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Adsorption of Zn (II) from aqueous solution by using chitin extraction from crustaceous shell

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Original Article

Abstract

Removal of toxic heavy metals from wastewater is an important environmental challenge. In this Study, Zn (II) removal from aqueous solution by chitin extraction from crustaceous shells (shrimp and crab) was investigated. The biosorption studies were determined as a function of contact time, pH, initial metal concentration, and the amount of adsorbent. Adsorption of Zn (II) increased with decreasing concentration of the adsorbents and reached maximum uptake at 0.5 g. Effect of pH was studied in the range of 3-7 and the optimum conditions for both adsorbents were found in the range of 5-7. Zn (II) adsorption for both adsorbent was evaluated by Langmuir and Freundlich Isotherms. Results indicated that the Freundlich isotherm model was the most suitable one for the adsorption process using chitin extracted of shrimp and crab shells. The pseudo-first order and pseudo second order kinetic models were used to describe the kinetic data. The adsorption capacity (q_{max}) calculated from Langmuir isotherm and the values of the correlation coefficient obtained showed that chitin extracted from shrimp shells has the largest capacity and affinity for the removal of Zn (II) compared with the chitin extraction from the crab shells.

KEYWORDS: Adsorption, Chitin crab shells, Chitin shrimp shells, Kinetics, Zn (II)

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Introduction

Industrial wastewaters generated from industrialization activities may contain different toxic heavy metals.[1] Zinc is one of the most important metals often found in effluents discharged from industries involved in acid-mine drainage, galvanizing plants and municipal wastewater treatment plants.[2] It is important for the physiological functions of living tissue and regulates many biochemical processes. However, too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting and anemia.[3] Therefore, selective separation of Zn (II) from aqueous solution, especially wastewater has drawn more and more attention in recent years. There are many techniques for Zn (II) removal, such as chemical precipitation, ion exchange, membrane filtration, electrolytic methods and

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reverse osmosis. However, these methods are limited for high operational cost and inefficient in the removal of some heavy metal ions.[4] In contrast, adsorption owing to its advantages such as a variety of adsorbent materials and high efficiency is recognized as an effective and economic method for removal of pollutants from wastewaters.[5] 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 activated carbon, ion exchange resins, natural and synthetic zeolites are used.[6,7] In recent years, the use of chitin extracted from crustacean shell as biosorbents and organic substrates has gained importance.[8]

Chitin is the most important natural polysaccharide after cellulose found in crustaceous shells or in cell walls of fungi.[9] This polymer has been recommended as a suitable absorbent resource material because of its excellent properties such as biodegradability, biocompatibility, adsorption property, flocculating ability, polyelectrolisity and its possibilities of regeneration in a number of applications. The chitin structure (Figure 1) has positively charged amine (NH_2) functional groups which are responsible for the polyelectrolyte behavior. Therefore, chitin could adsorb negatively charged material with its positively charged functional groups to give electric neutrality.[10] Moreover, it has been recognized that chitin has significant potential as a biosorbent for metal removal. For example, the uptake of Cd^{2+} by chitin has been reported to be 14.9 mg/g.[11] Zhou et al.[12] investigated the adsorption of lead, cadmium, and copper onto cellulose/chitin beads; these metals were adsorbed at pH ranging from 3 to 6. Hawke et al.[13] studied the uptake of iron and manganese from seawater onto chitin; results showed low manganese (II) removal (< 10%) at pH 6-8.7 and increased removal (> 90%) at pH 9.5, while iron (II) was removed at levels of 22-30% at pH 2-8.

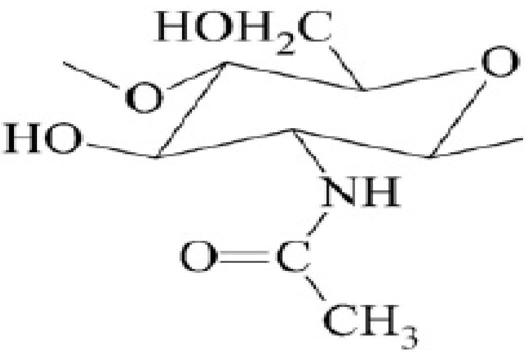

Figure 1. The basic structure of chitin[14]

In this work, we investigated the potential of chitin, extracted from shrimp and crab shells, to act as a biosorbent for Zn^{2+} removal from aqueous media. Chitin was prepared in the particle sizes range of 50-16 mesh and used in batch studies to quantify the effects of adsorbent dosage, contact time, pH and metal concentration on Zn^{2+} uptake performance.

