Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A COMPARATIVE STUDY FOR THE SORPTION OF Cu(II) IONS BY CHITIN AND CHITOSAN: APPLICATION OF EQUILIBRIUM AND MASS TRANSFER MODELS

Yeşim Sağ[a]; Yücel Aktay[a]
[a] Department of Chemical Engineering, Hacettepe University, Ankara, Turkey

To cite this Article Sağ, Yeşim and Aktay, Yücel(2002) 'A COMPARATIVE STUDY FOR THE SORPTION OF Cu(II) IONS BY CHITIN AND CHITOSAN: APPLICATION OF EQUILIBRIUM AND MASS TRANSFER MODELS', Separation Science and Technology, 37: 12, 2801 — 2822

To link to this Article: DOI: 10.1081/SS-120005467

URL: http://dx.doi.org/10.1081/SS-120005467

SEPARATION SCIENCE AND TECHNOLOGY, 37(12), 2801–2822 (2002)

A COMPARATIVE STUDY FOR THE SORPTION OF Cu(II) IONS BY CHITIN AND CHITOSAN: APPLICATION OF EQUILIBRIUM AND MASS TRANSFER MODELS

Yeşim Sağ* **and Yücel Aktay**

Department of Chemical Engineering, Hacettepe
University, Beytepe, Ankara, Turkey

ABSTRACT

The sorption of Cu(II) by chitin, a naturally occurring material, and chitosan, prepared from chitin, was investigated and compared. The effect of pH, initial metal ion concentration, particle size, sorbent concentration, and stirring rate on sorption capacity was characterized by measuring the sorption isotherms. Sorption data of chitin and chitosan were best modeled by the Langmuir and Redlich–Peterson isotherms, although they can be modeled by the Freundlich and BET sorption models. Next, batch studies were carried out to identify the rate-controlling steps for Cu(II) sorption. Single resistance models were used in the determination of the external film mass transfer step and the intraparticle diffusion step.

Key Words: Waste-water treatment; Cu(II) ions; Sorption; Chitin; Chitosan; Equilibrium sorption models; Mass transfer models

---

*Corresponding author. E-mail: kmu@hacettepe.edu.tr

www.dekker.com

INTRODUCTION

Chitosan, poly[β-(1 → 4)-2-amino-2-deoxy-D-glucopyranose], is a polymer composed of partially deacetylated (1 → 4)-2-acetamide-2-deoxy-β-D-glucose. It can be easily made by deacetylating chitin, poly[β-(1 → 4)-2-acetamido-2-deoxy-D-glucopyranose], found in the shell of crustaceans, the cell wall of fungi and bacteria, or the broth from industrial fungal processes (e.g., citric acid).[1,2] During the last two decades chitin, chitosan, and their derivatives have found numerous applications in medicine, pharmacology, biotechnology, food technology, and waste-water treatment.[2,3]

Compared with other polysaccharides, chitin is unreactive, intractable, and has low solubility in aqueous media, in contrast with chitosan. Therefore, its deacetylation process in production of chitosan generally requires quite vigorous conditions.[4,5] In fact, chitin cannot be sharply distinguished from chitosan, because fully acetylated and fully deacetylated chitins do not normally occur in nature and are difficult to prepare. In chitin and chitosan sorbents, degree of deacetylation, a proportion between amine and acetylamino groups, could be a key parameter in controlling sorption and desorption of sorbates.[5,6] Although several mechanisms have been proposed for the sorption of heavy metal ions by chitin or chitosan, such as precipitation mechanism, deposition of metal aggregate mechanism, ion-exchange, complexation, and simple sorption, its metal uptake mechanism has still not yet been fully explained.[1,7] Chitosan collects metal ions through chelation, due to the presence of an amino group of the 2-amino-2-deoxy-D-glocose (glocosamine) unit.[7] Although there is a disagreement in the literature regarding the coordination modes for the chitosan–copper complex, it has been recently confirmed by the technique of electrospray mass spectrometry that the Cu(II) is co-ordinated to the C(1)-alkoxide, the four amine nitrogens of chitosan tetrasaccharide and an anion.[8]

The aim of this study was to understand the mechanisms that govern Cu(II) uptake by chitin or chitosan, and to find appropriate models for the mass transfer and equilibrium of removal.

EXPERIMENTAL

Materials

Chitin prepared from crab shells (poly(*N*-acetyl-1,4-β-D-glucopyranosamine)] $(C_8H_{13}NO_5)_n$ (Fluka 22720) and chitosan [2-amino-2-deoxy-(1 → 4)-β-D-glucopyranan; poly(1,4-β-D-glucopyranosamine)] (Fluka 22742) were used for copper removal. Before utilization of the sorbent, the raw chitin and chitosan were grounded and sieved into three fractions as a function of particle diameter d_p (μm)—$250 < d_p < 420$, $420 < d_p < 595$, and $595 < d_p < 841$. Before and after sorption experiments, the chitin and chitosan particles were weighed and no weight loss of the sorbent was observed at any of the pH values examined. *Rhizopus arrhizus*, a filamentous fungus, was obtained from the U.S. Department of Agriculture Culture Collection. *R. arrhizus* was grown aerobically in batch culture at 30°C and prepared for biosorption as described previously.[9]

Preparation of Sorption Media and Sorption Studies

Cu(II) solutions were prepared by diluting 0.02 *M* of stock solution of copper(II), obtained by dissolving anhydrous $CuSO_4$ in distilled water. Initial concentrations of Cu(II) ions were varied over the 0.393–4.721 mmol L^{-1} ranges while the dry sorbent weight in each sample was constant at 1.0 g L^{-1}. Before mixing with the chitin or chitosan flakes or fungal suspension, the pH of each was adjusted to the required value for the sorption of Cu(II) ions, by adding 1 mol L^{-1} of H_2SO_4. Batch kinetic experiments were conducted at a constant temperature (25°C), in a rotary shaker, using 250 mL flasks. In order to investigate the effects of stirring rate, sorption studies were performed in a batch-baffled and magnetically stirred reactor. The working volume of the reactor was 100 mL. The stirring rate was varied between 200 and 800 rpm. Sorption studies were carried out as described previously.[10] The concentration of unadsorbed Cu(II) ions in the sorption medium was determined spectrophotometrically. The colored complex of Cu(II) ions with sodium diethyl dithiocarbamate was read at 460 nm.[11]

RESULTS AND DISCUSSION

Kinetic Aspects of Cu(II) Sorption onto Chitin or Chitosan

Effect of pH

The waste waters containing metal ions present commonly an acidic pH. Chelatant amino polymers like chitosan have a low efficiency in metal uptake in this pH range because of protonation of the amino groups. Moreover, the amino polymers, like chitosan, are soluble in strongly acidic media. On the other hand, chitin constitutes an interesting material since it bears approximately 30% amine residues and is insoluble in water, whatever the pH. A lower pH will cause the functional groups of chitin/chitosan to be

