

«Original Article»

Adsorption of Zn (II) from aqueous solution by using chitin extracted from shrimp shells

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Abstract

Background: Chitin and its derivatives (chitosan) are natural biopolymer produced from crustacean shell, which due to their active functional groups such as amine and hydroxyl have high ability to absorb heavy metals from water and wastewater. The aim of this study was to investigate zinc removal from aqueous solutions by using chitin extracted from shrimp shells.

Material and methods: To study the removal of zinc, chitin extracted from shrimp shells was used as biosorption in a batch system. In addition, the influence of pH, initial metal concentration, amount of adsorbent and contact time on adsorption process was investigated.

Results: The results of this research showed that the absorption capacity of zinc closely depended on the pH of solution, as zinc absorption concentration increased in terms of mg/g with increasing pH. The results of equilibrium studies revealed that zinc absorption process on the extracted chitin was desirable and followed the Freundlich isotherm model and pseudo second kinetic model. Moreover, Fourier Transform Infrared Spectroscopy (FTIR) results indicated that functional groups such as amine (-NH₂) and hydroxyl (-OH) had the highest effect on adsorption of zinc.

Conclusion: According to the obtained results, the chitin extracted from shrimp shells appeared to be a suitable adsorbent for removing zinc from aqueous solutions.

Keywords: Adsorption, Adsorption isotherm, Chitin, Kinetic model, Zinc

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Introduction

The release of large amounts of heavy metals into the natural environment has resulted in a number of ecological and health problems. Many industrial processes such as metal finishing, electroplating, non-ferrous metal works, paper, and petroleum produce wastewater flows containing heavy metals, which are toxic to the nature. Toxic metals can be distinguished from other pollutants, since they are not biodegradable and can be accumulated in living organisms. Some metals such as zinc and iron are regarded bioessential while others such as cadmium, mercury, and chromium are highly toxic. However, even bioessential metals may cause health and ecological problems if present at a considerable amount. One metal ion often released into the nature through industrial activities at concentrations of health and ecological concern is zinc (Zn (II)) (1-5).

Zinc is a trace element that is essential for life and act as a micronutrient when present in trace amounts. It is important for the physiological functions of living tissue, and controls many biochemical processes. However, too large amount of zinc can cause prominent health problems such as muscular stiffness, loss of appetite, stomach cramps, skin irritations, vomiting, nausea, and anemia (6,7). Therefore, WHO recommended the maximum acceptable concentration of zinc in drinking water to be 5.0 mg/l (8).

Several methods are available for removing Zn (II) from aqueous solutions. This includes chemical precipitation, electrolysis, ion exchange, reverse osmosis, and adsorption (9,10). These methods have some disadvantages such as expensive equipment and operations, production of toxic sludge and other wastes, requiring high amount of energy, and pre-treatment (11-13). Thus, an effective removal method needs to be inexpensive and economical. Recently, biosorption has achieved considerable importance as an alternative method for

the removal of Zn (II) from aqueous solution (14). Living or nonliving organisms are being used in biosorption. In this method, different materials such as chitinous materials e.g. shrimp, krill, squid, and crab shell, microbial biomass e.g. bacteria, fungi, and yeast, and algal biomass can be used (15). Among the many other low cost absorbents identified, chitin and its derivatives are nontoxic, biodegradable, biocompatible, antibacterial, and environmental friendly polymers with high molecular weight (16). Therefore, the purpose of this study was to investigate the efficacy of using chitin extracted from shrimp shell for the removal of zinc ions from aqueous solutions. The effects of different parameters, such as solution pH, adsorbent dose, and zinc ions concentrations on the sorption capacity were investigated. Comparison between sorption on chitin and other adsorbents was also studied.

