



**HAL**  
open science

## Mercury Sorption on Chitosan

Karol Campos, Guibal Eric, Francisco Peirano, M. Ly, Holger Maldonado

► **To cite this version:**

Karol Campos, Guibal Eric, Francisco Peirano, M. Ly, Holger Maldonado. Mercury Sorption on Chitosan. *Advanced Materials Research*, 2007, 20-21, pp.635-638. 10.4028/www.scientific.net/AMR.20-21.635 . hal-04663941

**HAL Id: hal-04663941**

**<https://imt-mines-ales.hal.science/hal-04663941v1>**

Submitted on 31 Oct 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Mercury Sorption on Chitosan

K. Campos<sup>1,a</sup>, E. Guibal<sup>2,b</sup>, F. Peirano<sup>3,c</sup>, M. Ly<sup>4,d</sup> and H. Maldonado<sup>5,e</sup>

<sup>1,2,3</sup>Ecole des Mines d'Alès, Laboratoire Génie de l'Environnement Industriel, 6 avenue de Clavières, F-30319 Alès Cedex, France

<sup>4,5</sup>Universidad Peruana Cayetano Heredia Lima, Perú

<sup>a</sup>Karol.Campos@ema.fr, <sup>b</sup>Eric.Guibal@ema.fr, <sup>c</sup>Francisco.Peirano@ema.fr, <sup>d</sup>MLy@golder.com.pe, <sup>e</sup>dquim2@upch.edu.pe

**Keywords:** Adsorption, chitosan, mercury ions, column size effect, concentration effect, fixed bed reactor, flow velocity effect particle size effect.

**Abstract.** Mercury sorption on chitosan was investigated in batch and continuous systems. Chitosan sorption properties were determined through sorption isotherms. Langmuir and Freundlich equations were used for the modeling of isotherms at pH 5. In batch systems, maximum sorption capacities reached 550 mg Hg/g. Sorption kinetics have been studied as a function of sorbent particle size and stirring rate. Dynamic removal of mercury was tested in a fixed bed reactor investigating the following parameters: particle size, column size, flow velocity and metal ion concentration. Clark and Adams-Bohart models were evaluated for the simulation of breakthrough curves. This study shows that chitosan is an effective sorbent for the treatment and recovery of mercury from dilute effluents at near neutral pH.

## Introduction

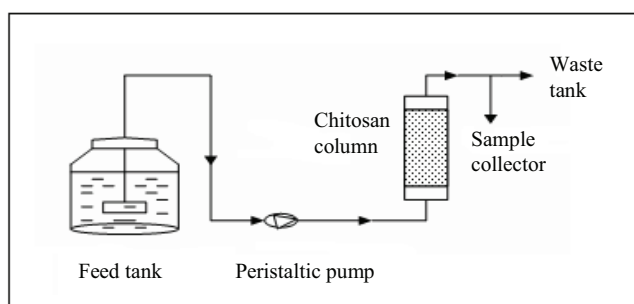
The necessity to reduce the amount of mercury ions in wastewater streams of industries, has led to an increasing interest for selective biosorbents [1, 2]. Biosorption is a technique that uses waste biomass or natural biopolymers (low-cost materials) to sequester heavy metal ions from aqueous [3, 4]; it usually comprises several mechanisms: adsorption, ion exchange, chelation, micro-precipitation, etc. This alternative process is competitive, effective and cheap [5]. Chitosan can be extracted from chitin, one of the most abundant biopolymer in nature. Chitosan is a linear polymer of D-glucosamine and characterized by high contents of amino and hydroxyl functional groups. Chitosan is well known for its high affinity for metal ions (it contains a large number of free amine groups that are very reactive for chelation of metal cations in the near-neutral pH range) [6, 7]. Other useful features of chitosan include its abundance, non-toxicity, hydrophilicity [8]. The objective of the present work is to investigate the adsorption of mercury from aqueous solution by chitosan using batch and continuous system. Previous experiments have shown that optimum pH was close to pH 5 [9]. A sorption isotherm has been performed for evaluating the maximum sorption capacity. And the influence of agitation speed was carried out in order to measure the contribution of external diffusion in kinetic control. In the case of fixed-bed systems the effects of design parameters such as bed height, flow rate, particle size, and metal initial concentration, have been investigated. The breakthrough profiles for the sorption of mercury in continuous system were analyzed using the Clark, and the Adams-Bohart models.