Materials and Methods

Shrimp shells were washed several times with water and dried at 50° C overnight in a dry heat incubator. Afterwards, they were mechanically grinded in a mixer and passed through two layers of gauze. One hundred grams of shrimp shell powder were submerged in 1 L of 10% (w/w) HCl at room temperature for 24 h. After filtration with filter paper, the residue was washed with distilled water to neutral. Then the residue was submerged in 1000 ml of 10% (w/w) NaOH at room temperature for 24 h for. Then, the shrimp shell residue was washed with distilled water for removal the proteins. A volume of 250 ml of 95% ethanol was consecutively used to remove ethanol-soluble substances from the obtained crude chitin. Finally, the shrimp shell residue was subjected to the above procedure for 2 times.[14]

Chitin was extracted from the exoskeleton of crab with 1 N NaoH for 24 h at room temperature. This process was repeated 2 times with alkaline solution. The material was washed with water until the pH became neutral and demineralization was then carried out with 1 N

HCl at room temperature. The pigments were oxidized with 1% potassium permanganate and 1% oxalic acid, and then the material was washed until its pH was neutral. The material was then dried at 100° C for 2 h.[15]

In order to understand the adsorption mechanism, several characterizations were carried out on the two adsorbents. Fourier transform infrared spectrophotometer was applied to determine the presence of adsorbent functional groups (4000-400/cm). Brunauer-Emmet-Teller (BET) method was used for the samples specific surface determination. Water binding capacity (WBC) and fat binding capacities (FBC) of chitin were measured using the method of Kucukgulmez et al.[16] The degree of acetylation (DA) was calculated from the absorbance (A) ratios by using the following equation:

$$DA\,(\%) = \frac{A_{1655}}{A_{3450}} \times 115 \qquad (1)$$

Finally, the pH values of the chitin samples were determined according to the ASTMD 4972-01 standard method while the ash content was determined by heating at 530° C for 20 h.

A stock solution of 1000 mg/l of Zn (II) ions was prepared using analytical-reagent grade zinc chloride salt. The stock solution was diluted to appropriate concentrations accordingly. Each experiment was carried out in duplicates, and the average values were presented. All filtrate was analyzed using atomic absorption spectrometer (AAS 5FL model, Germany).

The effect of initial pH on the adsorption of Zn (II) ions was conducted using 1 g of adsorbent with 250 ml of 50 mg/l Zn (II) ions solution. The pH of the solution was adjusted in the range 3-7 using 0.1 M HCl or 0.1 M NaOH. The adsorbent was stirred in the Zn (II) ions solution at 300 rpm for 180 min. Since the optimum pH has been determined, the effect of adsorbate concentration was studied by varying the amount of adsorbent from 0.5 to 10 g under the optimum pH and agitation period of 180 min. The effect of metal concentration was investigated by mixing 250 ml of Zn (II) solution with metal concentration various under optimal conditions. Adsorption kinetic studies were carried out by shaking 250 ml of 50 mg/l Zn(II) solution with different contact time (0.5-4 h).

The amount of adsorbed Zn (II) on adsorbent (q_e, mg/g), and percent removals (%R) were calculated as follows:

$$q = \frac{(C_0 - C_e)V}{W} \qquad (2)$$

$$\%R = \frac{(C_0 - C_e)V}{C_0} \qquad (3)$$

Where q is the adsorption amount (mg/g), C_0 and C_e the initial and final concentrations (mg/l), V the volume of solution (l) and W is the mass of biosorbent used (g).

Results and Discussion

Characterization of chitin extraction from crustaceous shell

Chitin was obtained from shrimp and crab shells with a yield of 25.21% and 37.5% respectively. According to Muzzarelli, crustaceous shells consist mainly of chitin, protein and calcium carbonate with an average composition of 15-40%, 20-40% and 20-50% by weight, respectively.[17] This means that the yield of chitin was high on the laboratory scale. On the other hand, this value is similar to other studies.[18-20] The calculated DA values of crab and shrimp chitin using the formula (1) were 58% and 90%, respectively. These differences in DA could be attributed to the different isolation conditions of chitin, demineralization step or the deproteinization step under different alkaline conditions.[21] Majtan et al. obtained same results and showed the DA values of bumblebee and shrimp chitin were 87.3% and 99.0%, respectively.[22] Moreover, previous studies have shown the DA of chitin from various marine sources, including 79.5% in the king crab shell, 95.1% in the squid shell, and 84.6% in the Lobster.[23] Water and FBC of different chitin derivatives (chitosan) were reported as 355-611% and 217-477 %, respectively, by Kucukgulmez et al.[16] The WBC and FBC of crustaceous chitin in the present study were compatible to those reported by Kucukgulmez et al.[16] The moisture content of chitin obtained from crustaceous shells was measured to be 2.8% as shown in table 1, which is in agreement with Abdulkarim et al.[24] The ash content of crab chitin was higher than that of shrimp shell, this could be attributed the presence of high acetyl group and $CaCO_3$ in the crab chitin sample. Furthermore, table 1 indicates that a very small amount of ash (0.8%) was found in the chitin shrimp. This proves that a demineralization process for the isolation of chitin from shrimp shells was enough.