Material and methods

Extraction of chitin from shrimp shells:

Shrimp shells were obtained from a local company located in Ahvaz City in Iran. The shells were washed several times and dried in sunlight for 1 day. Then the chitin was extracted from the shrimp shells as described before (17) using hydrochloric acid 10% at room temperature for 24 h to remove minerals (demineralization), and sodium hydroxide 10% at room temperature for 24 h to remove protein (deproteinization). The extracted chitin was washed and dried in sunlight and assayed to obtain moisture content, ash content, surface area, water binding capacities and fat binding capacities (17). Fourier transform infrared spectroscopy (FTIR) was used to determine the presence of functional groups in absorbent. Infrared spectra of chitin and chitin-zinc metal ion were obtained over a frequency range of 400–4000 cm^{-1} by a Bruker Tensor 27 IR spectrometer.

Batch adsorption studies

Influence of pH on metal adsorption capacity: To study the influence of pH on the Zn (II) adsorption capacity of the adsorbent, experiments were conducted at different initial pH values (3-7).

The effect of mass of the adsorbent: Effect of adsorbent mass was studied by using different masses of the adsorbent (0.5-10 g) for the batch experiment.

The effect of concentration of Zn (II): The effect of initial concentration of Zn (II) ions on the equilibrium adsorption of Zn (II) ions from aqueous solution was studied by using various concentrations of Zn (II) ions (50-500 mg/L). The experiment was performed by adding mass of the adsorbent in solutions containing various concentrations of Zn (II) ion for 180 minutes.

Adsorption isotherms: The adsorption isotherms for the Zn (II) removed were studied using initial concentration of Zn (II) between 50 and 500 mg/L at an adsorbent dosage level of 1g/250mL. The data obtained were then fitted to the Langmuir and Freundlich adsorption isotherm applied to equilibrium adsorption. Equations of these isotherms are: Freundlich (1)

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

Langmuir (2)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b q_m}$$

Where q_e and C_e are the equilibrium concentration of the adsorbent on the solid (mg/g) and in the liquid phases (mg/L), respectively; q_m is the maximum adsorption capacity (mg/g) according to the Langmuir model; b , K_f , and n are constants.

Kinetic studies: Sorption studies were carried out in 250 ml jar test flask at a solution pH of 7. The adsorbent were thoroughly mixed individually with 250 ml of solution containing 50 mg/L of Zn (II) ions. The suspension was shaken at room temperature and the filtrate collected

after 30-240 min was conserved for further analysis.

Determination of the concentration of Zn (II) ion: In each set of the experiment, the concentration of Zn (II) ion was determined using Atomic Absorption Spectroscopy (Analytic Jena AG, AAS 5FL model, Germany). Biosorption of the Zn (II) ions in the sorption system was calculated using the mass balance: (3)

$$q = \frac{(C_o - C_e)V}{w}$$

Where C_o and C_e are the initial and final concentrations (mg/L), V is the volume of aqueous solution (L) and W is the mass of adsorbent (g).

Results

Characterizations of chitin

In the present study, chitin was obtained from shrimp shells with a yield of 25.21%. According to mozzarella, Crustacean shells mainly consist of chitin, protein and calcium carbonate with an average composition of 15-40%, 20-40%, and 20-50% by weight, respectively (18). This means that on the laboratory scale, the yield of obtained chitin was high. Further characteristics of extracted chitin from shrimp shells such as moisture, ash, surface area, water, and fat binding capacities are shown in Table 1. To investigate functional groups of shrimp chitin, FT-IR spectrum analysis was done. The FT-IR spectra of shrimp chitin (Figure 1.a) exhibits an adsorption band from 3500 to 3200 cm^{-1} due to O-H and N-H stretching vibration; at 3000 to 2850 cm^{-1} assigned to -CH stretching vibrations; at 2517.95 and 2563.91 cm^{-1} assigned to O-H vibrations. The 1629.53 and 1633.61 cm^{-1} adsorption band is usually attributable to N-H deformation vibrations, while 1420 and 1419 cm^{-1} is due to -CH₃. Moreover, the band at 1063 and 1073 cm^{-1} is assigned to C-O stretching vibrations.

