

Evaluation of Glass Beads Coated with Chitosan for the Adsorption of Copper(II) Ions from Aqueous Solution

Juliana Q. Albarelli¹, Murilo T. Luna², Rodrigo S. Vieira² and Marisa M. Beppu^{1*} (1) School of Chemical Engineering, University of Campinas (UNICAMP), Cidade Universitária “Zeferino Vaz”, Caixa Postal 6066, Campinas, CEP 13083-970, SP Brazil. (2) Grupo de Pesquisas em Separações por Adsorção (GPSA), Departamento de Engenharia Química, Bloco 709, Campus do Pici, Universidade Federal do Ceará, Av. Mister Hull, Fortaleza, CEP 60455-760, CE Brazil.

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ABSTRACT: Chitosan, a natural polymer obtained from the de-acetylation of chitin, has been extensively studied in adsorption applications because its amino and hydroxyl groups can act as chelation sites. However, this material is rarely used as an adsorbent, mainly because of mechanical strength limitations. A possible means of making its use viable is the immobilization of chitosan onto solid matrices using particle-coating techniques. Studies have shown that the use of immobilized chitosan not only improves the mechanical strength of the adsorbent, but also enhances its mass-transfer properties. In this context, the present study has investigated the adsorption application of chitosan coated onto glass beads in batch and dynamic systems for the removal of copper ions from aqueous solution. The adsorption equilibrium properties were measured at different temperatures (25, 40, 50 and 60 °C) and the Langmuir, Freundlich and Langmuir–Freundlich models were used to fit the equilibrium data. Kinetic studies showed that adsorption equilibrium was attained after 10 h. The pseudo-first-order and pseudo-second-order kinetic models in both linear and non-linear forms together with the intra-particle diffusion model were used to fit the adsorption kinetics data. The best fit was obtained with the pseudo-second-order kinetic model, thereby suggesting that the limiting factor to mass transfer was chemical adsorption. The results indicate that chitosan immobilized onto glass beads demonstrate a good adsorption performance, with similar or even better results relative to other chitosan-based materials. Dynamic adsorption studies using the coated beads in a fixed bed system demonstrated the viability of their use for wastewater treatment.

1. INTRODUCTION

Contamination of the aquatic environment by heavy metal ions has become an issue of concern in view of the non-biodegradability and high toxicity of these materials. Of the known techniques for the removal of heavy metal ions in low concentration from wastewater, adsorption has been described as being the most efficient, low cost and easy operation (Kratochvil *et al.* 1997).

Several studies have been reported describing low-cost materials that can be applied as sorbents, including natural materials available in large quantities and industrial and agricultural wastes (Nghah *et al.* 2011; Crini 2005; Babel and Kurniawan 2003; Bailey *et al.* 1999). Chitosan,

* Author to whom all correspondence should be addressed. E-mail: beppu@feq.unicamp.br.

a natural polymer obtained from the de-acetylation of chitin, has been extensively studied for the removal of heavy metal ions from aqueous media because of its favourable adsorption capacity. Since the early 1970s, several articles have been published describing the use of this polymer for the adsorption of different metal ions. However, its use in large-scale adsorption processes presents some difficulties mainly related to its low mechanical strength. Guibal (2004) described many applications of chitosan sorbents, although the author reported that this adsorbent had not yet been applied on an industrial scale for wastewater treatment. In a recent review, Ngah *et al.* (2011) reported the use of chitosan composites for the adsorption of dyes and heavy metal ions, although the authors admitted that the majority of these studies had been restricted to the laboratory scale and for single component solutions.

A possible means of providing higher mechanical resistance and also improving the mass-transfer aspects is to immobilize chitosan onto a solid matrix using coating techniques. Some results using materials coated by chitosan such as clay (Gecol *et al.* 2006), perlite (Kalyani *et al.* 2005), PVC (Popuri *et al.* 2008), silica (Vijaya *et al.* 2008) and agro-industrial residues (Nomanbhay and Palanisamy 2005; Amuda *et al.* 2007) have already been reported. According to these studies, the use of immobilized chitosan enhanced its adsorption capacity. Of the various materials usually used as a solid support, glass beads are possibly one of the best choices because of their small dispersion particle size, mechanical strength and low cost (Liu *et al.* 2002). Interaction between the glass surface and the amino groups present in the chitosan structure could result in a successful interaction between the chitosan film and the support. Chitosan immobilization onto glass beads using coating techniques for adsorption proposes has not been reported in the literature to date.

In this context, this study was aimed at immobilizing chitosan onto glass beads and characterizing the resulting performance of the beads towards the adsorption of heavy metal ions from aqueous media. Copper(II) ions were used as a model due to their rapid adsorption and strong reactivity towards the amino groups present in chitosan relative to other metal ions (Zhao *et al.* 2002). Batch experiments were performed to study the equilibrium and kinetics of Cu(II) ion adsorption. Column adsorption experiments were conducted in order to evaluate the adsorption capacity towards Cu(II) ions in a dynamic system.

2. MATERIALS AND METHODS

2.1. Materials

The Cu(II) ion source was copper nitrate purchased from Vetec Química Fina Ltd., Brazil, an aqueous stock solution of the same being adjusted to the desired pH value through the use of NaOH or H₂SO₄ solutions (0.1 mol/l). Commercial glass beads were purchased from Labcenter, Brazil, while chitosan (commercial grade, high molecular weight, product number C 3646, with at least 85% de-acetylation) was purchased from Sigma-Aldrich, St. Louis, MO, U.S.A.

