Adsorption of Cu(II) and Cr(VI) ions by chitosan: Kinetics and equilibrium studies

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Abstract

The ability of chitosan as an adsorbent for Cu (II) and Cr (VI) ions in aqueous solution was studied. The experiments were done as batch processes. Equilibrium studies were done on both cross-linked and non-cross-linked chitosan for both metals. Cr (VI) adsorption behaviour could be described using the Langmuir isotherm over the whole concentration range of 10 to 1000 $mg \cdot l^{-1}$ Cr. The maximum adsorption capacity for both types of chitosan was found to be 78 $mg \cdot g^{-1}$ for the non-cross-linked chitosan and 50 $mg \cdot g^{-1}$ for the cross-linked chitosan for the Cr (VI) removal. For the Cu (II) removal the Freundlich isotherm described the experimental data over the whole concentration range of 10 to 1000 $mg \cdot l^{-1}$ Cu (II). The maximum adsorption capacity for both types of chitosan can be estimated to be greater than 80 $mg \cdot g^{-1}$. Cr (VI) removal was the highest at pH 5 but pH did not have a large influence on Cu (II). From these results it is clear that the adsorption of heavy metals is possible with chitosan, but that with this method, end concentrations of below 1 $mg \cdot l^{-1}$ can hardly be obtained.

Introduction

Industrial and mining wastewaters are important sources of pollution of heavy metals (Quek et al., 1998). The use of chromate and dichromate in metal plating and as corrosion control agents in cooling waters is quite extensive. It is well-known that Cr (VI) is toxic to living systems and must be removed from wastewater before it can be discharged. Current treatment for the removal of Cr (VI) involves acid catalysed chemical reduction to Cr^{3+}. The Cr^{3+} is then precipitated as hydroxide at alkaline conditions using either caustic or lime (Udaybhaskar et al., 1990). The presence of Cu (II) in wastewater is also a problem. Copper is used extensively by electrical industries, in fungicides and in anti-fouling paints. When Cu is ingested at high concentrations it can become toxic to humans, causing cancer and promoting oxidation. The present method for removal of Cu is to precipitate copper hydroxide by liming. But with this process, residual Cu remains a problem (Findon et al., 1993).

Owing to their wide use, the efficient removal of toxic metal ions from wastewater is an important and widely studied research area where a number of technologies have been developed over the years (Deans and Dixon, 1992). The most important of these methods include filtration, chemical precipitation, ion exchange, adsorption, electrodeposition and membrane systems. All these approaches have their inherent advantages and limitations. Although filtration and chemical precipitation are low-cost and effective in removing large quantities of metal ions quickly, neither is capable of removing trace levels of metal ions. Adsorption is also ineffective at very low concentrations of metal ions. Ion exchange can be used to reduce metal concentrations to the region of parts per million. In recent years studies on polymers, which bind metal ions, have increased significantly. Studies on the polymer-metal complexes are of great practical importance. Complexing abilities of polymers are used in nuclear chemistry, electrochemistry, hydrometallurgy and environmental protection (Kamiñski and Modrzejewska, 1997). Of particular significance among many methods of metal-ion separation is the one which combines two processes: complexing of a polymer with metal ions and ultrafiltration of the complexes though membranes of appropriate selectivity (Kamiñski and Modrzejewska, 1997).

A technique, which has been widely studied in the laboratory, but not widely applied industrially, is the use of chelation ion exchange. Chelation ion exchange takes advantage of the three-dimensional structure of the molecules to chelate and remove ions of a specific size in the presence of large quantities of other ions (Deans and Dixon, 1992). This approach is inherently attractive since only the toxic metal ions are removed while the harmless ions can be released into the environment. Some of the best chelation ion-exchange materials are biopolymers.

Biopolymers are industrially attractive for a number of reasons; *inter alia*, their capability of lowering transition metal-ion concentration to parts per billion concentrations, they are widely available and are environmentally safe. Such materials include cellulose, alginates, carrageenan, lignins, proteins, chitin and chitin derivatives. Another attractive feature of biopolymers is that they possess a number of different functional groups, such as hydroxyls and amines, to which metal ions can bind either by chemical or by physical adsorption (Deans and Dixon, 1992). Metal removal can be more effective by using chelation ion exchange as a polishing step after the majority of the metal ions have been removed. Since the metals used for chelation ion exchange will tend to have higher associated production costs, it is impractical to use them for removing massive quantities of heavy metals from water. However, it is possible to regenerate them *in situ*, by simply exposing the metal-laden materials to aqueous acid solutions, when desired. This study focuses on chitin derivatives for the removal of heavy metals such as Cr and Cu.

