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A study on biosorption of copper ions by fungal chitosan: an alternative to shrimp chitosan

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Abstract

Introduction: One of the main applications of chitosan is for heavy metals removal from waste waters. Industrially, chitosan is produced through deacetylation of chitin present in shellfish waste. Another source of chitosan is the cell wall of zygomycetes fungi with several advantages over shellfish wastes.

Materials and methods: Fungal chitosan purified from biomass of *Mucor indicus* and shrimp chitosan were applied and compared for removal of copper ions from aqueous solution. The effects of pH (3 to 5.5), copper ion concentration (5 to 52 mg l^{-1}), the amount of chitosan (200 to 3000 mg l^{-1}), adsorption time, temperature, and presence of other metal ions on the biosorption of Cu^{2+} were investigated.

Results: Maximum adsorption capacities for fungal and shrimp chitosans were 58.5 and 60.7 mg g^{-1}, respectively. The rate of copper adsorption by the fungal chitosan was significantly higher than that by the shrimp chitosan. Among pseudo-first order, pseudo-second order, intra-particle diffusion, and Elovich models, Ho's pseudo-second order model was the best model for fitting the kinetic data. The adsorption capacity increased for both types of chitosans by increasing the solution pH. However, temperature and presence of other ions did not show significant effects on the biosorption capacity of copper. The isotherm data were very well described by Langmuir, Freundlich, and Redlich-Peterson models.

Discussion and conclusion: Both fungal and shrimp chitosans can effectively be used for removal of copper ions from aqueous solutions. Adsorption process for fungal chitosan is fast, while the process is slower for the shrimp chitosan. Therefore, from the kinetics point of view, the fungal chitosan is preferable compared with the shrimp chitosan.

Key words: Biosorption, Copper, Fungal chitosan, Shrimp chitosan, Water treatment

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Introduction

Chitosan is a non-toxic and biodegradable polysaccharide containing amino and hydroxyl groups which makes it a suitable adsorbent for hazardous heavy metal removal. Industrially, chitosan is produced through deacetylation of chitin, which is mainly obtained from shellfish waste (1), with hot concentrated sodium hydroxide (2 and 3). Seasonal problems and limited supply in some regions reduce the industrial production of chitin and chitosan. Moreover, chitosan quality and the processing expenses are affected using a strong base solution at high temperatures to convert chitin to chitosan. An alternative source of chitosan is the cell wall of zygomycetes fungi (4 and 5). Fast fungal growth on inexpensive substrates regardless of season or location, lower concentration of inorganic material in fungal biomass, and enzymatic deacetylation of chitin to chitosan in the cell wall of zygomycetes instead of the expensive chemical deacetylation step for chitosan production are among the benefits of zygomycetes fungi over shellfish wastes for production of chitosan. Therefore, production of chitosan using fungi may be industrially advantageous and environmentally acceptable (6 and 7).

Copper is a serious water pollutant present in sewage of industries such as metal cleaning, paper and paperboard mills, and fertilizer production (8 and 9). Although trace amount of copper is essential as a nutrient, this metal is severely toxic and harmful for plants and humans at high concentrations (10 and 11). Maximum permissible limit of copper ions in drinking water is 2 mg l^{-1}, since it accumulates in the liver at higher concentrations (12).

Several reports are available studying the biosorption of copper ion using chitosan obtained by deacetylation of chitin available in crustacean such as shrimp (13 and 14) . However, to the best of our knowledge, there is no comparative report on the biosorption of Cu^{2+} by chitosan produced from deacetylation of shrimp chitin (shrimp chitosan) and chitosan extracted from the cell wall of fungi (fungal chitosan), and the maximum adsorption capacity (q_{max}) of fungal chitosan and the effects of operating parameters on copper removal by fungal chitosan have not been studied comprehensively.

In the current work, shrimp and fungal chitosans were used to remove copper ions. *Mucor indicus* biomass was used since it contains adequate quantities of chitosan (15). *M. indicus* is widely used in fermentation of lignocellulosic hydrolysates and production of a number of valuable materials, e. g., fishmeal, fungal extracts, and fatty acids (16). The high-quality fungal chitosan was separated and purified based on a recently developed method (17) using sulphuric acid, instead of conventional methods and using acetic acid or hydrochloric acid, which produce chitosan with a higher purity and yield. A comparative study on adsorption of copper ions by shrimp chitosan and chitosan extracted and purified from cell wall of the fungus were performed. Influences of different parameters on the biosorption of Cu^{2+} were studied. The Langmuir, Freundlich, Scatchard, Temkin, and Redlich-Peterson models were used to fit the equilibrium adsorption data. The adsorption rates were determined quantitatively and compared with pseudo-first order, pseudo-second order, intra-particle diffusion, and Elovich models.

