

Full Length Research Paper

Adsorption kinetics of cadmium and lead by chitosan

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An evaluation of the kinetics and capacity of chitosan to trap lead and cadmium ions in aqueous solution was carried out at 25°C using concentration and contact time as parameters. The experiments were done as batch process. Our results show that the adsorption process is concentration-driven with high capacity of chitosan for the adsorption of these metal ions. The Infra red spectroscopic study on the chitosan and the metal-chitosan complexes reveal a metal coordination based on the observed characteristic band changes. At initial lead concentrations of 1000, 500, 400, 250 and 100 mg/L, the adsorbed lead ion concentrations are 557, 265, 218, 132 and 65 mg/L, respectively. However, for the cadmium, the adsorbed concentrations are 263, 165, 152, 78 and 45 mg/L, respectively at the same initial concentrations. The lead and cadmium adsorption kinetic behavior could not be described using the Langmuir isotherm over the whole concentration range but Freundlich isotherm conforms to the experimental data.

Key words: Adsorption, chitosan, cadmium, lead, kinetics.

INTRODUCTION

A good number of industries are responsible for the release of heavy metals into the environment through their wastewater (Quek et al., 1998). Some of these heavy metals are extremely toxic elements and can seriously affect many living species especially human; therefore their removal from wastewater is important. 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 (Quek et al., 1998; Deans and Dixon, 1992; Grosse, 1986; Janson et al., 1982). However, these conventional technologies appear to be inadequate and expensive. In recent years studies on polymers which bind metals ions have increased significantly (Deans and Dixon, 1992; Grosse, 1998; Kaminski and Modrzejewska, 1997; Schmuhl et al., 2001; Findon et al., 1993). This approach is inherently attractive since only the toxic metals ions are removed while the harmless ions can be released into the environment.

Some of the best chelation ion-exchange materials are natural biopolymers (Brady et al., 1994; Schmuhl et al., 2001; Findon et al., 1993; Monser and Adhoum, 2002; Gotoh et al., 2004; Coughlin et al., 1990). Natural biopolymers are available in large quantities. Certain waste from agricultural operations may have potential to be used as low cost absorbents, as they represent unused resources, widely available and are environmentally friendly (Deans and Dixon, 1992). Among the many other low cost absorbents identified, Chitosan has the highest sorption capacity for several metal ions because 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 (Dean and Dixon, 1992; Findon et al., 1993; Ikhuoria and Omonmhenle, 2006; Bailey et al., 1999; Deshpande, 1986). Chitosan is a natural product derived from chitin (Figure 1), a polysaccharide foundation in the exoskeletons of shellfish like shrimps and crabs.

Lead is a heavy metal whose use in electrical industries, in fungicides and in anti-fouling paints is quite extensive. The removal of this toxic metal ion in wastewater has been an important issue for many years due to their environmental harm and threat to life (Xiao et al.,

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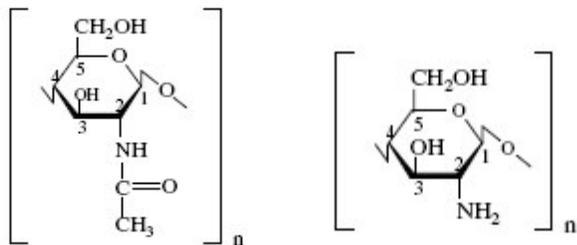


Figure 1: Chemical structures of chitin and chitosan

2006). The presence of cadmium ion in wastewater is also a problem. Cadmium is used extensively in phosphate fertilizer burning fuels, cement production, mining and metal processing operators (Jha et al., 1988).

Previous transport studies conducted suggested that metal ion is chelated with the NH_2 and OH groups in the chitosan chain (Findon et al., 1993). Chui et al. (1996) confirms that the amino sugars of chitin and chitosan are the major effective binding sites for metal ions, forming stable complex by co-ordination. The nitrogen lone pair electrons in the amino and N-acetyl amino groups can establish dative bonds with transition metal ions. Also, some hydroxyl groups in these biopolymers may function as donors; hence deprotonated hydroxyl groups can be involved in the co-ordination with metal ions (Kaminski and Modrzejewska, 1997; Chui et al., 1996).