Table 1. Physico-chemical characteristic of adsorbents

Characterization	Chitin shrimp shells	Chitin crab shells
Yield (%)	25.21	37.5
PZC	6.7	7.2
Moisture (%)	2.813	2.86
Ash content (%)	0.8	10.75
Water binding capacities (%)	452	402
Fat binding capacities (%)	387	306
Surface area (m^2/g)	3.95	3.2

PZC: Point of zero charge

The pH_Z values for chitin shrimp and chitin crab were 6.7 and 7.2, respectively. Based on these values, the prepared adsorbents were almost similar. However, for chitin crab the pH_Z was higher than the pH_Z of chitin shrimp. This could be due to the presence $CaCO_3$ in the crab chitin sample. The BET surface area of the crab and shrimp chitin was 3.2 and 3.95 m^2/g, respectively.

The infrared spectra of chitin from shrimp and crab are shown in figure 2. According this figure, Fourier transform infrared (FTIR) spectra of two chitins were quite similar. The spectra were characterized by three significant amide bands at 1632, 1574 and 1315/cm, which correspond to the amide I stretching of C = O, the amide II of N-H and amide III of C-N, respectively. The vibrational absorption bands at 1063 and 1073/cm are assigned to the C-O stretching. Bands at 3500 and 3200/cm corresponded to O-H and N-H stretching vibration, respectively. In addition, absorption bands at 3000-2850/cm assigned to -CH stretching vibrations; at 2517.95 and 2563.91/cm assigned to O-H vibrations. Moreover, figure 2 also shows the FTIR spectra of (a) chitin shrimp-Zn (II) and (b) chitin crab-Zn (II). With respect to the FTIR spectrum of chitin, the FTIR spectra of chitin-zinc ion show changes in the intensity of the adsorption bands at 3500-3300/cm, 1419/cm and 1632/cm attributable to -OH and $-NH_2$ groups. These changes indicate complex formation, which decreases the energies of the bonds due to the adsorbed zinc ions.

Effect of pH

The pH of an adsorption system is a crucial parameter in any adsorption system as it describes the mechanism involved in the adsorption process. Figure 3 shows the biosorption efficiency of Zn (II) at different pH values from 3 to 7. As shown in figure 3, the adsorption capacities were very low for adsorbents at pH < 4, due to an increase in the positively charged active sites (NH_3^+). Moreover, in this pH, electrostatic repulsion between the positive protons of the surface of chitin and H^+ lead to decrease of adsorption capacity. At pH > 5, a decrease in the protonation of the active sites increased the adsorption capacities for chitin shrimp and crab. According to these results the maximum adsorption of Zn (II) ions onto the two adsorbents occurred at pH 7, therefore, this pH value was selected as the optimum pH throughout this study. On the comparison between chitin shrimp and chitin crab the adsorption of zinc was much higher in chitin shrimp than that of chitin crab due to the DA high, maximum surface area and free amino groups. Karthikeyan et al.[25] reported the neutral condition for a favorable removal of Zn (II) using chitosan. According to Vijayaraghavan et al.[26] report, a strong adsorption of Zn (II) occurs