As the degree of deacetylation (DD) of chitinous material exceeds 50%, it becomes soluble in acidic aqueous solutions and is called chitosan (Tsaih and Chen, 1997). The characteristics of chitosan depend on the degree of deacetylation, the distribution of acetyl groups, chain length, and molecular mass distribution.

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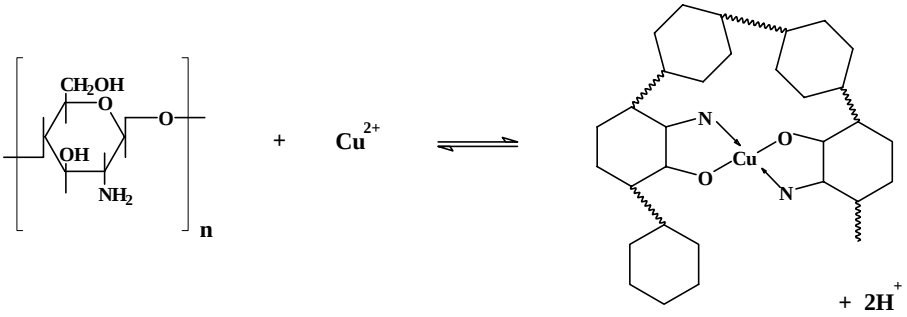


Figure 1
Formation of chitosan chelates with copper ions (Kamiñski and Modrzejewska, 1997)

Additionally, partially acetylated chitosan, which has about 50% D-glucosamine units, is only able to dissolve in water (Sugimoto et al., 1998). Chain flexibility of chitosan molecules in solution can be manipulated by using chitosan with different DDs, or solutions with differing pH and/or ionic strength to control the pore size, mechanical strength or permeability of the membranes or capsule-prepared chitosan (Tsaih and Chen, 1997). In 1999, Guibal et al. stated that the surface charge of chitosan varies drastically as a function of the pH of the solution. Decreasing the pH results in a drastic increase in the positive charge of the sorbent. This expected result is consistent with the pK_a of chitosan. The pK_a values of chitosan, ranges from 6.2 to 6.8 (Guibal et al., 1999). From the literature it is clear that chitosan can be used to remove numerous trace metals (Cu(II), Pb(II), U(VI), Cr(III), Cr(VI), Ni(II), Cd(II), Zn(II), Co(II), Fe(II), Mn(II), Pt(IV), Ir(III), Pd(II), V(V) and V(IV)) from wastewater. In these studies chitosan has been used in a variety of forms, which include chitosan beads, flakes and membranes (Findon et al., 1993; Deans and Dixon, 1992; Kamiñski and Modrzejewska, 1997; Onsøyen and Skaugrud, 1990; McKay et al., 1989).

Transport studies which were conducted by Findon et al. (1993) were not able to confirm the actual mechanism of Cu uptake by chitosan, but they considered it likely that the Cu is chelated with the NH_2 and NH groups in the chitosan chain.

The article of Chui et al. (1996) confirms that the amino sugars of chitin and chitosan are the major effective binding sites for metal ions, forming stable complexes by co-ordination. The nitrogen electrons present in the amino and N-acetylamino groups can establish dative bonds with transition metal ions. Some hydroxyl groups in these biopolymers may function as donors. Hence, deprotonated hydroxyl groups can be involved in the co-ordination with metal ions (Lerivrey et al., 1986).

Low pH would favour protonation of the amino sites, resulting in a reversal of charge, and would greatly diminish the metal-chelating ability of chitin and chitosan. This suggests that at a neutral pH more of the metal ions should be adsorbed by the chitosan.

According to Kamiñski and Modrzejewska (1997), it is well-known that chitosan forms chelates with metal ions by releasing hydrogen ions. Hence the adsorption of a metal ion on chitosan depends strongly on the pH of the solution. An example of the formation of a chitosan chelate with Cu ions is shown in Fig.1. Chitosan membranes produced by the phase-inversion method can be applied successfully to the removal of metal ions. The metal ions Cu(II), Cd(II), Co(II), Zn(II) and Ni(II) are almost completely retained by the membrane. In the case of Cr(VI) and Mn(II) ions, the separation depends on the pH and the process conditions (Kamiñski and Modrzejewska, 1997).

In this study, chitosan is used to remove Cr (VI) and Cu (II) from wastewater. A kinetic study was carried out using concentration, pH and stirring speed as parameters.

Experimental

In this study the following reagents were used: Chitosan (high, medium and low molecular mass) (*Aldrich Chemical Company, South Africa*); cupric chloride ($CuCl_2.2H_2O$) (*Saarchem, South Africa*); potassium dichromate ($K_2Cr_2O_7$) (*Merck NT laboratory supplies, South Africa*); hydrochloric acid (HCl) (*Saarchem, South Africa*); sodium hydroxide (NaOH) (*BDH Chemicals Ltd, South Africa*); 1-chloro-2:3-epoxy-propan (epichlorohydrin) (*BDH Chemicals Ltd, South Africa*). All the reagents used were of the highest possible grade. Millipore milli-Q deionised water, with a conductivity of 18.2 MΩcm was used for all reagent solutions.