2.2. Coating glass beads with chitosan

A 2.5% w/v chitosan coating solution was prepared by dissolving chitosan flakes in a 3.0% v/v solution of acetic acid. The glass beads were first stirred for 6 h at room temperature with a 3.0% v/v acetic acid solution, then drained and washed with de-ionized water. The acid-treated glass beads were added to the chitosan solution and maintained for 12 h at 4 °C. The chitosan-coated beads were then dropped into a 1 mol/l NaOH solution in order to neutralize the amino groups

and were then maintained at room temperature for 24 h. The beads were then separated from the NaOH solution by means of a plastic sieve and exhaustively washed with de-ionized and distilled water until the washing water possessed a neutral pH. The beads were finally stored in ultrapure water at 4 °C until being used in the experiments.

2.3. Characterization of the adsorbent

The coated glass beads were dried at room temperature for 24 h and then covered with a thin layer of gold using a sputter coater (SC7629 Polaron model, East Grinstead, U.K.) for observation by a scanning electron microscopy (SEM) (LEO-440i, Cambridge Instruments, England). A vacuum of 1.33×10^{-6} mbar and a voltage of 20 kV were used to generate the secondary electron image.

Fourier-transform infrared spectra of the adsorbent before and after the adsorption of Cu(II) ions were obtained over the wavenumber range 400–4000 cm^{-1} using an FT-IR Illuminate R2 spectrometer in conjunction with KBr pelleted samples.

2.4. Batch adsorption experiments

Studies regarding the adsorption kinetics was performed by soaking a known amount of adsorbent in 100 ml of a suitable Cu(II) ion solution (20, 100 and 200 mg/ℓ at pH 5.0) contained in a series of flasks. These flasks were maintained at different stirring rates (80, 150 and 200 rpm) at room temperature. Samples were collected at different time intervals and the metal ion concentration was determined by means of a Perkin-Elmer AA Analyst 100 atomic absorption spectrophotometer. The adsorption capacity of chitosan was calculated on the basis of the difference in the Cu(II) ion concentration in the bulk solution before and after adsorption, in accordance with equation (1):

$$Q = \frac{(C_i - C_f)V}{W} \quad (1)$$

where Q is the amount of Cu(II) ions adsorbed by the adsorbent (mmol/g), V is the volume of the Cu(II) ion solution (ℓ), C_i and C_f are the initial and final Cu(II) ion concentration (mmol/ℓ), and W is the weight of the dry chitosan beads (g).

In order to investigate the controlling mechanism of the adsorption process such as mass transfer and chemical reaction, the experimental data were fitted employing the pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intra-particle model. The estimated kinetic parameters were compared using a linear least-squares method and a non-linear method as described by Kumar and Sivanesan (2006). According to these authors, the difference between the linear and non-linear equations for the same set of experimental data is due to the variation in the error structure upon linearizing a non-linear equation. Thus, the error distribution may vary depending on the way the equation is linearized.

The non-linear and linear forms of the pseudo-first-order and pseudo-second-order kinetic models, together with the linear form of the intra-particle diffusion model are listed in equations (2)–(6) below:

Pseudo-first-order model:

$$\text{Non-linear form} \quad Q_t = Q_e(1 - e^{-k_1 t}) \quad (2)$$

$$\text{Linear form} \quad \log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (3)$$

Pseudo-second-order model:

$$\text{Non-linear form} \quad Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

$$\text{Linear form} \quad \frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (5)$$

Intra-particle diffusion:

$$\text{Linear form} \quad Q_t = k_i t^{0.5} \quad (6)$$

In these equations, Q_e is the value of the amount adsorbed per unit mass of adsorbent at equilibrium (mmol/l) as obtained from the adsorption isotherm, Q_t is the amount adsorbed (mmol/l) at any time t , k_1 (1/h) is the pseudo-first-order adsorption rate constant, k_2 [g/(mmol h)] is the pseudo-second-order adsorption rate constant, while k_i [mmol/(g h^{1/2})] is the constant of the intra-particle diffusion model proposed by Weber and Morris (1962), being a characteristic parameter that describes the initial stage of the adsorption process.

In order to determine the equilibrium isotherms, a known amount of adsorbent was soaked in 25 ml of a given Cu(II) ion solution at pH 5.0 and stirred mechanically at 150 rpm for 10 h at temperatures of 25, 40, 50 and 60 °C, respectively. Both the initial metal ion concentration and that in the solution after equilibrium had been attained were measured as described above. The adsorption equilibrium data obtained at different temperatures were fitted by the Langmuir, Freundlich and Langmuir–Freundlich equilibrium models (see below), with mathematical adjusts being undertaken using the Origin® software non-linear regression method.

The Freundlich, Langmuir and Langmuir–Freundlich models may be expressed mathematically as follows:

Freundlich model (Freundlich 1906):

$$Q = K_F C_e^{1/n} \quad (7)$$

Langmuir model (Langmuir 1918):

$$Q = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (8)$$

Langmuir–Freundlich model (Lazaridis 2003):

$$Q = \frac{Q_{\max} (K_{LF} C_e)^b}{1 + (K_{LF} C_e)^b} \quad (9)$$

where K_F (l/g) is the Freundlich constant that represents the adsorption capacity, $1/n$ is the heterogeneity factor, Q_{\max} (mmol/g) is the maximum adsorption capacity, K_L (l/mmol) is the

Langmuir equilibrium constant, K_{LF} (ℓ/mmol)^{1/b} is the Langmuir–Freundlich constant and b is the Langmuir–Freundlich heterogeneity constant.

