Application of nanochitosan and chitosan particles for adsorption of Zn(II) ions pollutant from aqueous solution to protect environment

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Abstract Existence of heavy metals like zinc within water source is considered as one of the most important environmental problems. Accumulating within alive tissues, zinc raises various diseases and disorders. Chitosan is a hydrophilic polymer which is raised from acetyl groups of chitin from alkaline solution: it is employed widely as a well-known adsorbent for removing heavy metal ions. Present study aimed at optimizing the production of chitosan nano size particles by method of calvo and compared the adsorption of Zn (II) ions by chitosan macro and nano size particles. Adsorption experiments were conducted in a batch system and the effects of temperature, pH, contact time and initial concentration of metal ions on productivity of adsorption of zinc ions have been considered. Performing analysis DLS revealed that mean size of nano chitosan particles is 19.84 nm. Optimal adsorption by chitosan and nano chitosan has been done in pH 7 and about of 5. Efficiencies of both adsorbent were increased by increasing contact time. Both adsorbent had maximum efficiency at the temperature of 25 °C. At the concentration of 10 mg/L of zinc metal ions, maximum effective removal of chitosan macro and nano size particles were 90.80 and 99.10 %, respectively. Maximum capacity of adsorption by chitosan macro and nano size particle was 196.07 and 370.37 mg/g, respectively. Adsorption kinetics followed a pseudo second order model. Nanochitosan compared to chitosan particles had higher removal efficiency for Zinc

metal ions due to nano size of particles, larger adsorption surfaces and more functional groups.

Keywords Heavy metals · Zinc · Nanochitosan · Adsorption · Adsorption isotherm · Adsorption Kinetic

Introduction

The pollution of water resources by heavy metals is considered as one the most important environmental problems (Abdelwahab et al. 2013). The most common metals ion founded within wastewater include lead, copper, zinc, cadmium, chromium, and nickel (Cristian et al. 2015). Zinc is employed widely as an important and necessary element in such industries as dyeing, casting, automobile manufacturing, batteries, dentistry, medicine, fungicide production, galvanize production units, processes of exploitation and melting of metals, thermoplastics and stabilizers (Brian Zieske 2015). The effect of zinc in the human body and electron transition within various enzymatic reactions has been clarified; thus, its tiny amount is necessary for human body. Large amount of this element, due to its biological aggregation, can lead to such diseases as genetic mutations and fetal deficiencies. Zinc deficit can lead to growth weakness, losing the sense of taste and deduction of generation system activities. The solutes of zinc have an astringent taste; they have corrosive influence on skin and inflammation effects on the digestive system. Chronic toxicity of zinc can cause muscle weakness, pain, upset stomach, unbalanced electrolytes, losing water of body, stomachache, dizziness; and kidney disability is a result of large size of zinc chloride (El-Shafey 2010; Jain 2013; Brian Zieske 2015).

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Various methods have been recommended for heavy metal removal out of wastewater among of which, filtration, reverse osmosis, chemical oxidation or reduction, activated carbon, sedimentation, coagulation, ion exchange, membrane processes, electro-dialysis, electrode position, and adsorption can be mentioned (Gakwisiri et al. 2012). The method of adsorption is widely used because of its easy function, low level of energy consumption, simple preservation, high capacity of adsorption and high efficiency for water and wastewater treatment (Jain et al. 2015). This method makes use of various adsorbent like activated carbon, charcoal ashes, bentonite, clay, algae, raw crab shell and bacteria (Wan Ngah et al. 2011; Ahlam et al. 2012; Patricia et al. 2013; Haider et al. 2014; Karnib et al. 2014; Chuanqiang et al. 2016). Recently, due to their availability, cost effectiveness and lack of toxicity, biopolymers have been adsorbent a proper adsorption of heavy metals by researchers (Haider et al. 2014). Chitin (N-acetyl-D- β -glucosamine) has been known as the second natural polysaccharide which can be found abundantly after cellulose. This polymer is a white, in flexible substance which can be found within the outer shells of such crustaceans as crabs, lobster, erythema, shrimp, and within some foods like grains, yeast, banana, and fungus (Jaa-farzadeh et al. 2014). Chitosan is a hydrophilic, cationic polymer which is obtained from removing acetylchitin groups from alkaline solution. Because of its adsorption and ion exchange, chitosan is able to combine with metal ions. Thus, it has gained variety of functions on adsorption of heavy metals. In order to obtain chitosan derivatives of higher adsorption capacity, it has been reformed through some chemical and physical processes (Wan Ngah et al. 2011; Ahmad et al. 2015). These processes have been conducted in order to improve reactivity of polymers or to raise adsorption kinetic. The unique characteristics of nano size particles—small size and large surface—have created high capacity for adsorption of metal ions (Singh et al. 2011). Adsorption of some metal ions like arsenic, gold, copper, nickel, lead, and cadmium by bio adsorbent chitosan has been investigated (Laus et al. 2010; Benavente et al. 2011; Singh et al. 2011; Sobhanardakani et al. 2016). The studies have demonstrated that chitosan, having amine and hydroxyl groups, can be used to remove heavy metal ions. On the other hand, a number of studies have been performed on metal ions adsorption by such derivatives of chitosan as chitosan grafted polyacrylonitrile, xanthate-modified magnetic chitosan and other derivatives of chitosan (Ramya et al. 2011; Zhu et al. 2012; Bassi and Shiv 2013; George and Dimitrios 2015).