The adsorption of Cr and Cu was carried out in a batch process at room temperature (25±1°C) except where stated otherwise. Cu (II) and Cr (VI) solutions were prepared in deionised water using $CuCl_2$ and $K_2Cr_2O_7$ respectively. Precisely 1g of sorbate (chitosan) was added to the reaction mixture of 300ml of metal solution. For the sorption isotherm studies the initial concentration of metal was varied from 10 to 1000 $mg \cdot l^{-1}$ metal. For each solution the concentration was studied as a function of time. The total time of an experiment was 2 h 40 min. During this time 10 samples were taken at given time intervals. To prevent the removal of chitosan from the solution, during sampling, a syringe was used as a filter. Samples were analysed by atomic absorption (AA) spectrometry.

The effect of the pH of the suspending medium on metal removal was studied by performing equilibrium sorption tests at different pH values. Adjustments to pH were made with 0.1 $mol \cdot dm^{-3}$ NaOH or 0.1 $mol \cdot dm^{-3}$ HCl. During these tests the metal concentration (100 $mg \cdot l^{-1}$), the amount of chitosan (1 g), the stirring speed (400 $r \cdot min^{-1}$) and the temperature (25°C) were kept constant.

The effect of the stirring speed (200, 400 and 600 $r \cdot min^{-1}$), and the influence of the pH (varied between pH 2 and 11) were also studied in order to determine the effect of these parameters on the removal of metal ions from the solution.

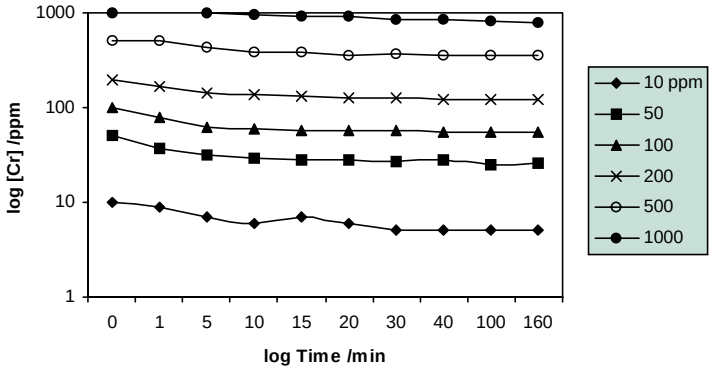
All pH values were measured with a Hanna instrument pH301 pH meter.

Equilibrium isotherms were determined using cross-linked chitosan. Cross-linking improves the stability of chitosan at a lower pH. The chitosan was cross-linked using epichlorohydrin. The procedure was as follows: 0.067 $mol \cdot dm^{-3}$ NaOH was added to 100 ml of an 0.01 $mol \cdot dm^{-3}$ epichlorohydrin solution. 3 g of high molecular mass chitosan was added. This mixture was then stirred for 3 h at 50°C. The cross-linked chitosan was filtered from the solution and washed with deionised water and dried. Adsorption tests were carried out on the cross-linked chitosan, in the metal concentration range of between 10 and 1000 $mg \cdot l^{-1}$.

Cr and Cu concentrations were analysed using a Varian spectrAA 250 coupled to a computer and printer. A hollow cathode lamp for chromium from Varian techtron and for the copper from Cathodeon was used as the radiation source.

Figure 2 (top right)
Adsorption kinetics of Cr (VI) on chitosan at different initial concentrations [Cr] = 10, 50, 100, 200, 500 and 1 000 mg·l^{-1}; Chitosan = 1 g; pH = 5; Stirring speed = 400 r·min^{-1}; T = 25°C

Figure 3 (bottom right)
Isotherm for the adsorption of Cr(VI) ions onto non cross-linked and cross-linked chitosan



Results and discussion

Sorption kinetics are important physicochemical parameters to evaluate the basic qualities of a good sorbent (such as whether or not the sorbent adsorbs metals). Removal of Cr (VI) by chitosan as a function of time at pH 5, at various initial Cr (VI) concentrations, is shown in Fig. 2. The results indicate that as the concentration of the Cr (VI) is increased, so does the time taken before equilibrium is reached. It also appears that at lower concentrations less Cr (VI) adsorbs onto the chitosan than at higher concentrations. The colour of the adsorbent changed from pale white to yellowish brown on adsorption of Cr (VI). At an initial Cr (VI) concentration of 1 000, 500, 200, 100, 50 and 10 mg·l^{-1}, the chromium removal was 200, 150, 78, 45, 24 and 5 mg·l^{-1} respectively.

