



Preparation of Nanochitosan as an Effective Sorbent for the Removal of Copper Ions from Aqueous Solutions

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ABSTRACT

Heavy metal ions in industrial effluents are considered as major source of pollution. In batch experiments, the effects of various parameters such as pH, contact time, initial concentration, and temperature on the adsorption of Cu (II) by nanochitosan (NCS) was investigated. Nanochitosan was prepared based on ionic gelation and characterized by means of Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) analysis. Maximum uptake of Cu (II) was recorded at pH=6. Accordingly, based on the experimental data for the amount of 100 mg/l of copper ions, maximum adsorption capacity by chitosan nanoparticles was 26.88 mg/g at 25°C. Equilibrium data for Cu (II) were fitted well by Langmuir adsorption model with maximum adsorption capacity of 33.33 mg/g at 25°C. The obtained data showed that the adsorption process kinetically proceeded according to pseudo second-order model. It was concluded that NCS had great potential to remove Cu (II) ions from the aqueous solutions at various concentrations of metal ions.

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1. INTRODUCTION

Today accumulation of excess heavy metal ions in environment has created great concern because of their increasing discharge, toxicity and other adverse effects on receiving waters. Heavy metals can accumulate in a live body and be harmful to humans and animals [1]; that may lead to serious diseases such as mental confusion, allergies, memory lost, irritability, balance problems and digestion. The effective removal of heavy metal ions from aqueous systems is very important for the protection of environment and public health [2]. For instance, potential sources of copper in industrial effluents include metal cleaning and plating baths, wood pulp production, fertilizer industry pulp, paper and paper board mills, etc [3]. High intake of copper may lead to headaches, low blood sugar, increase heart rate and nausea. It is also toxic to aquatic organisms in natural water even at very low concentration [4, 5]. A number of treatment processes including evaporation, coagulation, filtration, ion exchange, reduction electrolytic technologies adsorption and membrane

processing have been used for the removal of metal ions. Among them, adsorption technique has been proved to be one of the most effective and attractive processes [6-8]. Besides, biosorption is also recognized as an emerging technique for the treatment of water containing heavy metals. One of these biosorbant is chitosan that has a variety of potential applications [9]. Chitosan is the deacetylated product of chitin. Chitosan has very wide range of applications, such as prevention of water pollution, in medicine and biotechnology, in membrane separation and food technology [10]. The high content of amine groups makes possible chemical modification in chitosan with the purpose of improving its features as an effective adsorbent, with selective and high adsorption capacity [11]. Chitosan is also characterized by weak diffusion properties: long contact times are required to reach equilibrium. Sorption capacity can be controlled by sorbent particle size [12]. For solving these problems nanotechnology tools can be useful. Today nano techniques provide a ready solution for many water pollution problems [13]. The ability of controlling nanoparticle size is highly desirable for most applications in the field of nanotechnology [14]. In this

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research nanochitosan (NCS) produced are used for the removal of metal ions. NCS is environmentally friendly and bioactive material. It is frequently used as a controlled-release drug carrier for gene transfer in artificial organs and for immune prophylaxis. In addition, NCS has been used to improve the strength and wash ability of textiles and to confer anti-bacterial effect. NCS can be prepared in variety of experimental approaches [15]. Quan Gan [16] demonstrated protein encapsulation and controlled release using chitosan nanoparticle as carriers. Ramesh et al. [17] investigated the adsorption of Au(III), Pt(IV) and Pd(II) in glycerin modified cross-linked chitosan resin. Fan et al. [18] used ionic gelation to produce chitosan nanoparticles with 133~237 nm diameter.

In this work, removal of Cu(II) ions from aqueous solutions by nanochitosan was investigated. The NCS was prepared from a broad range of chitosan with low molecular weight via ionic gelation method. The samples were characterized with reliable techniques such as, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The effects of pH value, NCS dosage, contact time, and temperature on adsorption of metal ions were investigated.

2. MATERIAL AND METHODS

2.1. Materials Chitosan (CS) (MW= 50 ~ 190 kDa), degree of acetylation (75 ~ 85 %), was purchased from Sigma-Aldrich. Maleic acid (MA) and lead nitrate were purchased from Merck (Darmstadt, Germany).