The Freundlich and the Langmuir models are the simplest adsorption models with only two adjustable parameters. The parameter K_L in the Langmuir model is the ratio between the rates of adsorption and desorption at equilibrium. The Freundlich isotherm is an empirical model used to explain adsorption on heterogeneous surfaces that assumes an exponential distribution of active sites and energies. The Langmuir–Freundlich isotherm which has three adjustable parameters tends to the Langmuir isotherm when the heterogeneity parameter b is set to unity (Kyzas and Lazaridis 2009).

2.5. Column adsorption experiments

Column adsorption experiments were conducted employing a glass column of ca. 4.0 cm internal diameter and 20.0 cm length. Flow rates of 6.00, 3.00 and 2.00 $\text{m}\ell/\text{min}$ were used. The effluent solution was collected at different time intervals and the concentration of the metal ion in the effluent solution was monitored by atomic absorption spectroscopy.

The amount of metal ion adsorbed in the column (Q_{total}) up to saturation was calculated by mass balance from the breakthrough curves using equation (10), where the area under the curve $(1 - C/C_0)$ is proportional to the amount of metal ion adsorbed. The amount of metal ion retained in the bed up to the breakpoint — which corresponds to the useful capacity of the column (Q_u) — was calculated via equation (11):

$$Q_{\text{total}} = \frac{C_0 q}{1000m} \int_0^t \left(\frac{1 - C|_{z=L}}{C_0} \right) dt \quad (10)$$

$$Q_u = \frac{C_0 q}{1000m} \int_0^{t_b} \left(\frac{1 - C|_{z=L}}{C_0} \right) dt \quad (11)$$

where Q_{total} is the total adsorption capacity [$\text{mmol Cu(II) ions/g dry chitosan}$], Q_u is the adsorption capacity up to bed rupturing [$\text{mmol Cu(II) ion/g dry chitosan}$], m is the mass of dried chitosan (g), q is the volumetric flow of the solution ($\text{m}\ell/\text{min}$), $C|_{z=L}$ is the concentration of metal ion removed from the column (mmol/ℓ), C_0 is the initial metal ion concentration (mmol/ℓ), t_b is the time required to reach the breakpoint (min) and t is the total time (min).

The calculation of the mass-transfer zone (MTZ) was performed using equation (12), where H is the height of the adsorption column:

$$\text{ZTM} = H \left(1 - \frac{Q_u}{Q_{\text{total}}} \right) \quad (12)$$

3. RESULTS AND DISCUSSION

3.1. Characterization of the adsorbent

After coating, the glass beads were completely covered by a chitosan layer. Thus, the surface morphology of the coated glass beads as observed by SEM indicated the formation of a homogeneous chitosan film (see Figure 1 overleaf). The thickness of the chitosan film layer and

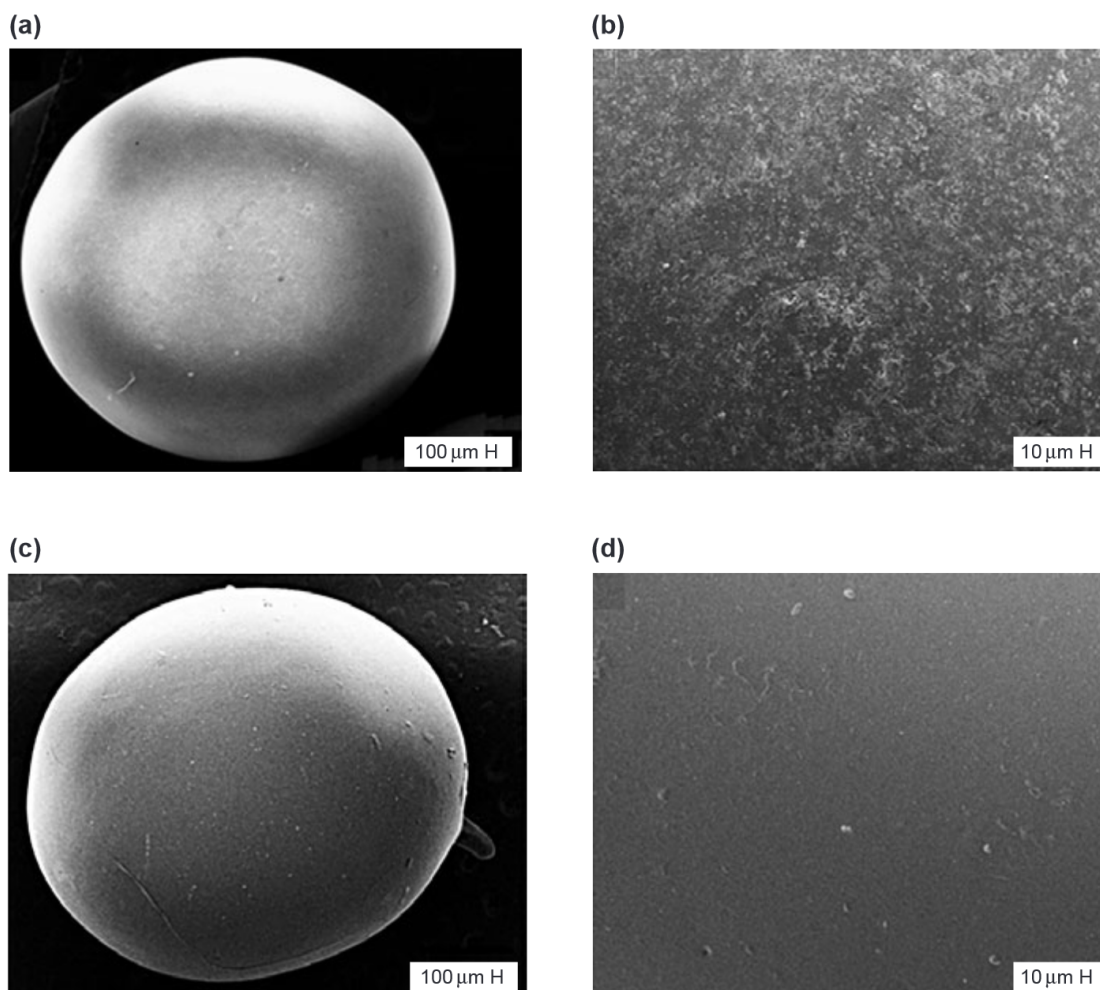


Figure 1. Glass beads before coating, (a) and (b), and after coating with chitosan, (c) and (d).