Figure 1.b also shows the FTIR spectra of chitin-Zn (II). The samples of chitin-zinc ion were prepared following the course of action in effect of initial pH. According to the figure, the FTIR spectra of chitin-zinc

ion show changes in the normal of the adsorption bands at 3500–3300 cm^{-1} , attributable to -OH and -NH₂ groups. In addition, the adsorption bands at 1419 cm^{-1} and 1632 cm^{-1} is attributable to -OH and -NH₂ groups, respectively. These changes indicate a complex formation, which decreases the energies of the bonds due to the metallic ions adsorbed.

Factors influencing the adsorption of Zn (II)

In this research, firstly the effects of the pH and initial metal concentration on removal efficiency of zinc were determined by considering the residual zinc after adsorption in the effluent. Then other parameters influencing the adsorption such as adsorbent dose and contact time were investigated.

The effect of initial pH

Figure 2 presents the effect of initial pH on the Zn (II) adsorption results at the initial 50 mg/L Zn (II) concentration. In this stage, the results indicated that with an increase in pH, the extent of Zn (II) uptake increased for the adsorbent.

The effect of initial metal ion concentration

Experiments were undertaken to evaluate the effect of the initial metal ion

concentration on zinc removal from the solution. The results obtained are presented in Figure 3. The results showed that the metal uptake increases with an increase in initial concentration of metal ion.

The effect of adsorbent dosage

The effect of adsorbent's dosage on the zinc removal efficiency showed that the uptake rate of zinc decreased from 5 to 0.5 mg/g with an increase in adsorbent dosage (figure 4).

Biosorption equilibrium and kinetics

The Langmuir and Freundlich models were used to describe the equilibrium sorption isotherms. The calculated results of these models are given in Table 2. According to this table the R^2 values suggests that the Freundlich isotherm provides a good model of biosorption system. To evaluate the kinetics of the adsorption process, the pseudo first-order and pseudo second-order models were tested to interpret the experimental data. The results listed in Table 3 indicated that the kinetics for the sorption of zinc on chitin followed pseudo-second order kinetics.

Table 1. Physico-chemical characteristic of adsorbents

Characterization	Chitin shrimp shells
Yield (%)	25.21
P_{zc}	6.7
Moisture (%)	2.813
Ash (%)	0.8
Water binding capacities (%)	452
Fat binding capacities (%)	387
Surface Area(m^2/g)	3.95

Table 2. Parameters of Langmuir and Freundlich isotherms for adsorption of Zn(II) on chitin

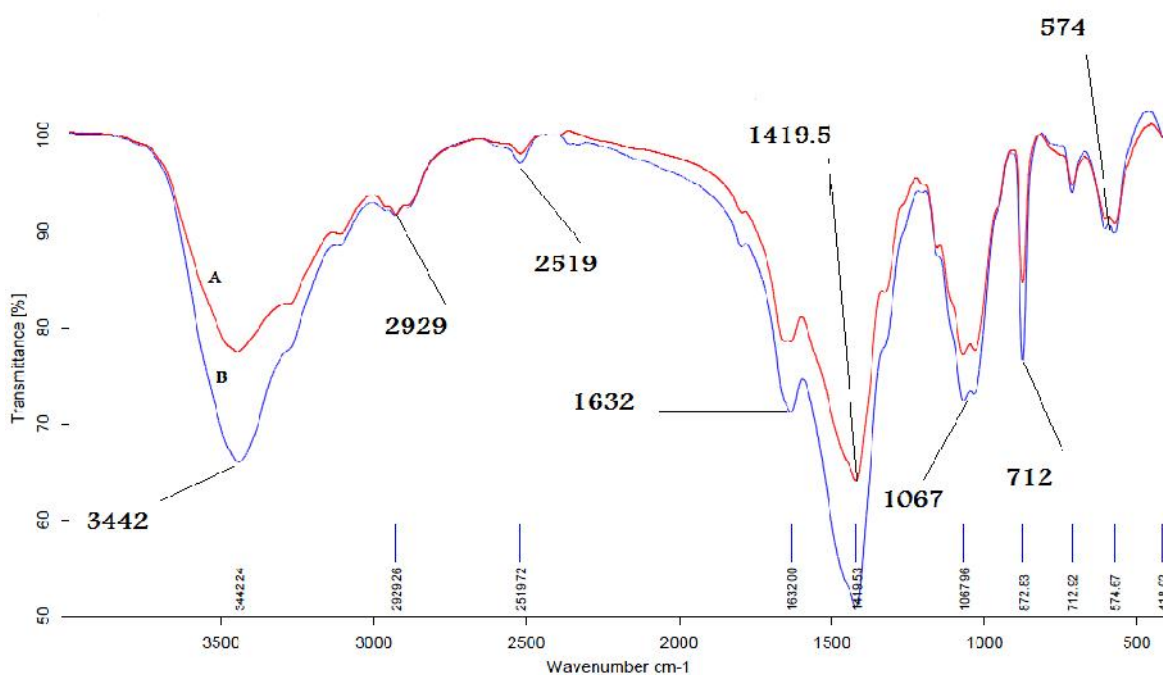
Adsorbent	Freundlich parameters			Langmuir constants			
	K_f	n	R^2	q_{max}	R_L	b	R^2
Prepared chitin	0.9664	1.15446	0.9992	270.270	0.52-0.915	0.00247	0.9783