Materials and methods

Shrimp chitosan

Low molecular weight shrimp chitosan with 60 cP viscosity (1% solution in 1% acetic acid), a product of BioLog Company Biotechnology and Logistics GmbH (Germany), was used in this research.

Fungal chitosan production and purification

Fungus *M. indicus* CCUG 22424 (Culture Collection, University of Göteborg, Sweden) was maintained on plates containing 40 g l^{-1} glucose, 10 g l^{-1} peptone, and 15 g l^{-1} agar and kept at 32°C for 5 days to grow and then stored at 4°C until use. Liquid cultivation was carried out in a fermentor containing 90 g l^{-1} date syrup (contained 7.2 % fructose, 7.0 % glucose, and 1.1% sucrose), 0.5 g l^{-1} ammonium phosphate and 3 g l^{-1} urea, and inoculated with 150 ml suspension containing 9 (±2) × 10^6 spores ml^{-1}. The temperature was kept at 32°C and 2 vvm sterile air was introduced into the fermentor to provide aerobic conditions as well as mixing. The medium pH was adjusted at 5.0 to 5.5 using H_2SO_4 and NaOH. After complete consumption of the sugars (about 43 h), the fungal biomass was harvested on a screen and washed with distilled water until a clear filtrate appeared.

The fungal chitosan was separated and purified according to a recently developed method (17) with slight modifications. The harvested biomass was soaked in 0.5 M NaOH (30 ml NaOH per gram of dry biomass) and autoclaved for 20 min at 121°C to obtain the Alkali Insoluble Material (AIM). Afterwards, AIM was washed several times with distilled water to reach pH 7 and was finally dried at 50°C. Then, 2.5 g dried AIM was soaked and mixed for 15 min in 250 ml 72 mM H_2SO_4 to remove the phosphates. The residue was then washed with distilled water and soaked in 250 ml 72 mM H_2SO_4 and placed in an oil-bath at 120°C for 70 min. The liquid phase was poured into 300 ml 0.15 M NaOH in an ice bath and then centrifuged to extract the low molecular weight fungal chitosan. The chitosan was dried at 50°C.

Shrimp and fungal chitosan were ground and sieved to obtain particles with sizes less than 0.5 mm.

Degree of deacetylation

The Deacetylation degrees of shrimp and fungal chitosans were measured according to the method developed by Mohammadi et al. (18) which were both 85%.

Biosorption experiments

A stock solution containing 1000 mg l^{-1} Cu^{2+} was prepared by dissolution of $CuSO_4$. $5H_2O$ in deionized water. The stock solution was diluted with deionized water to obtain solutions with desired concentrations. The solutions pH was adjusted using 0.1 M NaOH or 0.1 M H_2SO_4 before adding the chitosans. All experiments were carried out in 250 ml Erlenmeyer flasks containing 50 ml metal solution in a shaker-incubator at 135 rpm at certain temperatures. Control samples, without chitosan, with the same metal concentrations were also examined parallel to all tests. After reaching the equilibrium, the samples were centrifuged and concentration of the metal ions in the supernatant was measured.

Effect of initial pH of solution was examined by adding 0.03 g shrimp or fungal chitosan to a 50 ml Cu^{2+} solution (5 mg l^{-1}) at 32ºC. The experiments were carried out at pH 3.0, 3.5, 4.0, 4.5, 5.0, and 5.5. The mixtures were shaken to reach the equilibrium and the concentration of copper ions was measured.

Effects of chitosan loading were examined by addition of certain amounts of shrimp or fungal chitosan (0.01, 0.03, 0.05, 0.10, and 0.15 g) to 50 ml Cu^{2+} solutions (5 mg l^{-1}) at 32ºC and pH 4 and copper concentration was measured after equilibrium.

Effect of temperature on biosorption was examined by addition of 0.05 g shrimp or fungal chitosan to Cu^{2+} solution (50 ml) at pH 4 and different initial ions concentrations (5, 16, 28, 40, and 52 mg l^{-1}). The adsorption experiments were carried out at different constant temperatures of 13ºC, 32ºC, and 45ºC in a rotary shaker.

Effect of presence of chromium and lead ions on Cu^{2+} biosorption capacity of shrimp and fungal chitosan was also studied. Chitosan (0.03 g) was added to metal ions solution (50 ml), containing 5 mg l^{-1} of copper, chromium, and lead ions at pH 4 and 32ºC. Chromium and lead solutions were obtained by dissolution of $K_2Cr_2O_7$ and Pb $(NO_3)_2$ in deionized water, respectively.

