Chitosan Selectivity to Remove Cadmium (II), Cupper (II) and Lead (II) from Aqueous Phase: pH and Organic Matter Effects

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Abstract

The objective of this study was to investigate the selectivity of a chitosan, produced by a biological method from shrimp wastes (*Litopenaeus* sp.), for cadmium, cupper and lead in presence of natural organic matter at different solution pHs. The desorption grade of cadmium from saturated biosorbent was also investigated.

Adsorption isotherms, of one and three adsobates, were conducted in batch reactors at pH 4, 5 and 7 and 25 ^{o}C at an initial metal concentration of 5 to 100 mg/L. The chitosan utilized in this research has a molecular weight of 107.8 kDa and a degree of acetylation of 33.7%, and the clarified water used as solvent contained 10.7 mg/L of total organic carbon. On the other hand, desorption experiments were conducted in acidic conditions.

The results obtained in this study revealed that chitosan has a higher sorption capacity for copper follow by lead and cadmium, and hence, the biosorbent selectivity was as follows Cu>Pb≥Cd. This happened in both deonized and clarified water at pH 4. It was also found that cadmium removal by chitosan increased as pH rise from 4 to 7; 0.5, 3.3, and 6.0 mg/g for pH 4, 5 and 7, respectively, at an equilibrium concentration of 20 mg/L. On the other hand, experiments carried out in clarified water showed that the cadmium sorption capacity of chitosan was enhanced by the presence of natural organic matter; 6.7 mg/g in deinozed water and 19.9 mg/g in clarified water at an equilibrium concentration of 50 mg/L and pH 7. Finally, the preliminary desorption experiments conducted at pH 2 and 3, with HNO_3, reported 68 and 44.8 % of metal desorbed, accordingly.

These findings reveal that the chitosan tested in this study posses an acceptable sorption capacity for cadmium, copper and lead. It was found that this biosorbent is more selective for cupper follow by lead and cadmium, and that the cadmium sorption capacity increases as pH rises. It was also observed that the natural organic matter enhances the chitosan sorption capacity, and that the cadmium adsorption is partially reversible at acid pHs.

Introduction

Wastewaters from metal-mechanic industry, agriculture runoffs, municipalities, etc., pollute surface waters and aquifers with toxic metals, such as cupper, cadmium and lead, which drastically affects the aquatic and terrestrial life. The use of biosorbents, like chitin and its subproduct chitosan, to remove toxic compounds from water has reported acceptable results that have encouraged to optimize the production process and to improve the quality of these types of biosorbents.

In this study chitosan produced from shrimp wastes by a biological method (*Litopenaeus* sp.) was utilized to remove cadmium, cupper and lead in presence of natural organic matter at different solution pHs. The biosorbent regeneration was also studied.

Experimental

The chitosan utilized in this investigation has a molecular weight of 107.8 KDa and a deacetylation grade of 66.3 %. The chemicals used were analytical grade; Cd $(NO_3)_2$ $4H_2O$, Pb $(NO_3)_2$, Cu $(NO_3)_2$ H_2O, and the solution pH was adjusted by HNO_3 or NaOH. In order to determine the organic matter effect, deionized and clarified water (collected from a local water treatment plant named "los filtros – SLP") was used as a solvent to determine the sorption isotherms. On the other hand, the metal concentration in solution was determined by an Atomic Absorption Spectrophotometer (AAnalyst 400), and the total organic carbon (TOC) by a Shimadzu 5000A TOC analyzer.

The adsorption isotherms were determined in batch reactor as follows. A determined amount of biosorbent was placed in a bag made of Teflon mesh, and consequently this bag was submerged in a solution containing a determined concentration of metal at constant temperature. The solution was constantly mixed by a Teflon coated stir bar moved by a magnetic stirrer. The solution pH was adjusted daily until it remained constant, and once the equilibrium was reached the metal concentration was determined. Finally, the metal sorption capacity was computed by a mass balance and reported as mg of metal removed by g of biosorbent.