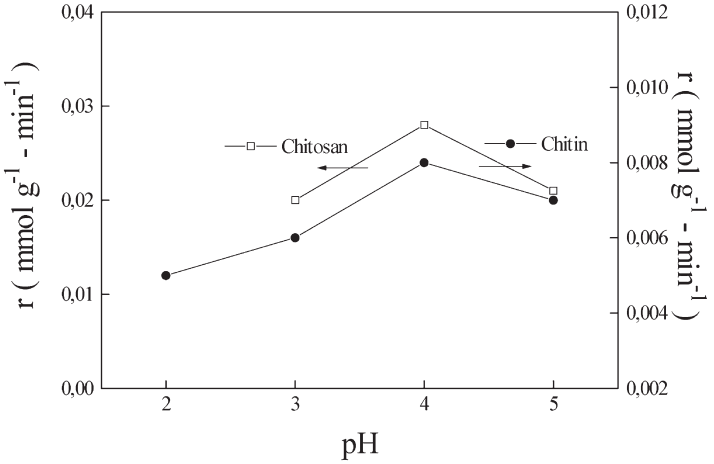

Figure 1. Effect of pH on the initial sorption rates of Cu(II) ions by chitin and chitosan (C_0, 0.952 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1 g L^{-1}).

protonated to a higher extent and result in a stronger repulsion for a positively charged ion in the solution. For that reason, Cu(II) ions were best adsorbed onto chitin/chitosan at pH in the range 4.0–5.0 (Fig. 1). At pHs higher than 5.0, Cu(II) ions precipitated because of the concentration of OH^- ions in the sorption medium and sorption studies could not be performed. Since a high deacetylation degree of chitosan brings an instability in strongly acidic solutions owing to the increased solubility, Cu(II) sorption onto chitosan could not be studied at pH 2.0.

Effect of Sorbent Concentration

As surface area is important in enhancing metal uptake, it is expected that by increasing the amount of biosorbent in a system, more and more metal ions would be removed. Although the adsorbed Cu(II) concentration increased with sorbent concentration, the amount of metal adsorbed per unit weight of chitin or chitosan, q, actually decreased with increase in the sorbent concentration. A concentration of 0.5 g L^{-1} of chitin or chitosan seems to be an optimum sorbent concentration. The rate of sorption was also reduced at high sorbent concentrations (Fig. 2), and hence more time was needed to reach equilibrium. In addition, the extent of desorption of sorbed ions from sorbent will increase with increase in sorbent concentration, as a result of collision of sorbent particles, and the potential of multilayer sorption will be reduced.

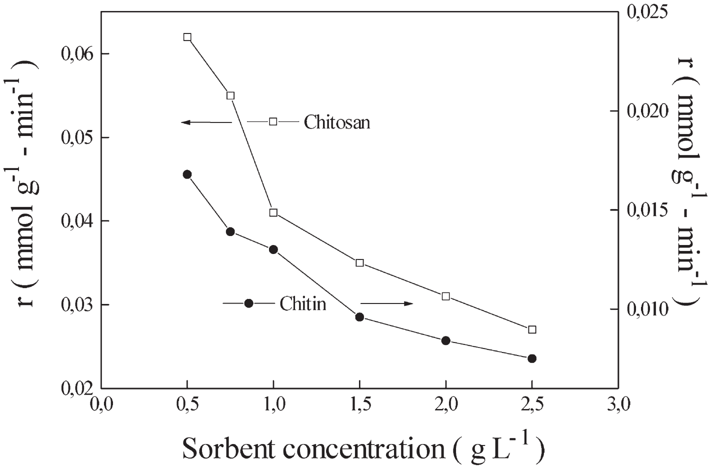

Figure 2. Effect of sorbent concentration on the initial sorption rates of Cu(II) ions by chitin and chitosan (pH, 4.0; C_0, 1.905 mmol L^{-1}; particle size, 250–420 μm).

Effect of Stirring Rate

The effect of stirring speed (n) on the initial sorption rates of Cu(II) was evaluated in terms of Reynolds number ($N_{\mathrm{Re}} = nD_{\mathrm{a}}^2\rho/\mu$) calculated from the diameter (D_{a}) and peripheral speed of the impeller (nD_{a}). Agitation influences the distribution of the solute in the bulk solution but can also act on the formation of the external boundary film. Increasing the Reynolds number from 2900 to 11,600 increased slightly the initial sorption rates of Cu(II) ions onto chitin (Fig. 3). In the case of chitosan, at N_{Re} numbers lower than 5800, there was insufficient agitation to ensure the uniform distribution of sorbent and solute. Increasing the Reynolds number beyond 5800, however, did not raise the initial sorption rates of Cu(II) ions onto chitosan, indicating that external film mass transfer was not the rate-limiting step in a well-agitated vessel. At N_{Re} numbers higher than 11,600, the strong shear forces may have interfered with sorption, damaging the chitosan particles.

Equilibrium Aspects of Cu(II) Sorption onto Chitin or Chitosan

Effect of pH

Equilibrium isotherms were measured to determine the capacity of chitin and chitosan for Cu(II) ions. The three most common types of equilibrium

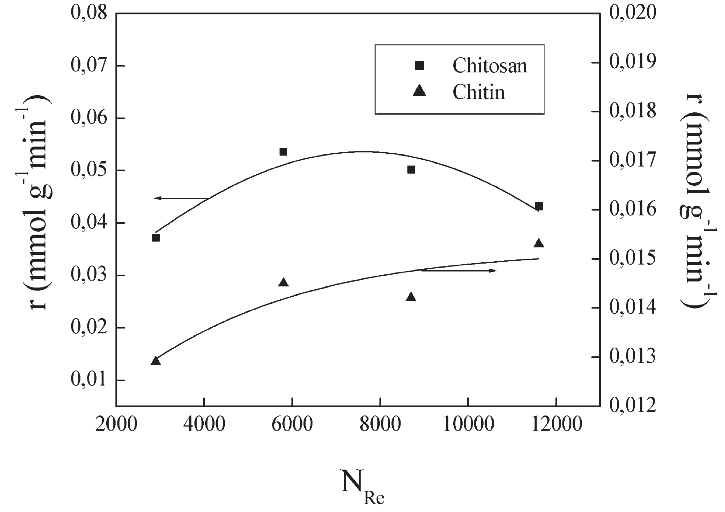

Figure 3. Effect of stirring rate on the initial sorption rates of Cu(II) ions onto chitin and chitosan (pH, 4.0; C_0, 1.905 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1 g L^{-1}).

sorption models for monolayer saturation capacity are the Langmuir, Freundlich, and the Redlich–Peterson. The BET model describing multilayer sorption was also applied to sorption equilibrium data of Cu(II) ions onto chitin and chitosan.

The Langmuir equation has been used extensively for dilute solutions in the following form,[12,13]

$$q_{\mathrm{eq}} = \frac{q_{\mathrm{s}} b C_{\mathrm{eq}}}{1 + b C_{\mathrm{eq}}} \tag{1}$$

q_{eq} is the amount of solutes sorbed per unit weight of sorbent at equilibrium concentration, C_{eq}, and $a = q_{\mathrm{s}} b q_{\mathrm{s}}$ is the maximum amount of sorbed material required to give a complete monolayer on the surface, and b is a measurement of relative sorption affinity.

The Freundlich expression is an empirical equation based on sorption onto a heterogeneous surface.[12,13]

$$q_{\mathrm{eq}} = a^0 C_{\mathrm{eq}}^{b^0} \tag{2}$$

a^0 is an indication of the sorption capacity of the sorbent, b^0 indicates the effect of concentration on the sorption capacity and represents the sorption intensity.