In order to study the kinetics of biosorption, samples of shrimp or fungal chitosan (0.03 g) were added to a 50 ml Cu^{2+} solution (5 mg l^{-1}). The pH and temperature were set at 4 and 32ºC, respectively. The moment of chitosan addition to the solution was considered as time zero. Each data was achieved from individual flask at different times.

Adsorption isotherms were evaluated by addition of 0.05 g shrimp or fungal chitosan to Cu^{2+} solution (50 ml) at 32ºC and pH 4. Initial concentrations of the metal solutions were 5, 16, 28, 40, and 52 mg l^{-1}. In order to describe adsorption isotherm, Langmuir, Freundlich, Redlich-Peterson (19), Temkin (20), and Scatchard (21) models were used and the best model was identified. In all equations, q_e (mg g^{-1}) is adsorption capacity, which is the equilibrium amount of adsorbed solute per unit weight of chitosan, q_{max} (mg g^{-1}) is the amount of adsorbed ions to saturate unit mass of chitosan, and C_e (mg l^{-1}) is the equilibrium concentration of metal ions.

The Langmuir model is expressed as:

(1) $q_e = \frac{q_{max} K C_e}{1 + K C_e}$

Where K (l mg^{-1}) is a constant related to the energy or net enthalpy of adsorption. The linear form of this equation is as follows:

(2) $\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} K C_e}$

Freundlich model is:

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

Where K_F ((mg/g) / (mg/l) $^{1/n}$) and n show the capacity of adsorption and its intensity, respectively. The linear form of this model is: (4) $ln q_e = ln K_F + \frac{1}{n} ln C_e$

Temkin model is:

(5) $q_e = \frac{RT}{b_T} (\ln C_e + \ln A_T)$

Where A_T (l g^{-1}) and b_T (kJ mol^{-1}) are the model's constants. R is the universal gas constant, and T (K) is the temperature.

Scatchard model is:

(6) $\frac{q_e}{C_e} = q_m . k_b - k_b q_e$

Where q_m (mg g^{-1}) and K_b (l mg^{-1}) are Scatchard model's parameters.

Redlich-Peterson model is:

(7) $q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$

Where K_R (l g^{-1}), a_R (l mg^{-1}) $^{\beta}$ and β are the model's parameters. Exponent of β is between 0 and 1. This equation can also be expressed as below:

(8) $\frac{C_e}{q_e} = \frac{1}{K_R} + (\frac{a_R}{K_R}) C_e^{\beta}$

Measurement of copper ions

Concentration of copper ions in all solutions was measured by an atomic absorption spectrometer (210 VGP, Buck Scientific Co. England). Adsorption capacity was calculated as**:**

(9) $q_e = \frac{(C_0 - C_e)V}{m}$

Where V (l) is the volume of the solution which is 0.05 l in all experiments, m (g) is the mass of chitosan used, and C_0 and C_e (mg l^{-1}) are the concentration of copper ions before and after biosorption, respectively.

Statistical analysis

All experiments were carried out in duplicate and the average values were reported. Effect of chitosan type on adsorption capacity in all experiments was analyzed using PASW Statistics 18. T-test and analysis of variance (ANOVA) was performed at 5% level of significance.

Results

Kinetics of Cu^{2+} removal

In order to investigate the kinetics of biosorption, shrimp and fungal chitosans were added to a solution with 5 mg l^{-1} copper ions. The concentration of ions and biosorption capacity of copper at different times are presented in Fig. 1(a) and (b), respectively. The results showed a very high initial rate of copper ions adsorption on both types of chitosan. Afterwards, the rate of biosorption decreased and finally, the system reached to equilibrium. The copper ions were removed under two steps, a rapid phase followed by a slower one (22) For shrimp chitosan, the adsorption capacity increased rapidly and 70% of initial copper ions adsorbed in the first 3 h and then decreased gradually to reach equilibrium in about 24 h. For the purified fungal chitosan, the equilibrium was reached after 3 h (Fig. 1).

In order to study the kinetics of adsorption, pseudo-first order (23), Ho's pseudo-second order (23), intra-particle diffusion (24), and Elovich (23) models were evaluated. Ho's model is the best model for description of kinetic data for shrimp and fungal chitosans, since correlation factors are higher than 0.99 (Table 1). Ho's model is:

(10) $\frac{t}{q_t} = \frac{1}{K q_e^2} + \frac{t}{q_e}$

Table 1- Different models correlation factor (R^2) and Ho's model parameters for the biosorption of Cu^{2+} by shrimp and fungal chitosans

Chitosan type	Model						experimental q_e (mg/g)
	Pseudo-first order R^2	Pseudo-second order			Elovich R^2	Intra-particle diffusion R^2	
		R^2	K (g/mg/min)	calculated q_e (mg/g)			
Shrimp	0.8602	0.9980	0.0023	7.85	0.9868	0.9129	7.58 ± 0.02
Fungal	0.7157	0.9998	0.0146	7.31	0.7253	0.4422	7.25 ± 0.03