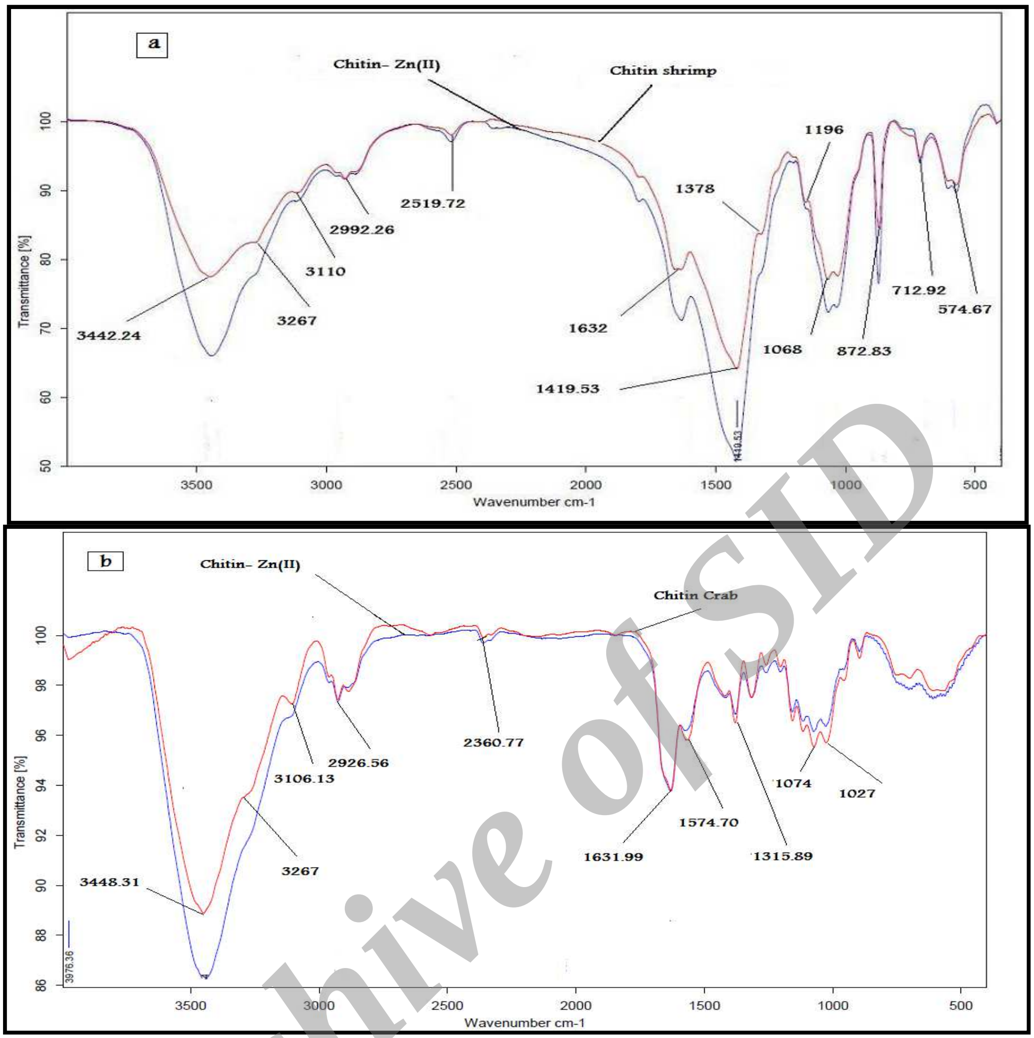

Figure 2. Infrared spectra of (a) chitin shrimp-Zn (II), and (b) chitin crab-Zn (II)

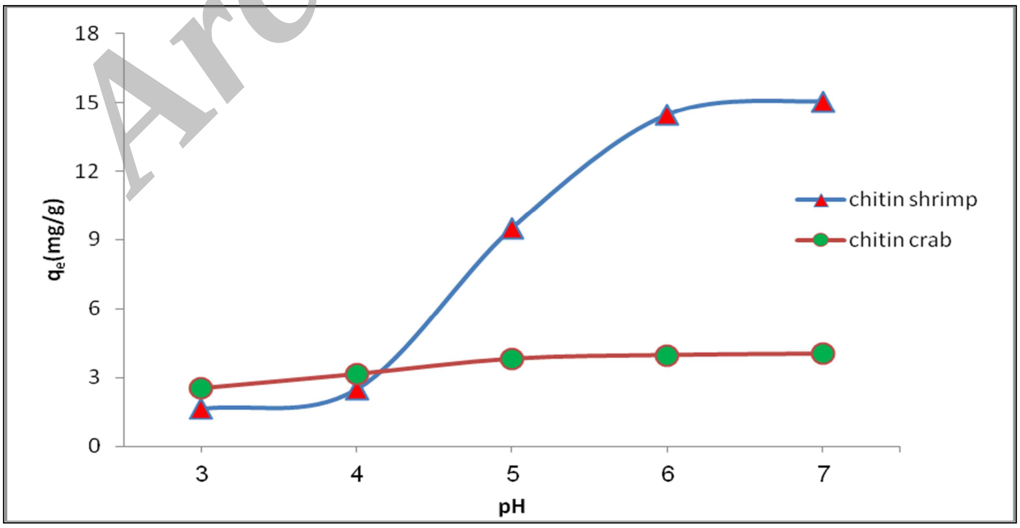

Figure 3. pH effect on zinc uptake by chitin crustaceous shell

on the crab shell particles in pH = 6. Lee et al.[27] reported that the presence of acetyl groups (DA high) in polymer increased their ability to bind with ferric ion.

Effect of initial metal concentration

Figure 4 shows the effect of initial metal concentration on the adsorption kinetics of the chitin at pH 7. An increase in the initial metal concentration leads to an increase in the adsorption capacity of the Zn (II) on chitin. This is due to the increase in the driving force of the concentration gradient, as an increase in the initial metal concentration. Figure 4 also shows that the adsorption of Zn (II) was much higher in chitin shrimp than that of chitin crab. This may be due to availability of DA and higher special surface area, or larger adsorption site compared with chitin crab. Gonçalves et al.[28] studied the adsorption of food dyes in a binary system by chitosan with different deacetylation degrees. Their results showed that the best conditions for the adsorption of food dyes onto chitosan were DD of 95%. Kurita[29] have shown that removal of mercury and copper ions increased with increasing deacetylation degrees of chitin. Wuertz et al.[30] demonstrated that the DA of polymers can affect the binding capacity for cations. Ho et al.[31] studied adsorption of metal ions on tree. In this study, it is confirmed that the adsorption efficiency is dependent on the specific surface area.

Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of Zn (II) was shown in figure 5. It could be seen from figure 5 that the removal efficiency of Zn (II) considerably increased with the increase of adsorbent dosage. This was due to the greater availability of exchangeable sites for Zn (II) ions. However, the adsorption capacity decreased with increasing the adsorbent dosage. This was due to the higher number of unsaturated adsorption sites as the adsorbent dosage was increased. Bhattacharya et al.[32] studied the effect of adsorbent dose on the Zn (II) adsorption capacity. Their results showed that with increasing adsorbent dosage more surface area is available for adsorption due to increasing in active sites on the adsorbent.

Adsorption kinetics

Figure 6 shows the change in the adsorption capacity of Zn (II) by chitin crustaceous shell as a function of time at pH 7. The adsorption capacity increases with the increase in contact time and the adsorption equilibrium occurs after 3 h.

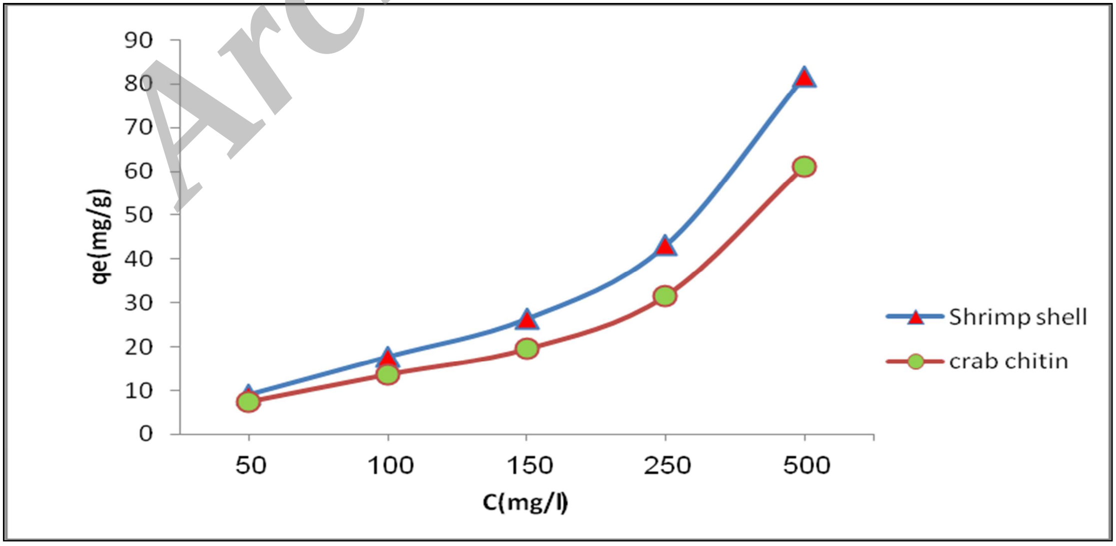

Figure 4. Effect of initial metal concentration on zinc uptake by chitin crustaceous shell

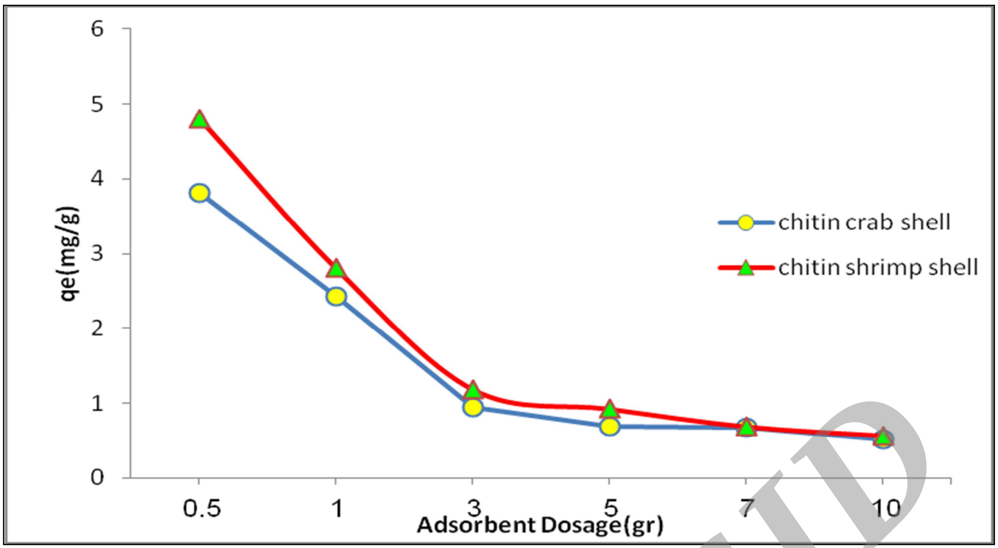

Figure 5. Effect of adsorbent dosage on the adsorption of Zn (II)

The kinetic data in table 2 is explicitly analyzed according to pseudo first-order and second-order. The R^2 and q_e values (Table 2) complied with experimental results, show that the pseudo second-order equation is the best one. Arshad et al.[33] studied the kinetics of adsorption Zn onto neem biomass. They found that pseudo-second order model provided better correlation than pseudo first-order model. Li et al.[4] computed the pseudo-second order model for their experimental data of studies on adsorption characteristics of Zn removal by magnetic chitosan modified with diethylenetriamine.