## Experimental

**Batch experiments.** Isotherms were performed by mixing a given amount of chitosan (10-50 mg) with 150 mL of mercury solution (concentration varying between 10 and 150 mg/L). The chitosan was supplied by France Chitine as a flaked material, with a deacetylation percentage of about 87%, and a molecular weight close to 125, 000 g/mol. The flasks were agitated at 500 rpm on a reciprocal shaker. The initial solution pH was adjusted using H<sub>2</sub>SO<sub>4</sub> and NaOH at optimal pH (pH = 5). After

72 h of agitation, the samples were filtered. Residual concentration was determined using ICP-AES. The amount of metal adsorbed on chitosan was calculated using the mass balance equation. The equilibrium data were modeled using the Langmuir [10, 11] and Freundlich [12, 13] isotherm equations. The kinetics were performed at different agitation speeds 200, 350, and 500 rpm and different particle sizes  $G1 < 125 \mu\text{m} < G2 < 250 \mu\text{m} < G3 < 355 \mu\text{m}$ .

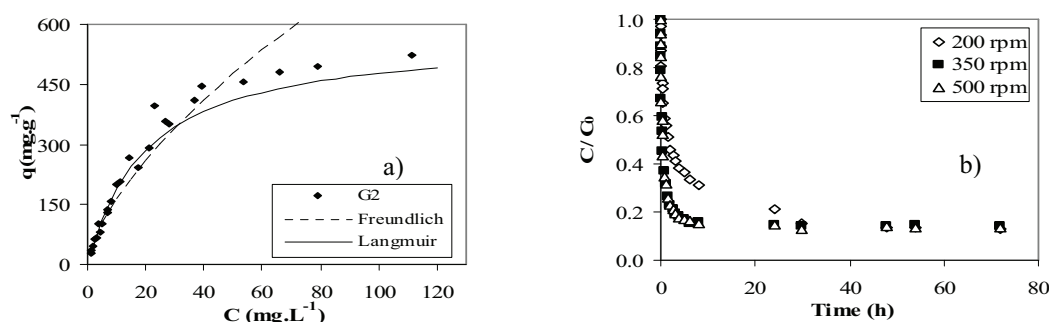
**Column experiments.** Continuous-flow sorption experiments were conducted in a glass column with internal diameter of 7 mm and different lengths (Figure 1). Since the ratio of column diameter to particle diameter is high, the effects of channelling are negligible. Glass beads (2 mm in diameter) were placed at the top of the column in order to provide a uniform flow. The study focused on the effect of important variables at optimal pH (pH=5), including bed height (4.6-14.2 cm), flow rate of mercury solution (0.64-1.9 mL/min – linear flow rate  $U_o$  between 1-3  $\text{m.h}^{-1}$ ), mercury concentration (25-75 ppm). The columns were filled with G1-G3 fractions, additionally G4 size fraction (355-500  $\mu\text{m}$ ) was also carried out. The mass of sorbent was set at 0.5, 1 and 1.5 g (corresponding to depths  $Z$  of 4.6, 9.2 and 14.2 cm respectively, G2). The solution was pumped upflow at varying volumetric flow rate (0.64-1.9 mL/min). The effluent samples were taken at different intervals. The results were modeled using the Adams-Bohart model [14, 15] and the Clark model [16, 17].



**Figure 1.** Fixed-Bed system: Schematic diagram of experimental set up.

## Results and discussion

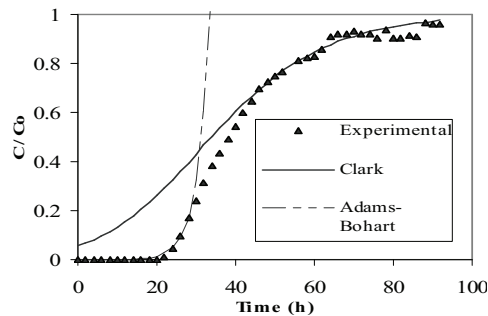
**Batch system.** The adsorption isotherm and linearized Langmuir and Freundlich adsorption isotherms are illustrated in Fig. 2 a) The Langmuir isotherm equation [10, 11] ( $r^2=0.99$ ) fitted better the adsorption process of Hg (II) by chitosan than the Freundlich equation [12, 13] ( $r^2=0.96$ ).



**Figure 2.** a) Mercury adsorption isotherm (pH=5,  $T=20^\circ\text{C}$ , particle size G2). b) Effect of agitation speed on kinetics (pH=5, mercury solution 50 mg/L, Chitosan solution 300 mg/L).