Report on the evaluation of heavy metal adsorption on chitosan is relatively scarce; more details are therefore required on the kinetics and thermodynamics of this adsorption process. This study presents the potential application of biopolymers to the problem of heavy metal pollution abatement by using chitosan to remove lead and cadmium metal ions from aqueous solution. A kinetic study was also carried out using concentration and stirring speed at pH 4.5 as parameters.

MATERIALS AND METHODS

Chitin (from crab shells) was obtained from Sabo model market in Lagos State, Nigeria. All other chemicals used were of analytical grade. The N-deacetylation method of Coughlin et al. (1990) was used with slight modification. The crab shells were ground in a wooden mortar and sieved particles in the size range 0.35 – 0.5 mm were first soaked in a 5% HCl solution for 1 h, at room temperature to remove calcium salts (demineralization). After rinsing with distilled water, the decalcified chitin was transferred to a 50% NaOH solution at 100°C, under constant stirring for 3 h. The sample was washed with deionised water, filtered and dried at 50°C for 24 h under vacuum. The chitosan samples were characterized using Fourier Transform Infra-red spectrometer (Niconet Avator 330 by Thermoelectron Corporation).

Sorption of lead and cadmium metal ions on chitosan

The adsorptions of the lead metal was carried out in a batch process at room temperature, 100 mg of chitosan was added to 25 ml of each solution. Kinetic and equilibrium sorption of Pb^{2+} and Cd^{2+}

ions on chitosan was carried out at 25°C using various initial concentrations of the metal ions. The sorption of the metal ions was examined at time intervals under conditions of vigorous agitation. Contact time was varied between 2 to 12 h. The sorption kinetics was done at pH 4.5 according to the method of Schmuhl et al. (2001). Pb^{2+} and Cd^{2+} concentrations were analyzed using atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

FT-IR analysis

The spectra of chitosan, chitosan-Cd and chitosan-Pd polymeric complexes are shown in Figure 2. The band amide 1 ($\nu_{\text{C=O}}$) around 1637 cm^{-1} stretching frequency, characteristic of chitosan with acetylated units is present in all the spectra. However, in chitosan-metal complexes, a new band around 1625-1635 cm^{-1} appears. These bands correspond to the bending in plane (scissoring) of N-H which also appear as a shoulder at around 1605 cm^{-1} . This observed red shift is due to interaction of chitosan with the metal ions. The broad bands in the region 3000-3600 cm^{-1} could be attributed to the stretching of OH groups of the chitosan and overlapping stretching bands of NH. With the chitosan-metal complexes, the bands are unfolded and the stretching of O-H is observed between 3418 and 3450 cm^{-1} while the stretching of N-H is observed between 3260 and 3266 cm^{-1} .

In addition, a significant change is observed in the region from 1000 to 1200 cm^{-1} . In the free chitosan heteropolymer, a broad band around 1068 cm^{-1} appears which could be associated with the stretching of C-O bond. In the presence of metal ions, the band shifted and appear between 1113 and 1116 cm^{-1} which correspond to the stretching of C-O bond of C3 from chitosan (secondary OH, Figure 1) as well as the band between 1025 and 1030 cm^{-1} corresponding to the stretching of C-O bond of C6 from chitosan (primary OH) verifying the complexation of the chitosan to Cd (II) and Pb (II) not only via the amine groups, but also through the OH groups. Also in this region, two important bands were identified in the chitosan-metal polymeric complexes. The stretching frequencies between 1064 and 1075 cm^{-1} correspond to the asymmetric stretching of C-O bonds.

In the spectra of chitosan-mixed metal complexes of Cd (II) and Pb (II) in solutions of equimolar concentrations shown in Figure 3, it is observed that the spectra present has similar features with those of single metal ions. As suggested by Taboada et al. (2003), this observation could be due to lack of metal-metal interaction and the form of retention is therefore similar when the metal ions are either in mixture or separated.

Adsorption capacity of chitosan

Sorption kinetics is an important physiochemical parameter to evaluate the basic qualities of a good sorbent.