Table 3. Pseudo-first-order and pseudo-second-order kinetic constants for adsorption of Zn (II) on chitin

Adsorbents	$q_e(\text{exp})$ mg/g	Pseudo first order kinetics			Pseudo second order kinetics		
		$K_1(10^{-4})$	q_e	R^2	$K_2(10^{-4})$	q_e	R^2
Chitin	7.64	149	10.01	0.9577	5.4	12.562	0.9815

Table 4. Comparison of zinc uptake capacity

Biosorbent	Zinc uptake (mg/g)
Bentonite	52.91
Red mud	12.59
Blast furnace slag	17.65–98.08
Biosolids	36.87
Scarp rubber	100
Powered waste sludge	168
Neem bark	137.67
Neem leaves	147.08
Peat	9.28–12.1
Bacillus subtilis	137
Sargassa sp.	70
Fungal biomass	98
Lignin	95
Amberlite IRC-718	156.89
Lewatit TP-207	89.56
Chitin (this study)	270.270

**Fig 1. FTIR spectra of (a) the chitin shrimp shells and (b) chitin-Zn (II)**

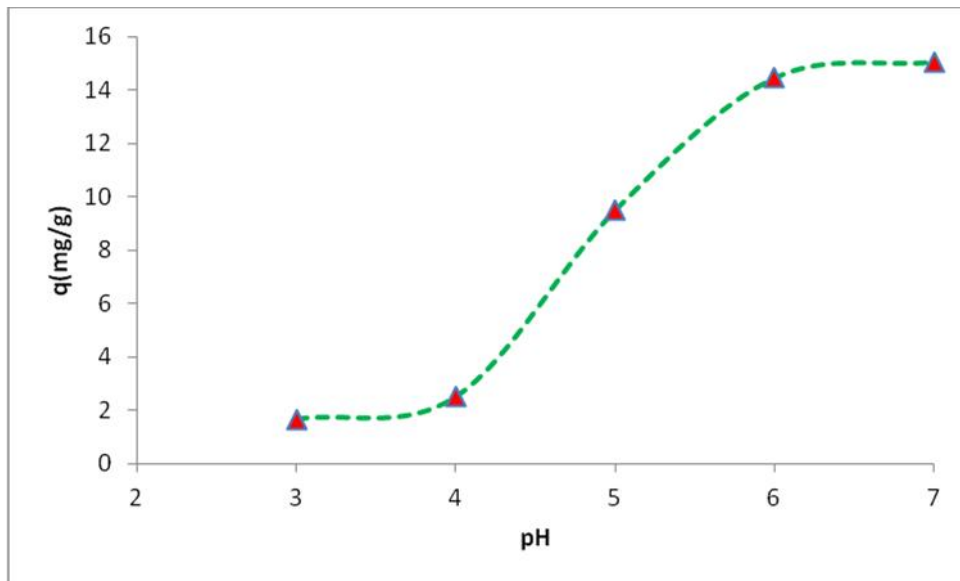


Fig 2. The effect of pH on Zn (II) uptake capacity

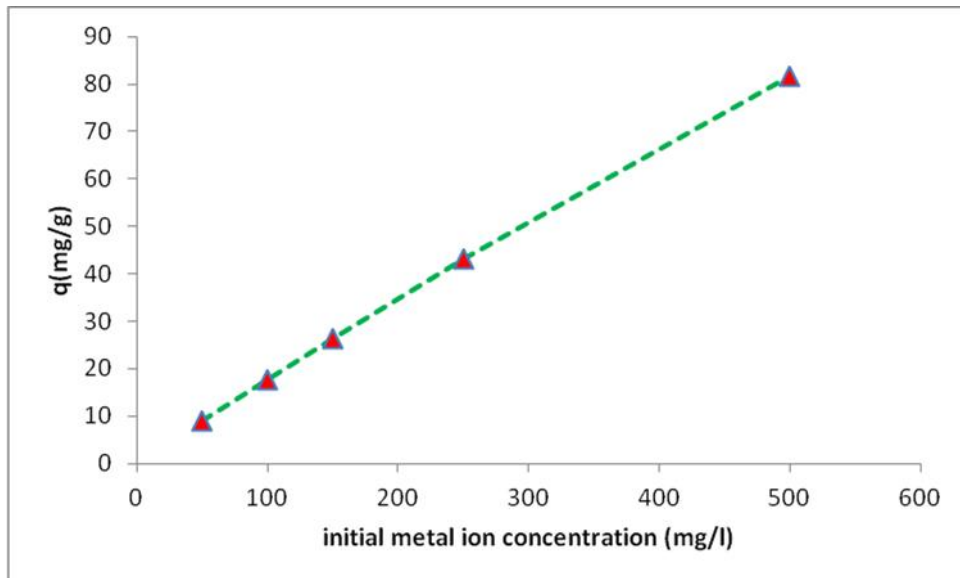


Fig 3. The effect of initial metal ion concentration onto Zn (II) uptake capacity