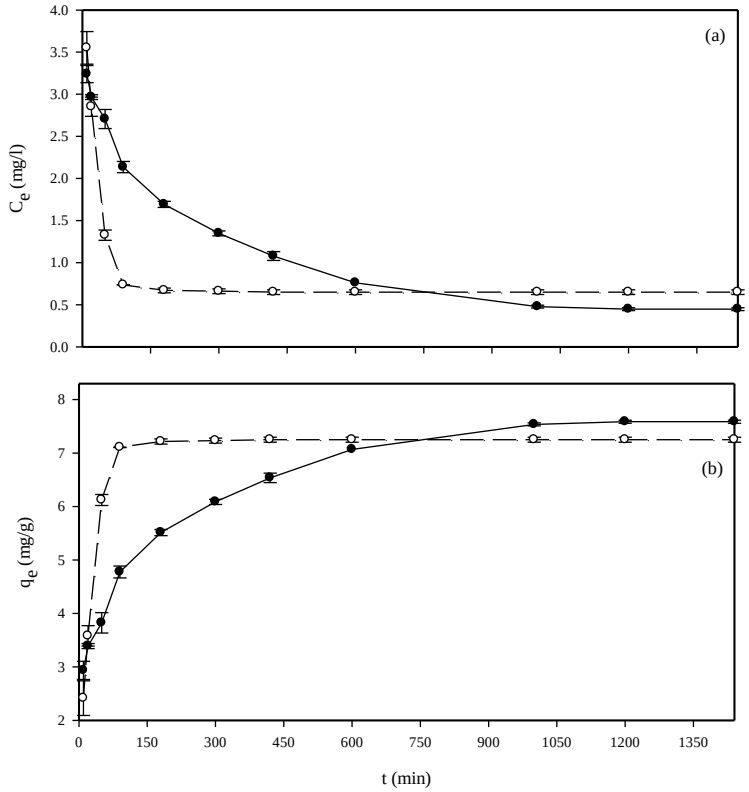

Fig. 1- Time distribution of copper ions concentration (a) and biosorption capacity (b) in solutions containing shrimp (●) and fungal (○) chitosans

where q_t (mg g^{-1}) is the amount of adsorbed metal ions per unit weight of adsorbent at time t (min), and K is the pseudo second-order reaction rate constant of adsorption (g mg^{-1} min^{-1}). Linear regression analysis was used to fit the kinetic data to Ho's model and q_e and K for both types of chitosan were calculated (Table 1). As this table demonstrates, Ho's model is able to predict the kinetic data very well.

Effects of pH on the biosorption

Effects of initial solution pH, in the range of 3.0 to 5.5, on biosorption capacity for both types of chitosan were investigated (Fig. 2). The biosorption of copper by chitosan should be studied within the range of 3.0 - 5.5 since copper can precipitate as copper hydroxide at pH higher than 5.5. On the other hand, the chitosan can be dissolved in acidic solution at pH lower than 3 (25).

The biosorption capacity of chitosans was highly dependent on pH. With increasing the pH from 3.0 to 5.5, the biosorption capacity (q_e) increased from less than 2 to about 7.5 mg g^{-1} for fungal chitosan and from less than 5 to more than 8 mg $g,^{-1}$ for shrimp chitosan. Analysis of variance showed that adsorption capacity is not dependent on chitosan type (Table 2)

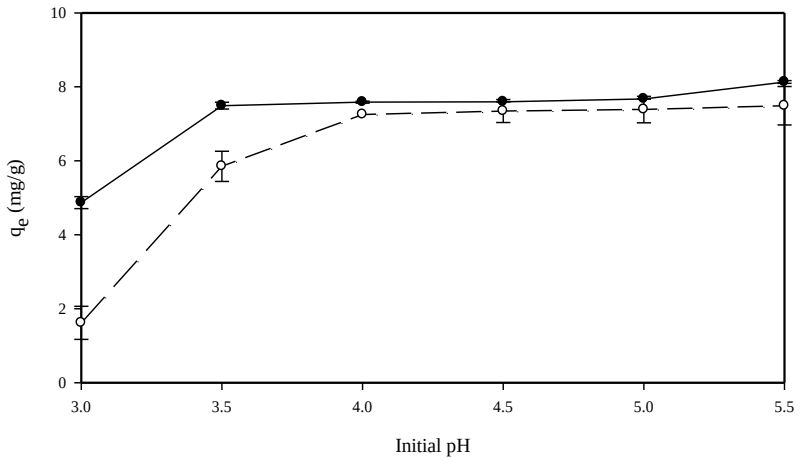

Fig. 2- Effect of initial pH on biosorption of copper ion by shrimp (●) and fungal (○) chitosans