Kinetics results show that the intraparticle diffusion was not the main limiting step, the curves overlaid for particles G1, G2 and G3 (not shown). In order to evaluate the contribution of external diffusion the velocity of agitation was varied between 200 and 500 rpm. Fig. 2 b) shows that increasing agitation speed improved sorption rate (above 350 rpm the sorption kinetics stabilized). When increasing the agitation speed, the diffusion rate of mercury ions from the bulk liquid to the liquid boundary layer surrounding particles became higher because of an enhancement of turbulence and a decrease of the thickness of the boundary layer [18].

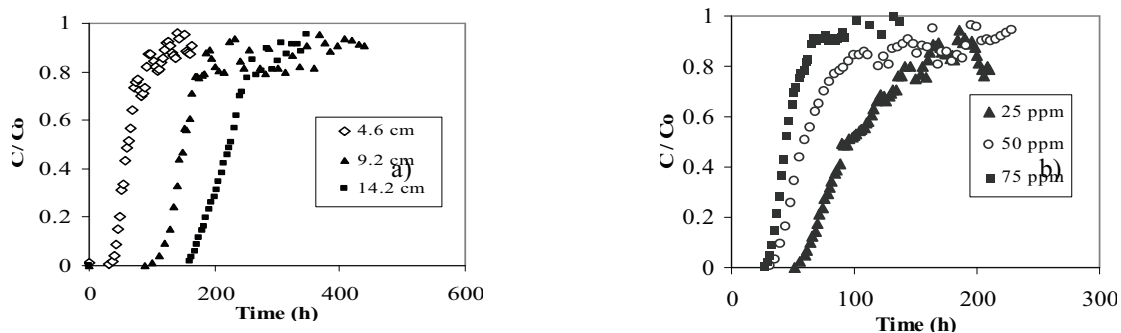
**Column system.** Experimental design methodology was carried out and only the most representative data have been shown. The simulated breakthrough curves are given in Fig.3. Adams-Bohart model was applied to experimental data for the description of the initial part of the breakthrough curve ( $C/C_o < 0.15$ ). Sorption capacity of the chitosan increases with increasing the depth, initial concentration, flow rate, but in the case of particle size, lower size particles are more favorable for mercury uptake but the pressure drop increases with decrease in the particle size. The Clark model fitted well the experimental results, but the initial part of the breakthrough curve was not defined; Aksu [16] and Hamdaoui [19] also observed that for  $C/C_o < 0.07$  the model could not apply to experimental data.



**Figure 3.** The breakthrough curve of Hg (II) sorption by chitosan with Adams-Bohart and Clark model. ( $C_o=50$  ppm,  $v=1.9$  mL/min,  $Z=6.1$  cm, particle size G3).

*Effect of column depth.* Breakthrough time and exhaustion time increased linearly with column depths (Figure 4a), for selected G2 size fraction. Increasing the depth of the columns increased the residence time, which improved the saturation of the sorbent.

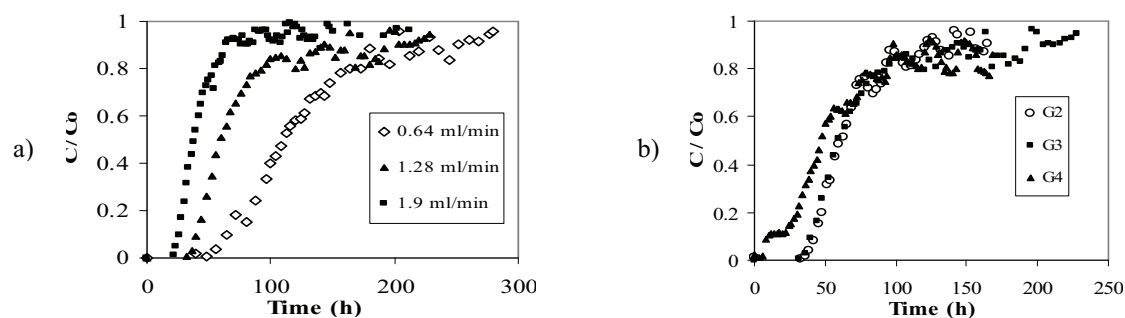
*Effect of metal concentration.* In Figure 4 b) shows the breakthrough profiles for the adsorption of mercury at initial concentrations (with selected G3 size fraction). With decreasing the inlet Hg (II) concentration the breakthrough curves were delayed and the treated volume increased at breakthrough. Lower concentration gradient caused slower transport [20, 21].