In a two-component system (sorbent and solution) a graph of the solute concentration in the solid phase C_{ads} (mg·g^{-1}) can be plotted as a function of the solute concentration in the liquid phase C_{eq} (mg·dm^{-3}) at equilibrium. Since the data for the curve are obtained at a single temperature, the curve is an isotherm. In a solid-liquid system, positive sorption results in the removal of solute from the bulk solution and the concentration at the surface of the solid, until the remaining solute in the solution is in dynamic equilibrium with the solute on the solid surface. At equilibrium there is a defined distribution of the solute between the liquid and the solid phases, which can generally be expressed by one or more isotherms (Findon et al., 1993). Figure 3 shows the isotherm of the sorption of chromium ions by non cross-linked and cross-linked chitosan.

The isotherm is characterised by the initial region, which is represented as being concave to the concentration axis. The isotherm is beginning to reach a plateau, which can typically be described by the Langmuir isotherm (Parfitt and Rochester, 1983).

The results of the Cr (VI) concentration dependence study were subjected to analyses by means of both Langmuir and Freundlich adsorption isotherms. It became clear that the Langmuir equation fitted the data better than the Freundlich equation by describing the data over the entire concentration range. The Langmuir equation (Eq. (1)), which is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies, is expressed as:

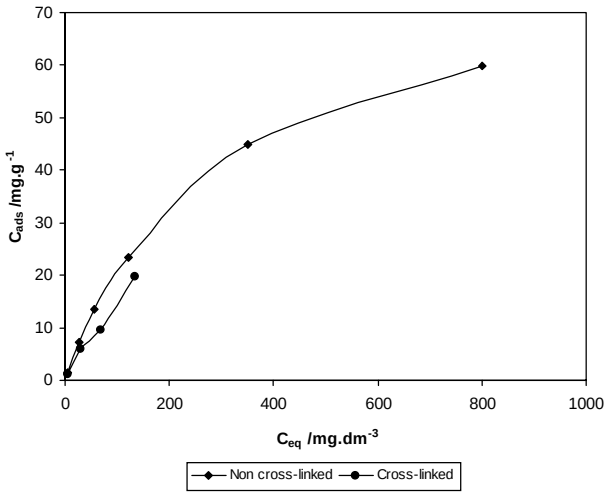
$$C_{ads} = (K_L C_{eq})/(1 + bC_{eq}) \quad (1)$$

In this study the following linearised form of the Langmuir isotherm was used.

$$C_{eq}/C_{ads} = bC_{eq}/K_L + 1/K_L \quad (2)$$

and

$$C_{max} = K_L/b \quad (3)$$



where:

C_{ads} = amount of Cr (VI) adsorbed (mg·g^{-1})
C_{eq} = equilibrium concentration of Cr (VI) in solution (mg·dm^{-3})
K_L = Langmuir constant (dm^3·g^{-1})
b = Langmuir constant (dm^3·mg)
C_{max} = maximum .CR (VI) to adsorb onto 1 g chitosan (mg·g^{-1})

The constant b in the Langmuir equation is related to the energy or the net enthalpy of the sorption process. The constant K_L can be used to determine the enthalpy of adsorption.

A plot of C_{eq}/C_{ads} vs. C_{eq} yielded a straight line (see Fig. 4), confirming the applicability of the Langmuir adsorption isotherm.

The values of K_L and b were obtained by a least square fit and were calculated to be $K_L = 0.29 \pm 0.09$ dm^3·g^{-1}, $b = 0.0037 \pm 0.0003$ dm^3·mg and $C_{max} = 78 \pm 30$ mg·g^{-1}.

The chitosan was cross-linked with epichlorohydrin to stabilise the chitosan at a lower pH level. Experiments were done on the cross-linked chitosan to establish whether cross-linking effects the adsorption process. Figure 4 shows the Langmuir isotherm fitted on the data derived from the cross-linked chitosan. By comparing the two lines in Fig. 4, one can see that the ability of the cross-linked chitosan to adsorb Cr (VI) is less than that of the chitosan that is not cross-linked.

The values of K_L and b, were found to be $K_L = 0.21$ dm^3·g^{-1}, $b = 0.0004$ dm^3·mg and $C_{max} = 50$ mg·g^{-1}. Because of the limited amount of data points, statistical treatment of the data was not relevant. When comparing these values to the non-cross-linked chitosan value for K_L, b and C_{max}, it is clear that the non-cross-linked chitosan has the potential to adsorb about 30 mg more of the metal per gram of chitosan. This is consistent with the fact that when chitosan is cross-linked some of the binding sites are used for the cross-linking.