2.2. Preparation of Nanochitosan NCS was prepared according to method developed by de Moura et al. [14]. Firstly, CS and MA were dissolved in distilled water for 30 min under magnetic stirring (VELP, SCIENTIFICA, Europe) at 300 rpm, heated for 3 h in a constant bath temperature (70 °C). Next, 0.2 mmol of K₂S₂O₈ was added to the solution while continuously stirring at 70 °C for 7 h; then cooled in ice bath till a milky emulsion was obtained. The suspension was centrifuged for 15 min at 16000 rpm and then freeze dried using a freeze dryer.

2.3. Characterizations of the Nanochitosan

2.3.1. FT-IR Analysis NCS was analyzed on Shimadzu Spectrum model 8400s FTIR spectra in the range of 400 to 4000 cm⁻¹. The NCS powdered in KBr was used to prepare pellets.

2.3.2. Scanning Electron Microscopy (SEM) The morphology of the NCS and CS samples was analyzed by SEM (scanning electron microscopy) on a KYKY model EM3200. In a SEM, the specimen is vacuumed.

An electron beam passes through a couple of condenser lenses, which apply a magnetic field to narrow the beam and apertures (holes) to block stray electrons. The beam causes some electrons to be ejected, which can then be detected and amplified to produce an image of the sample surface.

2.4. Metal Ion Uptake Experiments

2.4.1. Instrumentation A SensAA atomic absorption spectrometer (GBC scientific equipment, Australia) equipped with a lead and copper hollow cathode lamps was used. The instrument was set at 324.7 nm for Cu.

2.4.2. Batch Experiments Batch experiments were performed by placing 0.125 g of dry NCS in series of Erlenmeyer flasks containing 50 ml of 50 ppm metal solution and flasks were agitated on a shaker (KS 4000i control, IKA) at 180 rpm. For optimization of pH, contact time, adsorbent dosage and initial concentration, batch experiments were performed at room temperature, 25 °C. Adsorption experiments for the removal of Cu (II) were conducted in pH range of 3–6, adsorbent dosage (2.5-7.5 g/l), contact time from 0-180 min, metal concentration (10–100 mg/l) and temperature 25-45 °C. The pH of solution was adjusted by adding 0.1M HCl and 0.1M NaOH solution for the required pH value. The biosorption kinetics and isotherms data were collected under optimized condition of pH and contact time. For the best result, experiments were carried out in triplicates and the mean values were reported. After separation by centrifugation (HERMLE Z 233 M-2, Germany) at 8000 rpm, the residual concentration of the metal ions was determined by atomic absorption spectrometer. In all of the above experiments, the adsorption values were calculated from the change in solution concentration using the following equation [19]:

$$q = (C_0 - C_e) \times \frac{V}{m} \quad (1)$$

where q is the amount (mg/g) of metal ions adsorbed by the NCS, C_0 and C_e (mg/l) are the metal concentrations in the solution initially and after adsorption, respectively, V (l) is the volume of added solution and m (g) is the mass of the adsorbent (dry) used. The removal efficiency calculated as:

$$R \% = 100 \times \frac{(C_0 - C_e)}{C_0} \quad (2)$$

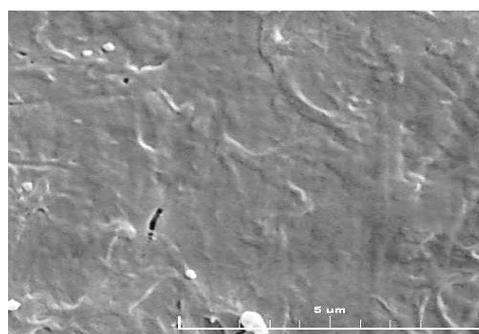
3. RESULTS AND DISCUSSION

3.1. Synthesis of Nanochitosan The characteristics of the prepared NCS with several concentrations of CS and pH of the solution were evaluated. The results