Table 2- Analysis of variance for dependence of adsorption capacity on chitosan type

	Sum of Squares	df	Mean Square	*F-value*	*P-value*
Between Groups	3.413	1	3.413	1.019	0.337
Within Groups	33.501	10	3.350		

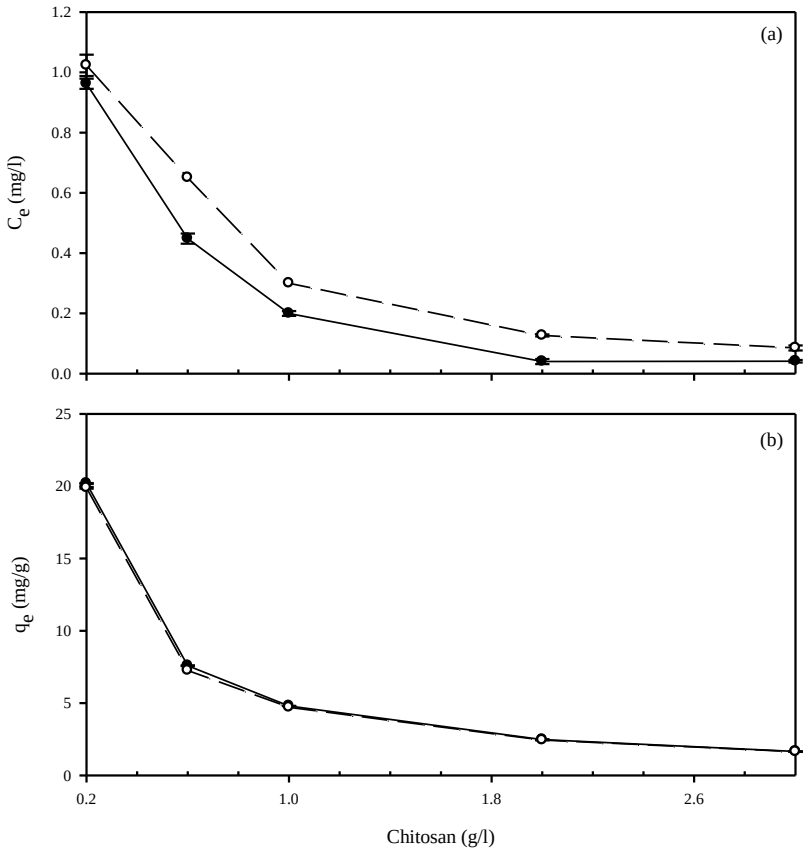

Fig. 3- Effect of chitosan amount on equilibrium copper ion concentration (a) and biosorption capacity (b) for shrimp (●) and fungal (○) chitosans

Effects of adsorbent concentration

Effects of adsorbent concentration on Cu^{2+} removal were studied (Fig. 3(a) and (b)). As expected, the amount of adsorbed Cu^{2+} increased with increasing the amount of adsorbent. Increasing the amount of chitosan also resulted in lower adsorption capacity (q_e) for both shrimp and fungal chitosans.

Effects of temperature on biosorption

Effects of temperature on biosorption capacity of chitosans were investigated (Table 3). According to analysis of variance (Table 4), temperature did not have a significant effect on adsorption capacities of both shrimp and fungal chitosans. The adsorption capacity was slightly increased for shrimp chitosan with increasing the process temperature from 13ºC to 45ºC, while it was slightly decreased for the fungal chitosan. Besides, fungal chitosan has a slightly better adsorption capacity than shrimp chitosan at 13ºC.

Adsorption isotherm

Adsorption capacity as a function of equilibrium concentration of metal ions (C_e) is shown (Fig. 4). As can be seen, adsorption capacity increased with increasing the initial copper ions concentration. Furthermore, adsorption percentage decreased by increasing Cu^{2+} concentration (Fig. 5).

The parameters of the models for biosorption of Cu^{2+} by shrimp and fungal chitosans are calculated (Table 5). As correlation factors show (R^2> 0.99), Langmuir, Freundlich, and Redlich-Peterson models accurately described the isotherm data for both types of chitosan.