This study aimed at (1) optimizing the production of chitosan nano size particles by method of calvo, (2) comparing the removal of zinc metal ions by chitosan and synthesized nano chitosan out of aqueous solutions, (3)

investigation of temperature, pH, contact time and initial concentrations of metal ions influences on the efficiency of zinc adsorption, isotherm and kinetics.

Materials and methods

Sodium tripolyphosphate (STPP), zinc nitrate ($\text{Zn}(\text{NO}_3)_2$), acetic acid (CH_3COOH), sodium chloride (NaCl), hydrochloric acid (HCl) and sodium hydroxide (NaOH) all were supplied from the German Merck company. Chitosan with mean molecular weight and degree of deacetylation 85 % was bought from Chinese Sigma Aldrich Company (Sureshkumar et al. 2011; Sivakami et al. 2013).

RH basic hot plate magnet mixer (IKA Co. Germany) for initial mixing of solution and used in the adsorption experiments. Centrifuge model EBA 8 (HETTICH Co. Germany) was used to separate adsorbent particle from solution. pH was measured by means of pH meter Jenway 3510. Flame atomic absorption spectrophotometer (FAAS) SpectrAA-200 (Schimadzu Co. Japan) was used to determine the concentration of remained metal ions of samples. Dynamic light dispersion plant (Zetasizer MAL 1094694), made in England for measuring mean size of synthesized nano particles. Field Emission Scanning Electron Microscope (FE-SEM HETTICH S4160) for considering morphology of obtained chitosan macro and nano size particles were employed. In order to investigate functional groups and comparing molecular structures of chitosan macro and nano size particles, as well as transformations raised from zinc metal ions adsorption, FTIR test by Perkin Elmer spectrum two (Japanese) were used.

Chitosan nano particle preparation

Chitosan nano particles were prepared using calvo method. According to this method, chitosan of mean molecular weight was solved under mild-stirring conditions within acetic acid 1.5 % at the exposure of sodium chloride. Various concentrations of chitosan (1, 1.5, 2, 2.5, 3 g/L) were resulted. Chitosan solution pH was set on (4.5, 5, 5.5 and 6). STPP solution was obtained of concentration of 1 g/L in deionized water. pH of STPP solution set on 5. In order to prepare chitosan nano particles, STPP solution was added in drops to the stirring chitosan solution in volume ratio of 14:1 (CTS: STPP); then, resulted solution was stirred in the room temperature for periods of (5, 25, 45, 65 and 85 Min) with 750 rpm. In order to obtain chitosan nano particles with the smallest size, 140 mg of chitosan was dissolved in 75 mL of acetic acid 1.5 %, and then, 210 mg of sodium chloride was added to the solution, slowly. Then, 5 mL of sodium tripolyphosphate solution of concentration 1 g/L was added in drops; after 25 min of

mixing with the rate of 750 rpm, a milky solution was obtained, pH of which was 4.65 and contained chitosan nano particles (Calvo et al. 1997; Sivakami et al. 2013; Singh et al. 2014).

Metal ions solution preparation

The solution of 1000 mg/L of heavy metal employed in experiments of capturing weight of metal salt and comparing with expected amount of metal existence within solution was supplied. The salt uses for zinc metal was zinc nitrate of molecular formula $\text{Zn}(\text{NO}_3)_2$. To do this, 2.9 g of zinc salt was solved in deionized water and then became volume 1000 mL within volumetric flask. Metal solutions needed for subsequent experiments were obtained from this solution.

Adsorption experiments

Throughout the experiment, the volumes of samples were set as 100 mL.

Adsorption by chitosan macro size particles

A 250 mL Erlenmeyer flask was filled by 100 mL of zinc nitrate ($\text{Zn}(\text{NO}_3)_2$) aqueous solution, then 140 mg of chitosan was added; also pH was set by NaOH and HCl solutions. After this step the flask was sealed and placed on magnetic mixers at speed of 300 rpm at certain temperatures. After desirable time, adsorbent was separated by centrifuging the solution under speed of 6000 rpm for 30 min, and then concentrations of remained ions were measured by flame atomic absorption spectrophotometer (Sivakami et al. 2013; Jain 2013; Nabila et al. 2014).

Adsorption by chitosan nano particles

By addition of 5 mL of STPP solution (1 g/L) to 70 mL of chitosan solution (140 mg chitosan plus 210 mg NaCl in 1.5 % acetic acid) under magnetic stirring (750 rpm) at room temperature, a milky dispersion with a pH of 4.65 was obtained which contain chitosan nano particle. Then 25 mL of zinc nitrate solution with different concentration was added and the result solution was poured in a 250 mL Erlenmeyer flask. The sealed flask was placed on magnetic mixers at speed of 300 rpm at certain temperatures. After passing desirable time, adsorbent was separated and its concentration was measured. In adsorption experiment HCl and NaOH solutions were used to set pH of solution (Sivakami et al. 2013; Nabila et al. 2014).