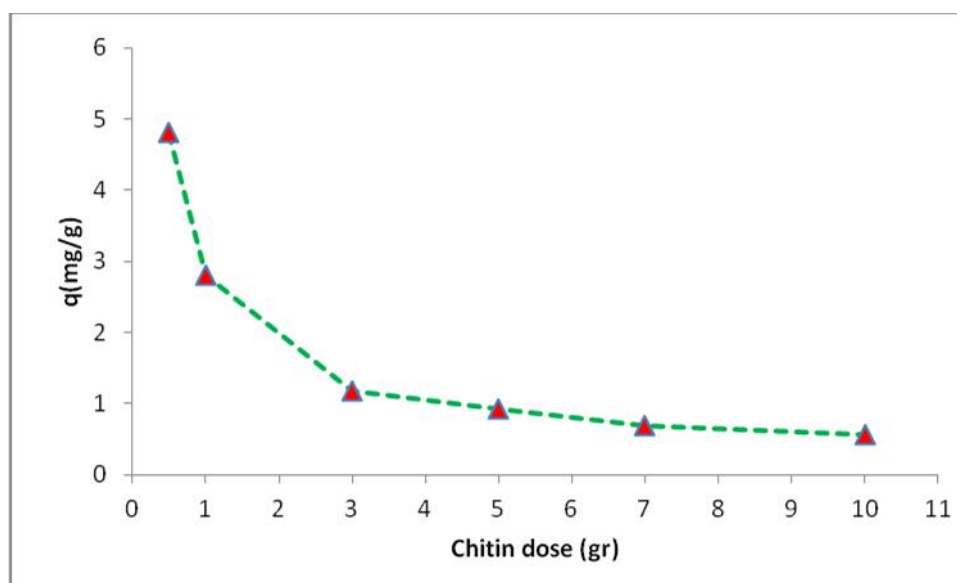


Fig 4. The effect of chitin dose onto Zn (II) uptake capacity

Discussion

The influence of pH on adsorption capacity

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, the speciation of metal in water, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. Thus, in this research, we evaluated the effect of pH on the adsorption of Zn (II) by chitin. The obtained results showed that adsorption capacity of chitin raises by increasing initial pH from 3 to 7. This increase in adsorption can be explained by considering the surface charge of the adsorbent material. At acidic pH values adsorption is low because of competition between H^+ ions and metal ions for the binding sites of the adsorbent and where surfaces have strong positive charge similar to that of the Zn ions. Moreover, at low pH, the amine groups of chitin are protonated to varying degrees, reducing the number of binding sites available for zinc uptake (18,19). As a result, zinc uptake is low in the presence of high concentrations of protons. While at higher pH, the ligands ($-COOH$, $-NH_2$) attract

positively charged zinc ion, and binding occurs due to an effective ion exchange mechanism that involves an electrostatic interaction between the positively charged groups in chitin and zinc ion (20,21). These observations are in agreement with Pinto et al. and Liu et al. (16, 22).

The effect of initial Zn(II) concentration on adsorption capacity

The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases (23). The effect of initial concentration of metal on Zn (II) removal was determined by equilibrating chitin at an initial concentration of metal ranging from 50 to 500 mg/l. The experimental data in this stage demonstrated that Zn (II) uptake increased with metal concentration, but the removal efficiency decreased. This effect of initial Zn (II) concentration on adsorption efficiency can be explained as follows: at low concentrations of metal, metal ion adsorption involves higher energy sites. As concentrations of metal increases, the higher energy sites are saturated and adsorption begins on a lower energy sites, resulting in a decrease in the

adsorption efficiency (23). These results are similar to those reported by Wasewar et al. and Kalyani et al. (19, 23).

The effect of adsorbent dose

