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Adsorption kinetics of mercury in Batch system and its removal in columns packed with chitosan

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Abstract: This project involves the adsorption kinetics of Hg^{2+} and the removal of this metallic ion from aqueous solutions using chitosan-packed columns. The adsorption kinetics experiments considered the following independent variables: the metallic ion concentration, particle size and mass of chitosan. In the case of the removal of metallic ion at different metallic ion concentration using packed columns, the volumetric flow rate, the particle size of the adsorbent, the pH solutions and temperature were kept constant in all experiments. The results showed that the adsorption kinetics are independent from the parameters evaluated and in all cases, the pseudo-second order model was the best fit for the experimental data. The packed columns experiments displayed that the adsorbent was more effective at higher metallic ion concentrations.

Keywords: Adsorption kinetics; chitosan-packed column; mercury removal

Introduction

In Nicaragua, the small-scale artisanal mining use mercury for the extraction of gold (güiriseros). The process involves grinding-milling-amalgamation in stone mills and subsequently, the obtained amalgam (Au-Hg) is burned outdoors for the gold-mercury separation. During 100 years of mining activity in Santo Domingo and La Libertad, Chontales, approximately 40 tons of mercury have been released to the environment, and it is considered that approximately 45% has discharged in rivers bordering (Picado, 2004).

A study about mercury contamination of groundwater and superficial water performed in 2007 for the Libertad, Chontales revealed people had been consuming groundwater contaminated with this metal for many years. The results of this study also showed that mercury was present at all eight sampling points where collected and at four of those points, the Hg concentration exceeded the CAPRE (Regional Committee for Drinking Water for Central America) guidelines for drinking water (Benavente et al., 2007).

An alternative for the removal of heavy metals is the use of chitosan, since several studies have shown that this adsorbent material is able to fix a great variety of metals (Muzzarelli, 1977). The main objective of this study is to determine the effectiveness of chitosan for the removal of mercury using packed columns. For this, the adsorption kinetics of mercury were determined and the removal of mercury (Hg^{2+}) was carried out in chitosan- packed columns at different concentrations.

Material and Methods

Chitin was extracted from shrimp waste by desproteinization, demineralization and depigmentation at laboratory level. This product was deacetylated in 50 wt% NaOH for 1 h at 110 8C (15%, w/v) to obtain chitosan. Infrared spectroscopy was used to determine its deacetylation degree and viscosimetry was used to determine its molecular weight.

Kinetic studies were performed in batch experiments at initial pH 6 ± 0,5, at three initial metallic ion concentrations (20, 50 and 100 μg/l), at two different mass of adsorbent (2,0 y 5,0 g) and chitosan particle sizes of 0,22–0,45 mm. Simplified models were used to determine the rate-controlling step.

Experimental studies in chitosan-packed columns were carried out in a cylindrical column (34 cm in height and 2,5 cm in internal diameter). A Watson-Marlow 502S peristaltic pump was used to adjust the flow rate and to feed the column with the metallic ion solution. The experiments were performed with two different metallic ion concentration (2,0 y 10,0 μg/l). Mercury concentration was determined by GBC 932 Plus Atomic Absorption, using a HG3000 Hydride Generator.

Results and Conclusions

The IR spectrum of chitosan is showed in Figure 1.1. According to the FTIR spectrum of chitosan, the absorbance values at 3432 cm^{-1} and at 1654 cm^{-1} were 0,555 and 0,296, respectively. A degree of deacetylation of 60% was obtained applying the Domszy and Roberts equation (Domszy and Roberts, 1985).

Please include Figure 1.1 here.

The molecular weight of chitosan was calculated by applying Mark-Houwink equation (Ravi Lumar, 2000), which implies the determination of the intrinsic viscosity. To obtain this parameter, the Huggins equation that relates the reduced viscosity (η_{sp}) to the concentration (C_2) was applied (Parada et al., 2004). Figure 1.2 shows Huggins representation to obtain the value of the intrinsic viscosity [η]. The results indicated that the molecular weight of chitosan is 1,02 x 10^6 g/mol.

Please include Figure 1.2 here.

Pseudo-first order and pseudo-second order models were tested with experimental data for mercury adsorption. The results indicated that the behavior of the adsorption kinetics was independent of the evaluated variables. In all cases, the pseudo-second order model was the best fit to the experimental data, indicating that the control step is the adsorption into the overall rate of the metallic adsorption process. The Figure 1.3 shows mercury adsorption capacity as a function of time at different mass of absorbent and the parameters adsorption capacity (q_e) and Pseudo-second order rate constant (k_2), corresponding to the pseudo-second order equation, are depicted in Table 1.1.

Please include Figure 1.3 here.

Please include your Table 1.1 here.

Figure 1.4 shows the breakthrough curve for mercury adsorbed onto chitosan at different ion concentration. The results indicate that for a system of packed columns, chitosan adsorbs better the mercury metallic ion at high concentrations than at low concentrations.

Please include Figure 1.4 here.