Adsorption process was performed in order to determine the effects of temperature, optimal pH, contact time, initial concentration of zinc ions, and determination of adsorption

kinetic coefficients and isotherm constants. The samples were taken at the times 5, 15, 25, 35, 45, 55, 65, and 75 min for chitosan nano size particles, and at the times 10, 35, 60, 85, 110, 135, 160 and 185 min for chitosan macro size particles, of which, at the times 65 and 160 min, adsorption reach to equilibrium for chitosan nano and macro size particles, respectively. Effect of pH in the ranges of 2–6 and 4–8 for chitosan nano and macro size particles, initial concentration of metal ions at the range of 10–1000 mg/L, and effect of temperature at the range of 15–55 °C were considered for chitosan macro and nano size particles (Sureshkumar et al. 2011; Sivakami et al. 2013; Jain 2013; Nabila et al. 2014).

In order to capture the equilibrium adsorption capacity of the adsorbent, the following equation was employed:

$$q_e = \frac{v(c_0 - c_e)}{m} \quad (1)$$

Where: q_e = amount adsorbed per unit weight of adsorbent at equilibrium (mg/g), V = volume of metal bearing solution (L), C_0 = initial metal concentration (ppm), C_e = final metal concentration (ppm), m = amount of biomass (g) (Jain 2013).

Adsorption and adsorbent's ability to absorb heavy metal ions out of aqueous solutions were measured by Langmuir and Freundlich isotherm models. Langmuir's model suggests that adsorption has been performed within monolayer or constant number of surface adsorption sites; all adsorption sites have equal energies, and it is assumed that structure of adsorbent is homogenous (Chen et al. 2008).

Langmuir's equation is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

Where: q_e = amount adsorbed (mg/g), C_e = equilibrium concentration of the metal ion (mg/L), q_m = maximum amount of adsorbed metal ion per unit mass of sorbent (mg/g), K_L = is the Langmuir constant related to the energy of adsorption (L/mg).

Freundlich's model illustrates adsorption within heterogeneous systems. This model follows Eq. 3 (Ramesh et al. 2008).

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where: q_e = Amount adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e = Equilibrium concentration of adsorbate in solution after adsorption (ppm), K_F = Empirical freundlich constant or capacity factor (L/g), n = Freundlich's exponent which demonstrates severity of adsorption.

In order to take a better understanding of dynamics of metal ions adsorption on chitosan macro and nano size

particles, Lagergren pseudo first order kinetic and Ho pseudo second order kinetic were employed for illustrating data. Equation of pseudo first order model is presented as (Dang et al. 2009):

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (4)$$

Where: q_t = Amount of metal adsorbed at any time (mg/g), q_e = Amount of metal adsorbed at equilibrium time (mg/g), K_1 = Pseudo first order rate constant (min^{-1}).

Integrating above equation, its linear form appears (Dang et al. 2009):

$$\ln(q_e - q_t) = -K_1 t + \ln q_e \quad (5)$$

Equation of pseudo second order model is (Dang et al. 2009):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (6)$$

Integrating of which yields following linear form of that (Dang et al. 2009):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

In the Eqs. 5–7, t is the time of sampling on the base of minutes, and K_2 is the pseudo second order rate constant.

Results and discussion

Effect of different concentrations of chitosan on the size of chitosan nano particles

In order to consider the effect of this parameter, experimental conditions were designed in which, 5 mL of sodium tripolyphosphate with concentration 1 g/L and pH 5 was added to 70 mL of chitosan solution with concentration of 1, 1.5, 2, 2.5 and 3 g/L and pH 5 at the exposure of sodium chloride under magnetic mixing conditions for stirring period of 15 min and rate of 750 rpm; the obtained results are presented in Table 1. When chitosan concentration increase from 1 to 1.5 and 2 g/L size of particles shrink; whereas when chitosan concentration changes from 2 to 2.5 and 3 g/L, size of nano particles grow. In general, when weight of chitosan increases up to sodium tripolyphosphate, chitosan concentration within solution and subsequently, viscosity of the solution raise. As a result, resistance of liquid phase increases

against dispersion and size of nano particles grow. In other words, increase of chitosan weight ratio up to sodium tripolyphosphate leads to the reduction of density of the substance producing cross links within the solution; and also, chitosan molecules of positive charge rise within solution, due to increase of raised viscosity. Thus, because of strong hydrogenic inter-chaine bindings which are formed among chitosan molecules, they have a little tendency to do cross links with sodium tripolyphosphate. Therefore, by reducing cross links size of nano particles increase. By reduction of weight ratio chitosan: sodium tripolyphosphate, the density of substance forming cross links within solution raises; and tripolyphosphate ions can easily cross link to positive charged amine groups which leads to formation of perfect cross links of chitosan molecules and reduction of particles size. To reduce weight ratio chitosan: tripolyphosphate for reduction of particles size is possible in a certain level. More reduction of this ratio will lead to reduction of chitosan concentration and increasing of density of the substance forming cross links. In the other words, rising of density of tripolyphosphate within solution will result in nano particles get close to each other's and amassed. Finally size of particles will grow (Mi et al. 1999; Kaloti and Bohidar 2010).