its porosity could not be precisely measured by SEM because freeze-drying would have been necessary to preserve the structure of the film rather than the slow drying process that we employed (Vieira and Beppu 2006b). Freeze-drying could not be performed due the severe conditions of pressure and temperature fluctuations necessary, which could damage the coating and lead to its detachment from the glass surface.

FT-IR analyses revealed that all the functional groups, such as $-\text{NH}_2$ and $-\text{OH}$, originally present in the spectrum of chitosan, were preserved after the coating process and were available for interaction with metal ions. Peaks were observed at 3250 cm^{-1} ($-\text{OH}$ and $-\text{NH}$ stretching), 2862 cm^{-1} ($-\text{CH}$ stretching), 1627 cm^{-1} ($-\text{NH}$ bending in $-\text{NH}_2$), 1370 cm^{-1} ($-\text{NH}$ deformation vibration in $-\text{NH}_2$), and 1015 cm^{-1} ($-\text{C}-\text{O}-\text{C}-$ stretching). Similar results have been obtained previously for natural chitosan (Vieira and Beppu 2006a; Popuri *et al.* 2008).

3.2. Kinetics of metal ion adsorption and the effect of stirring rate in batch experiments

The effect of Cu(II) ion concentration on the adsorption kinetics of chitosan-coated glass beads was analyzed (see Figure 2 overleaf), from which it is seen that the Cu(II) ion concentration in the solution attained an equilibrium value after 10 h. This result is in accordance with others cited in the literature for adsorption using materials coated by chitosan (Vijaya *et al.* 2008; Popuri *et al.* 2008).

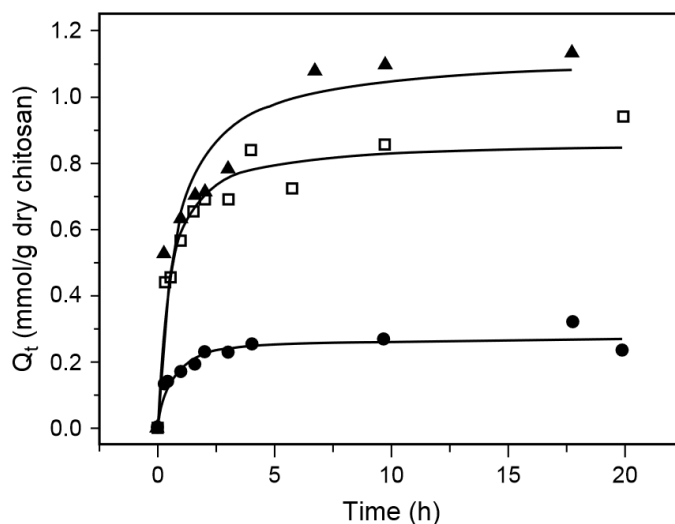


Figure 2. Adsorption kinetics for different initial Cu(II) ion concentrations: (●) 20 ppm, (□) 100 ppm and (▲) 200 ppm.

As the initial Cu(II) ion concentration in the solution increased, the rate of removal of Cu(II) ions through adsorption decreased. Thus, the Cu(II) ion removal rate was approximately 90% for a 20 mg/l solution, whilst Cu(II) ion removal from the 200 mg/l solution was only around 45%. When lower amounts of metal ions are present in the solution, competition for the active sites on chitosan is lower and hence the chances of the metal ions binding to the adsorbent surface are higher. A higher concentration of metals ions in solution leads to saturation of the surface active sites, forcing the metal ions to diffuse inside the polymer matrix and pores in order to interact with the adsorbent. Thus, although the final uptake of Cu(II) ions is higher as the solution concentration increases, the removal rate decreases probably as a result of the limitations of mass transfer in accessing the active sites of the adsorbent.

The linear forms of the pseudo-first- and pseudo-second-order models were initially applied for fitting the kinetic adsorption data. If these equations are appropriate, then linear plots of $\log(Q_e - Q_t)$ versus t and t/Q_t versus t , respectively, would be expected. The calculated rate constants (k_1 and k_2), the predicted Q_e values and the correlation coefficients R^2 obtained by the least-squares correlation method for the linear and non-linear forms of these models are listed in Table 1. The linear form of the pseudo-first-order model did not describe the experimental results. In this case, the maximum amount of metal ion adsorbed (Q_e) as obtained by the Langmuir equation is reported. This value can be influenced by the error distribution. In contrast, the non-linear form exhibited an R^2 value that was higher than that found for the linear form, since Q_e was estimated by the least-squares method in this case. In general, the pseudo-first-order model describes a reversible solid/liquid equilibrium process and can only be applied over the initial stages of the adsorption process, since it fails to represent the whole process. The results were not well fitted by Weber and Morris model. This indicates that the process was not controlled solely by internal diffusion of the metal ions into the adsorbent, but mainly by external diffusion (Nghah and Fatinathan 2008).