The adsorption isotherms

In order to determine the adsorption capacity the chitin crustaceous shell for Zn (II), and to identify the nature of this adsorption, the equilibrium adsorption isotherm is of basic importance. The Langmuir and Freundlich adsorption isotherm models were used to depict equilibrium sorption isotherms, and the calculated results of these models are given in table 3. As shown in table 3, the R^2 value of the Freundlich isotherm was greater than that of the Langmuir isotherm for the adsorption of Zn (II). This indicates that the adsorption of Zn (II) on chitin particles is better described by the Freundlich model than the Langmuir model. Kalyani et al.[34] reported that adsorption of zinc and copper on Gallus Domesticus shell powder followed both Freundlich and Langmuir models. Souag et al.[35] and Israel et al.[36] computed the Freundlich adsorption isotherm for their experimental data.

In order to anticipate the Zn (II) adsorption efficiency by chitin crustaceous shell and to understand whether the process is favorable or unfavorable for the Langmuir type adsorption process, the isotherm shape can be classified by the dimensionless equilibrium parameter (R), and can be calculated as following:

$$R_L = \frac{1}{1+bC_0} \qquad (4)$$

Where R_L, C_o, and b are the dimensionless equilibrium parameter or separation factor, the initial Zn (II) concentration (mg/l), and the Langmuir constant (mg/l), respectively. The value of RL (constant separation factor) indicates the shape of the isotherms to be either linear (RL = 1), favorable (0 < RL < 1), irreversible (RL = 0) or unfavorable (RL > 1). The data obtained in table 3 represent a favorable adsorption for both adsorbents.

A comparison of the maximum capacity q_{max} of chitin crustaceous shell with those of some other adsorbents reported in the literature is

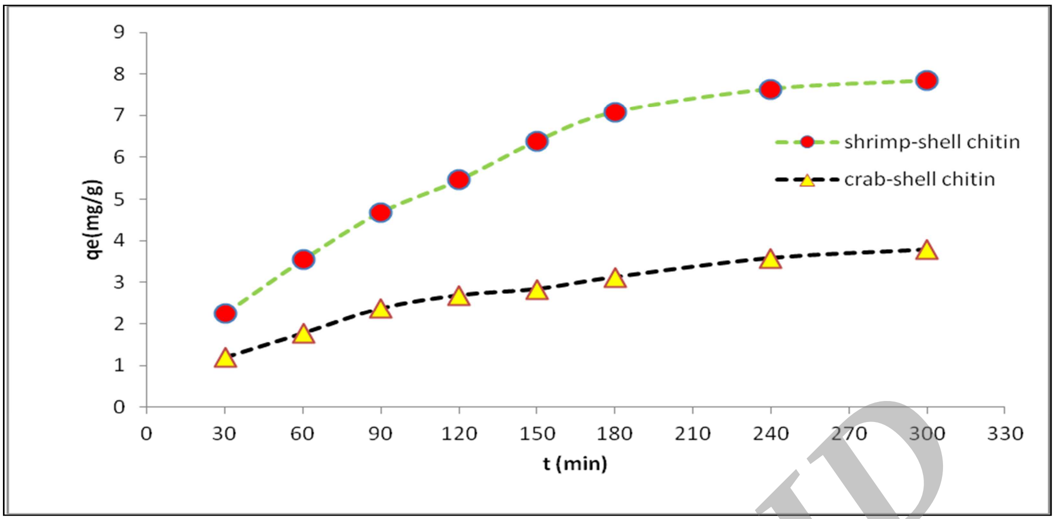

Figure 6. Influence of contact time on Zn (II) uptake by chitin crustaceous shell

Table 2. Kinetic model constants during Zn (II) biosorption at pH 7

Adsorbents	q_e (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 shrimp shells	7.64	149	10.01	0.9577	5.4	12.562	0.9815
Chitin crab shells	3.58	156	4.8128	0.9686	23	4.677	0.9918

K_1: The pseudo-first order rate constant (1/min); q_e: The amount of metal sorption at equilibrium (mg/g); R^2: Correlation coefficient; K_2: The pseudo-second order rate constant (g/mg/min)

Table 3. Langmuir and freundlich isotherm constants and correlation coefficients

Adsorbents	RL	Freundlich model			Langmuir model		
		K_f	n	R^2	q_m	b	R^2
Chitin shrimp shells	0.447-0.89	0.9664	1.1544	0.9992	270.270	0.00247	0.9783
Chitin crab shells	0.52-0.915	0.6013	1.2119	0.9973	181.181	0.00184	0.7391

RL: Constant separation factor; R^2: Correlation coefficient; K_f: Freundlich isotherm constant; q_m: The maximum adsorption capacity (mg/g); n: The Freundlich constant; b: The Langmuir constant

given in table 4. Differences of metal uptake are due to the differences in properties of each adsorbent such as structure, functional groups and surface area.