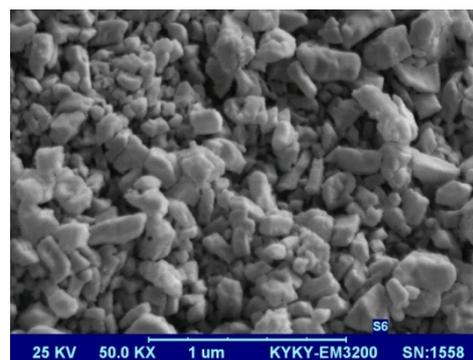
indicated that when concentration of chitosan increased, the particle size also increased. Wen Fan [18] found that the formation of chitosan nanoparticles was depended on concentration of chitosan solution, mass ratio of chitosan to cross-linking agent and pH of the chitosan solution. This fact was also confirmed in present work in order to avoid formation of micro-particles, the concentration of chitosan and pH of the solution need to be adjusted. Using developed method which was the same methodology applied by Bodnar et al. [20] and de Moura et al. [14], to produce NCS, 2 g CS in was dissolved in 1 g MA solution at pH 5. In slightly acidic solution, the amino groups of CS and carboxyl groups of MA were protonated which may affect the size of nanoparticles [14]. The electrostatic interactions with MA-CS led to formation of nanoparticles through the polymerization of MA in the presence of CS molecules. When the MA polymerization reached a certain level, the formation of CS-MA nanoparticles occurred with linkages between negative charge of MA carboxyl groups and positive charge of CS amino groups. Figure 1 demonstrates FT-IR spectra of NCS with various functional groups. The interaction of CS and MA are illustrated in this figure. The CS spectrum presents characteristic peaks at 3435 cm^{-1} assigned to stretching vibration of NH_2 and OH groups; the bands at 1660 and 3050 cm^{-1} is assigned to N-H and NH_2 group; the peak at 1700 cm^{-1} is associated with C=O and the band at 1080 cm^{-1} is related to C-O stretching vibration [19]. The two new bands located at 1638 and 1545 cm^{-1} are assigned to COO^- and NH^{+3} groups, respectively. These indicate ionic interaction between MA and CS associated with the formation of nanoparticles [14]. The bands at 1700 and 1600 cm^{-1} are assigned to C=O and (C-C) which confirm the presence of MA in the nanoparticles compositions.

3. 2. Scanning Electron Microscopy (SEM) Analysis

The SEM of NCS and CS particles are shown in Figure 2; it seems that these nanoparticles have a very homogeneous morphology than chitosan. The obtained average particle size was less than 200 nm for mass ratio of CS/MA=2:1 and pH value of 5 for the prepared solution.



Chitosan



Nanochitosan

Figure 2. SEM of Chitosan and Nanochitosan (mass ratio of CS/MA= 2:1, pH=5)

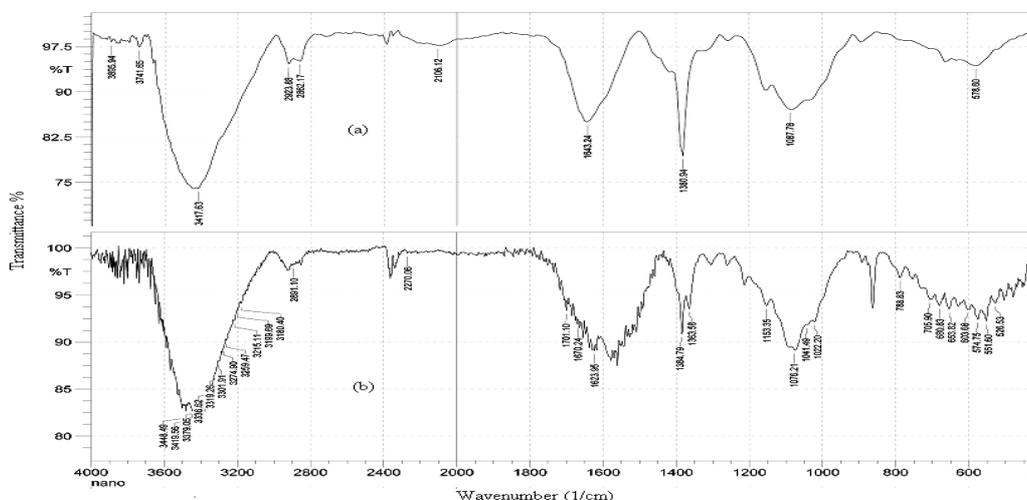


Figure 1. FTIR spectra of (a) Chitosan and (b) Nanochitosan.