Table 3- Effect of temperature on adsorption capacity of shrimp and fungal chitosans

	C_e (mg/l) at 32ºC		shrimp chitosan q_e (mg/g)			fungal chitosan q_e (mg/g)		
C_0(mg/l)	Shrimp	Fungal	13ºC	32ºC	45ºC	13ºC	32ºC	45ºC
5	0.20± 0.00	0.30±0.00	4.87	4.80	4.86	4.81	4.70	4.64
16	0.81±0.00	1.37±0.05	15.02	15.19	15.28	15.66	14.64	13.75
28	1.86± 0.08	2.83±0.32	25.52	26.15	26.70	27.58	25.18	23.43
40	3.54± 0.11	4.31±0.31	35.74	36.46	36.60	38.45	35.69	35.41
52	4.97± 0.02	5.92±1.48	43.53	47.25	47.16	46.11	46.08	45.65

Table 4- ANOVA for dependence of Adsorption capacity of shrimp and fungal chitosan on temperature

	Sum of Squares		df	Mean Square		*F-value*		*P-value*	
	shrimp	fungal	shrimp & fungal	shrimp	fungal	shrimp	fungal	shrimp	fungal
Between Groups	4.15	9.75	2	2.07	4.87	0.008	0.018	0.992	0.982
Within Groups	3213.4	3271.7	12	267.8	272.6				

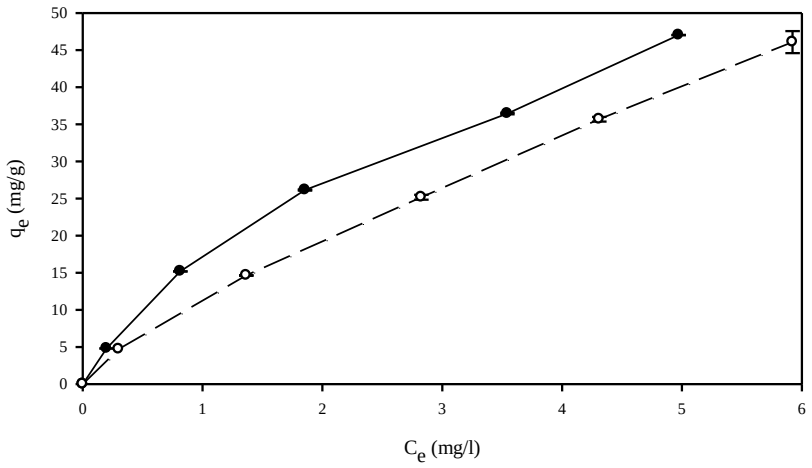

Fig. 4- Equilibrium biosorption of copper ions by shrimp (●) and fungal (○) chitosans

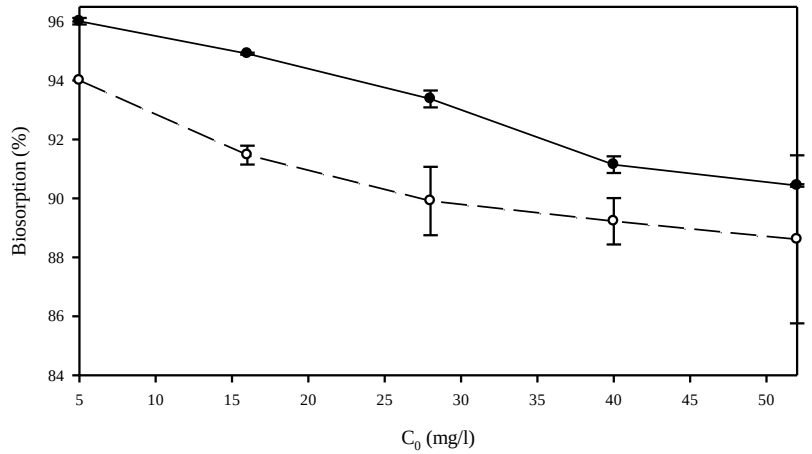

Fig. 5- Effect of copper ions concentration on adsorption percent by shrimp (●) and fungal (○) chitosans

Table 5 - Different models isotherm constants for biosorption of Cu^{2+} onto shrimp and fungal chitosans at 32ºC

Model		Shrimp chitosan	Fungal chitosan
Langmuir	R^2	0.9994	0.9959
	q_{max} (mg/g)	60.74	58.52
	K (l/mg)	0.43	0.29
Freundlich	R^2	0.9930	0.9997
	n	1.42	1.31
	K_F ((mg/g) / (mg/l) $^{1/n}$)	15.89	11.65
Temkin	R^2	0.9411	0.8936
	RT/b_T	12.59	13.07
	A_T (l/g)	5.61	3.50
Scatchard	R^2	0.9501	0.7953
	q_m (mg/g)	68.99	84.07
	K_b (l/mg)	0.35	0.17
Redlich-Peterson	R^2	0.9912	0.9988
	β	0.63	0.10
	K_R (l/g)	32.87	-8.49
	a_R (l/mg) $^{\beta}$	0.92	-1.74

Effects of presence of chromium and lead ions

The effects of chromium and lead ions on biosorption of Cu^{2+} by shrimp and fungal chitosans were also studied (Table 6). The results showed that adsorption capacity of copper ions did not considerably change in the presence of other ions for both types of chitosan. Thus, both types of chitosan can be successfully used for selective removal of copper ions from wastewaters and effluents containing the heavy metal ions.