Effect of stirring period duration on the size of chitosan nano particles

In order to this, 5 mL of sodium tripolyphosphate solution with the concentration of 1 g/L and pH 5 was added to 70 mL of chitosan solution having concentration 2 g/L and pH 5 at the exposure of sodium chloride and under magnetic mixing conditions at the rate of 750 rpm for periods of 5, 25, 45, 65 and 85 min; obtained results are presented in Table 2. At first, some particles with large size were resulted; the reasons of their appearance were imperfect reaction between chitosan and tripolyphosphate and existence of micro size particles of chitosan. The smallest nano size particles were obtained during 25 min stirring period, as a result of perfection of reaction between chitosan particles and tripolyphosphate. Also, increasing stirring period more than 25 min result in a little growing of particles size; this trend can be attributed to increase of possibility of free molecules attending in reaction within solution. Conducted studies have demonstrated that increasing reaction time causes nanoparticles to grow (Singh et al. 2008).

Table 1 Effect of different concentrations of chitosan on chitosan particles size

Concentrations of chitosan (g/L)	1	1.5	2	2.5	3
Particle size (nm)	227.09	115.3	26.12	119.8	284.3

Table 2 Effect of stirring period duration on chitosan particles size

T (min)	5	25	45	65	85
Particle size (nm)	672.17	24.08	47.24	53.2	68.45

Effect of pH of chitosan solution on the size of chitosan nano particles

In order to consider the effect of chitosan solution pH on the size of nano particles, 5 mL of sodium tripolyphosphate solution with concentration of 1 g/L and pH 5 was added to 70 mL chitosan solution with concentration of 2 g/L and pH 4.5, 5, 5.5 and 6 at the exposure of sodium chloride, under magnetic mixing conditions at the rate of 750 rpm for stirring period of 25 min. Obtained results are presented in Table 3. Sodium tripolyphosphate solved within deionized water, produces ions OH^- and $\text{P}_3\text{O}_{10}^{5-}$ which were present within sodium tripolyphosphate solution, simultaneously. Within high pH, in order to attach chitosan NH_3^+ groups, ions OH^- compete with ions $\text{P}_3\text{O}_{10}^{5-}$. Ions OH^- , due to their small size, can penetrate easily into chitosan and make a sedimentary layer; whereas, ions OH^- decrease by acidification of pH, and as a result, ions $\text{P}_3\text{O}_{10}^{5-}$ remains in the solution. Therefore, chitosan can easily make cross links to sodium tripolyphosphate and produce small sized nano particles (Mi et al. 1999; Kaloti and Bohidar 2010).

Size distribution of chitosan nano particles

According to the conducted experiments, for obtaining chitosan nano particles with the smallest sizes, the most proper concentration of chitosan is 2 g/L; pH of chitosan solution should be 4.5; time of 25 min, is needed for stirring; concentration of sodium tripolyphosphate solution should be 1 g/L and its pH be 5; sodium chloride of concentration 3 g/L is needed; the volume ratio of chitosan:STPP should be 14:1; and acetic acid of the weight 1.5 % should employed; all of which would result information of nano particles with mean diameter 19.84 nm, as shown on the Fig. 1.

FTIR analysis

Figure 2 illustrates FTIR spectrum of chitosan (a) and chitosan banded with zinc ions (b). Peak of 3439.90 cm^{-1} is related to functional groups of $-\text{OH}$ and $-\text{NH}$ within chitosan figuration. Also, existence of peak in wave length of 1637.20 cm^{-1} is the result of existence of amine group

Table 3 Effect of pH of chitosan solution on chitosan particles size

PH	4.5	5	5.5	6
Particle size (nm)	19.84	24.08	37.09	49.31

within structure of the material. Peak of 621.07 cm^{-1} is related to functional group of $-\text{CH}$. Through FTIR spectrum of chitosan banded with metal ions, peak of 3441.67 cm^{-1} is related to functional groups of $-\text{NH}$ and $-\text{OH}$. Also, peaks of 1637.27 and 658.05 cm^{-1} are related to functional groups of amine and $-\text{CH}$. As can be observed, resulted energy droppings in all three peaks are due to adsorption of metal ions by these functional groups.

Figure 3 shows FTIR spectrum of chitosan nano size particles (a) and zinc-loaded chitosan nano particles (b). The peak of 344.85 cm^{-1} is related to functional groups of $-\text{NH}$ and $-\text{OH}$. Disappearing of peak of 1637.20 cm^{-1} and appearing of peak of 1638.07 cm^{-1} is because of ionic connection among ammonium and phosphoric ions. Also, peak of 1279 cm^{-1} is created due to $\text{P}=\text{O}$ within molecular structure of chitosan nano particles. The peak of 625.14 cm^{-1} reveals the existence of functional groups of $-\text{CH}$. Through FTIR spectrum of nano particles of chitosan banded with metal ions, the peak of 3443.68 cm^{-1} is related to the functional groups of $-\text{NH}$ and $-\text{OH}$. And, the peak of 1638.58 cm^{-1} is related to the binding of ammonium and phosphoric ions; while the peak of 695.76 cm^{-1} is related to the functional group of $-\text{CH}$. Through all mentioned peaks due to adsorption of zinc metal ions, energy droppings of functional groups are observed. Also, the peak of 1279 cm^{-1} , because of binding of phosphoric groups and metal ions of zinc, has been disappeared.

Morphology of chitosan and chitosan nano particles

FE-SEM images of chitosan macro and nano size particles are presented in Fig. 4. In the figure of chitosan nano size particles, the volume ratio of chitosan to sodium tripolyphosphate 14:1 and pH is 4.65. Many pores throughout chitosan macro and nano size particles which can be observed clearly in the figure, have made more increasingly functionality for this material within adsorption.