3. 3. Effect of various Parameters on the Heavy Metal Ions Removal

3. 3. 1. Effect of pH One of the important parameters in adsorption processes is the pH of the solution which can affect active sites for adsorption of metal ions on the surface of adsorbent and chemical structure of metals in aqueous phase [18]. In this study, keeping all other parameters constant, the effect of pH in the range of 3–6 on the adsorption of Cu (II) ions on NCS and CS was investigated. Figure 3 illustrates the effect of pH on the adsorption of Cu (II) ions by NCS and CS. It was observed that the adsorption of Cu (II) ions increased while pH of the solution was increased to pH=6. In acidic pH less than 3 the adsorbent surface was entirely covered with H_3O^+ which strongly competed with metal ions for adsorption sites. In this situation, H_3O^+ competes with Cu (II) ions for the adsorbent site, which prevent adsorption of Cu (II) ions by NCS and CS. Adsorption of Cu (II) decreased as the acidity of solution increased [21]. In the range of $3 < pH < 6$, the concentration of H_3O^+ ions decreases, which caused to expedite quickly and efficiently the adsorption of metal ions. It was observed that the adsorption of Cu (II) ions by NCS and CS decreased at pH values greater than 6. At $pH > 6$, Cu^{2+} retention decreased because small amount of Cu^{2+} started to deposit on $Cu(OH)_2$. This also supports the chelation of Cu^{2+} on NCS and CS [21]. It was observed that adsorption rate of Cu (II) was high when pH value was 6.

3. 3. 2. Effect of Contact Time Figure 4 shows the removal efficiency of Cu (II) ions by NCS and chitosan in batch adsorption experiments. The results demonstrate that metal density in the solution decreased with increasing the contact time and the solution reached to equilibrium in less than 60 and 120 min for NCS and CS, respectively. So for further experiments, the contact time was selected 60 and 90 min for NCS and CS, respectively. The maximum adsorption of Cu (II) ions was attained at the end of adsorption process. Also, the results indicate that adsorption process was preliminary quick which caused a large amount of adsorption. In the second step, the percentage of removal changed insignificantly.

It was reported that long time was required for copper sorption from aqueous solutions by chitosan nanofibers [22]. In contrast, in present study, the removal of Cu (II) ions from aqueous solutions was achieved in a short contact time. This was attributed to high surface reactivity and large surface area of the NCS. The results showed that adsorption capacity of Cu (II) by NCS was higher than CS; while Cu (II) showed lower affinity toward CS as expected in this research.

3. 3. 3. Effect of Initial Concentration of Metal Ions on Adsorption Another effective parameter on

removal of Cu (II) is initial concentration of metal ions in the solution. As Figure 5 shows at $pH=6$ and 10 ppm concentration of metal ions the maximum adsorption of Cu (II) was about 92.67 and 67% for NCS and CS, respectively. Above 75 mg/l, adsorption capacity of Cu (II) began to be stable and showed slight decrease. NCS showed better adsorption than CS, because NCS had larger surface area than CS. In addition, NCS had a crosslink agent of carboxyl groups as a result of acid maleic.

3. 4. Comparison of NCS with other Adsorbents to Remove Copper Ions

In order to have good understanding about the adsorption capacity of NCS, experiments were conducted for several adsorbents such as cross linked and non cross linked chitosan-coated bentonite beads, chitosan-coated magnetic nanoparticles, cross linked chitosan with both epichlorohydrin (ECH) and triphosphate (TPP), cross linked magnetic chitosan beads, chitosan nano-hydroxyapatite composite and chitosan/clinoptilolite composite. Table 1 shows the experimental results of several adsorbents based on removal efficiency.

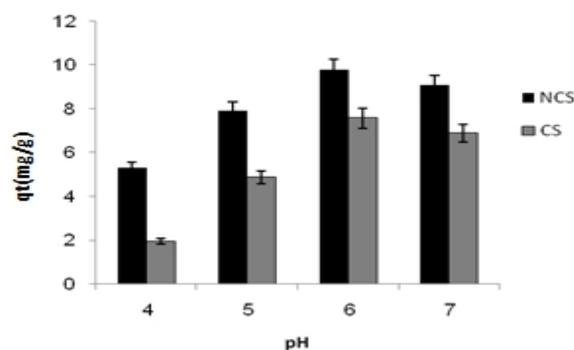


Figure 3. Effect of pH on the removal efficiency of Cu (II) ions by NCS and CS. (initial concentration 50 mg/l, adsorbent mass 5 g/l, shaking rate 180 rpm and temperature 298 K).