Conclusion

The results of the present investigation show that chitin crustaceous shell has considerable potential for the removal of Zn (II) ions from aqueous solution. The adsorbed amounts of Zn (II) increased with a decrease in adsorbent dosage due to the decreasing number of unsaturated adsorption sites. The solution pH plays a significant role in influencing the capacity of an adsorbent towards Zn (II) ions. An increase in the pH of solutions leads to a significant increase in the adsorption capacities

Table 4. Comparison of maximum capacity of chitin crustaceous shell for zinc adsorption with other adsorbents

Adsorbent	Uptake (mg/g)	Reference
Bentonite	52.91	37
Red mud	12.59	37
Bacillus subtilis	137.00	37
Fungal biomass	98.00	37
Lignin	95.00	37
Scarp rubber	100.00	37
Crab carapace	172.50	37
Amberlite IRC-718	156.89	37
Chitosan	58.83	37
Lewatit TP-207	89.56	33
Biosolids	36.87	33
Powered waste sludge	168.00	33
Neem bark	137.67	33
Neem leaves	147.08	33
Chitin shrimp shells	270.27	This study
Chitin crab shells	181.18	This study

of Zn (II) on the chitin crustaceous shell. The adsorbed amounts of Zn (II) ions increased with increase in contact time and reached the equilibrium after 180 min. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms. The Freundlich isotherm was demonstrated to provide the best correlation for the adsorption of Zn (II) on the chitin crustaceous shell. The pseudo-first-order and second-order kinetic models were used to describe the kinetic data. The dynamical data fit well with the second-order kinetic model. The uptake of zinc by chitin crustaceous shell in this study is comparable with other adsorbents reported in the literature. The results showed that zinc uptake by chitin crustaceous shell in this study was significantly higher than most of the selected biosorbents.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

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References

1. Veli S, Alyuz B. Adsorption of copper and zinc from aqueous solutions by using natural clay. J Hazard Mater 2007; 149(1): 226-33.
2. King P, Anuradha K, Lahari SB, Prasanna KY, Prasad VS. Biosorption of zinc from aqueous solution using Azadirachta indica bark: equilibrium and kinetic studies. J Hazard Mater 2008; 152(1): 324-9.
3. Fu F, Wang Q. Removal of heavy metal ions from wastewaters: a review. J Environ Manage 2011; 92(3): 407-18.
4. Li H, Bi S, Liu L, Dong W, Wang X. Separation and accumulation of Cu(II), Zn(II) and Cr(VI) from aqueous solution by magnetic chitosan modified with diethylenetriamine. Desalination 2011; 278(1-3): 397-404.
5. Aydin YA, Aksoy ND. Adsorption of chromium on chitosan: Optimization, kinetics and thermodynamics. Chemical Engineering Journal 2009; 151(1-3): 188-94.
6. Apiratikul R, Pavasant P. Batch and column studies of biosorption of heavy metals by Caulerpa lentillifera. Bioresour Technol 2008; 99(8): 2766-77.
7. Sari A, Tuzen M, Soylak M. Adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay. J Hazard Mater 2007; 144(1-2): 41-6.
8. Pinto PX, Al-Abed SR, Reisman DJ. Biosorption of heavy metals from mining influenced water onto chitin products. Chemical Engineering Journal 2011; 166(3): 1002-9.
9. Brugnerotto J, Lizardi J, Goycoolea FM, Arguelles-Monal W, Desbrieres J, Rinaudo M. An infrared investigation in relation with chitin and chitosan characterization. Polymer 2001; 42(8): 3569-80.
10. Ahmad AL, Sumathi S, Hameed BH. Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC. Chemical Engineering Journal 2006; 118(1-2): 99-105.
11. Benguella B, Benaissa H. Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies. Water Res 2002; 36(10): 2463-74.
12. Zhou D, Zhang L, Zhou J, Guo S. Cellulose/chitin bead for adsorption of heavy metals in aqueous solution. Water research 2004; 38(11): 2643 50.
13. Hawke D J, Sotolongo S, Millero F J. Uptake of Fe(II) and Mn(II) on chitin as a model organic phase. Marine chemistry 1991; 33(3): 201-212.
14. Du Y, Zhao Y, Dai S, Yang B. Preparation of water-soluble chitosan from shrimp shell and its antibacterial activity. Innovative Food Science & Emerging Technologies 2009; 10(1): 103-7.
15. Yen MT, Yang JH, Mau JL. Physicochemical characterization of chitin and chitosan from crab shells. Carbohydrate Polymers 2009; 75(1): 15-21.
16. Kucukgulmez A, Celik M, Yanar Y, Sen D, Polat H, Kadak AE. Physicochemical characterization of chitosan extracted from Metapenaeus stebbingi shells. Food Chemistry 2011; 126(3): 1144-8.
17. Kim SK. Chitin, Chitosan, Oligosaccharides and Their Derivatives: Biological Activities and Applications. New York, NY: Taylor & Francis Group; 2010.
18. Benavente M, Moreno L, Martinez J. Sorption of heavy metals from gold mining wastewater using chitosan. Journal of the Taiwan Institute of Chemical Engineers 2011; 42(6): 976-88.
19. Sagheer FAA, Al-Sughayer MA, Muslim S, Elsabee MZ. Extraction and characterization of chitin and chitosan from marine sources in Arabian Gulf. Carbohydrate Polymers 2009; 77(2): 410-9.
20. Wang Y, Chang Y, Yu L, Zhang C, Xu X, Xue Y, et al. Crystalline structure and thermal property characterization of chitin from Antarctic krill