Table 6- Biosorption of Cu^{2+} in a solution containing one, two and three metal ion(s)

q_e (mg Cu^{2+} adsorbed per g of chitosan)				
Metal ion(s)	Cu	Cu+Cr	Cu+pb	Cu+pb+Cr
Shrimp chitosan	8.08 ± 0.0642	8.11 ± 0.0033	7.46 ± 0.0125	8.09 ± 0.001
Fungal chitosan	8.07 ± 0.0833	8.15 ± 0.0617	8.13 ± 0.0008	8.15 ± 0.0458

Discussion and conclusion

Chitosan extracted from the cell wall of *M. indicu*s was used for copper removal from aqueous solutions and compared with chitosan obtained from shrimp wastes.

For both chitosans, there was a very high initial rate of copper ions adsorption. Afterwards, the rate of biosorption decreased and finally, the system reached to equilibrium. The reason for the fast initial rate of adsorption is related to the availability of high number of free absorbent sites on the chitosan surface and also high copper ions concentration gradient between the bulk and the surface (26). At the beginning of biosorption, chitosan amino groups on the surface play an important role as copper coordination sites (22 and 27). The rate is reduced when the sites are occupied and the sorbate needs to penetrate to inner layers of the biosorbent.

For shrimp chitosan, the equilibrium was reached after 24 h. Similar result was observed in removal of copper ions by chemically modified chitosan in which the adsorption capacity reached to an equilibrium state within 24 h (26). Longer times to reach the equilibrium were also reported in removal of copper ions by chitosan (22 and 28). For the purified fungal chitosan, the equilibrium was reached after 3 h (Fig. 1). Similar result was obtained in copper uptake by chitosan flake (29) and nickel removal by bacteria (30). Therefore, biosorption was faster for the fungal chitosan than the shrimp chitosan. Shrimp chitosan is produced through deacetylation of shrimp chitin with hot concentrated sodium hydroxide. Therefore, using a strong base solution at high temperature affects chitosan quality. Moreover, the molecular weight of shrimp chitosan was higher than fungal chitosan. These may make it difficult for copper ions to penetrate into inner layers of chitosan which leads to the slower copper adsorption by shrimp chitosan in comparison with fungal chitosan. From the kinetics point of view, the fungal chitosan is preferable compared with the shrimp chitosan, since reaching to the equilibrium in a short

period of time is an important factor for designing a reactor leading to a smaller reactor volume (31).

Ho's pseudo- second order model could describe the kinetic data of both shrimp and fungal chitosans. Generally, most of the reports studying removal of copper ions were best fitted into the pseudo second order model (8, 26, 32 and 33).

The operating pH was a very effective parameter on the biosorption capacity of chitosans. With increasing the pH from 3.0 to 5.5, the biosorption capacity (q_e) increased for both chitosans. At low pH, the competition between H_3O^+ and copper ions decreases the adsorption capacity (27). With increasing the pH, the negative charge of the chitosan surface increases and makes it easier for positive copper ions to bind on chitosan surface (34). Generally, pH is an important parameter since it affects the surface charge of chitosan (21). Chitosan chelates with copper ions and releases hydrogen ions. Therefore, adsorption of copper ions on chitosan depends strongly on pH in aqueous solutions (22 and 35). The optimum pH for copper removal for both types of chitosans was found to be 5. 5 which is in agreement with the result of another investigation (21). Statistical analysis showed that adsorption capacity is not dependent on chitosan type.

With increasing the amount of chitosans, the amount of adsorbed Cu^{2+} increased, while adsorption capacity (q_e) for both shrimp and fungal chitosans decreased. Surface area is an important parameter for metal uptake; thus, higher concentration of chitosan provides higher copper ions removal by increasing the number of adsorption sites as well as the adsorption surface area (32). However, increasing the chitosan loading resulted in aggregation of the chitosan and consequently, underutilization of chitosan, which led to a lower biosorption capacity (32). Similar trends were observed as results of increasing adsorbent concentration in a number of studies (32, 33 and 36). According to analysis of variance, adsorption capacities of both chitosans are not statistically different.