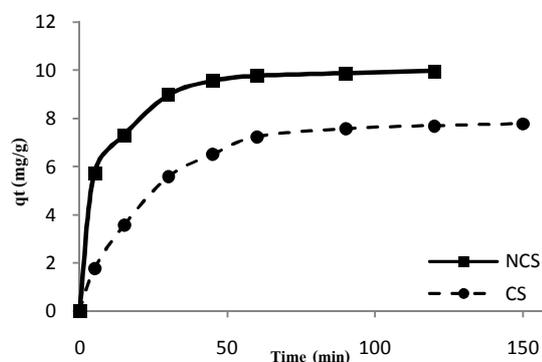


Figure 4. Effect of contact time on the removal efficiency of Cu (II) ions by NCS and CS. (initial concentration 50 mg/l, adsorbent mass 5 g/l, shaking rate 180 rpm and temperature 298 K).

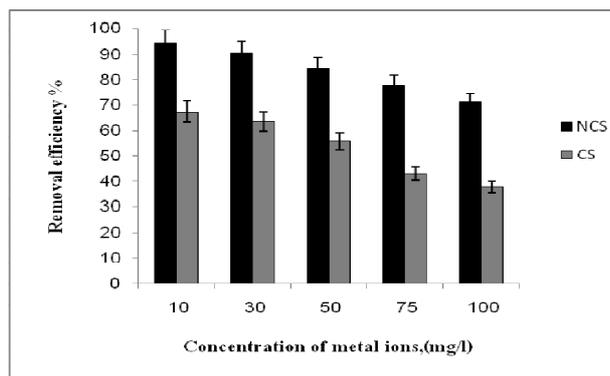


Figure 5. Effect of concentration of metal ions (mg/l) on the removal efficiency of Cu (II) ions by NCS and CS. (pH=6, adsorbent mass 2.5 g/l, shaking rate 180 rpm and temperature 298 K).

TABLE 1. Comparison between NCS and other adsorbents

Adsorbent	Removal efficiency (%)	Adsorption capacity (mg/g)
Nanochitosan (Present study)	94.37	33.33
Non cross linked chitosan-coated bentonite beads [25]	99.87	12.21
Cross linked chitosan-coated bentonite beads [25]	99.98	9.43
Chitosan-coated magnetic nanoparticles [26]	96.8	144.9
Cross linked chitosan with both epichlorohydrin (ECH) and triphosphate (TPP) [24]	100	---
Cross-linked magnetic chitosan beads [1]	---	78.13
Chitosan nano-hydroxyapatite composite [9]	---	6.2
Chitosan/clinoptilolite composite [22]	---	11.32 (mmol/g)

3. 5. Adsorption Isotherms Adsorption isotherms are essential in order to determine the adsorption potential [23]. Figures 6 and 7 show experimental data of Cu (II) on NCS at different temperatures with initial Cu(II) concentration of 50 mg/l for Langmuir and Freundlich isotherms. The adsorption curves indicate that the uptake of Cu(II) decreased as the temperature increased. The adsorption data were plotted according to Langmuir model:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (3)$$

The linearized Lagmuir adsorption model is shown in the following equation:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{1}{q_m} C_e \quad (4)$$

Also, the Freundlich isotherm is expressed as follows:

$$q_e = k_F C_e^{1/n} \quad (5)$$

The linearized Freundlich adsorption model is also shown by the following equation:

$$\log q_e = \log k_F + \frac{1}{n} (\log C_e) \quad (6)$$

where q_e is the amount of adsorbed metal ions per gram of adsorbent in the bulk solution and C_e is the equilibrium concentration of Cu(II) in the bulk solution, in mg/g and mg/l, respectively. The constants q_m and k_L are constants of Langmuir equation, in mg/g and l/mg, respectively. q_m is the maximum adsorption capacity of the monolayer formed on the adsorbent while k_F and n are the constants of Freundlich equation incorporating adsorption capacity and intensity, in l/g, respectively [24]. Langmuir and Freundlich isotherms for the adsorption of Cu (II) ions from aqueous solution on NCS are plotted in Figures 6 and 7. The constant parameters in two adsorption isotherms with the correlation coefficients are presented in Table 2. The linear relationships are statistically significant, which indicate the applicability of the two adsorption isotherms and the monolayer coverage of Cu(II) on the NCS surface. Adsorption capacity obtained from the Langmuir isotherm was 33.33 mg Cu(II) per gram NCS for Cu(II) concentration of 50 mg/l.