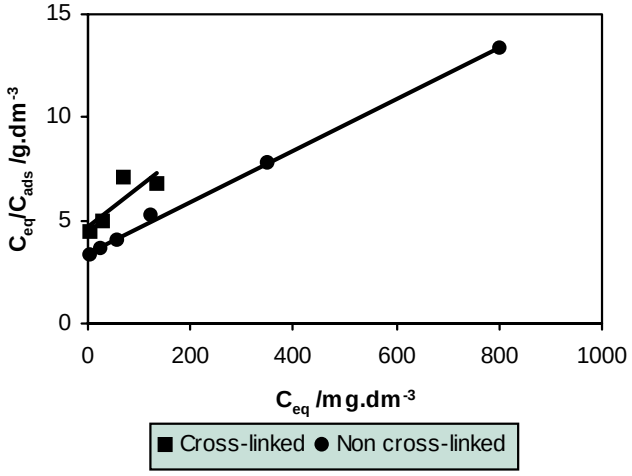


Figure 4
Langmuir plot for the adsorption of chromium onto non cross-linked and cross-linked chitosan

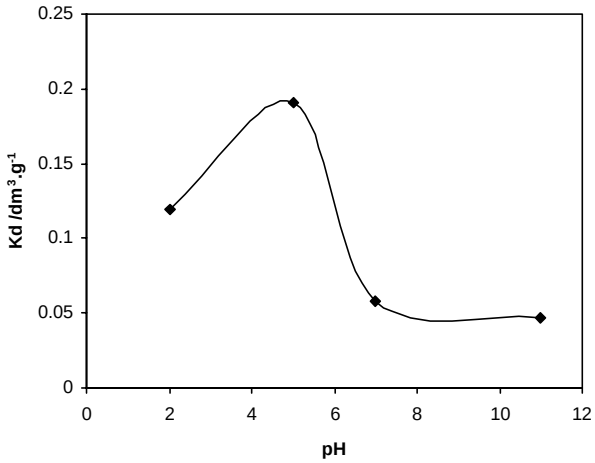


Figure 5
Effect of pH on the adsorption of Cr (VI) on chitosan

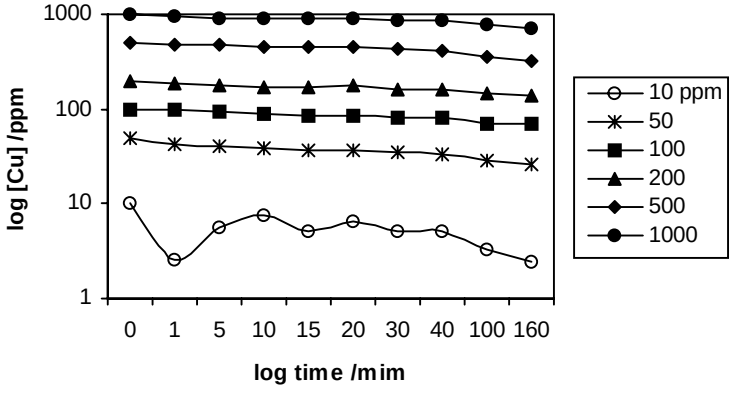


Figure 6
Adsorption kinetics for copper adsorption onto chitosan at various initial concentrations
[Cu] = 10, 50, 100, 200, 500 and 1 000 mg·l^{-1}; Chitosan = 1.0 g; pH = 5; Stirring speed = 400 r·min^{-1}; T = 25°C

Effect of the stirring speed and pH

The variation in the adsorption of Cr as a function of stirring speed was studied using 100 mg·l^{-1} chromium solutions with 1 g of chitosan. The effect of three speeds was investigated: 200, 400 and 600 r·min^{-1}. It appeared that stirring speed has no influence on the adsorption of Cr.

The removal of Cr (VI) from wastewater by adsorption is highly dependent on the pH of the solution, which affects the surface charge of the adsorbent, the degree of ionisation, and the speciation of the adsorbate species. It was therefore important to study the effect of pH on the adsorption of Cr (VI). Adsorption was determined over the pH range 1 to 11, using 1g chitosan and 100 mg·l^{-1} chromium solution. The results obtained are presented in Fig. 5. It is clear that the maximum adsorption of Cr (VI) occurred at pH 5, and decreased at lower and higher pH. Above pH 7 a plateau is observed.