Temperature did not have a significant effect on adsorption capacities of both shrimp and fungal chitosans. Similar results were obtained for adsorption of copper ions on *Mucor rouxii* (former name of *M. indicus*) biomass within the temperature range of 10-50ºC indicating that adsorption capacity did not depend on temperature (21). Yang and Zall (37) studied the adsorption of copper ions on chitosan for temperatures within the range of 5 to 55ºC. They obtained apparent activation energy of about 400 cal mol^{-1} for the adsorption of copper ions. The low activation energy indicates that the temperature does not influence the sorption isotherm.

Langmuir, Freundlich, and Redlich-Peterson models accurately described the isotherm data for both types of chitosan. Based on published research results, Langmuir model was able to describe isotherm data for adsorption of copper ions on *M. rouxii* (21) and *Rhizopus oryzae* biomass (32). According to statistical analysis, performances of both chitosans in copper ions removal are similar. Besides,

the maximum adsorption capacities predicted by Langmuir equation are nearly the same for both chitosans (Table 5).

Adsorption capacity increased with increasing the initial copper ions concentration (Fig. 4). It could be due to higher mass transfer driving force (concentration gradient). Furthermore, adsorption percentage decreased with increasing Cu^{2+} concentration (Fig. 5). The reason could be due to saturation of adsorption sites as a result of high copper ions concentration (38).

Adsorption capacity of copper ions did not considerably change in the presence of other ions for both types of chitosan Three different cases in adsorption of multi-metal ions solutions are possible: (a) synergism in which the mixture is more effective than individual ions, (b) antagonism in which the mixture is less effective than individual ions, and (c) non-interaction in which mixing has no effect (39). The effects of chromium and lead ions on Cu^{2+} removal were found to be non-interactive. A set of experiments were also performed to study the biosorption of single-metal ion solutions at the condition of interactive experiment using the shrimp and fungal chitosans. The results showed that fungal chitosan did not adsorb lead or chromium ions (data not shown). Similar result was observed on biosorption of lead ions by shrimp chitosan while this was able to adsorb chromium ions. The effect of chromium on biosorption of copper ions on shrimp chitosan was non-interactive. However, the interactions of multi-metal ions solutions in biosorption are very complex and needs further detailed studies.

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بررسی جذب زیستی یون‌های مس توسط کیتوزان قارچی: جایگزینی برای کیتوزان میگویی

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چکیده

مقدمه: یکی از کاربردهای اصلی کیتوزان در حذف فلزات سنگین از پساب‌هاست. در صنعت، کیتوزان از دی استیله شدن کیتین موجود در ضایعات سخت پوستان تولید می‌شود. منبع دیگر کیتوزان دیواره سلولی قارچ‌های زیگومایست است که مزیت‌های بیشتری نسبت به ضایعات سخت پوستان دارد.

مواد و روش‌ها: کیتوزان قارچی استخراج و خالص شده از زیست توده *موکور ایندیکوس* و کیتوزان میگویی برای حذف یون‌های مس از محلول آبی استفاده و مقایسه شدند. تأثیر اسیدیته (۳ تا ۵/۵)، غلظت یون مس (۵ تا ۵۲ میلی‌گرم بر لیتر)، مقدار کیتوزان (۲۰۰ تا ۳۰۰۰ میلی‌گرم بر لیتر)، زمان جذب، دما و حضور سایر یون‌های فلزی بر جذب زیستی بررسی شد.

نتایج: بیشینه ظرفیت‌های جذب برای کیتوزان‌های قارچی و میگویی به ترتیب ۵۸/۵ و ۶۰/۷ میلی‌گرم بر گرم به دست آمد. سرعت جذب مس توسط کیتوزان قارچی از کیتوزان میگویی به میزان درخور توجهی بالاتر بود. از میان مدل‌های شبه مرتبه اول، شبه مرتبه دوم، نفوذ درون ذره‌ای و الوویچ، مدل شبه مرتبه دوم هو بهترین مدل برای تطبیق بر داده‌های سینتیکی است. برای هر دو نوع کیتوزان، ظرفیت جذب با افزایش اسیدیته محلول افزایش یافت. دما و حضور سایر یون‌هاف تأثیر در خور توجهی بر ظرفیت جذب مس نداشت. داده‌های هم دما نیز به خوبی با مدل‌های لانگمایر، فرندلیچ و ردلیچ-پترسون توصیف شد.

بحث و نتیجه‌گیری: هر دو کیتوزان قارچی و میگویی می‌توانند به طور موثری برای حذف یون‌های مس از محلول‌های آبی به کار گرفته شوند. فرآیند جذب برای کیتوزان قارچی سریع بوده، در حالی‌که این فرآیند برای کیتوزان میگویی کندتر است. بنابراین، از نقطه نظر سینتیکی کیتوزان قارچی نسبت به میگویی ارجح است.

واژه‌های کلیدی: جذب زیستی، مس، کیتوزان قارچی، کیتوزان میگویی، تصفیه آب

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