TABLE 2. The Langmuir equation and the Freundlich equation for adsorption of Cu (II) ions

Adsorbent	NCS	
Langmuir Isotherm Results	q_m (mg/g)	33.33
	k_L (l/mg)	0.1820
	R^2	0.9960
	R_L	0.108
Freundlich Isotherm Results	n	1.92
	k_F	5.420
	R^2	0.964

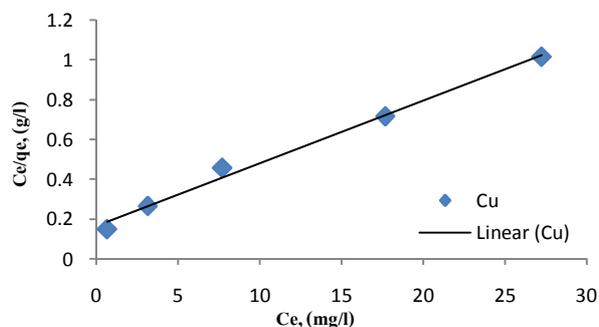


Figure 6. Langmuir isotherm plot for the adsorption of Cu (II) ions on NCS.

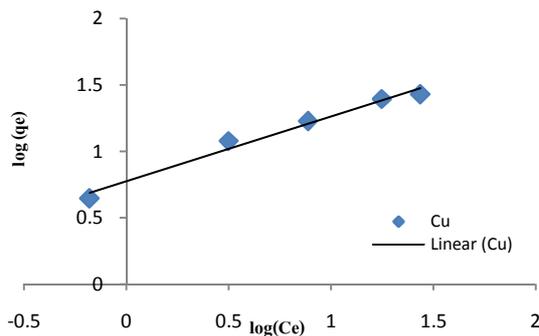


Figure 7. Freundlich isotherm plot for the adsorption of Cu (II) ions on NCS.

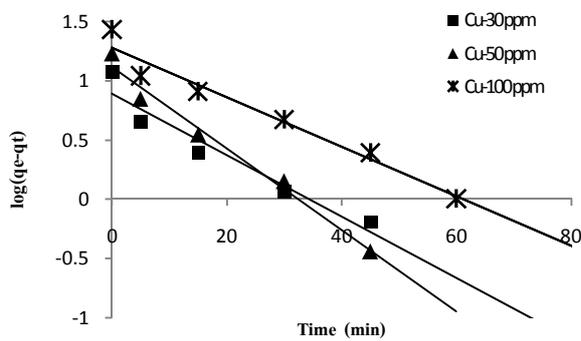


Figure 8. Pseudo-first-order model for adsorption of Cu (II) ions on NCS (pH=6, adsorbent mass 2.5 g/l, shaking rate 180 rpm and temperature 298 K).

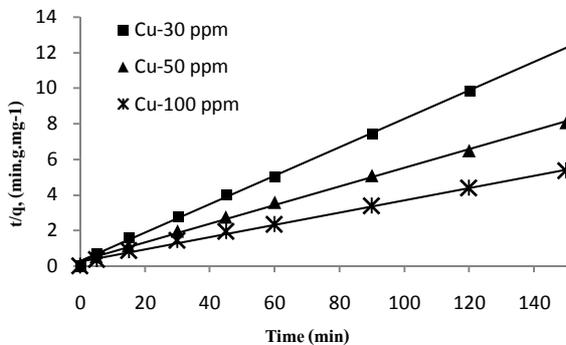


Figure 9. Pseudo-second-order model for adsorption of Cu (II) ions on NCS (pH=6, adsorbent mass 2.5 g/l, shaking rate 180 rpm and temperature 298 K).

A separation factor is essential characteristics of the Langmuir isotherm which is defined as [25]:

$$R_L = \frac{1}{(1 + k_L C_i)} \tag{7}$$

The value of R_L indicates the shape of Langmuir isotherm and the nature of adsorption process. It is considered as a favorable process when ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) and irreversible ($R_L = 0$). In present study, the value of R_L calculated for the initial Cu (II) concentrations is 0.108, that means, the adsorption of Cu (II) on NCS is a favorable process. The Freundlich constants k_f and n are 5.420 L/g and 1.92, respectively. It is known that value of n between 1 and 10 represents an appropriate adsorption.