Equation (4) was used to calculate the distribution ratio (K_d) (see Fig. 5).

$$K_d = ((C_i - C_f)/C_f)* V/W \quad (4)$$

where:

K_d = distribution ratio (dm^3·g^{-1})
C_i = metal concentration, liquid phase before equilibrium (mol·dm^{-3})
C_f = metal concentration after equilibrium (mol·dm^{-3})
V = volume of liquid (dm^{-3})
W = mass of chitosan (g)

Representing the chitosan as CM, the dissociation equation of the amine groups of the chitosan could be represented by (Jha *et al.*, 1988):

$$CM^+:H + H_2O \leftrightarrows CM: + H_3O^+ \quad (5)$$

The pH_{zpc} of chitosan prepared from lobster shells has been reported to be between 6.2 and 6.8 (Guibal et al., 1999). From the pK_a value, it can be calculated that the extent of protonation is 9, 50, 91, and 99 % at a pH of 7.3, 6.3, 5.3, and 4.3, respectively. Cr (VI) forms stable complexes such as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2+}, and $HCr_2O_7^-$; the fraction of any particular species is dependent upon the chromium concentration and pH (Udaybhaskar et al., 1990).

Below the pK_a value of chitosan, the sorbent is positively charged, while the sorbate is negatively charged. This leads to an electrostatic interaction, i.e. attraction between the sorbent and the sorbate. Above the pK_a value the sorbent and sorbate will be negatively charged and, hence, Cr (VI) removal should be reduced drastically. The experimentally observed decrease in the Cr (VI) removal at a higher pH can be explained by the rapid changes in protonated and unprotonated forms of chitosan. The decrease in K_d at pH 2 may be due to the fact that the chitosan is unstable at lower pH.

Copper interactions with chitosan

Equilibrium studies

Removal of Cu (II) by chitosan was studied as a function of time and the concentration of Cu at pH 5. Figure 6 shows the adsorption with various initial concentrations of Cu (II). The results indicate that the time taken to reach

equilibrium is longer as the concentration of the Cu (II) increases. It also shows that at higher concentrations the amount of Cu (II) adsorbed is much higher than at lower concentrations. The colour of the sorbent during adsorption changed from pale white to light blue. At the initial concentrations of 10, 50, 100, 200, 500, and 1 000 mg·l^{-1} Cu (II) solutions, the amount of Cu (II) adsorbed onto the chitosan was 7.6, 24, 32, 60, 176 and 285 mg·l^{-1} respectively.

In Fig. 7 the isotherm for the adsorption of Cu (II) ions onto chitosan is shown. As in the case of Cr (VI) the Langmuir equation (Eq. (3)) was used to describe the data derived from the adsorption of copper onto chitosan over the entire concentration range studied. But in the case of Cu (II), the Langmuir equation did not describe the adsorption ($R^2 = 0.385$). However, a Freundlich equation plot of log C_{ads} vs. log C_{eq} yielded a straighter line as shown in Fig. 8 ($R^2 = 0.95$). The linearity of the plot supports the applicability of the Freundlich adsorption isotherm in this study. The Freundlich equation (Eq. (60) which is used to describe heterogeneous surface energies, is expressed as:

$$C_{ads} = PC_{eq}^{1/n} \quad (6)$$

In this study the following linearised form of the Freundlich equation was used.

$$\log C_{ads} = \log P + 1/n \log C_{eq} \quad (7)$$

where:

C_{ads} = amount of Cu (II) adsorbed (mg·g^{-1})
C_{eq} = equilibrium concentration in solution (mg·dm^{-3})
1/n = Freundlich constant (mg·g^{-1})
P = Freundlich constant (g·dm^{-3})

From Fig. 8 it is evident that the values of 1/*n* and *P*, which are rough measurements of the adsorption intensity and adsorption capacity of the adsorbent, have been determined by the least-square fit and were found to be 0.64±0.08 mg·g^{-1} and 0.98±0.16 g·dm^{-3} respectively. Compared to literature sources (see Table 1) the lower value of 1/*n* signifies that the forces which are exerted on the surface of the chitosan during Cu (II) adsorption are weak. The low value of *P* confirms the weak affinity of the chitosan for the Cu (II). The maximum adsorption capacity is greater than 80 mg·g^{-1} (see Fig. 7 and Table 1) at 700 mg·dm^{-3} of copper in the solution. At higher concentrations this maximum can be higher.

The chitosan was cross-linked with epichlorohydrin to increase its stability at lower pH and experiments were conducted in order to determine the influence of cross-linking on the adsorption. Figure 8 shows the Freundlich isotherm derived from the data using the cross-linked chitosan.

From the Freundlich plot the values for 1/*n* and *P* can be calculated. The values for 1/*n* and *P* for cross-linked chitosan are 0.98±0.08 mg·g^{-1} and 0.12±0.10 mg·dm^{-3} respectively. The 1/*n* value suggests that the adsorption forces of Cu (II) acting on the surface of the cross-linked chitosan are stronger compared to those of the non-cross-linked chitosan. However, according to the *P* values the affinity of Cu (II) for cross-linked chitosan and non-cross-linked chitosan is about the same. The maximum capacity of the non cross-linked and cross-linked chitosan can be estimated from Fig. 7. The estimated values for both, non-cross-linked and cross-linked chitosan, are greater than 80 mg·g^{-1}.