Results and discussion

The cadmium sorption capacity of chitosan at 25 ^{o}C increased as pH rise from 4 to 7. For example, at an equilibrium concentration of 40 mg/L and pH 4 the sorption capacity was 1.8, and it increased to 5.75 and 6.6 mg/L at pH 5 and 7, respectively (Figure 1).
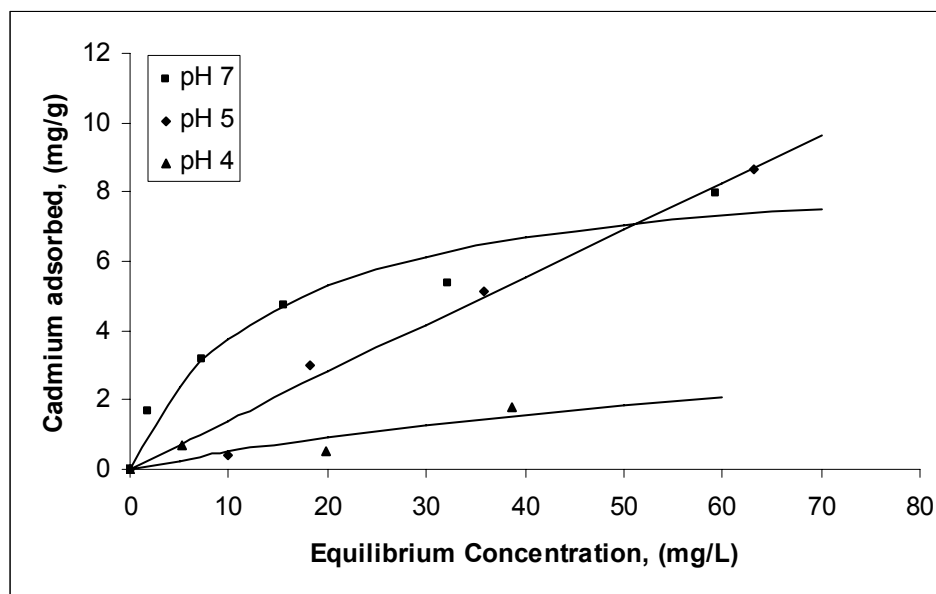

Figure 1. Cd Adsorption isotherms for chitosan in deionized water at different pHs and 25 ^{o}C

On the other hand, the chitosan sorption capacity of a mixture of Cd, Cu and Pb at a equal initial concentration (in moles) was also determined. This experiment was conducted in both deinonized (Figure 2) and clarified (Figure 3) water to determine the organic matter effect on the sorption capacity. It was found that at pH 4 chitosan is more selective for cupper, followed by cadmium and lead, which is in agreement with result reported by Huang C. et al.(1996). More importantly, these results showed that the presence of natural organic matter did not affect selectivity but it did increase the cupper sorption capacity about three times.
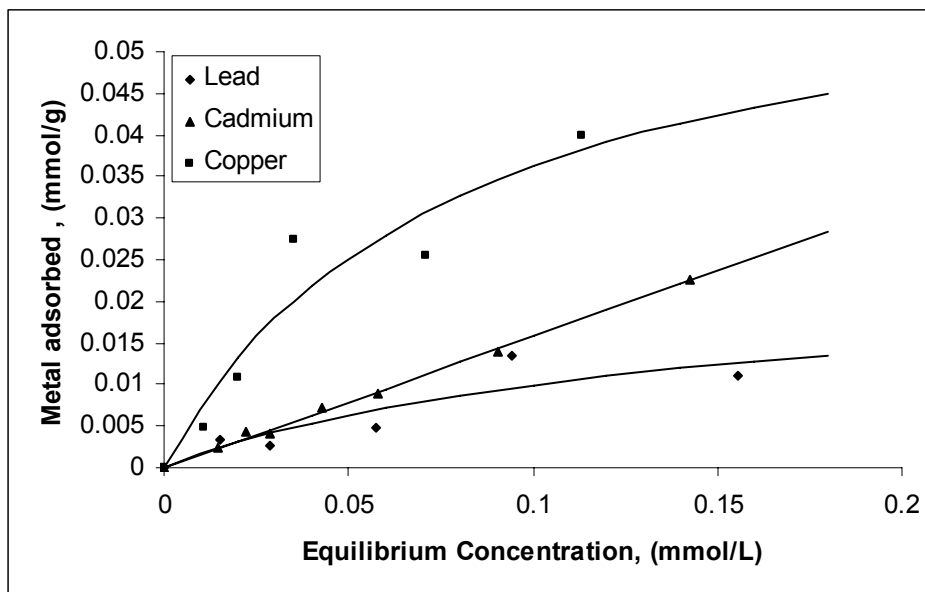