**Figure 4.** a) Effect of bed height ( $C_o= 50$  ppm,  $v=1.28$  ml/min, particle size G2, pH=5).  
b) Effect of metal concentration ( $v=1.28$  ml/min,  $Z=6.2$  cm, particle size G3, pH=5).

*Effect of flow rate.* In Figure 5 a) breakthrough and exhaustion occurred faster at higher flow rates. Also as the flow rate increased, metal concentration in the effluent increased rapidly resulting in much sharper breakthrough curves. This behavior may be due to insufficient residence time of the solute in the column and to diffusion limitations [22].

*Effect of particle size.* Figure 5 b) shows that particle size had a limited impact on the breakthrough curves. The curves almost overlapped, indicating that intraparticle diffusion does not control the dynamic sorption of mercury on chitosan. This result is consistent with those obtained in batch system.



**Figure 5.** a) Effect of flow rate ( $C_0=50$  ppm,  $Z=6$  cm, particle size G3, pH=5).  
 b) Effect of particle size ( $C_0=50$  ppm,  $v=1.28$  ml/min).

## Conclusion

Sorption capacities as high as  $550 \text{ mg Hg g}^{-1}$  were obtained at pH close to 5. Langmuir equation fitted well experimental data. The size of sorbent particles hardly affected kinetic profiles (for both batch and column systems), indicating that intraparticle diffusion was not the main limiting step in the process. Both agitation speed and flow rate strongly influenced the time required to reach equilibrium in batch and the slope of the breakthrough curve. The concentration of mercury also influenced the slope of the curve while increasing the depth of the column (increasing the amount of sorbent) did not affect the slope and only shifted the breakthrough volumes.

## Acknowledgements

Authors thank the Franco-Peruvian Collaboration program Raul Porras Barrenechea for financial support.

## References

- [1] Y. Kawamura, H. Yoshida, S. Asai and H. Tanibe: J. Chem. Eng. Japan Vol. 31 (1) (1998), p. 1
- [2] D. Karunasagar, M. V. Balarama and S. V. Rao: J. Hazard. Mater. Vol. B118 (2005), p. 133
- [3] M. Tsezos: Hydrometallurgy Vol. 59 (2001), p. 241
- [4] A. Hammami, F. Gonzalez, A. Ballester, M. L. Blázquez. and J. A Muñoz: Submitted to J. Env. Management (2006)
- [5] B. Volesky: *Sorption and Biosorption*, (Bx-sorbex Inc. St. Lambert, Quebec 2003)
- [6] E. Guibal: Sep. Purif. Tech. Vol. 38 (2004), p. 43
- [7] R. Juang, F. Wu, and R. Tseng: Wat. Res. Vol. 33 (10) (1999), p. 2403
- [8] R. Kumar: React. Funct. Polym. Vol. 46 (2000), p. 1
- [9] F. Peirano: MSc. Project. Marseille University (2003)
- [10] I. Safarik: Wat. Res. Vol. 29 (1) (1995), p. 101
- [11] A. Saglam, Y. Yalcinkaya, A. Denizli, M.Y. Arica, O. Genc and S. Bektas: Microchem. J. Vol. 71 (2002), p. 73
- [12] Y. Kaçar, C. Arpa, S. Tan and A. Denizli: Process Biochem. Vol. 37 (2002), p. 601
- [13] M. Chiou and H. Li: J. Hazard. Mater. Vol. B93 (2002), p. 233
- [14] H. Tran and F. Roddick: Wat. Res. Vol. 33 (13) (1999), p. 3001
- [15] S. Ghorai and K. Pant: Sep. Purif. Technol. Vol. 42 (2005), p. 265
- [16] Z. Aksu and F. Gonen: Process Biochem. Vol. 39 (2004), p. 599
- [17] Y. Sag and Y. Aktay: Process Biochem. Vol. 36 (2001), p. 1187
- [18] J. Shen and Z. Duvnjak: Process Biochem. Vol. 40 (2005), p. 3446
- [19] O. Hamdaoui: J. Hazard. Mater. Vol. B138 (2006), p. 293
- [20] M. Tsezos: Hydrometallurgy Vol. 59 (2001), p. 395
- [21] R. Han, W. Zou, H. Li, Y. Li and J. Shi: J. Hazard. Materials Vol. B137 (2006), p. 934
- [22] E. Guibal, C. Milot and Jean Roussy: Wat. Env. Res. Vol. 71 (1) (1999), p. 10