(Euphausia superba). Carbohydr Polym 2013; 92(1): 90-7.
21. Susana Cortizo M, Berghoff CF, Alessandrini JL. Characterization of chitin from Illex argentinus squid pen. Carbohydrate Polymers 2008; 74(1): 10-5.
22. Majtan J, Bilikova K, Markovic O, Grof J, Kogan G, Simuth J. Isolation and characterization of chitin from bumblebee (Bombus terrestris). Int J Biol Macromol 2007; 40(3): 237-41.
23. Cardenas G, Cabrera G, Taboada E, Miranda SP. Chitin characterization by SEM, FTIR, XRD, and 13C cross polarization/mass angle spinning NMR. Journal of Applied Polymer Science 2004; 93(4): 1876-85.
24. Abdulkarim A, Isa MT, Abdulsalam S, Muhammad AJ, Ameh AO. Extraction and Characterisation of Chitin and Chitosan from Mussel Shell. Civil & Environmental Research 2013; 3(2): 108-14.
25. Karthikeyan G, Anbalagan K, Andal NM. Adsorption dynamics and equilibrium studies of Zn (II) onto chitosan. J Chem Sci 2004; 116(2): 119-27.
26. Vijayaraghavan K, Winnie HYN, Balasubramanian R. Biosorption characteristics of crab shell particles for the removal of manganese(II) and zinc(II) from aqueous solutions. Desalination 2011; 266(1-3): 195-200.
27. Lee JW, Ashby RD, Day DF. Role of acetylation on metal induced precipitation of alginates. Carbohydrate Polymers 1996; 29(4): 337-45.
28. Gonçalves JO, Duarte DA, Dotto GL, Luiz AA. Use of Chitosan with Different Deacetylation Degrees for the Adsorption of Food Dyes in a Binary System. CLEAN - Soil, Air, Water 2014; 42(6): 767-74.
29. Kurita K. Controlled functionalization of the polysaccharide chitin. Progress in Polymer Science 2001; 26(9): 1921-71.
30. Wuertz S, Muller E, Spaeth R, Pfleiderer P, Flemming HC. Detection of heavy metals in bacterial biofilms and microbial flocs with the fluorescent complexing agent Newport Green. J Ind Microbiol Biotech 2000; 24(2): 116-23.
31. Ho YS, Huang CT, Huang HW. Equilibrium sorption isotherm for metal ions on tree fern. Process Biochemistry 2002; 37(12): 1421-30.
32. Bhattacharya AK, Mandal SN, Das SK. Adsorption of Zn(II) from aqueous solution by using different adsorbents. Chemical Engineering Journal 2006; 123(1-2): 43-51.
33. Arshad M, Zafar MN, Younis S, Nadeem R. The use of Neem biomass for the biosorption of zinc from aqueous solutions. J Hazard Mater 2008; 157(2-3): 534-40.
34. Kalyani G, Babu Rao G, Saradhi V, Kumar YP. Equilibrium and kinetic studies on biosorption of zinc onto Gallus Domesticus shell powder. ARPN Journal of Engineering and Applied Sciences 2006; 4(1): 39-49.
35. Souag R, Touaibia D, Benayada B, Boucenna A. Adsorption of Heavy Metals (Cd, Zn and Pb) from Water Using Keratin Powder from Algerien Sheep Hoofs. European Journal of Scientific Research 2009; 35(3): 416-25.
36. Israel U, Eduok UM. Biosorption of zinc from aqueous solution using coconut (Cocos nucifera L) coir dust. Archives of Applied Science Research 2012; 4(2): 809-19.
37. Lu S, Gibb SW, Cochrane E. Effective removal of zinc ions from aqueous solutions using crab carapace biosorbent. Journal of Hazardous Materials 2007; 149(1): 208-17.