The pseudo-second-order model was linearized as proposed by Ho and McKay (2004). Kumar and Sivanesan (2006) have described four different variants of the pseudo-second-order linear equation where the error distribution changed according to the way in which the equation was linearized. It will be seen from Table 1 that the value of R^2 arising from the fit of the linear pseudo-second-order model to the observed adsorption kinetics was higher than

TABLE 1. Fitting of the Experimental Adsorption Kinetic Data for the Adsorption of Cu(II) Ions onto Glass Beads Coated with Chitosan by Various Models in the Linear and Non-linear Forms

Model/Parameters	Initial Cu(II) ion concentration		
	20 mg/ℓ	100 mg/ℓ	200 mg/ℓ
Pseudo-first-order model			
<i>Linear form</i>			
R ²	0.264	0.631	0.871
k ₁ (1/h)	0.006	0.051	0.154
Q _e (mmol/g)	1.084	0.727	0.815
<i>Non-linear form</i>			
R ²	0.854	0.873	0.825
k ₁ (1/h)	1.411	1.626	0.752
Q _e (mmol/g)	0.257	0.785	1.057
Pseudo-second-order model			
<i>Linear form</i>			
R ²	0.996	0.994	0.990
k ₂ [g/(mmol h)]	2.032	1.496	0.699
Q _e (mmol/g)	0.245	0.951	1.309
<i>Non-linear form</i>			
R ²	0.919	0.945	0.907
k ₂ [g/(mmol h)]	7.651	2.586	1.167
Q _e (mmol/g)	0.279	0.868	1.130
Intra-particle diffusion model			
R ²	0.853	0.707	0.527
k _i [mmol/(g h ^{1/2})]	0.229	0.169	0.043

the value found for the application of the non-linear pseudo-second-order model, indicating that the type of linearization involved with this model provided an adequate fit. According Ngah *et al.* (2004), the pseudo-second-order model provides a good fit to the data arising from most adsorption processes if it is assumed that the limiting step is chemical adsorption. Table 1 indicates that the value of k_2 diminished as the initial concentration of Cu(II) ions in the system increased. This fact demonstrates that the adsorption process occurred at a faster rate at low Cu(II) ion concentrations, probably as a result of the reduced competition for chitosan active sites as described above.

The influence of external diffusion on the adsorption process was evaluated by performing kinetic experiments employing different stirring rates (80, 150 and 200 rpm). Figure 3 overleaf depicts the kinetic results as described by the pseudo-second-order model while Table 2 presents the calculated kinetic parameters. According to these results, the kinetic rate decreased on increasing the rate of stirring, indicating that the adsorption rate was controlled by external diffusion. On increasing the stirring rate, turbulence in the solution also increased; eventually this led to a reduction in the thickness of the external solution boundary layer. The highest stirring rate of 200 rpm caused detachment of the chitosan coating from the glass surface. Even though this could at first be seen as a limitation, this detachment phenomenon could be of interest as a means of

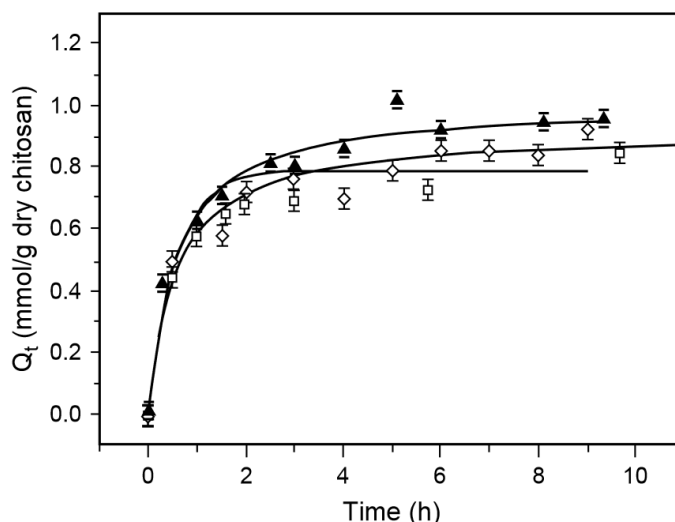


Figure 3. Effect of stirring rate on the adsorption kinetics of Cu(II) ions onto chitosan-coated glass beads. Data points correspond to the following stirring rates: \diamond , 80 rpm; \square , 150 rpm; \blacktriangle , 200 rpm. Initial conc. of Cu(II) ion solution = 100 mg/l.

TABLE 2. Influence of the Stirring Rate on the Values of the Pseudo-second-order Kinetic Parameters for the Adsorption of Cu(II) Ions onto Glass Beads Coated with Chitosan

	Stirring rate		
	80 rpm	150 rpm	200 rpm
R^2	0.947	0.924	0.976
k_2 [g/(mmol h)]	2.860	1.982	1.821
Q_e (mmol/g)	0.871	0.918	1.009

disposing of chitosan after its use as an adsorbent. After detachment of the biopolymer coating, the glass beads could be used in another coating/adsorption cycle.

The data listed in Table 2 indicate that an increase in the stirring rate led to an improvement in the adsorption capacity, as observed by Ngah *et al.* (2002) using natural chitosan beads for the removal of Cu(II) ions. These authors observed that on increasing the rate of stirring from 70 rpm to 200 rpm, a 50% increase in the removal of the metal ion occurred.