Another isotherm equation such as a three-parameter isotherm proposed by Redlich–Peterson seems to be more adequately fit the broad range of equilibrium data.[14,15]

$$q_{\mathrm{eq}} = \frac{K_{\mathrm{R}} C_{\mathrm{eq}}}{1 + a_{\mathrm{R}} C_{\mathrm{eq}}^{\beta}} \tag{3}$$

If β is equal to 1, then Eq. (3) becomes the Langmuir equation. If $a_{\mathrm{R}} C_{\mathrm{eq}}^{\beta}$ is much greater than 1, then it becomes the Freundlich equation. If $a_{\mathrm{R}} C_{\mathrm{eq}}^{\beta}$ is much less than 1, which occurs at low concentrations, then it becomes a linear isotherm equation.

The theoretical BET model for multilayer sorption is:[16,17]

$$q_{\mathrm{eq}} = \frac{Q_{\mathrm{m}} B C_{\mathrm{eq}}}{(C_{\mathrm{s}} - C_{\mathrm{eq}})\left[1 + (B - 1)\left(\frac{C_{\mathrm{eq}}}{C_{\mathrm{s}}}\right)\right]} \tag{4}$$

where C_{s} is the saturation concentration of the solute, and B a constant relating to the energy of interaction with the surface.

The sorption constants of Cu(II) ions onto chitin and chitosan calculated according to the Langmuir, Freundlich, Redlich–Peterson, and the BET sorption models at different pH values are listed in Tables 1 and 2. The values of the sorption constants obtained from the sorption isotherms confirmed optimum pH value determined from the initial sorption rates for the uptake of Cu(II) ions. The correlation coefficients (R) were generally very high for the various models. However, the Langmuir model provided the best fit with experimental and predicted values at all pH values for the sorption of Cu(II) ions onto chitin (Fig. 4), while the best fit for chitosan was obtained by using the Redlich–Peterson model.

The shape of an isotherm can indicate the favorability of sorption of solute by the sorbent. The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, r, which is defined by Eq. (5):

$$r = \frac{1}{1 + bC_0} \tag{5}$$

where C_0 is an initial metal concentration in solution. This parameter could predict whether sorption of the Cu(II) ions on chitin or chitosan was "favorable" or "unfavorable," such as unfavorable isotherm if $r > 1$, linear isotherm if $r = 1$, favorable isotherm if $0 < r < 1$, and irreversible isotherm if $r = 0$. In a real sorption process, however, r values always lie between 0 and 1, and as the r value approaches zero, the sorption becomes more favorable (Table 3).

As also seen from the values of the sorption isotherm coefficients and the separation factors, chitosan is a more favorable sorbent than chitin, especially in

Table 1. Change of the Sorption Isotherm Coefficients of the Langmuir, Freundlich, Redlich–Peterson, and BET Models with pH for the Sorption of Cu(II) Ions onto Chitin,

	Langmuir Model				Freundlich Model			Redlich–Peterson Model				BET Model		
pH	q_s (mmol/g)	b (L/mmol)	a (L/g)	R^2	a^0 (mmol$^{1-b^0}$L$^{b^0}$/g)	b^0 (mmol$^{1-b^0}$L$^{b^0}$/g)	R^2	K_R (L/g)	a_R (mmol$^{\beta+1}$/g L$^{\beta}$)	β	R^2	Q_m (mmol/g)	B	R^2
3.0	0.719	0.208	0.149	0.995	0.118	0.765	0.992	0.164	0.360	0.683	0.985	0.122	20.002	0.964
4.0	1.012	0.234	0.237	0.999	0.184	0.728	0.990	0.239	0.256	0.919	0.998	0.169	56.370	0.914
5.0	0.768	0.220	0.169	0.994	0.132	0.763	0.989	0.208	0.563	0.533	0.981	0.134	19.016	0.973

Particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.

Table 2. Change of the Sorption Isotherm Coefficients of the Langmuir, Freundlich, Redlich–Peterson, and BET Models with pH for the Sorption of Cu(II) Ions onto Chitosan

pH	Langmuir Model				Freundlich Model			Redlich–Peterson Model				BET Model		
	q_s (mmol/g)	b (L/mmol)	a (L/g)	R^2	a^0 (mmol$^{1-b^0}$L$^{b^0}$/g)	b^0 (mmol$^{1-b^0}$L$^{b^0}$/g)	R^2	K_R (L/g)	a_R (mmol$^{\beta+1}$/g L$^{\beta}$)	β	R^2	Q_m (mmol/g)	B	R^2
3.0	1.737	0.691	1.200	0.983	0.645	0.609	0.984	1.407	1.046	0.700	0.979	0.471	52.300	0.976
4.0	3.035	1.477	4.482	0.969	1.605	0.545	0.959	4.463	1.573	0.896	0.980	1.042	38.866	0.966
5.0	1.859	0.814	1.514	0.997	0.750	0.586	0.988	1.822	1.318	0.759	0.998	0.598	29.747	0.976

Particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.

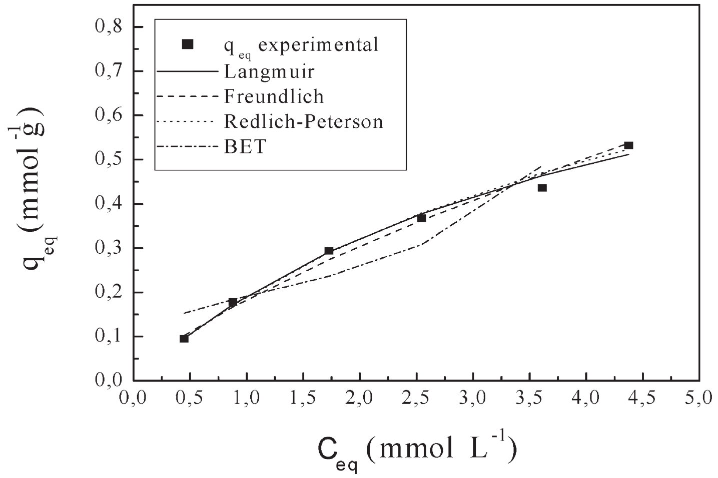

Figure 4. Comparison of the Langmuir, Freundlich, Redlich–Peterson, and BET sorption isotherms for Cu(II) sorption onto chitin at pH 4.0 (particle size, 250–420 μm; sorbent concentration 1 g L^{-1}).

the case of copper. The excellent sorption behavior of chitosan for metal ions is due to: (i) the high hydrophilicity of chitosan with a large number of hydroxyl groups; (ii) the large number of primary amino groups content with high activity; and (iii) the flexible structure of the polymer chains of chitosan, which enables a suitable configuration for complexation with metal ions.