To determine the needed chitin quantity for a maximal removal of zinc, the effect of chitin dosage on zinc removal was tested through conducting experiments with adsorbent dose varying from 0.5 to 10 g while keeping other parameters (pH, agitation speed, and contact time constant). The obtained results demonstrated that adsorption capacity of the adsorbent generally decreased when the dose increased, while the removal efficiency of zinc ions increased. This effect of adsorbent dose on adsorption efficiency can be explained by increasing unsaturated sorption sites for zinc ions as adsorbent loading is increased. These observations are in agreement with previously reported results by Wasewar et al. (19).

Comparison of Zn(II) removal efficiency with different adsorbents reported in literature

The adsorption capacities of the chitin for the removal of Zn (II) are compared with those of other adsorbents reported in literature and the values of adsorption capacities are presented in Table 4. Although the data collated in Table 4 may not represent equivalent or optimized conditions or with various zinc removal mechanisms in each case, it still provides a useful comparison for engineers in making practical decision for selecting a suitable

biosorbent. According to Table 4, the chitin adsorbent shows a good adsorption capacity when compared to the adsorption capacity of various low-cost adsorbents for zinc removal (24).

Conclusion

In this study, adsorption experiments for the removal of Zn (II) from aqueous solutions were carried out using chitin extracted from shrimp shells. The obtained results indicated that the pH was the main factor affecting metal removal and affected the adsorption rate onto chitin. Optimum pH values for maximum zinc removal for chitin were found to be 7. Moreover, the results showed that increasing the amount of adsorbent increased Zn (II) removal due to the increase in number of adsorption sites. Maximum removal of Zn (II) was obtained at adsorbent dose of 10 g for the chitin adsorbent. After comparing the experimental results of the Freundlich and Langmuir models, it was revealed that the Freundlich model gave a better correlation coefficient. In addition, the pseudo second order equation fit the experimental data well for the studied ion.

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