3.3. Adsorption equilibrium in batch experiments

The adsorption isotherm is important in understanding the distribution of the adsorbate when equilibrium is established. Figure 4 overleaf presents the equilibrium adsorption isotherms obtained at different temperatures, where the curves depicted show the fit obtained by applying the Langmuir data to the experimental data. The parameters arising from the application of the Langmuir, Freundlich and Langmuir–Freundlich models are listed in Table 3. The R^2 values were obtained by the least-squares method.

The experimental data were best fitted by the Langmuir isotherm, indicating that the adsorption on the surface probably occurred as a monolayer. This model is consistent with the suggestion that

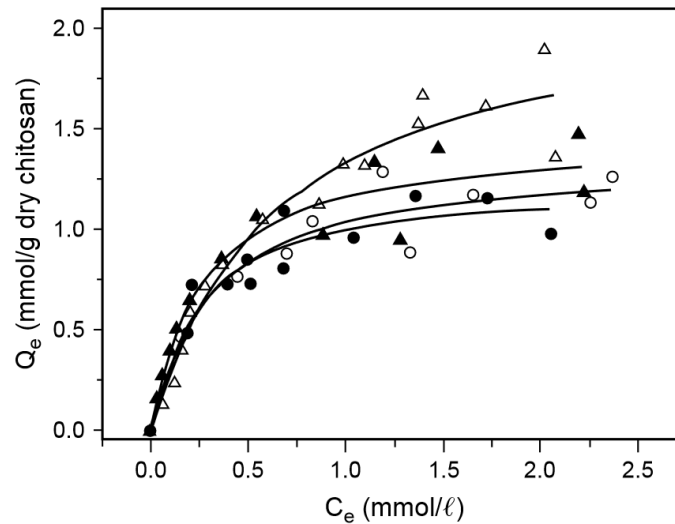


Figure 4. Isotherms for the adsorption of Cu(II) ions onto chitosan-coated glass beads at several temperatures. Data points correspond to the following temperatures: ●, 25 °C, ○, 40 °C, ▲, 50 °C, △, 60 °C. Initial conc. of Cu(II) ion solution = 100 mg/l. The continuous lines represent the application of the Langmuir model to the experimental data.

TABLE 3. Parameters Calculated by Fitting the Equilibrium Adsorption Data by the Langmuir, Freundlich and Langmuir–Freundlich Models

Model/Parameters	Temperature			
	25 °C	40 °C	50 °C	60 °C
Langmuir				
Q_{\max} (mmol/g)	1.26	1.33	1.41	2.33
K_L (l/mmol)	3.78	3.34	4.10	1.38
R^2	0.91	0.95	0.94	0.98
Freundlich				
K_F (l/g)	0.86	0.87	1.32	1.55
1/n	3.33	2.70	2.56	2.43
R^2	0.87	0.91	0.93	0.93
Langmuir–Freundlich				
Q_{\max} (mmol/g)	1.176	1.319	1.492	2.068
K_{LF} (l/mmol) ^{1/b}	4.382	3.441	3.685	1.784
b	1.17	1.06	0.96	1.05
R^2	0.897	0.943	0.925	0.951

the chelation of the Cu(II) ions occurs specifically onto the amino groups on the adsorbent surface. This result also accords with the fact that the Langmuir model provides a good description of adsorption systems involving low concentrations of adsorbate.

In the case of the Freundlich isotherm, it is commonly accepted that the smaller the value of the 1/n coefficient, the smaller is the affinity of the metal ion to the adsorbent. The maximum adsorption capacity of the adsorbent (Q_{\max}) obtained from fitting the Langmuir model increased on increasing the temperature. This increase in adsorption capacity can be related to the increase in external mass transfer with temperature. In general, in systems where the adsorption capacity

decreases with increasing temperature, physisorption contributes more significantly to the adsorption process than chemisorption. The values of K_L and K_{LF} , calculated from the Langmuir and the Langmuir–Freundlich models, decreased with increasing temperature. Over the temperature range studied, the values of K_L and K_{LF} were greater than 1.0, thereby indicating that the adsorption equilibrium was shifted towards adsorption. However, on increasing the temperature, K_L decreased in value, indicating that the adsorption/desorption equilibrium became more reversible in character.

The parameter K_L can be used to describe the affinity between the metal ion and the adsorbent through the curvature of the sorption isotherm as measured in terms of R_L , a dimensionless parameter. At all studied temperatures, the value of the parameter R_L indicated that the adsorption of Cu(II) ions onto chitosan-coated glass beads was favourable ($0 < R_L < 1$) (Table 4). However, as the initial concentration of Cu(II) ions in the aqueous solution increased, the value of the parameter R_L decreased, indicating a tendency towards an irreversible isotherm. The increase in temperature favoured the reversibility of the reaction as previously verified by the analysis of the K_L parameter.

The maximum adsorption capacity of chitosan-coated glass beads for Cu(II) ions calculated for 25 °C can be compared to the maximum capacity of other chitosan-based adsorbents (see Table 5). It will be seen from the data listed that the value of Q_{max} obtained in the present study was similar to that determined by Popuri *et al.* (2008) who studied chitosan coated on PVC and by Ngah and Fatinathan (2008) using chitosan beads. The highest adsorption capacity recorded in Table 5 is for chitosan coated onto perlite, probably due to the fact that perlite itself possessed an ability to adsorb

TABLE 4. Values of R_L as Calculated from Kinetic Data for the Adsorption of Cu(II) Ions onto Chitosan-coated Glass Beads at Different Temperatures

Initial Cu(II) ion conc., C_i (mg/l)	R_L parameter ^a at			
	25 °C	40 °C	50 °C	60 °C
20	0.46	0.49	0.44	0.70
80	0.17	0.19	0.16	0.37
140	0.11	0.12	0.10	0.25
200	0.08	0.09	0.07	0.19

^a $R_L = 1/(1 + K_L C_i)$ where K_L = Langmuir parameter and C_i is the initial Cu(II) ion concentration.