In conclusion, this study shows that the adsorption kinetics are independent from the parameters evaluated and the pseudo-second order model was the best fit for the experimental data. The packed columns experiments displayed that the adsorbent was more effective at higher metallic ion concentrations.

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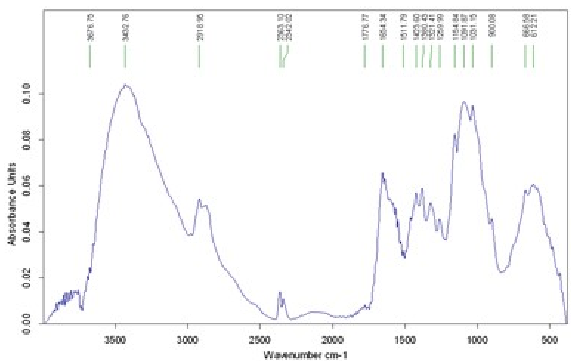


Figure 1.1 Spectrum of chitosan produce a laboratory level.

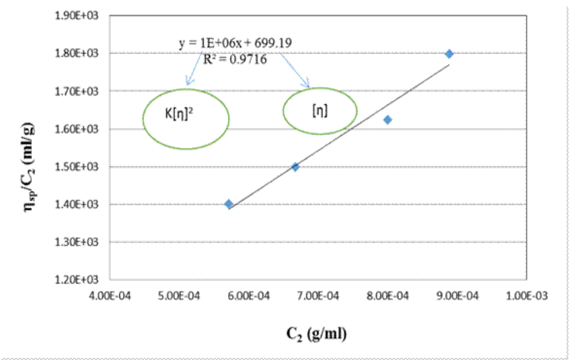
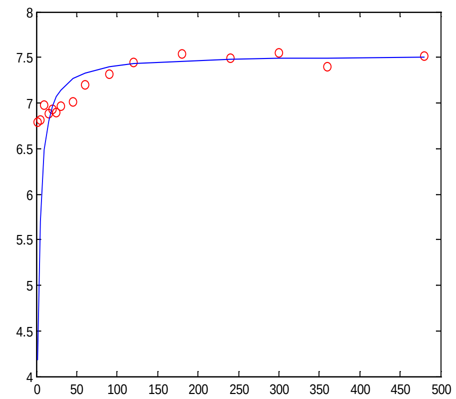
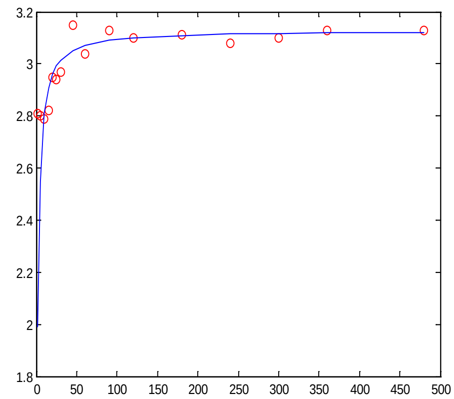


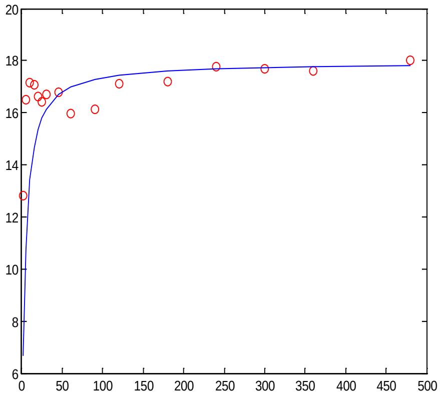
Figure 1.2 Huggins representation to obtain the value of the intrinsic viscosity [η].



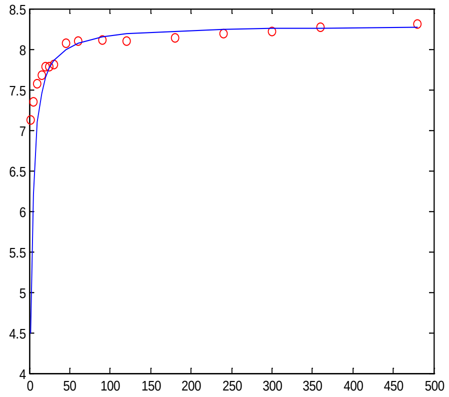
(a) 20 µg/l and 2 g of adsorbent.



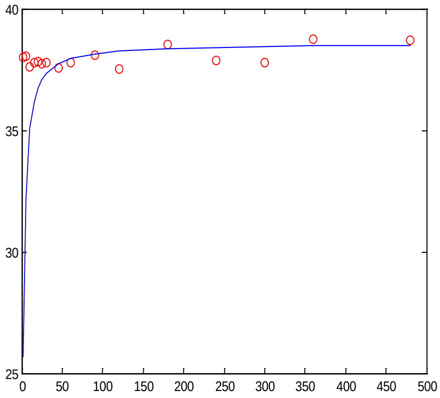
(b) 20 µg/l and 5 g of adsorbent.