3. 4. Adsorption Kinetics Kinetic models such as pseudo-first-order and pseudo-second-order models are used in order to examine the controlling mechanism for the adsorption process for Equations (8) and (9), respectively [26].

Pseudo-first-order model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{8}$$

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

where q_t (mg/g) is the adsorption at time t (min); q_e (mg/g) is the adsorption capacity at adsorption equilibrium; and k_1 (min^{-1}) and k_2 ($\text{g}/\text{mg}\cdot\text{min}$) are the kinetic rate constants for the pseudo-first-order and the pseudo-second-order models, respectively. The kinetic adsorption of Cu (II) ions was fitted to Equations (8) and (9), and the calculated data results are in Table 3. The correlation coefficients (R^2) for the pseudo-second-order adsorption model were higher than the pseudo-first-order rate equation. Therefore, the adsorption of copper ions is well represented by the pseudo-second-order kinetic model. The pseudo-second-order rate constants are slightly different for the five initial Cu (II) concentrations, so that the effect of initial concentration is low.

TABLE 3. Adsorption kinetic parameters for Cu ions adsorption onto NCS

Initial Cu conc. (mg/l)	q_e, exp (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (1/min)	q_e, cal (mg/g)	R^2	k_2 (g/mg·min)	q_e, cal (mg/g)	R^2
10	4.43	0.1105	3.98	0.913	9.1×10^{-2}	4.505	0.998
30	11.94	0.0599	7.798	0.932	2.48×10^{-2}	12.5	0.997
50	16.92	0.0783	13.121	0.981	1.79×10^{-2}	17.544	0.996
75	24.74	0.0598	17.782	0.937	1.12×10^{-2}	25.641	0.998
100	26.88	0.0484	19.055	0.962	7.12×10^{-3}	28.572	0.993

4. CONCLUSION

NCS was successfully prepared by polymerization of MA solution in the presence of low molecular weight CS. The nanoparticle was prepared with mass ratio of CS/MA = 2:1 and pH of the solution was adjusted at 5. SEM analysis showed that chitosan nanoparticles have a very homogeneous morphology with average particle size less than 200 nm. Also, this research paper indicates that the size of nano particles caused to increase the surface of adsorbent. It may also help to reach a high efficiency of heavy metal removal. It seems that adsorption by NCS is a promising alternative to replace conventional adsorbents in removal of hazardous heavy metal ions. The optimum pH value for the adsorption of Cu (II) ions was 6. Langmuir adsorption model showed maximum adsorption capacity of 33.33 mg/g of Cu at 25°C. The kinetic mechanism for the adsorption of metal ions followed pseudo-second-order model which provided the best experimental data correlation for this ions. This field of research hopes that NCS can be applied commercially instead of only laboratory scale.

5. ACKNOWLEDGEMENTS

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Preparation of Nanochitosan as an Effective Sorbent for the Removal of Copper Ions from Aqueous Solutions

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یونهای فلزی موجود در پساب های صنعتی به عنوان منبع اصلی آلودگی در نظر گرفته می شود. در آزمایشات سیستم ناپیوسته، اثر پارامترهای مختلف مانند pH، زمان تماس، غلظت اولیه و دما بر جذب مس (II) توسط نانو کیتوزان (NCS) مورد بررسی قرار گرفت. نانو کیتوزان بر اساس روش ژل شدن یونی تهیه شد و با استفاده از دستگاه طیف سنجی مادون قرمز (FTIR) و دستگاه میکروسکوپ الکترونی (SEM) مورد تجزیه و تحلیل قرار گرفت. حداکثر جذب مس (II) در pH = 6 بدست آمد. بر اساس داده های تجربی برای مقدار 100 mg/l از یون های مس، حداکثر ظرفیت جذب نانوذرات کیتوزان 26/88 mg/g در دمای 25 درجه سلسیوس صورت پذیرفت. مطالعات تعادلی بر روی داده های آزمایش نشان داد مدل لانگمایر رفتار داده های تجربی را بهتر از مدل فرندلیچ توصیف می کند. اطلاعات به دست آمده نشان داد که معادلات سینتیکی بر اساس معادله سینتیکی شبه مرتبه دوم می باشد. هم چنین نشان داده شد که NCS دارای پتانسیل بسیار خوبی برای حذف یون های مس (II) از محلول های آبی دارای غلظت های مختلف از یون های فلزی است.

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