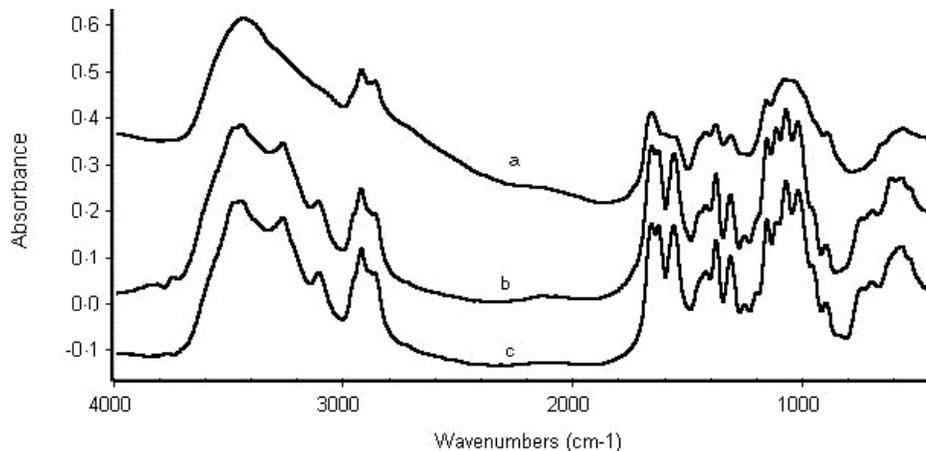


Figure 2. FT-IR Spectra of a: Chitosan, b: Chitosan-Cd complex and c: Chitosan-Pb complex.

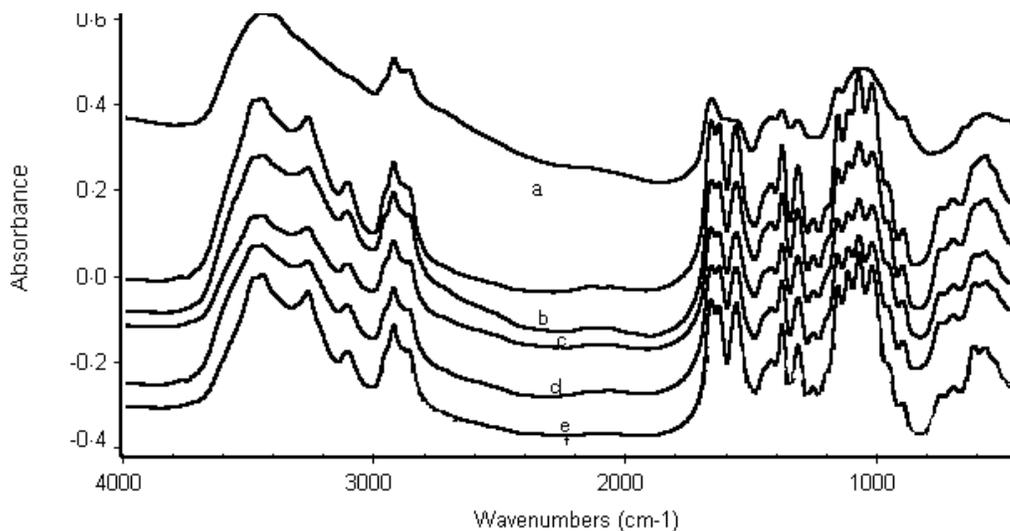


Figure 3. FT-IR Spectra of Chitosan-mixed metal complexes Cd and Pd in solutions of equimolar concentrations (a: 0, b: 100, c: 250, d: 400, e: 500 and f: 1000 mg/L).

Removal of Pb^{2+} and Cd^{2+} by chitosan as a function of time at various initial metal concentrations indicate that as the concentration is increased so does the time taken before equilibrium is attained. At lower concentrations less metal ion (Cd^{2+} or Pb^{2+}) adsorbs onto the chitosan than at higher concentrations (Figures 4 and 5). At initial concentrations of 100, 250, 400, 500 and 1000 mg/L, the amount of Pb^{2+} sorbed was 73, 144, 149, and 211 mg/L, respectively. For the Cd^{2+} , it was 45, 78, 52, 165 and 263 mg/L at the same initial concentrations, respectively. The variation of the amount of Pb^{2+} and Cd^{2+} ions removed from initial metal concentration by Chitosan is shown in Table 1.

These results clearly indicate that chitosan can remove Pb^{2+} and Cd^{2+} ions from aqueous solution. The amount of

$Pb(II)$ ion adsorbed on the chitosan is higher than that of $Cd(II)$ ion. This trend is explained on the basis of their ionic radii ($Cd = 0.92\text{\AA}$ and $Pb = 1.21\text{\AA}$) and the hydration energy of $Pb(II)$ ion which is lower than that of $Cd(II)$ ion. Reports have shown that adsorption may be related directly to loss of outer hydration sphere that precedes hydrolysis of metal ions (Ikhuoria and Omonmhenle, 2006). Hence, $Pb(II)$ ion will have better access to the chitosan surface than $Cd(II)$ ion.

