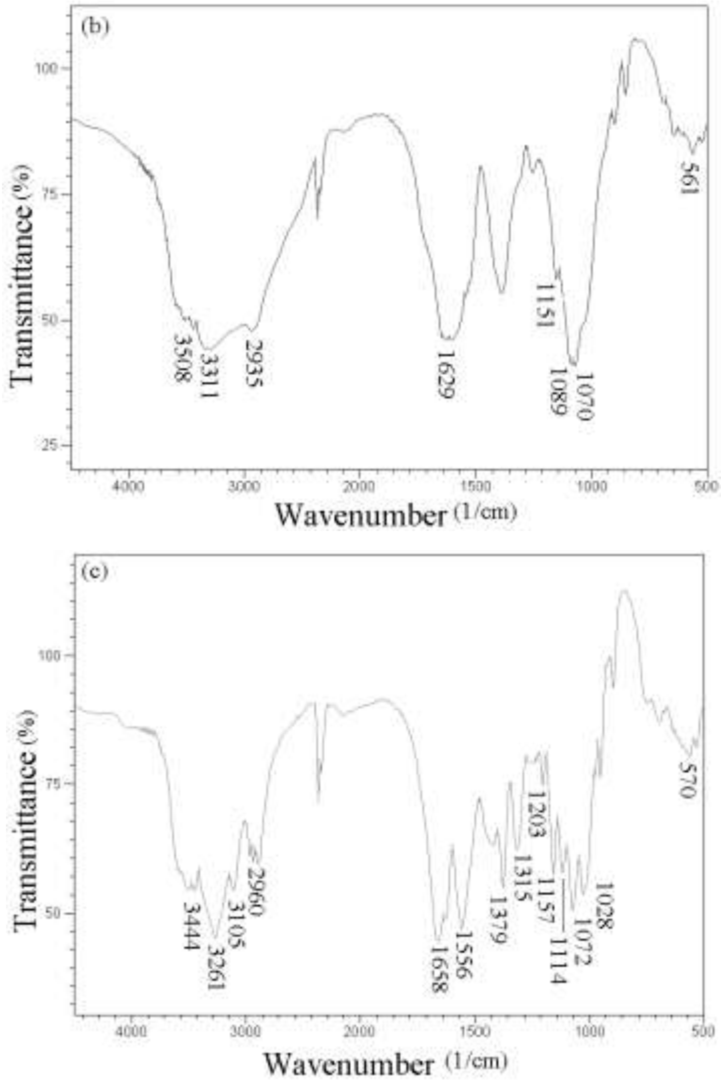


Figure 5: FT-IR analysis of chitosan: (a) before adsorption process, (b) chitosan with Fe(III), (c) chitosan with Cr(VI). (pH=4, chitosan dosage=3.0 mg mL^{-1}, particle size=260 µm, contact time=7h).

In FIGURE 5(a) it can be observed at 3487 and 3265 cm^{-1} the overlapping stretches of axial O–H and N–H, typical of the chitosan molecule. The peak at 2960 cm^{-1} is related to the axial stretching of C-H. The sharp and less intense band centered at 1658 cm^{-1} shows the carbonyl stretch, from the chitin, demonstrating that chitosan was not completely deacetylated. The angular deformation of the amine can be seen in an intense and sharp band in the region of 1556 cm^{-1}. The band 1379 cm^{-1} refers to an angular deformation of asymmetric CH_3 grouping of chitin. The peaks at 1315 and 1203 cm^{-1} are relative to the symmetric angular deformation of C–H. The bands 1157, 1114, 1072 and 1028 cm^{-1} indicate the stretching of the

C–O bond. The peak at 576 cm^{-1} can be related to the torsional oscillation of the N–H bond present in the group $(NH_3)^+$ of chitosan.

In FIGURE 5(b) (chitosan adsorbed with Fe(III)) the peaks in the region of 2935 and 3508 cm^{-1} showed changes in the shape and in the values of wave number compared to the original spectrum of chitosan (FIGURE 5(a)). This indicates that hydroxyl and amino groups of chitosan were responsible for the interaction with Fe(III). The participation of the amino group can be confirmed by modifying of the stretch at 576 cm^{-1} (Fig. 5 (a)) to 561 cm^{-1} (FIGURE 5 (b)), which shows the Fe–N binding [18]. The participation of O–H grouping can be confirmed by the modification of the peaks in the region between 1028 and 1157 cm^{-1}.

In FIGURE 5(c) (chitosan adsorbed with Cr(VI)) it was observed changes in the region between 3100 and 3450 cm^{-1}, however, the shape of the bands was not changed, showing the localized interaction of Cr(VI) with chitosan amino groups. The interaction of Cr(VI) with $(NH_3)^+$ of chitosan can be confirmed by modification of band 576 cm^{-1} (FIGURE 5(a)) to 570 cm^{-1} (FIGUR. 5(c)).

4. CONCLUSIONS

In this work, chitosan obtained from shrimp wastes was used to remove Fe(III) and Cr(VI) from aqueous solutions. For both metals, the more suitable condition was at pH = 4, chitosan dosage of 3.0 mg mL^{-1}, particle size of 260 µm and contact time of 7 h, and under these conditions, the percentages of ions removal were 85.1% and 42.1% to Fe(III) and Cr(VI), respectively.

The kinetic study showed that the Avrami model was the more appropriate to represent the experimental data for both ions. The maximum adsorption capacities were 1.151×10^{-3} and 1.264×10^{-3} mol g^{-1} for Fe(III) and Cr(IV), respectively. The FT–IR analysis showed that the hydroxyl and amino groups of chitosan were responsible for the interaction with Fe(III). Localized interactions of Cr(VI) with chitosan amino groups were verified.

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