Figure 2. Metal adsorption isotherms for chitosan at pH 4 and 25 ^{o}C in deionized water
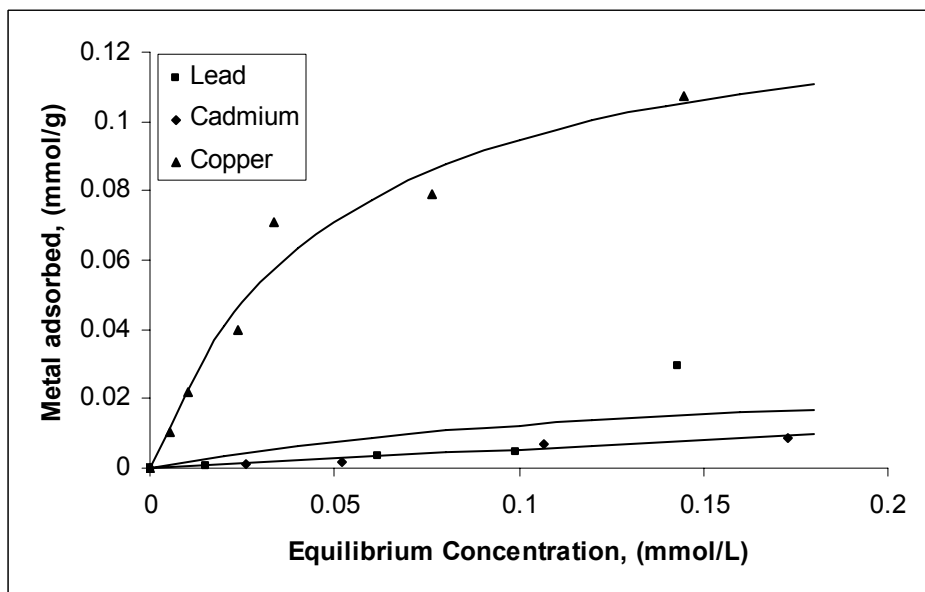

Figure 3. Metal adsorption isotherms for chitosan at pH 4 and 25 ^{o}C in clarified water

It is to be mentioned that the effect of natural organic matter on the cadmium sorption capacity was also studied, and it was found that the sorption capacity of this element increased 2.2 times when organic matter was present.

Based on these finding, the following sorption mechanisms were proposed. In acidic conditions -OH groups are dissociated and $-NH_2$ groups are protonated, hence, the remaining $-O^-$ can adsorb, by electrostatic interaction, metal ions (Me^{2+}). Plus the electrostatic attractions between the free electron pairs of the nitrogen of the protonated amino group and the divalent ions can form chelate complexes, as it has been described by R. Bassi et al. (2000). On the other hand, when organic matter is present, this can bond to the chitosan $-NH_3^+$ groups through its dissociated oxygen-containing groups charged negatively, additionally, these groups can also adsorb Me^{2+} (Gotoh T. et al. 2004; Deng S. and Bai R. 2003) which contributes to the metal removal. The latest could explain why the presence of organic matter increased the divalent metals sorption capacity of chitosan.

The desorption experiments conducted at pH 2 and 3 revealed that bout 68 and 44.8%, respectively, of Cd initially adsorbed by chitosan was desorbed. These results suggested that the cadmium removal by chitosan was conducted by both physical (electrostatic attraction) and chemical (covalent bond) adsorption, and because of this the cadmium adsorbed by chitosan is partially reversible.

Conclusions

It was concluded that the cadmium sorption capacity of chitosan increases as the solution acidity decreases. Plus the natural organic matter enhances the cadmium and cupper sorption capacity from two to three times, and it does not alter the chitosan selectivity; Cu>Cd≥Pb. On the other hand, the cadmium adsorption by chitosan is partially reversible, which suggests that the cadmium sequestration in this case is conducted by physical and chemical adsorption.

References

Huang,C.; Chiem,Y.; Liou,M.R.; "Adsorption of Cu (II) and Ni (II) by palletized biopolymer"; Journal of Hazardous Materials 45 (1996) 265-277

Bassi, R.; Prasher, S. O.; Simpson, B. K.; "Removal of selected Metal Ions from Aqueous Solutions Using Chitosan Flakes"; Separation Science and Technologu, 35 (4), 547-560 (2000)

Gotoh,T.; Matsushima,K.; Kikuchi, K.I.; "Preparation of alginate-chitosan hybrid gel beads and adsorption of divalent metal ions"; Chemosphere 55 (2004) 135-140

Deng,S.; Bai,R.; "Aminated Polyacrylonitrile Fibers for Humic Acid Adsorption: Behaviors and Mechanisms"; Environ. Sci. Technol. 37, 5799-5805 (2003)