Effect of Particle Size

In general, with variation in particle size, the values of the sorption isotherm coefficients did not differ greatly, these values generally differed only

Table 3. Separation Factor Values at Different pH Values and Particle Sizes

	pH[a]			Particle Size[b] (μm)	
	3.0	4.0	5.0	420–595	595–841
Chitin	0.49	0.47	0.48	0.48	0.50
Chitosan	0.23	0.12	0.20	0.18	0.22

[a] C_0, 4.721 mmol L^{-1}; particle size 250–420 μm; sorbent concentration 1.0 g L^{-1}.
[b] C_0, 4.721 mmol L^{-1}; pH, 4.0; sorbent concentration 1.0 g L^{-1}.

by an order of magnitude (Tables 4 and 5). Although the difference in the values of the sorption isotherm coefficients was only slight, overall a trend was established in that as the particle size increased, the Langmuir constants, q_s, b, a, the Freundlich constant a^0, the Redlich–Peterson constant, K_R (Fig. 5), and the BET constant Q_m decreased. Maximum uptake is a function of the specific area or external surface of the sorbent. As the particle size is decreased, the external surface of the chitin or chitosan flakes increased. As also confirmed by the separation factors given in Table 3, the optimum particle size range for both chitin and chitosan is 250–420 μm.

Mass Transfer Aspects of Cu(II) Sorption onto Chitin or Chitosan

External Mass Transfer Diffusion Model

The model used in this study is the boundary method. This model expresses the evaluation of the concentration of the solute in the solution, C (mmol L^{-1}), as a function of the difference in the concentrations of the metal ion in the solution, and at the particle surface, C_s (mmol L^{-1}), according to the equation of Weber and Morris:[18–23]

$$\frac{dC}{dt} = -\beta_L S(C - C_s) \tag{6}$$

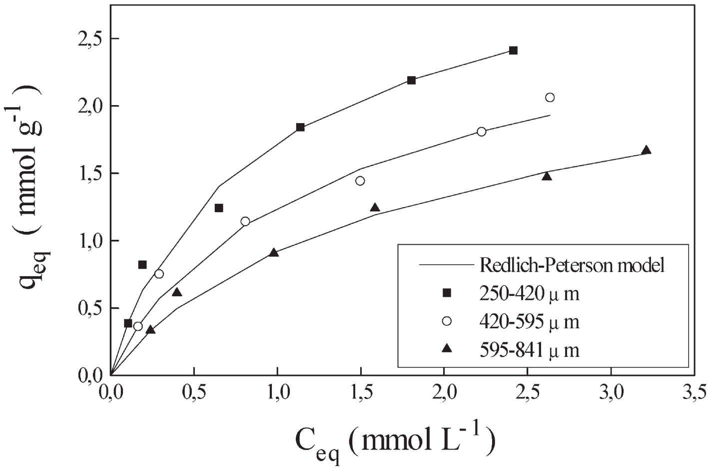

Figure 5. The Redlich–Peterson sorption isotherms obtained at different particle sizes for Cu(II) sorption onto chitosan (pH 4.0; sorbent concentration, 1 g L^{-1}).

Table 4. Change of the Sorption Isotherm Coefficients of the Langmuir, Freundlich, Redlich–Peterson, and BET Models with Particle Size for the Sorption of Cu(II) Ions onto Chitin

	Langmuir Model				Freundlich Model			Redlich–Peterson Model				BET Model		
Particle Size (μm)	q_s (mmol/g)	b (L/mmol)	a (L/g)	R^2	a^0 (mmol$^{1-b^0}$ L$^{b^0}$/g)	b^0 (mmol$^{1-b^0}$ L$^{b^0}$/g)	R^2	K_R (L/g)	a_R (mmol$^{\beta+1}$/g L$^{\beta}$)	β	R^2	q_m (mmol/g)	B	R^2
250–420	1.012	0.234	0.237	0.999	0.184	0.728	0.990	0.239	0.256	0.919	0.998	0.169	56.37	0.914
595–420	0.938	0.226	0.212	0.995	0.166	0.732	0.989	0.22	0.303	0.825	0.992	0.163	23.619	0.954
841–595	0.828	0.214	0.177	0.976	0.14	0.750	0.967	0.182	0.288	0.691	0.977	0.132	22.191	0.975

pH, 4.0; sorbent concentration $1.0\,\mathrm{g\,L^{-1}}$.

Table 5. Change of the Sorption Isotherm Coefficients of the Langmuir, Freundlich, Redlich–Peterson, and BET Models with Particle Size for the Sorption of Cu(II) Ions onto Chitosan

	Langmuir Model				Freundlich Model			Redlich–Peterson Model				BET Model		
Particle Size (μm)	q_s (mmol/g)	b (L/mmol)	a (L/g)	R^2	a^0 (mmol$^{1-b^0}$ L$^{b^0}$/g)	b^0 (mmol$^{1-b^0}$ L$^{b^0}$/g)	R^2	K_R (L/g)	a_R (mmol$^{\beta+1}$/g L$^{\beta}$)	β	R^2	q_m (mmol/g)	B	R^2
250–420	3.035	1.477	4.482	0.969	1.605	0.545	0.959	4.463	1.573	0.896	0.980	1.042	38.866	0.966
595–420	2.775	0.974	2.703	0.966	1.206	0.560	0.956	2.755	1.193	0.866	0.979	0.807	60.155	0.971
841–595	2.371	0.718	1.703	0.978	0.889	0.579	0.968	1.778	0.926	0.840	0.984	0.650	78.826	0.947

pH, 4.0; sorbent concentration $1.0\,\mathrm{g\,L^{-1}}$.

where β_L is the mass transfer coefficient and S the specific surface area for mass transfer. In a well-agitated system, the solute and sorbent particle concentration in the liquid phase is assumed to be uniform, so that the solute concentration, m, is determined from the measured mass of chitin or chitosan, w, and the volume of particle free liquid, v, according to the equation:

$$m = \frac{w}{v} \tag{7}$$

Assuming smooth, spherical particles, the surface area for mass transfer, S, is obtained from m, using the equation:

$$S = \frac{6m}{d_p \rho_{app}} \tag{8}$$

where d_p is the particle diameter and ρ_{app} the apparent volume mass of the sorbent. Making some assumptions such as a surface concentration C_s negligible at $t = 0$, a concentration in solution tending to the initial concentration C_0 and also negligible intraparticle diffusion, Eq. (6) is simplified to

$$\left[\frac{d(C/C_0)}{dt}\right]_{t \to 0} = -\beta_L S \tag{9}$$

In a plot of C/C_0 vs. time, β_L is determined from the slope as $t \to 0$. External film mass transfer coefficients were determined for chitin and chitosan as a function of initial Cu(II) ion concentration, particle size, stirring rate, sorbent concentration, and pH are presented in Tables 6 and 7.