Sorption efficiency

The distribution coefficient of an adsorbent is defined as the ratio of the metal ion adsorbed to the amount in the li-

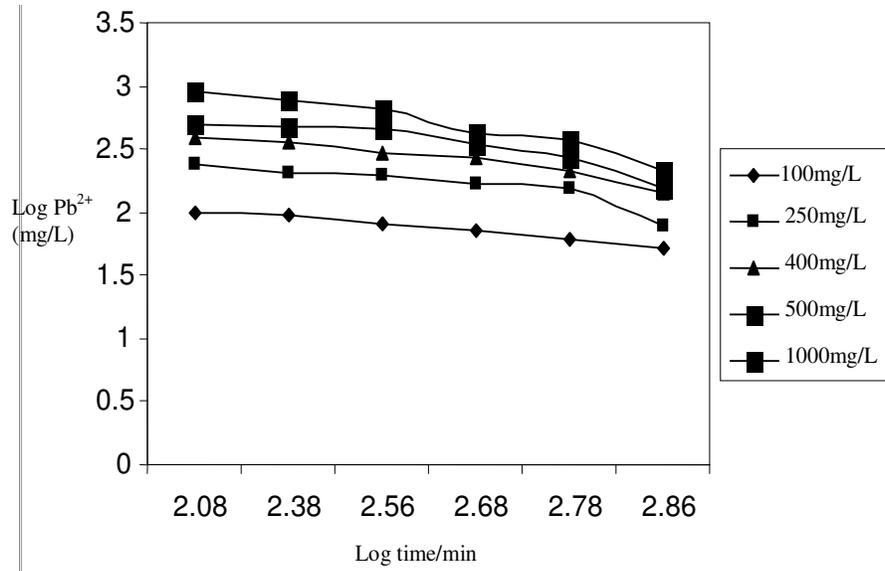


Figure 4. Adsorption kinetics of lead ions on chitosan at different initial concentrations $[Pb^{2+}] = 100, 250, 400, 500, 1000$ (mg/l), pH 4.5, stirring speed = 180 rpm.