TABLE 5. Maximum Copper(II) Ion Adsorption Capacity of Different Chitosan-based Adsorbents

Chitosan-based adsorbent	Q_{max} (mmol/g of dry adsorbent)	Reference
Chitosan coated on glass beads	1.26	This study
Chitosan coated on perlite	3.09	Kalyani <i>et al.</i> (2005)
Chitosan membrane	2.0	Vieira <i>et al.</i> (2007)
Chitosan coated on PVC beads	1.38	Popuri <i>et al.</i> (2008)
Chitosan spheres	1.02	Ngah and Fatinathan (2008)
Chitosan/alginate spheres	1.06	Ngah and Fatinathan (2008)
Chitosan/PVA	0.75	Ngah <i>et al.</i> (2004)
Chitosan spheres	0.53	Ngah <i>et al.</i> (2004)
GLU–chitosan spheres	0.49	Ngah and Fatinathan (2008)

cations (Aguiar *et al.* 2002). The lowest adsorption capacities are those recorded for natural chitosan beads and for chitosan cross-linked with glutaraldehyde (GLU). This is attributed to the restricted diffusion of the adsorbate into the adsorbent bulk. Furthermore, parameters such as the degree of de-acetylation of chitosan, chitosan concentration and coating thickness may exhibit positive or negative effects on the final adsorption capacity of chitosan.

3.4. Column studies

The main characteristics of the column packed with chitosan-coated glass beads employed in these studies are listed in Table 6.

The influence of the feed rate on the adsorption behaviour was analyzed with the resulting breakthrough curves being depicted in Figure 5. Initial experiments conducted with a flow rate of 6.00 ml/min attained the breakthrough point very rapidly in just 7 min. Consequently, lower flow rates of 2.00 ml/min and 3.00 ml/min were examined. Table 7 presents the analyzed data obtained for the breakthrough curves. The highest rate of removal (% Rem) occurred when a lower flow rate (2.00 ml/min) was applied. This would be expected since the higher residence time of the solution inside the column would increase the contact time between the adsorbent and the Cu(II) ions, thereby favouring adsorption of the latter. Although it is possible that lower flows could result in better removal rates, the removal capacity of the column per hour would decrease and hence significantly reduce its efficiency in time.

TABLE 6. Characteristics of Column Packed with Chitosan-coated Glass Beads

Property	Value
column diameter (cm)	4.00
bed length (cm)	16.00
column volume (cm ³)	201.06
bulk density (g/cm ³)	1.57
particle volume (cm ³)	149.21
bed porosity	0.26

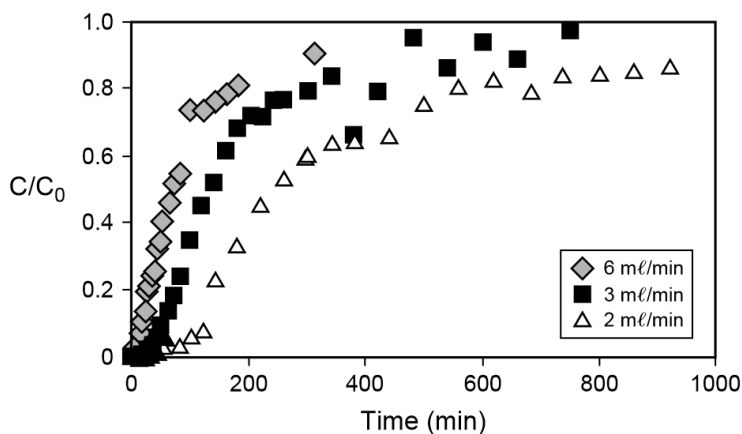


Figure 5. Breakthrough curves obtained for different flow rates in a column study of the adsorption of Cu(II) ions onto chitosan-coated glass beads. Initial conc. of Cu(II) ion solution = 100 mg/l.

TABLE 7. Analysis of the Adsorption Capacity of Chitosan-coated Glass Beads in a Dynamic Adsorption System

	Flow rate		
	6.00 mL/min	3.00 mL/min	2.00 mL/min
t (min)	180.00	340.00	620.00
V _u (mL)	395.00	393.00	493.00
Q _u (g/m ³)	125.36	136.24	197.99
MTZ (cm)	6.41	5.66	5.87
% Rem	11.35	11.98	12.68

The mass-transfer zone (MTZ) for a flow rate of 2.00 mL/min was 5.87 cm. The value of the adsorption capacity per volume of the column (Q_u) shows that approximately 200 g of Cu(II) ions was adsorbed per m³ of column containing adsorbent when the best studied flow rate was employed. The results are similar to those reported by Popuri *et al.* (2008) who studied the removal of Cu(II) ions in an adsorption column using chitosan coated onto PVC beads. These authors reported saturation of the adsorbent at a flow rate of 2.00 mL/min in a column of 300 mL volume, i.e. four-times smaller than that proposed in the present study. Osifo *et al.* (2009) studied the use of chitosan beads of 0.9 mm diameter cross-linked with glutaraldehyde for the removal of Cu(II) ions in adsorption columns. The time of removal up to saturation of the adsorbent was 23 h at a flow rate of 7.2 mL/min. Although the column used by Osifo *et al.* was about 2% higher than the one used in the present study and parameters such as the flow rate, diameter and porosity of the adsorbent interfered with the adsorption capacity, the capacity found by the authors was 20-times greater than that obtained using chitosan coated onto glass beads as the adsorbent. This can probably be attributed to the large amount of adsorbent material within the column used by Osifo *et al.* compared with the amount of chitosan in the column filled with chitosan-coated glass beads employed in the present work. In addition, the diameter of the non-immobilized chitosan adsorbent was much smaller than that of the immobilized one. This implies a higher surface area and thus more active sites available for adsorption onto the chitosan surface.