A plot of C/C_0 vs. time is given for variation of initial metal ion concentration in Fig. 6. Since, increasing the metal concentration in the solution reduced the diffusion of metal ions in the boundary layer, both the initial rate of external diffusion ($\beta_L S$), and the β_L decreased with increasing C_0. The initial external diffusion rate was increased by lowering the particle size of the sorbent. This increase in the initial external diffusion rates was only slight, as previously observed from the values of the sorption isotherm coefficients. For that reason, the values of β_L decreased with increasing the external surface area, S. Increasing the Reynolds number from 2900 to 5800 increased the β_L value; this was an expected result as increased turbulence reduces the film boundary layer surrounding the chitin particle. Increasing the Reynolds number beyond 5800, however, did not raise the β_L value (Fig. 7). The slight effect of agitation implies that external mass transfer is not the sole rate-limiting phase, and confirms that intraparticle diffusion resistance needs to be included in the analysis of overall sorption. The initial rate of external diffusion increased with increasing sorbent concentration because of increasing surface area. With increase in sorbent concentration, the ratio of Cu(II) ions available to sorbent present is reduced,

Table 6. External Film Mass Transfer Coefficient (β_L) for the Sorption of Cu(II) Ions onto Chitin

	C_0[a] (mmol L^{-1})						Sorbent Concentration[b] (g L^{-1})						Particle Size[c] (μm)			pH[d]			Stirring Rate[e] (N_{Re})			
Variable	0.541	1.056	2.019	2.914	4.046	4.905	0.50	0.75	1.00	1.50	2.00	2.50	250–420	420–595	595–841	3.0	4.0	5.0	2,900	5,800	8,700	11,600
$\beta_L S$ (sec^{-1}) × 10^3	0.13	0.12	0.10	0.09	0.09	0.11	0.07	0.09	0.10	0.12	0.15	0.16	0.09	0.08	0.06	0.07	0.10	0.07	0.10	0.12	0.11	0.12
β_L (cm sec^{-1}) × 10^3	0.68	0.62	0.51	0.47	0.45	0.56	0.75	0.65	0.51	0.43	0.39	0.33	0.47	0.62	0.67	0.37	0.51	0.39	0.55	0.61	0.57	0.64

[a] pH, 4.0; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.
[b] pH, 4.0; C_0, 2.019 mmol L^{-1}; particle size, 250–420 μm.
[c] pH, 4.0; C_0, 2.914 mmol L^{-1}; sorbent concentration, 1.0 g L^{-1}.
[d] C_0, 2.019 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.
[e] pH, 4.0; C_0, 1.905 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.

Table 7. External Film Mass Transfer Coefficient (β_L) for the Sorption of Cu(II) Ions onto Chitosan

	C_0[a] (mmol L^{-1})						Sorbent Concentration[b] (g L^{-1})						Particle Size[c] (μm)			pH[d]			Stirring Rate[e] (N_{Re})			
Variable	0.494	1.015	1.894	2.979	3.994	4.827	0.50	0.75	1.00	1.50	2.00	2.50	250–420	420–595	595–841	3.0	4.0	5.0	2,900	5,800	8,700	11,600
$\beta_L S$ (sec^{-1}) × 10^3	0.49	0.46	0.36	0.30	0.33	0.28	0.26	0.33	0.36	0.41	0.47	0.53	0.30	0.28	0.23	0.25	0.36	0.24	0.30	0.46	0.41	0.37
β_L (cm sec^{-1}) × 10^3	4.60	4.27	3.40	2.84	3.12	2.62	4.81	4.16	3.40	2.58	2.21	1.98	2.84	3.93	4.69	2.33	3.40	2.20	2.83	4.33	3.81	3.43

[a] pH, 4.0; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.
[b] pH, 4.0; C_0, 1.894 mmol L^{-1}; particle size, 250–420 μm.
[c] pH, 4.0; C_0, 2.979 mmol L^{-1}; sorbent concentration, 1.0 g L^{-1}.
[d] C_0, 1.894 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.
[e] pH, 4.0; C_0, 1.905 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.

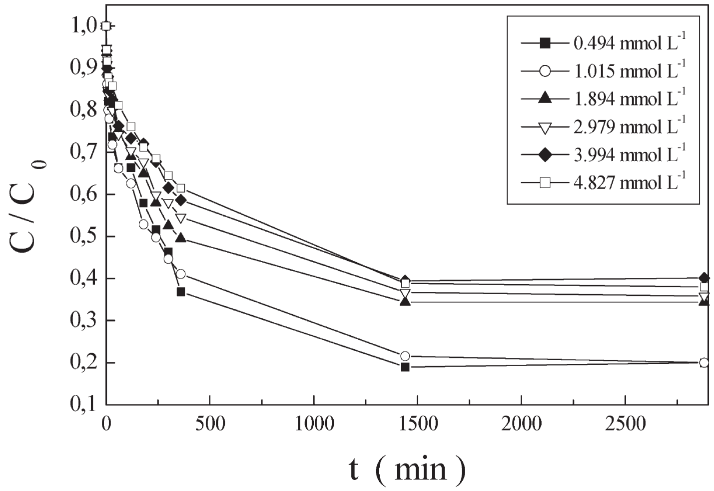

Figure 6. External mass transfer resistance model. Effect of initial Cu(II) ion concentration on kinetics of Cu(II) sorption by chitosan (pH, 4.0; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}).

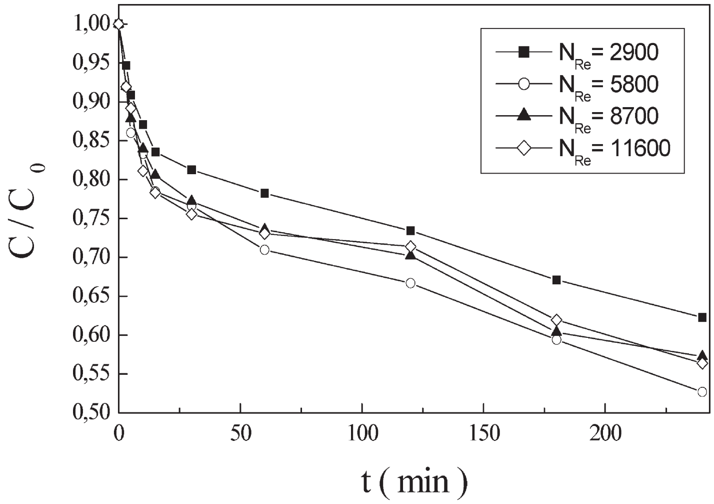

Figure 7. External mass transfer resistance model. Effect of stirring rate on kinetics of Cu(II) sorption by chitosan (pH, 4.0; C_0, 1.905 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}).

hence the percentage of Cu(II) ions available for sorption is smaller than in situations where the sorbent concentration is lower. The distance between the sorbent particles is also long at lower sorbent concentrations, resulting in an increase in active sorption area. For that reason, higher external film mass transfer coefficients were obtained at lower sorbent concentrations by an effective mixing.

The external film mass transfer coefficients, β_L, for chitin and chitosan were 0.51×10^{-3} and 3.40×10^{-3} cm sec^{-1} with an external diffusion rate of 0.10 and 0.36 sec^{-1}, respectively, at medium values of all the variables examined (at pH 4.0, 250–420 μm particle size range, 2 mmol L^{-1} initial Cu(II) ion concentration, and 1.0 g L^{-1} sorbent concentration). The external film mass transfer coefficients of chitin and chitosan had a mean value of 0.60×10^{-3} and 3.73×10^{-3} cm sec^{-1}, respectively. For copper sorption onto chitosan, McKay et al. calculated a β_L coefficient equal to 4×10^{-3} cm sec^{-1}.[23] Findon et al. reported external diffusion coefficients changing between 63.6×10^{-3} and 5.4×10^{-3} cm sec^{-1} with experimental parameters for copper sorption by chitosan.[18]

Intraparticular Mass Transfer Diffusion Model

In the model developed by Weber and Morris[21] and McKay and Poots,[22] the fractional approach to equilibrium varies according to a function of $(D_t/r^2)^{0.5}$, where D is the diffusion coefficient in the solid and r the particle radius. So, intraparticle diffusion is determined by a dependence on the square root of time, $t^{0.5}$, and is estimated from plots of q vs. $t^{0.5}$.[18,19] If intraparticle diffusion is a rate-controlling step, then the plots should be linear; the slope of the linear section is determined and is defined as an intraparticle diffusion rate parameter, K (mmol g^{-1} sec$^{-1/2}$). As intraparticle diffusion predominates in the range 10–60% of the sorption region, correlations only take into account this range. For that reason, linearization was carried out using the initial time of contact between 0 and 360 min. Then a decreasing rate of sorption produces another curved portion leading to an equilibrium plateau.