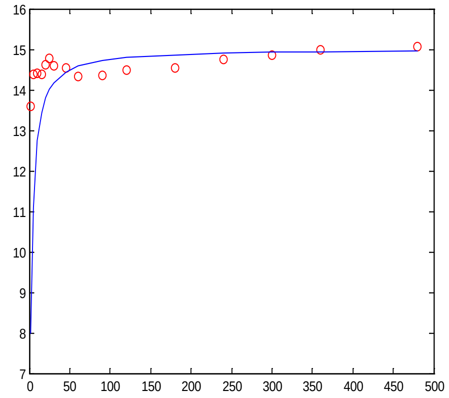
(c) 50 µg/l and 2 g of adsorbent.



(d) 50 µg/l and 5 g of adsorbent.

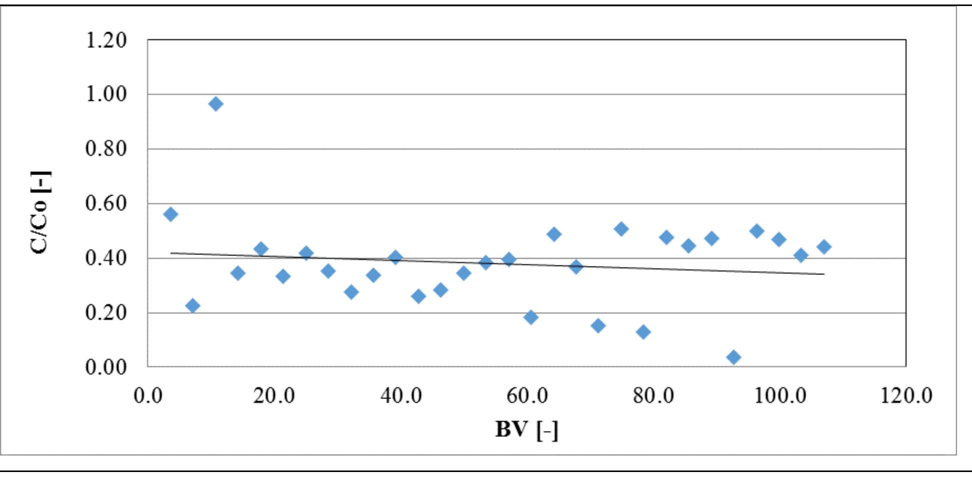


(e) 100 µg/l and 2 g of adsorbent.

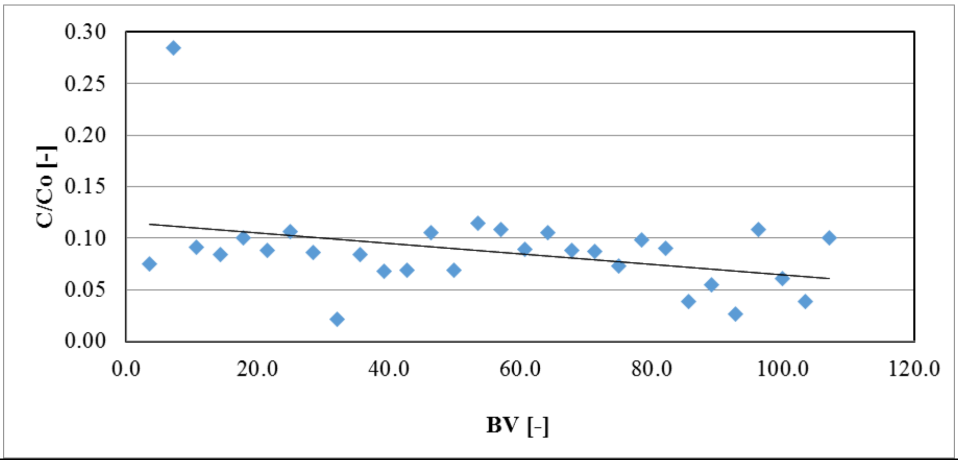


(f) 100 µg/l and 5 g of adsorbent.

Figure 1.3 Comparison between experimental data and non-linear modelled results using pseudo-second order equation, for adsorption kinetics of Hg (II) in chitosan, at different concentrations and different mass of adsorbent.



(a) Mercury ion concentration (Co = 2,0 µg/l)



(b) Mercury ion concentration (Co = 10,0 μg/l)

Figure 1.4 Ion metallic adsorption in chitosan-packed columns at 1.1 ml/s solution flowrate.

Table 1.1 Correlation values for the simplified models and values of q_e y k_2 for mercury kinetics adsorption determined according to Pseudo-second order model at different mass of adsorbent.

Co (μg/l)	Mass of adsorbent (g)	Pseudo-first model (R^2)	Pseudo-second model (R^2)	Pseudo-second model Parameters	
				k_2 (g/(μg·min))	q_e (μg/g)
20	2	0.6878	0.9998	0.1329	12.04
20	5	0.8042	0.9999	0.3195	3.58
50	2	0.6099	0.9916	0.0558	60.20
50	5	0.3273	0.9994	0.1205	14.08
100	2	0.0777	0.9992	0.0259	38.73
100	5	0.8074	0.9994	0.0666	26.47