Even with the evident positive aspects of chitosan immobilization, the coating of solid matrices led to a decreased adsorbent capacity of the column mainly because of the presence of inert material (substrate). A possible solution to this problem would be the use of smaller inert supports, increasing the surface area and consequently the amount of immobilized chitosan. Another alternative would be to use rigid and highly porous structures to increase the surface area available for chitosan attachment.

The adsorption capacity of the column filled with chitosan-coated glass beads could become attractive for large-scale adsorption processes, in which the use of chitosan in its non-immobilized form is not possible due to the low mechanical strength of the adsorbent.

4. CONCLUSIONS

The results reported demonstrate the potential of using chitosan coatings on glass beads in adsorption systems for the removal of Cu(II) ions from aqueous systems. The immobilization of chitosan onto glass beads has the advantage of improving the mechanical strength of the adsorbent and enhancing mass transfer, with no decrease in the adsorption properties of chitosan. The batch

results demonstrated the good performance of chitosan-coated glass beads, with similar or even better results compared to chitosan beads on their own or other chitosan-coated materials. Immobilization favours the use of this adsorbent in adsorption processes and enables the possible application of chitosan in larger-scale adsorption columns.

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REFERENCES

- Aguiar, M.R.M.P., Novaes, A.C. and Guarino, A.W.S. (2002) *Quím. Nova* **25**, 1145.
- Amuda, O.S., Giwa, A.A. and Bello, I.A. (2007) *Biochem. Eng. J.* **36**, 174.
- Babel, S. and Kurniawan, T.A. (2003) *J. Hazard. Mater.* **97**, 219.
- Bailey, S.E., Olin, T.J., Bricka, R.M. and Adrian, D.D. (1999) *Water Res.* **33**, 2469.
- Crini, G. (2005) *Prog. Polym. Sci.* **30**, 38.
- Freundlich, H.M.F. (1906) *Z. Phys. Chem.* **57**, 385.
- Gecol, H., Miakatsindila, P., Ergican, E. and Hiibel, S.R. (2006) *Desalination* **197**, 165.
- Guibal, E. (2004) *Sep. Purif. Technol.* **38**, 43.
- Ho, Y.S. and McKay, G. (2004) *Water Air Soil Pollut.* **158**, 77.
- Kalyani, S., Priya, J.A., Rao, P.S. and Krishnaiah, A. (2005) *Sep. Sci. Technol.* **40**, 1483.
- Kratochvil, D., Volesky, B. and Demopoulos, G. (1997) *Water Res.* **31**, 2327.
- Kumar, K.V. and Sivanesan, S. (2006) *J. Hazard. Mater.* **134**, 277.
- Kyzas, G.Z. and Lazaridis, N.K. (2009) *J. Colloid Interface Sci.* **331**, 32.
- Lagergren, S. (1898) *K. Sven. Vetenskapsakad. Handl.* **24**, 1.
- Langmuir, I. (1916) *J. Am. Chem. Soc.* **38**, 2221.
- Lazaridis, N.K. (2003) *Water Air Soil Pollut.* **146**, 127
- Liu, X.D., Tokura, S., Haruki, M., Nishi, N. and Sakairi, N. (2002) *Carbohydr. Polym.* **49**, 103.
- Ngah, W.S.W. and Fatinathan, S. (2008) *Chem. Eng. J.* **143**, 62.
- Ngah, W.S.W., Endud, C.S. and Mayanar, R. (2002) *React. Funct. Polym.* **50**, 181.
- Ngah, W.S.W., Kamari, A. and Koay, Y.J. (2004) *Int. J. Biol. Macromol.* **34**, 155.
- Ngah, W.S.W., Teong, L.C. and Hanafiah, M.A.K.M. (2011) *Carbohydr. Polym.* **83**, 1446.
- Nomanbhay, S.M. and Palanisamy, K. (2005) *E.J. Biotechnol.* **8**, 43.
- Osifo, P.O., Neomagus, H.W.J.P., Everson, R.C., Webster, A. and Gun, M.A. (2009) *J. Hazard. Mater.* **167**, 1242.
- Popuri, S.R., Vijaya, Y., Boddu, V.M. and Abburi, K. (2008) *Bioresour. Technol.* **100**, 194.
- Vieira, R.S. and Beppu M.M. (2006a) *Colloids Surf. A* **279**, 196.
- Vieira, R.S. and Beppu M.M. (2006b) *Water Res.* **40**, 1726.
- Vieira, R.S., Guibal, E., Silva, E.A. and Beppu, M.M. (2007) *Adsorption* **13**, 603.
- Vijaya, Y., Popuri, S.R., Boddu, V.M. and Krishnaiah, A. (2008) *Carbohydr. Polym.* **72**, 261.
- Weber Jr., W.J. and Morris Jr., J.C. (1963) *J. Sanit. Eng. Div., Am. Soc. Civil Eng.* **89**, 31.
- Zhao, K.S., Asami, K. and Lei, J.P. (2002) *Colloid Polym. Sci.* **280**, 1038.