For the sorption of Cu(II) ions by chitin and chitosan, Tables 8 and 9, respectively, give K, determined for each variable tested. Increasing the Cu(II) concentration in the solution promoted the diffusion in the chitin or chitosan particles and resulted in an increase in the intraparticular diffusion rate (Fig. 8). Increasing the particle size resulted in a greater time to reach equilibrium. The solute needed more time to diffuse to the interior of the particle. Moreover, the initial external diffusion rate was observed to increase by lowering the particle size of the sorbent, the intraparticle diffusion rate also increased in the same conditions. A 0.5 g L^{-1} chitin or chitosan concentration and pH 4.0 seems to be important sorption parameters in overcoming both external and internal mass

Table 8. Intraparticle Diffusion Rate Parameter (K) for the Sorption of Cu(II) Ions onto Chitin

	C_0[a] (mmol L^{-1})						Sorbent Concentration[b] (g L^{-1})						Stirring Rate[c] (N_{Re})				Particle Size[d] (μm)			pH[e]		
Variable	0.541	1.056	2.019	2.914	4.046	4.905	0.50	0.75	1.00	1.50	2.00	2.50	2,900	5,800	8,700	11,600	250–420	420–595	595–841	3.0	4.0	5.0
K (mmol g^{-1} sec$^{-1/2}$) × 10^3	0.26	0.74	1.93	1.99	2.53	3.61	2.33	2.20	1.93	1.71	1.40	1.16	1.77	2.31	2.28	2.21	1.99	1.90	1.54	0.91	1.93	1.22

[a] pH, 4.0; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.
[b] pH, 4.0; C_0, 2.019 mmol L^{-1}; particle size, 250–420 μm.
[c] pH, 4.0; C_0, 1.905 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.
[d] pH, 4.0; C_0, 2.914 mmol L^{-1}; sorbent concentration, 1.0 g L^{-1}.
[e] C_0, 2.019 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.

Table 9. Intraparticle Diffusion Rate Parameter (K) for the Sorption of Cu(II) Ions onto Chitosan

	C_0[a] (mmol L^{-1})						Sorbent Concentration[b] (g L^{-1})						Stirring Rate[c] (N_{Re})				Particle Size[d] (μm)			pH[e]		
Variable	0.494	1.015	1.894	2.979	3.994	4.827	0.50	0.75	1.00	1.50	2.00	2.50	2,900	5,800	8,700	11,600	250–420	420–595	595–841	3.0	4.0	5.0
K (mmol g^{-1} sec$^{-1/2}$) × 10^3	1.79	3.72	6.00	8.47	9.88	11.54	8.84	7.65	6.00	4.97	4.05	3.41	5.80	6.73	6.14	5.80	8.47	7.42	6.73	4.27	6.00	3.82

[a] pH, 4.0; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.
[b] pH, 4.0; C_0, 1.894 mmol L^{-1}; particle size, 250–420 μm.
[c] pH, 4.0; C_0, 1.905 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.
[d] pH, 4.0; C_0, 2.979 mmol L^{-1}; sorbent concentration, 1.0 g L^{-1}.
[e] C_0, 1.894 mmol L^{-1}; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}.

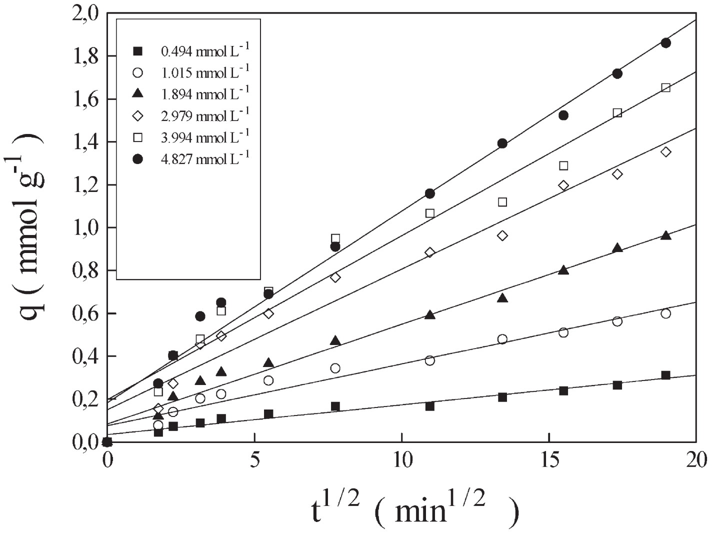

Figure 8. Intraparticular mass transfer diffusion model of Weber and Morris. Effect of initial Cu(II) ion concentration on kinetics of Cu(II) sorption by chitosan (pH, 4.0; particle size, 250–420 μm; sorbent concentration, 1.0 g L^{-1}).

transfer resistances. At pH 4.0 high affinity of Cu(II) for the sorbents caused both the external and internal mass transfer coefficients to increase. Variation of stirring rate had no effect on the *K* value. This is not unexpected as agitation typically influences only the external transport step. Discontinuity in experimental points or deviations from the linear solid lines represent several diffusion ranges for the sorption of Cu(II). Some of the models present multi-linearity, i.e., several portions of the curve are linear in a restricted range. This could indicate that two or more phenomena are occurring successively. A real approach of global diffusion generally prefers a combined model. The existence on the same curve of various lines suggests that various intraparticle diffusion rate parameters can be determined.[24–26] This result can be attributed to diffusion in pores of different class sizes.[23] This distinction is also related to the size of the ion. It is also important to note that Cu(II) sorption by chitin or chitosan exhibits, under linearized form, a positive and significant ordinate intercept, indicating the influence of external rate control, as especially observed at higher initial Cu(II) ion concentrations.