Effect of pH on Zn^{2+} adsorption

Figure 5 shows the effect of pH on the adsorption of metal ions of zinc by chitosan macro and nano size particles. As can be observed, increasing pH causes the increase of zinc ions removal out of aqueous solution which is due to predominance free species of zinc ions within solution that are involved in adsorption process; the highest removal amount in pH was 7. In pH higher than 7, zinc ions in the form of $\text{Zn}(\text{OH})_2$ begin to sediment; thus, removing decreases (Karthikeyan et al. 2004). In the case of adsorption of zinc metal ions by chitosan nano particles, increasing pH causes increasing of metal ions removal, so that the most removal percentage of pH is about of 5. There

Fig. 1 Size distributions of chitosan nano particles with mean size of 19.84 nm

	Size (d.nm):	% Number:	St Dev (d.nm):
Z-Average (d.nm): 19.84	Peak 1: 19.23	100.0	6.238
Pdl: 0.600	Peak 2: 0.000	0.0	0.000
Intercept: 0.931	Peak 3: 0.000	0.0	0.000
Result quality : Good

Fig. 2 FTIR spectra of chitosan macro size particles (a) and zinc-loaded chitosan particles (b)

is a competition between Zn^{2+} and H^{+} to bind with amine and triphosphoric groups, so at low pH lots of adsorption sites are protonated, and sorption capacity of chitosan macro size particles and chitosan nanosize particles for Zn will reduce (Trahar et al. 1997). Adsorption of metal ions depends largely on protonation or non-protonation of amine and phosphoric groups of chitosan nano particles (Sreejalekshmi et al. 2009). When pH decreases within the solution, amine groups present in chitosan nano particles begin to protonated of various degrees; thus, the number of points available for chelating metal ions decrease, and leads to electro-statically repulsion of metal cations (Chu 2002). Whereas, within higher pH, ligands of adsorbent, like $\text{P}_3\text{O}_{10}^{5-}$, can increase density of negative

charge on the surface of ligands and, as a result, electrostatic adsorption of positive- charged metal ions on the surface of ligands increase and adsorption percentage rises. Within pH higher than 5, due to increase of OH^{-} ions, penetration of ions into the structure of chitosan nano particles makes some sedimentary layers, and leads to reduction of adsorbent surface and amount of metal ions removing (Mi et al. 1999; Kaloti and Bohidar 2010).

Effect of the initial concentration of the metal ions on Zn^{2+} adsorption

Removal percentage of metal ions by chitosan macro and nano size particles, affected by initial concentration of

Fig. 3 FTIR spectra of chitosan nano particles (a) and zinc-loaded chitosan nano particles (b)

Fig. 4 FE-SEM pictures of chitosan macro size particles (a) and chitosan nano size particles (b)

Fig. 5 Effect of pH on Zn²⁺ adsorption, $C_0 = 1000$ mg/L, 300 rpm, 25 °C

Fig. 6 Effect of initial metal ion concentration on Zn²⁺ adsorption, 300 rpm, 25 °C, chitosan pH = 7, nanochitosan pH = 5

metal ions, at the range of 10–1000 mg/L and pH of 7 and 5 and concentration of 2 g/L of adsorbent was considered. Figure 6 illustrates the effect of initial concentration on the adsorption percentage of zinc ions. Increase of initial concentration of metal ions leads to reduction of removal percentage; the highest removing percentages by chitosan macro and nano size particles at the concentration of 10 mg/L of zinc metal ions and 2 g/L of adsorbent were 90.80 and 99.10 %, respectively; and pH were 7 and 5. Rising initial concentration of metal ions causes gradient

driving force of concentration to increase, so adsorption capacity rises, too. At the low concentrations, about all metal ions react to active adsorption points of adsorbent, while there are some free adsorption points at the surface of adsorbent. At the high concentrations of metal ions, each of active adsorption points is surrounded by many metal ions. Therefore, taking more adsorption points leads to increase of adsorption capacity. At the higher concentrations, adsorption capacity is almost constant which is resulted from saturated points of adsorption (Sari et al. 2007). The

poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of zinc to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial zinc concentration. Therefore, it was evident from the results that zinc adsorption was dependent on the initial metal concentration (Jain 2013).

Adsorption isotherm results

The equilibrium data for the adsorption are commonly known as adsorption isotherms. It is essential to know them so as to compare the effectiveness of different adsorbent material under different operational conditions and also to design and optimize an adsorption system. Langmuir and Ferendlich models of adsorption are represented in Figs. 7 and 8. Both of them conform to the fit date of adsorption, but observing figures and data of Table 4, it is clarified that Langmuir's model can better predict metal ions adsorption by chitosan macro and nano size particles. So, it can be concluded that adsorbent surface in both micro and nano dimensions are homogeneous; and surface adsorption is often done in the form of monolayer. In the case of chitosan macro size particles, correlation coefficient of adsorption of metal ions in Langmuir's model and maximum capacity of adsorb of zinc metal ions were obtained as 0.9920 and 196.07 mg/g respectively. Also, the amounts of chitosan nano size particles are 0.9940 and 370.37 mg/g.