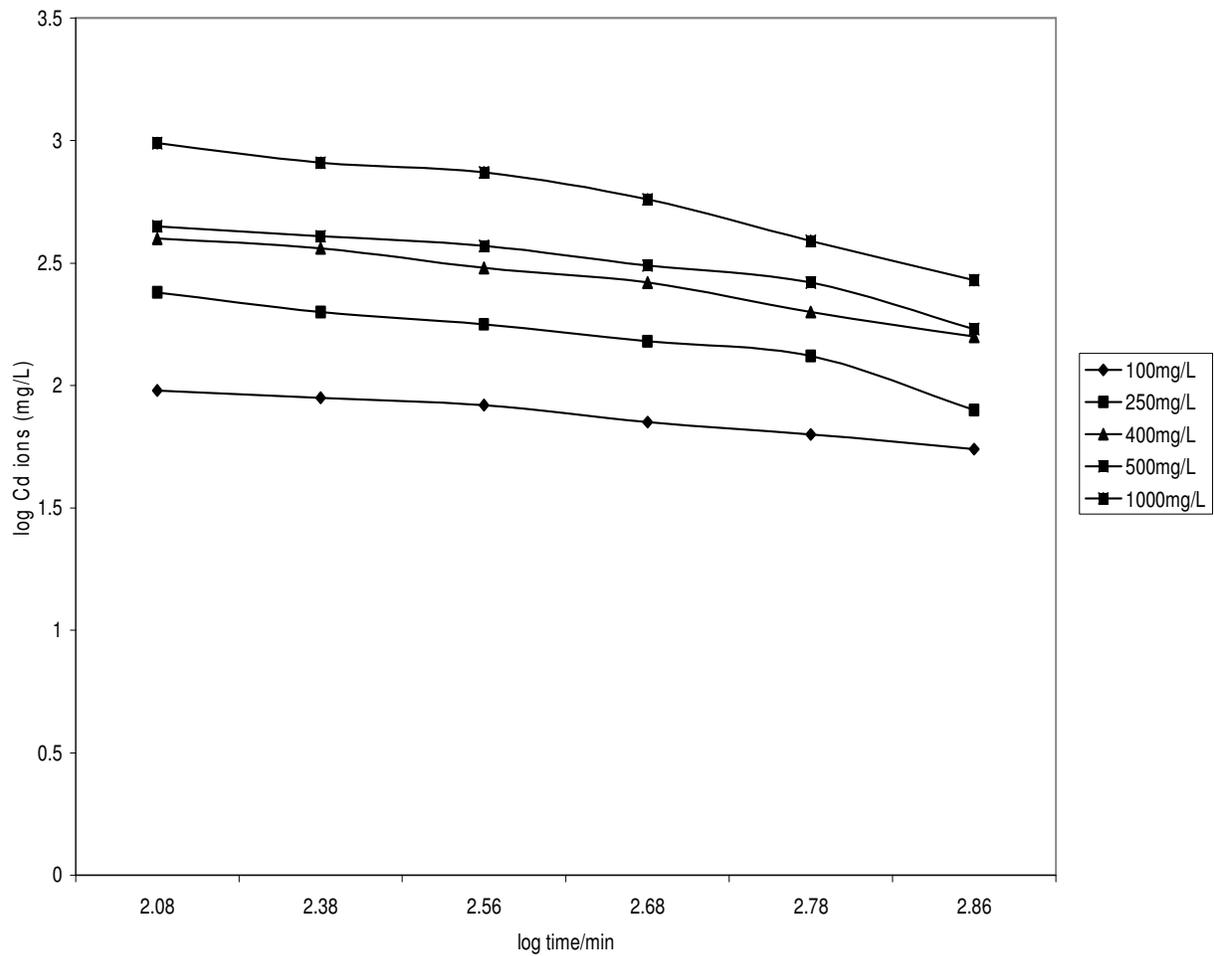


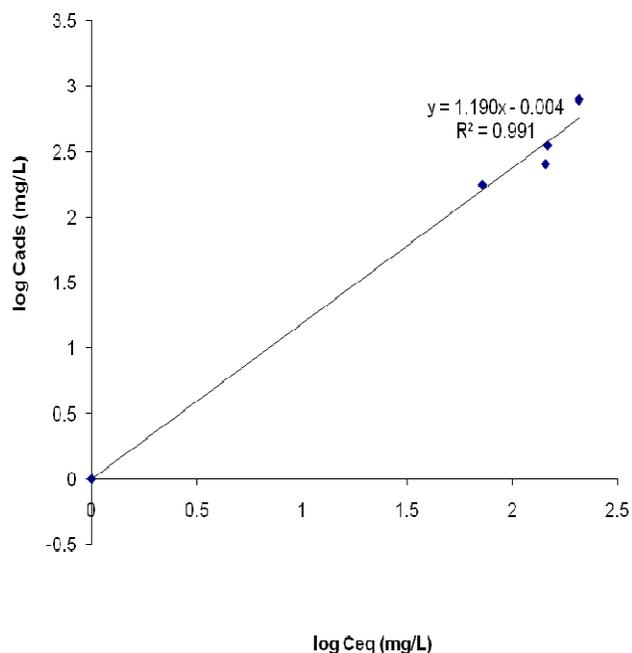
Figure 5. Adsorption kinetics of cadmium ions on chitosan at different initial concentrations $[Cd^{2+}] = 100, 250, 400, 500, 1000$ (mg/l), pH 4.5, stirring speed= 180 rpm.

Table 1. Equilibrium sorption of metal ions on Chitosan at 25 °C, pH 4.