The intraparticle diffusion rate parameters, *K*, for chitin and chitosan were determined as 1.93×10^{-3} mmol g^{-1} $sec^{-0.5}$ (0.12 mmol g^{-1} $hr^{-0.5}$) and 6.00×10^{-3} mmol g^{-1} $sec^{-0.5}$ (0.36 mmol g^{-1} $hr^{-0.5}$), respectively, at medium values of all the parameters examined. Intraparticle diffusion rate parameters for chitin and chitosan had a mean value of 1.77×10^{-3} mmol g^{-1} sec$^{-0.5}$ (0.11 mmol g^{-1} hr$^{-0.5}$) and 6.09×10^{-3} mmol g^{-1} sec$^{-0.5}$ (0.36 mmol g^{-1} hr$^{-0.5}$), respectively. Cu(II) sorption by chitosan appears to be less controlled by diffusion mechanisms than Cu(II) uptake by chitin. Low sorption capacity of chitin may also be a result of poor diffusion of Cu(II) ions in the chitin. Yang and Zall estimated intraparticle diffusion rate of Cu(II) ions onto chitosan and chitin by a diffusion equation similar to the model of Weber and Morris and obtained a higher rate constant, 2.31 mmol g^{-1} hr$^{-0.5}$ for chitosan and 0.79 mmol g^{-1} hr$^{-0.5}$ for chitin.[15] Findon et al. obtained intraparticle diffusion rate parameters changing in a wide range (0.10–1.29 mmol g^{-1} hr$^{-0.5}$) with the variables tested for Cu(II) sorption by chitosan.[18]

Comparison of the Cu(II) Sorption by Chitin and Chitosan with *R. arrhizus*

R. arrhizus that belongs to the Mucorales family possessing usually higher chitin/chitosan content in the cell wall is known for its strong metal-sorbent properties, which are common to the whole genus. Chitin/chitosan productivity of *Rhizopus* species can be as high as 58% of the cell-wall mass.[27] Using pure chitin and chitosan gave a Cu(II) binding capacity of 0.368 mmol (g chitin)$^{-1}$ and 2.413 mmol (g chitosan)$^{-1}$. The Cu(II) uptake capacity of *R. arrhizus* was 0.456 mmol (g dry cell)$^{-1}$. Thus, the Cu(II) uptake capacity of chitosan was considerably higher than that of *R. arrhizus*, while pure chitin had a Cu(II) uptake capacity slightly lower than that of the whole fungal biomass (Fig. 9). The equilibrium relationship for the sorption of Cu(II) ions by *R. arrhizus* was also studied by examining the closeness of fit of various sorption isotherm models. The best fit between the experimental equilibrium uptake values and model predictions was observed by using the Langmuir model. The b value, reflecting the affinity between the whole cells of *R. arrhizus* and Cu(II) ions was 1.465 L mmol^{-1}. The saturation amount of Cu(II) adsorbed, q_s, per unit weight of *R. arrhizus* at equilibrium and the separation factor were 0.569 mmol g^{-1} and 0.833 L g^{-1}, respectively. The Cu(II) uptake capacity of pure chitosan was about three to five fold greater than that of the whole cells of *R. arrhizus*. Although chitin only constitutes 17% of the cells,[28] it seems to be responsible for 83–96% of the total Cu(II) removal, depending on initial metal ion concentration. The percentages of the total sorption on whole cells that can be mainly attributed to sorption to the cell walls, chitin and chitosan were found to be 31, 20, and 83%, respectively. In particular, in the case of Cu(II), maximum metal uptake capacities of chitosan and chitin derivatives reported in the literature[3,29,30] are generally higher than those of pure whole cell cultures.

The copper sorption abilities and the uptake efficiencies can be increased by modifications to chitosan, such as grafting of specific functional group—

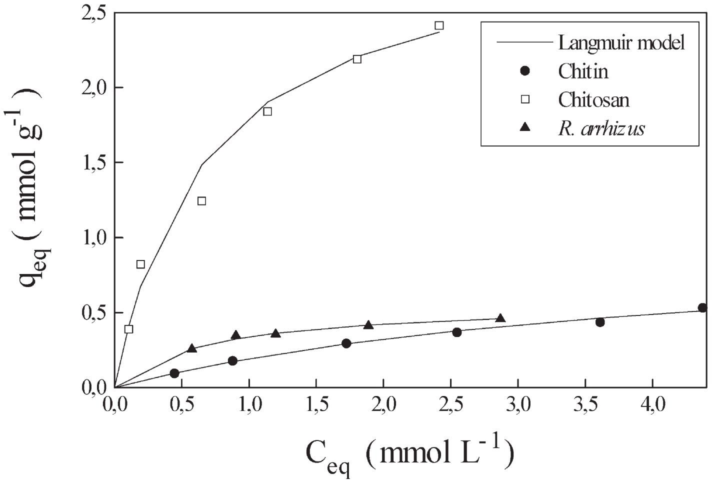

Figure 9. Comparison of the Langmuir Sorption Isotherms for Cu(II) Sorption by *R. arrhizus*, chitin, and chitosan (pH, 4.0; sorbent concentration, 1.0 g L^{-1}).

pyridine,[8] preparation of chitosan-based adsorption gels,[3] and crosslinked chitosan resin.[30] Only a few chitin-based derivatives have been prepared, because of its inherent intractability and very low solubility in aqueous media. The Cu(II) sorption capacities of chitin and chitosan used in this study are notably higher than those of pure or modified chitin and chitosan derivatives, reported previously in the literature.[3,8,18,29,30–32]

CONCLUSIONS

The ability of chitin or chitosan to sorb Cu(II) ions from aqueous solutions was studied, taking into account kinetic, equilibrium, and mass transfer aspects. An external mass transfer coefficient and an intraparticle diffusion rate parameter were determined for a number of system variables including pH, initial metal ion concentration, particle size, sorbent concentration, and stirring rate. The initial and equilibrium uptake strongly depends on pH, optimum sorption was reached at pH 4.0. At lower pH, the competition between protons and Cu(II) ions limits efficiency in removing Cu(II). Variation of initial metal ion concentration from low (about 30 mg L^{-1}) to high (300 mg L^{-1}) had also a notable influence on the kinetics. Increasing the particle size resulted in a decrease in the initial rates of sorption and equilibrium uptake. It implies that the sorption phenomenon is mainly a surface exchange. On the other hand, the stirring rate had no remarkable effect on the uptake kinetics of Cu(II) ions. This observation leads to the conclusion that external mass transfer resistance is not the major limiting phenomenon. Intraparticle diffusion rate parameters were significantly lower than those obtained in water or porous solids,[33] indicating a poor intraparticular diffusion into the chitin or chitosan or into the pores. It implies that a combined effect of the two mechanisms or the coexistence of various mechanisms are probable. Equilibrium isotherm studies revealed that the Cu(II) sorption onto chitin and chitosan was best described by the Langmuir and Redlich–Peterson models.

The sorption capacity of chitosan for Cu(II) ions was four to five times higher than that of chitin. The sorption behavior of the latter towards heavy metal ions depends on its degree of deacetylation. In addition, chitosan gave relatively higher external mass transfer rates and intraparticle diffusion rates than chitin. A large fraction of industrial waste waters containing heavy metal ions is discharged in strong acidic condition. This acidic effluent could severely limit the use of chitosan as a sorbent in removing metal ions due to chitosan's dissolution tendency in the effluent. To reduce such a problem, various crosslinking agents had been used to stabilize chitosan. However, such treatments reduce the metal sorption capacity of chitosan, and could considerably increase the application cost. In addition, the cost of pure chitosan is also higher than that of chitin. The copper sorption capacity of chitin used in this study is higher than that of some modified chitosans.[8,18,30] For that reason, chitin besides chitosan can also be effectively used in the treatment of Cu(II) ions.

ACKNOWLEDGMENT

The authors wish to thank TÜBİTAK, the Scientific and Technical Research Council of Turkey, for the partial financial support of this study (Project No: YDABÇAG, 199Y095).