Effect of contact time on Zn^{2+} adsorption and adsorption kinetic results

One of the selection criterions of adsorbent is high rate of adsorption. The effect of contact time on zinc adsorption

process was determined by conducting adsorption experiments at different contact time between the adsorbate and adsorbent in the range of 10–185 and 5–75 min for chitosan macro and nano size particles. The concentration of metal ions was 1000 mg/L; pH was kept as 7 and 5 for chitosan macro and nano size particles, and temperature 25 °C. Figure 9 presents the graph of effect of contact time on the adsorption level. The figure depicts that the rate of percent removal of zinc was higher at the beginning. This may be due to the larger surface area of the adsorbent being available at beginning for the adsorption of zinc ions. According to the Figure, raising contact time in both adsorbent causes them to perform more effectively. Equilibrium time and maximum efficiency of chitosan macro size particles are 160 min and 26 %, while of chitosan nano size particles are 65 min and about 50 %, respectively. The reason for this is that nano size particles adsorption surfaces are larger and increasing of their functional groups. It is clear for the results that the adsorption of zinc was dependent on contact time.

In order to consider adsorption kinetics, pseudo first order and pseudo second order models were employed for illustrating data Figs. 10 and 11 and Table 5 represent the results of two models; these values correspond to the experimental data. Ho pseudo second order kinetic model yielded more accepted approximation of experimental data ($R^2 > 0.99$) according to which, adsorption rate depends on chemical adsorption.

Effect of the temperature on Zn^{2+} adsorption

The temperature effect on removal of zinc ion using chitosan macro and nano size particles was studied within the range of 15–55 °C. Other parameters such as dose of initial metal ions and pH of solution were kept constant. Figure 12 illustrates the effect of temperature on the efficiency of zinc adsorption according to which, the

Fig. 7 Langmuir isotherm model fitting chitosan (a) and nanochitosan (b), 300 rpm, 25 °C, chitosan pH = 7, nanochitosan pH = 5

Fig. 8 Ferendlich isotherm model fitting chitosan (a) and nanochitosan (b), 300 rpm, 25 °C, chitosan pH = 7, nanochitosan pH = 5

Table 4 Isotherm parameters for Zn^{2+} adsorption by chitosan macro and nano size particles

	Micro size			Nano size		
Langmuir	q_m (mg/g)	α_L (L/mg)	R^2	q_m (mg/g)	α_L (L/mg)	R^2
	196.07	0.0159	0.9920	370.37	0.0335	0.9940
Freundlich	K_f (L/mg)	b_f	R^2	K_f (L/mg)	b_f	R^2
	7.06	0.5299	0.9734	21.19	0.4955	0.9803

Fig. 9 Effect of contact time on Zn^{2+} adsorption, $C_0 = 1000$ mg/L, 300 rpm, 25 °C, chitosan pH = 7, nanochitosan pH = 5

maximum efficiency of both adsorbent has been obtained at 25 °C. Binding energy of water and chitosan surface is so strong, and temperature rising can reduce energy these binding (Momenzadeh et al. 2011). Subsequently, this phenomenon yields increase of adsorption efficiency. Then, temperature rising can increase solubility of water, and on the other hand, when temperature raises, zinc ions tend to move from solid phase to solution phase which can increase solutes of water. As a result, driving force of adsorption decreases which leads to adsorption capacity reduction (Momenzadeh et al. 2011).

Fig. 10 The pseudo first order (Lagergren) model fitting chitosan (a) and nanochitosan (b), $C_0 = 1000$ mg/L, 300 rpm, 25 °C, chitosan pH = 7, nanochitosan pH = 5

Fig. 11 The pseudo second order (H_o) model fitting chitosan (a) and nanochitosan (b), $C_0 = 1000$ mg/L, 300 rpm, 25 °C, chitosan pH = 7, nanochitosan pH = 5

Table 5 Kinetic parameters for Zn^{2+} adsorption by chitosan macro and nano size particles

Adsorption parameter	Lagergren's pseudo first order kinetics			Ho pseudo second order kinetic		
	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg.min)	R^2
Chitosan macro size particles	178.98	0.0312	0.9697	192.30	0.0003	0.9964
Chitosan nano size particles	347.92	0.0867	0.9800	357.14	0.0005	0.9971

Fig. 12 Effect of temperature on Zn^{2+} adsorption, $C_0 = 1000$ mg/L, 300 rpm, chitosan pH = 7, nanochitosan pH = 5

Conclusion

The manner of adsorption Zn (II) out of aqueous solution by chitosan macro and nano size particles was studied. Nono chitosan particles of mean size 19.84 nm were produced. Adsorption Zn (II) out of aqueous solution was sensitive to pH changes and the highest removing by chitosan macro and nano size particles within pH were 7 and about of 5. Langmuir's isotherm model can predict adsorption of zinc metal ions by chitosan macro and nano size particles, very well. Maximum capacity of adsorption by chitosan macro size particles was 196.07 mg/g, while it was 370.37 mg/g for chitosan nano size particles. Adsorption kinetics followed a pseudo second order model

either on chitosan macro size particles or chitosan nano size particles, also by decreeing size of the chitosan particles to nano size, required time to reach equilibrium was decreased from 160 min (for chitosan macro size particles) to 65 min for chitosan nano size particles. The maximum zinc ions removal happened at about 25 °C for both chitosan macro and nano size.