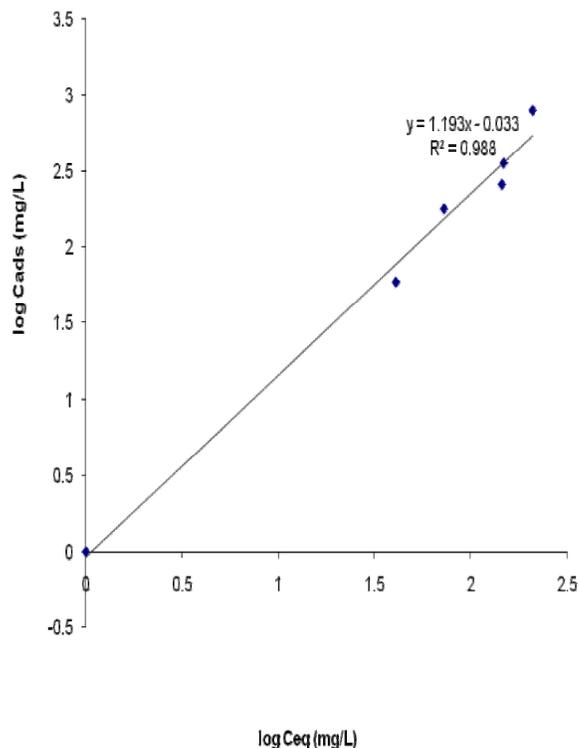
Initial metal ion conc. (mg/L)	Amount of metal ion adsorbed (mg/L)	
	Pb (II) ion	Cd (II) ion
100	65	51
250	132	103
400	218	198
500	265	249
1000	557	499

Table 2. Distribution Coefficient (K_d) of metal ions at 25 °C.

Metal ions	Equilibrium concentration of metal ions (mg/L)	Distribution coefficient (K_d)
Pb ²⁺	35 – 443	1.857 – 1.257
Cd ²⁺	49 – 501	1.041 – 1.0004

**Figure 6.** Freundlich plot of adsorption of Pb²⁺ onto chitosan.

quid phase. Values of the distribution coefficient lower than 1.0 shows low sorption efficiency. In this study, the values of the distribution coefficient of the distribution coefficient of the metal ion between the chitosan and the aqueous phase are dependent on the initial metal ion concentrations and are higher than 1.0 as presented in Table 2. The estimated values of the distribution coefficient (K_d) in Table 2 indicates high efficiency of the chitosan for the treatment of waste water containing Pb²⁺ and Cd²⁺ ions with chitosan.

**Figure 7.** Freundlich plot of adsorption of Cd²⁺ onto chitosan.

Sorption isotherm

The results of the Pb (II) and Cd (II) metal ions concentration dependence study were subjected to analyses by means of both Langmuir and Freundlich adsorption isotherms. It became clear that the Freundlich equation fitted the data better than the Langmuir equation by describing the data over the entire concentration range. The Freundlich equation plot of $\log C_{ads}$ vs. $\log C_{eq}$ which is valid for heterogeneous layer sorption on a surface containing multiple numbers of sites, predicting a heterogeneous distribution of sorption energies, yielded a straighter line as shown in Figures 6 and 7 ($R^2 = 0.991$ and 0.988 , respectively). The linearity of the plot supports the applicability of the Freundlich adsorption isotherm in this study.

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

$$\log C_{ads} = \log P + 1/n \log C_{eq}$$

where C_{ads} = amount of Pb (II) and Cd (II) adsorbed ($\text{mg}\cdot\text{g}^{-1}$), C_{eq} = equilibrium concentration in solution ($\text{mg}\cdot\text{dm}^{-3}$), $1/n$ = Freundlich constant ($\text{mg}\cdot\text{g}^{-1}$) and P = Freundlich constant ($\text{g}\cdot\text{dm}^{-3}$)

From Figures 6 and 7, it is evident that the values of $1/n$ and P , which are measurements of the adsorption

intensity and adsorption capacity of the adsorbent, have been determined by the least-square fit and were found to be 1.19 and 0.93 mg/L for lead, 1.15 and 0.93 mg/L for cadmium, respectively. Compared to literature sources (Schmuhl et al., 2001), the average values of $1/n$ signify that the forces which are exerted on the surface of the chitosan during Pb (II) and Cd (II) metal ions adsorption are moderate. The values of P confirm the affinity of the chitosan for the metal ions. The maximum adsorption capacity is greater than 100 mg·g⁻¹ at 1000 mg·dm⁻³ of Pb (II) and Cd (II) metal ions in the solution. At higher concentrations this maximum can be higher.

Conclusion

This study showed that chitosan absorbs heavy metals, in particular, lead and cadmium ions, and hence can be used to remove not only lead and cadmium but also other heavy metals from aqueous effluents. Chitosan as a result of its bioavailability would be economically useful for the treatment of wastewater containing heavy metals. Generally, the adsorption process for both metals is concentration driven.

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