REFERENCES

1. Volesky, B. Biosorption by Fungal Biomass. In *Biosorption of Heavy Metals*; Volesky, B., Ed.; CRC Press: Boca Raton, FL, 1990; 139–172.
2. Jiang, H.; Liang, J.; Grant, J.T.; Su, W.; Bunning, T.J.; Cooper, T.M.; Adams, W.W. Characterization of Chitosan and Rare-Earth-Metal-Ion Doped Chitosan Films. Macromol. Chem. Phys. **1997**, *198*, 1561–1578.
3. Tikhonov, V.E.; Radigina, L.A.; Yamskov, Y.A. Metal-Chelating Chitin Derivatives via Reaction of Chitosan with Nitrilotriacetic Acid. Carbohydr. Res. **1996**, *290*, 33–41.

4. Macaskie, L.E.; Dean, A.C.R. Metal-Sequestering Biochemicals. In *Biosorption of Heavy Metals*; Volesky, B., Ed.; CRC Press: Boca Raton, FL, 1990; 199–248.
5. Kim, C.Y.; Choi, H-M.; Cho, H.T. Effect of Deacetylation on Sorption of Dyes and Chromium on Chitin. J. Appl. Polym. Sci. **1997**, *63*, 725–736.
6. Gonzalez-Davila, M.; Millero, F.J. The Adsorption of Copper to Chitin in Seawater. Geochim. Cosmochim. Acta **1990**, *54*, 761–768.
7. Ngah, W.S.W.; Isa, I.M. Comparison Study of Copper Ion Adsorption on Chitosan, Dowex A-1, and Zerolit 225. J. Appl. Polym. Sci. **1998**, *67*, 1067–1070.
8. McKay, G.; Ho, Y.S.; Ng, J.C.Y. Biosorption of Copper from Waste Waters: A Review. Separ. Purif. Method **1999**, *28*, 87–125.
9. Sağ, Y.; Kutsal, T. The Selective Biosorption of Chromium(VI) and Copper(II) Ions from Binary Metal Mixtures by *R. arrhizus*. Process Biochem. **1996**, *31*, 561–572.
10. Sağ, Y.; Kutsal, T. Fully Competitive Biosorption of Chromium(VI) and Iron(III) Ions from Binary Metal Mixtures by *R. arrhizus*: Use of the Competitive Langmuir Model. Process Biochem. **1996**, *31*, 573–585.
11. Snell, F.D.; Snell, C.T. *Colorimetric Methods of Analysis*, 3rd Ed.; Van Nostrand: New York, 1959; Vol. 2, 78–139.
12. Hayward, D.O.; Trapnell, B.M.W. *Chemisorption*, 2nd Ed.; Butterworth: London, 1964; 67–159.
13. Smith, J.M. *Chemical Engineering Kinetics*, 3rd Ed.; McGraw-Hill: New York, 1981; 310–326.
14. Bellot, J.C.; Condoret, J.S. Modelling of Liquid Chromatography Equilibria. Process Biochem. **1993**, *28*, 365–376.
15. Yang, T.C.; Zall, R.R. Absorption of Metals by Natural Polymers Generated from Seafood Processing Wastes. Ind. Eng. Chem. Prod. Res. Dev. **1984**, *23*, 168–172.
16. Yu, J-W.; Neretnieks, I. Single-Component and Multicomponent Adsorption Equilibria on Activated Carbon of Methylcyclohexane, Toluene, and Isobutyl Methyl Ketone. Ind. Eng. Chem. Res. **1990**, *29*, 220–231.
17. Veglio, F.; Beolchini, F. Removal of Metals by Biosorption: A Review. Hydrometallurgy **1997**, *44*, 301–316.
18. Findon, A.; McKay, G.; Blair, H.S. Transport Studies for the Sorption of Copper Ions by Chitosan. J. Environ. Sci. Health **1993**, *A28*, 173–185.
19. Jansson-Charrier, M.; Guibal, E.; Roussy, J.; Delanghe, B.; Le Cloirec, P. Vanadium (VI) Sorption by Chitosan: Kinetics and Equilibrium. Water Res. **1996**, *30*, 465–475.
20. Weber, W.J.; Mathews, A.P. Effects of External Mass Transfer and Intraparticle Diffusion on Adsorption Rates in Slurry Reactors. In *AIChemE*

Symp. Ser.; American Institute of Chemical Engineers: New York, 1962; Vol. 73, 91–94.

21. Weber, W.J.; Morris, J.C. Advances in Water Pollution Research: Removal of Biologically-Resistant Pollutants from Waste Waters by Adsorption. In *Proc. Int. Conf. on Water Pollution Symp.*; Pergamon Press: Oxford, 1962; Vol. 2, 231–266.
22. McKay, G.; Poots, V.J.P. Kinetics and Diffusion Processes in Colour Removal from Effluent Using Wood as an Adsorbent. J. Chem. Tech. Biotechnol. **1980**, *30*, 279–292.
23. McKay, G.; Blair, H.S.; Findon, A. Sorption of Metal Ions by Chitosan. In *Immobilisation of Ions by Biosorption*; Eccles, H., Hunt, S., Eds.; Ellis Horwood: Chichester, UK, 1986; 59–69.
24. Van Vliet, B.M.; Weber, W.J., Jr.; Hozumi, H. Modelling and Prediction of Specific Compounds Adsorption by Activated Carbon and Synthetic Adsorbents. Water Res. **1980**, *14*, 1719–1728.
25. Mathews, A.P.; Weber, W.J., Jr. Modeling and Parameter Evaluation for Adsorption in Slurry Reactors. Chem. Eng. Commun. **1984**, *25*, 157–171.
26. McKay, G.; Bino, M.J. Application of Two Resistance Mass Transfer Model to Adsorption Systems. Chem. Eng. Res. Dev. **1985**, *63*, 168–174.
27. Tsezos, M.; Volesky, B. The Mechanism of Uranium Biosorption. Biotechnol. Bioeng. **1982**, *24*, 385–401.
28. Zhou, J.L. Zn Biosorption by *Rhizopus arrhizus* and Other Fungi. Appl. Microbiol. Biotechnol. **1999**, *51*, 686–693.
29. McKay, G.; Blair, H.S.; Findon, A. Equilibrium Studies for the Sorption of Metal Ions onto Chitosan. Indian J. Chem. **1989**, *28A*, 356–360.
30. Kondo, K.; Nakagawa, S-I.; Matsumoto, M.; Yamashita, T.; Furukawa, I. Selective Adsorption of Metal Ions on Novel Chitosan-Supported Sulfonic Acid Resin. J. Chem. Eng. Jpn. **1997**, *30*, 846–851.
31. Aly, A.S.; Jeon, B.D.; Park, Y.H. Preparation and Evaluation of the Chitin Derivatives for Wastewater Treatments. J. Appl. Polym. Sci. **1997**, *65*, 1939–1946.
32. Vasconcelos, M.T.S.D.; Azenha, M.A.O.; Cabral, J.P.S. Comparison of Availability of Copper(II) Complexes with Organic Ligands to Bacterial Cells and to Chitin. Environ. Toxicol. Chem. **1997**, *16*, 2029–2039.
33. Perry, R.H.; Green, D. *Perry's Chemical Engineers' Handbook*, 6th Ed.; Mc-Graw Hill: New York, 1984.

Received April 2001
Revised January 2002