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References

- Abdelwahab O, Amin NK, El-Ashtouky ESZ (2013) Removal of zinc ions from aqueous solution using a cation exchange resin. *Chem Eng Res Des* 91(1):165–173. doi:[10.1016/j.cherd.2012.07.005](https://doi.org/10.1016/j.cherd.2012.07.005)
- Ahlam M, Nida M, Ahmad L (2012) Kinetic, equilibrium and thermodynamic studies of the biosorption of heavy metals by ceratonia siliqua bark. *Am J Chem* 2(6):335–342. doi:[10.5923/j.chemistry.20120206.07](https://doi.org/10.5923/j.chemistry.20120206.07)
- Ahmad M, Ahmed S, Swami B, Ikram S (2015) Adsorption of heavy metal ions: role of chitosan and cellulose for water treatment. *Int J Pharm* 2(6):280–289. doi:[10.13040/IJPSR.0975-8232.IJP](https://doi.org/10.13040/IJPSR.0975-8232.IJP)
- Bassi R, Shiv O (2013) Removal of selected metal ions from aqueous solutions using chitosan flakes. *Sep Sci Technol* 35(4):547–560. doi:[10.1081/SS-100100175](https://doi.org/10.1081/SS-100100175)

- Benavente M, Moreno L, Martinez J (2011) Sorption of heavy metals from gold mining wastewater using chitosan. *J Taiwan Inst Chem Eng* 42(6):976–988. doi:10.1016/j.jtice.2011.05.003
- Brian Zieske D (2015) Aqueous zinc removal using nano-particle treated natural fibers. MSc Thesis, environmental engineering. http://digitalcommons.mtech.edu/grad_rsch/25/
- Calvo P, Remunan-Lopez C, Vila-Jato JL, Alonso MJ (1997) Novel hydrophilic chitosan-polyethylene oxide nanoparticles as protein carriers. *J Appl Polym Sci* 63(1):125–132. doi:10.1002/(SICI)1097-4628(19970103)63:1<125::AID-APP13>3.0.CO;2-4
- Chen AH, Liu SC, Chen CY, Chen CY (2008) Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin. *J Hazard Mater* 154(1–3):184–191. doi:10.1016/j.jhazmat.2007.10.009
- Chu KH (2002) Removal of copper from aqueous solution by chitosan in prawn shell: adsorption equilibrium and kinetics. *J Hazard Mater* 90(1):77–95. doi:10.1016/S0304-3894(01)00332-6
- Chuanqiang Z, Xiangxiang G, Jie H, Rong G (2016) Removal of Pb(II) and Zn (II) from aqueous solutions by raw crab shell: a comparative study. *Water Environ Fed* 88:374–383. doi:10.2175/106143016X14504669768174
- Cristian P, Violeta P, Ralusa I (2015) Removal of zinc ions from model wastewater system using bicopolymer membranes with fumed silica. *J Water Process Eng* 8:1–10. doi:10.1016/j.jwpe.2015.08.001
- Dang VBH, Doan HD, Dang-Vu T, Lohi A (2009) Equilibrium and kinetics of biosorption of cadmium(II) and copper(II) ions by wheat straw. *Bioresour Technol* 100:11–19. doi:10.1016/j.biortech.2008.05.031
- El-Shafey EI (2010) Removal of Zn(II) and Hg(II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk. *J Hazard Mater* 175:319–327. doi:10.1016/j.jhazmat.2009.10.006
- Gakwisiri C, Raut N, Al-Saadi A, Al-Aisri S, Al-Ajmi A (2012) A critical review of removal of zinc from wastewater. *Lect Notes Eng Comput Sci* 2197(1):627–630. <https://doaj.org/article/501a74fd1dfa4f759000abd70f52cea0>
- George Z, Dimitrios N (2015) Recent modifications of chitosan for adsorption applications: a critical and systematic review. *Mar Drug* 13:312–337. doi:10.3390/md13010312
- Haider M, Vakili M, Dahlan I (2014) Waste material adsorbents for Zinc removal from wastewater: a comprehensive review. *Int J Chem Eng* 2014:1–13. doi:10.1155/2014/347912
- Jaafarzadeh N, Mengelizadeh N, Hormozinejad M (2014) Adsorption of Zn (II) from aqueous solution by using chitin extracted from shrimp shells. *Jentashapir J Health Res* 5(3):131–139. http://jjhres.com/?page=article&article_id=27333
- Jain G (2013) Removal of copper and zinc from wastewater using chitosan. MSc Thesis, Department of Chemical Engineering, National Institute of Technology Rourkela. <http://ethesis.nitrkl.ac.in/5310/>
- Jain R, Weiss S, Franzen C, Farges F (2015) Adsorption of zinc by biogenic elemental selenium nanoparticles. *Chem Eng J* 260:855–863. doi:10.1016/j.cej.2014.09.057
- Kaloti M, Bohidar HB (2010) Kinetics of coacervation transition versus nanoparticle formation in chitosan-sodium tripolyphosphate solutions. *Colloids Surf B* 81(1):165–173. doi:10.1016/j.colsurfb.2010.07.006
- Karnib M, Kabbani A, Holail H, Olama Z (2014) Heavy metals removal using activated carbon, silica and silica activated carbon composite. *Energy Proced* 50:113–120. doi:10.1016/j.egypro.2014.06.014