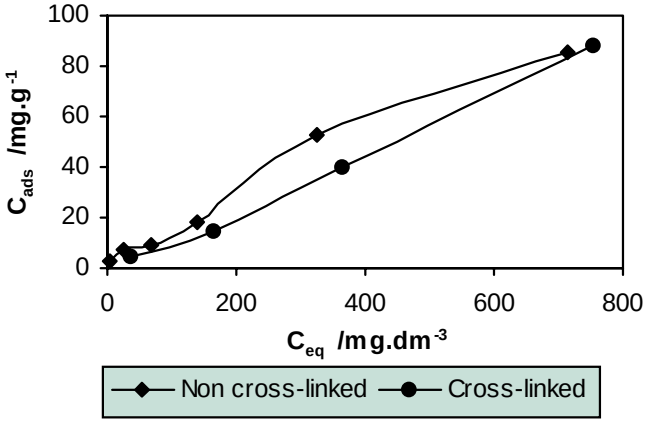


Figure 7
Isotherm for the adsorption of Cu (II) ions onto non-cross-linked and cross-linked chitosan

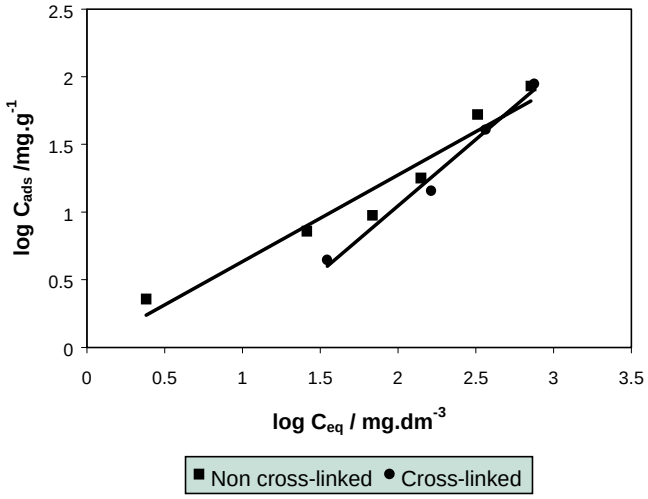


Figure 8
Freundlich plot for the adsorption of Cu (II) onto non-cross-linked and cross-linked chitosan

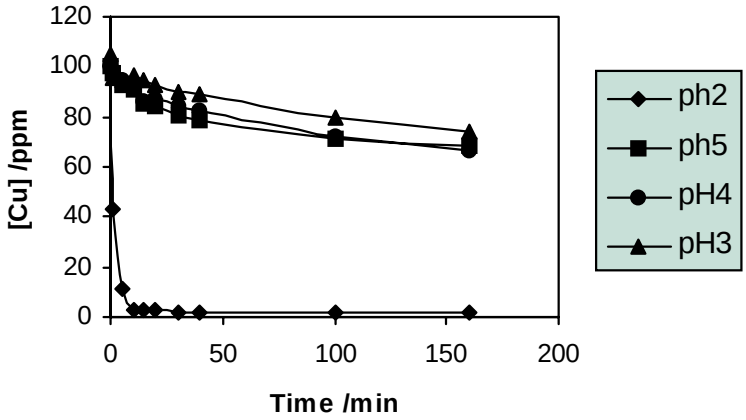


Figure 9
Effect of pH on the adsorption of Cu onto chitosan
[Cu] = 100 mg·l^{-1}; Chitosan = 1.0 g; pH = 2, 3, 4 and 5; Stirring speed = 400 r·min^{-1}; T = 25°C

TABLE 1
Langmuir and Freundlich constants derived from literature and experimental data (Udaybhaskar et al., 1990; Findon et al., 1993 and McKay et al., 1989)

Source	Langmuir constants			Freundlich constants		
	K_L ($dm^3 \cdot g^{-1}$)	b ($dm^3 \cdot mg^{-1}$)	C_{max} ($mg \cdot g^{-1}$)	P ($g \cdot dm^{-3}$)	1/n ($mg \cdot g^{-1}$)	C_{max} ($mg \cdot g^{-1}$)
Findon et al. (1993) (Cu)	1.17	0.02	59	2.44	1.64	
McKay et al. (1989) (Cu)	6.83	0.03	288			
Udaybhaskar et al. (1990) (Cu)	34.9	0.62	56.3			
Experimental data (Cu)				0.98 ± 0.16*	0.64 ± 0.08*	>80*
This study				0.12 ± 0.10	0.98 ± 0.08	>80
Experimental data (Cr)	0.29 ± 0.09*	0.0037 ± 0.0003*	78 ± 30*			
This study	0.21**	0.004**	50**			

* Data of non-cross-linked chitosan
** To less data point to carry out statistics

Effect of the stirring speed and pH

The variation in the stirring speed in the adsorption of Cu (II) onto chitosan was also studied. The stirring speed was varied from 200 to 600 $r \cdot min^{-1}$. Higher stirring speed slightly increased the rate of Cu (II) solution.