- Karthikeyan G, Anbalagan K, Muthalakshmi Andal N (2004) Adsorption dynamics and equilibrium studies of Zn (II) onto chitosan. *J Chem Sci* 116(2):119–127. doi:10.1007/BF02708205
- Laus R, Costa T, Szpoganicz B (2010) Adsorption and desorption of Cu(II), Cd(II) and Pb(II) ions using chitosan cross linked with epichlorohydrin-triphsphate as the adsorbent. *J Hazard Mater* 183:233–241. doi:10.1016/j.jhazmat.2010.07.016
- Mi FA, Shyu SS, Lee ST, Wong TB (1999) Kinetic study of chitosan tripolyphosphate complex reaction and acid-resistive properties of the chitosan tripolyphosphate gel beads prepared by in liquid curing method. *J Polym Sci, Part B: Polym Phys* 37(14):1551–1564. doi:10.1002/(SICI)10990488(19990715)37:14<1551::AID-POLB1>3.0.CO;2-H
- Momenzadeh H, Tehrani-Bagha AR, Khosravi A, Gharanjig K, Holmberg K (2011) Reactive dye removal from wastewater using a chitosan nano dispersion. *Desalination* 271(1–3): 225–230. doi:10.1016/j.desal.2010.12.036
- Nabila S, Elhaes H, Hanan S, Hotaby W, Ibrahim M (2014) A novel structure for removal of pollutants from wastewater. *Spectrochim Acta, Part A* 121:216–223. doi:10.1016/j.saa.2013.10.063
- Patricia NM, Wellington S, Meiry GF, Herve M (2013) Adsorption of zinc from aqueous solutions using modified Brazilian gray clay. *Am J Anal Chem* 4:510–519. doi:10.4236/ajac.2013.49065
- Ramesh A, Hasegawa H, Sugimoto W, Maki T, Ueda K (2008) Adsorption of gold(III), platinum(IV) and palladium(II) onto glycine modified cross linked chitosan resin. *Bioresour Technol* 99(9):3801–3809. doi:10.1016/j.biortech.2007.07.008
- Ramya R, Shanmugapriyal A, Ramasubramaniam S, Sudha PN (2011) Studies on removal of Cr(VI) and Cu (II) ions using chitosan grafted-polyacrylonitrile. *Schol Res Libr* 3:424–435. <http://scholarsresearchlibrary.com/aasr-vol3-iss3/AASR-2011-3-3>
- Sari A, Tuzen M, Uluzlu D, Soyak M (2007) Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass. *Biochem Eng J* 37(2):151–158. doi:10.1016/j.bej.2007.04.007
- Singh NS, Ningthoujam RS, Devi LR, Yaiphaba N, Sudarsan V, Singh SD, Vatsa RK, Tewari R (2008) Luminescence study of Eu³⁺ doped GdVO nanoparticles: Concentration, particle size, and core/shell effects. *J Appl Phys* 104:104307. <http://dx.doi.org/10.1063/1.3026612>
- Singh P, Bajpai J, Bajpai AK, Shrivastava RB (2011) Removal of arsenic ions and bacteriological contamination from aqueous solutions using chitosan nanospheres. *Indian J Chem Technol* 18:403–413. <http://hdl.handle.net/123456789/13035>
- Singh K, Singh A, Mishra A (2014) Effect of crosslinking agent on the size of polymeric nanoparticles. *World J Pharm Pharm Sci* 3:1416–1420. <http://www.wjpps.com/download/article/1417605092>
- Sivakami MS, Gomatehi T, Venkatesan J (2013) Preparation and characterization of nano chitosan for treatment wastewaters. *Int J Biol Macromol* 57:204–212. doi:10.1016/j.ijbiomac.2013.03.005
- Sobhanardakani S, Zandipak R, Mohammadi MJ (2016) Removal of Ni(II) and Zn(II) from aqueous solutions using chitosan. *Arch Hygien Sci* 5(1):47–55. <http://jhygiene.muq.ac.ir/article-1-68-en.html>
- Sreejalekshmi KG, Krishnan KA, Anirudhan TS (2009) Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: kinetic and equilibrium isotherm studies. *J Hazard Mater* 161(2–3): 1506–1513. doi:10.1016/j.jhazmat.2008.05.002
- Sureshkumar MK, Radhakrishnan K, Nuwar J (2011) Adsorptive removal of Cr(III) from aqueous solution using tripolyphosphate cross-linked chitosan beads. *J Radioanal Nucl Chem* 289:275–285. doi:10.1007/s10967-011-1074-2
- Trahar WJ, Senior GD, Heyes GW, Creed MD (1997) The activation of sphalerite by lead: a flotation perspective. 1997. *Int J Miner Process* 49:121–148. doi:10.1016/S0301-7516(96)00041-5

- Wan Ngah WS, Teong LC, Hanafiah MAKM (2011) Adsorption of dyes and heavy metal ions by chitosan composites: a review. *Carbohydr Polym* 83:1446–1456. doi:[10.1016/j.carbpol.2010.11.004](https://doi.org/10.1016/j.carbpol.2010.11.004)
- Zhu Y, Hu J, Wang J (2012) Competitive adsorption of Pb(II), Cu (II) and Zn (II) onto xanthate-modified magnetic chitosan. *J Hazard Mater* 221:155–161. doi:[10.1016/j.jhazmat.2012.04.026](https://doi.org/10.1016/j.jhazmat.2012.04.026)