A further study was done to determine the effect of pH on the removal of Cu (II) by chitosan. From Fig. 9 it is clear that pH does not play an important role in the removal of Cu (II) except at pH 2. Above pH 5 the copper precipitates from the solution and for this reason the study was just done to pH 5. At pH 2 excellent Cu (II) removal was achieved. This can be attributed to the fact that at pH 2 and below the chitosan is soluble. In other words, the reaction mixture was homogeneous.

Comparison of results with literature

In previous studies by Findon et al. (1993) and McKay et al. (1989) the Langmuir and Freundlich isotherm constants have been calculated for the adsorption process of Cu (II). These values as well as the values obtained from this study are represented in Table 1. In the literature no quantitative results could be found for Cr (VI). For Cu (II) the adsorption results have been described with the Langmuir isotherm. However, Cu (II) adsorption in this study could be better described with the Freundlich isotherm. This may mean that the commercial chitosan we used has more heterogeneous types of adsorption sites. Also, the Freundlich adsorption constants are difficult to compare with the Langmuir adsorption constants. However, the maximum adsorption capacity (C_{max}) is comparable with literature values, especially for the non-cross-linked chitosan system.

The adsorption rate constant for Cr (VI) seems to be somewhat lower than that of copper, because the value of *b* is almost an order of magnitude smaller ($b = k_{ads}/k_{des}$) than that found in the literature (see Table 1). However, the adsorption capacity C_{max} seems not be influenced by the kinetics and is about the same as for Cu (II) reported in the literature. Another point is that chromium adsorption is more homogeneous than copper. Probably some heterogeneous sites are not available to chromium.

The Cu (II) and Cr (VI) impurity levels after adsorption are in all cases higher than 1 $mg \cdot l^{-1}$. This is too high according to the DWAF Guidelines (1998), which stipulate maximum levels of 0.02 $mg \cdot l^{-1}$ and 0.1 $mg \cdot l^{-1}$ for Cr (VI) and Cu (II) respectively. This means that the practical and industrial significance of this introductory study is not that high. This study was, however, continued by manufacturing chitosan composite membranes with a phase inversion method (Steenkamp et al., 2000). This composite membrane was capable of adsorbing Cu (II) to a non-detectable level due to a more porous structure of the chitosan layer and a better process control. Because the inaccuracy of the AA analysis method is about 0.1 $mg \cdot l^{-1}$, it is still not clear whether Cu (II) adsorption impurity levels of 0.1 $mg \cdot l^{-1}$ or less can be obtained. About 1 kg of chitosan is needed to treat 1 kl of water with a Cu (II) impurity level of 100 $mg \cdot l^{-1}$. This means that, economically speaking, it is necessary to regenerate chitosan because this biopolymer is more expensive than other adsorbents like activated carbon.

Literature on the evaluation of heavy metal adsorption on chitosan is relatively scarce. More details are required on the kinetics and thermodynamics of this adsorption process.

Conclusions

- This study showed that chitosan adsorbs heavy metals, in particular Cr (VI) and Cu (II) ions. From the experimental data it is clear that the adsorption process for both metals is different owing to the fact that Cr (VI) adsorption is described by the Langmuir isotherm and Cu (II) adsorption by the Freundlich isotherm. However the adsorption process for both metals seems to be concentration-driven.

- It seems that the adsorption of Cr(VI) is not influenced by external factors such as stirring speed. However, Cu(II) adsorption is more influenced by such factors.
- The most effective pH for the removal of Cr (VI) was at pH 5 and for Cu (II) removal the pH range was from 3 to 5.
- From the experimental data it is observed that the metal concentration for copper can be lowered by means of the batch process from 10 $mg \cdot l^{-1}$ to 2.4 $mg \cdot l^{-1}$ and for the chromium it can be lowered to 5 $mg \cdot l^{-1}$. These impurity levels are higher than the required levels stipulated by the DWAF Guidelines (1998).
- Adsorption capacity for Cr (VI) and Cu (II) is comparable to literature values (50 to 100 $mg \cdot g^{-1}$), but the adsorption mechanism and adsorption sites seem to be different, especially for Cr (VI).

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