

# The Adsorption of Mercuric Ions by Chitosan

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## SYNOPSIS

The adsorption of mercuric ions by chitosan was investigated. The study of the adsorption kinetics shows that the rate of adsorption of mercuric ions on chitosan can be interpreted in terms of intraparticle diffusion as the rate-limiting step. The experimental data of adsorption equilibrium from mercuric chloride solutions correlate well with the Langmuir isotherm equation, although at high-solute concentrations, a multilayer type of adsorption with the subsequent increase in the uptake is observed. Column experiment confirms the ability of chitosan for the removal of mercuric ions from solutions in the absence of a high concentration of chlorides.

## INTRODUCTION

Chitosan, essentially poly-D-glucosamine, is a polymer obtained by extensive deacetylation of chitin. It is capable of adsorbing a number of metal ions, including  $\text{Hg}^{2+}$ . There are studies about the interaction of this metal ion with chitosans obtained from crab, prawn, squid, and squilla<sup>1,2</sup> and, more recently, with that prepared from lobsters.<sup>3</sup> Nevertheless, there are very few reports in the literature about the physicochemical characteristics of the adsorption process of mercuric ions on this polysaccharide. In the present work, some of the physicochemical parameters of this interaction are evaluated at the equilibrium as well as under dynamic conditions.

## EXPERIMENTAL

### Materials

Chitosan was obtained from shells of lobsters (*Panulirus argus*) by a procedure described elsewhere.<sup>4</sup> The deacetylation degree ( $90 \pm 1\%$ ) was evaluated independently by IR spectroscopy<sup>5</sup> and thermal analysis.<sup>6</sup> Particle sizes ranging from 1.25 to 2.5 mm were employed unless otherwise stated.

Mercuric chloride solutions were prepared from analytical grade  $\text{HgCl}_2$  (Merck). In all cases, the working pH was that of the solution.

### Methods

Equilibrium adsorption experiments were performed suspending 200 mg of the polymer in 20 mL of the corresponding solution and stirring at 25°C during 180 min. The solid was separated by filtration and the amount of mercury remaining in solution was determined in an SP-9 Philips atomic absorption spectrophotometer at  $\lambda = 253 \text{ nm}$  with an air/acetylene flame. Concentrations below  $10 \text{ mgHg}^{2+} \text{ L}^{-1}$  were determined by means of the cold-vapor technique.

Dynamic experiments were performed as follows: Glass columns,  $4 \times 1.4 \text{ cm}$ , were filled with chitosan particles (approximately 1 g of polymer). The columns were fed with 8–10  $\text{mg L}^{-1}$  mercuric chloride solutions at a flow rate of  $0.55 \text{ mL min}^{-1}$  using a peristaltic pump. The concentration of mercuric ions in the effluent was determined as described above.

## RESULTS AND DISCUSSION

It has been reported<sup>3</sup> that shaking chitosan for 3 h with the mercuric chloride solution guarantees the attainment of adsorption equilibrium, but no infor-

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mation has been supplied about the kinetics of this process. Figure 1 shows the results obtained by stirring chitosan in a solution of  $2.4 \cdot 10^3 \text{ mgHg}^{2+} \text{ L}^{-1}$ . The relatively rapid initial rate of adsorption is seen to decrease markedly during the first minutes of interaction, and after about 100 min, a gradual approach to the limiting adsorption is observed. López del Alba et al.<sup>7</sup> reported equilibration times of 10–15 min, but these authors employed smaller particle sizes (0.15–0.08 mm).

Chitosan can be considered a microporous material. When an amorphous polymer is below its glass transition, the thermal movements of the chain segments are restricted in such a way that pores resulting from irregularities in molecular packing actually exist.<sup>8</sup> Because of the relatively bulky chitosan chains, pores are large enough to let small molecules and ions through.

During the adsorption of materials in solution on porous adsorbents, there are essentially three consecutive stages involved<sup>9</sup>: transport of the adsorbate to the external surface of the adsorbent, diffusion of the adsorbate into the pores of the adsorbent, and adsorption of the solute on the internal surface of the adsorbent. This last stage is, in general, relatively rapid, and if the stirring is made sufficiently high, the adsorption rate will be controlled by the rate of diffusion of the solute into the capillary pores of the adsorbent.

The pattern found for the rate of adsorption in Figure 1 can be explained if it is supposed that the kinetics of the process is controlled by the diffusion of the solute in the capillary pores of chitosan. This mechanism has been previously postulated for the adsorption of metal ions on natural polymers generated from seafood processing wastes.<sup>10</sup>

Weber and Morris<sup>9</sup> pointed out that a functional relationship common to the majority of the intra-

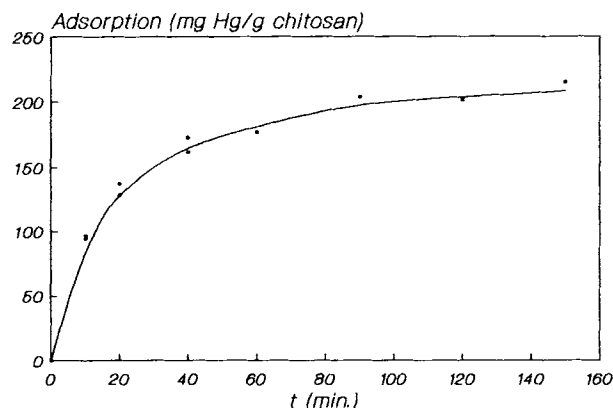


Figure 1 Rate of adsorption of  $\text{Hg}^{2+}$  on chitosan.

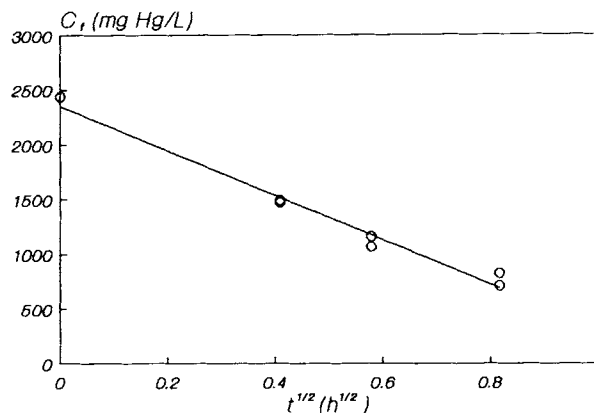
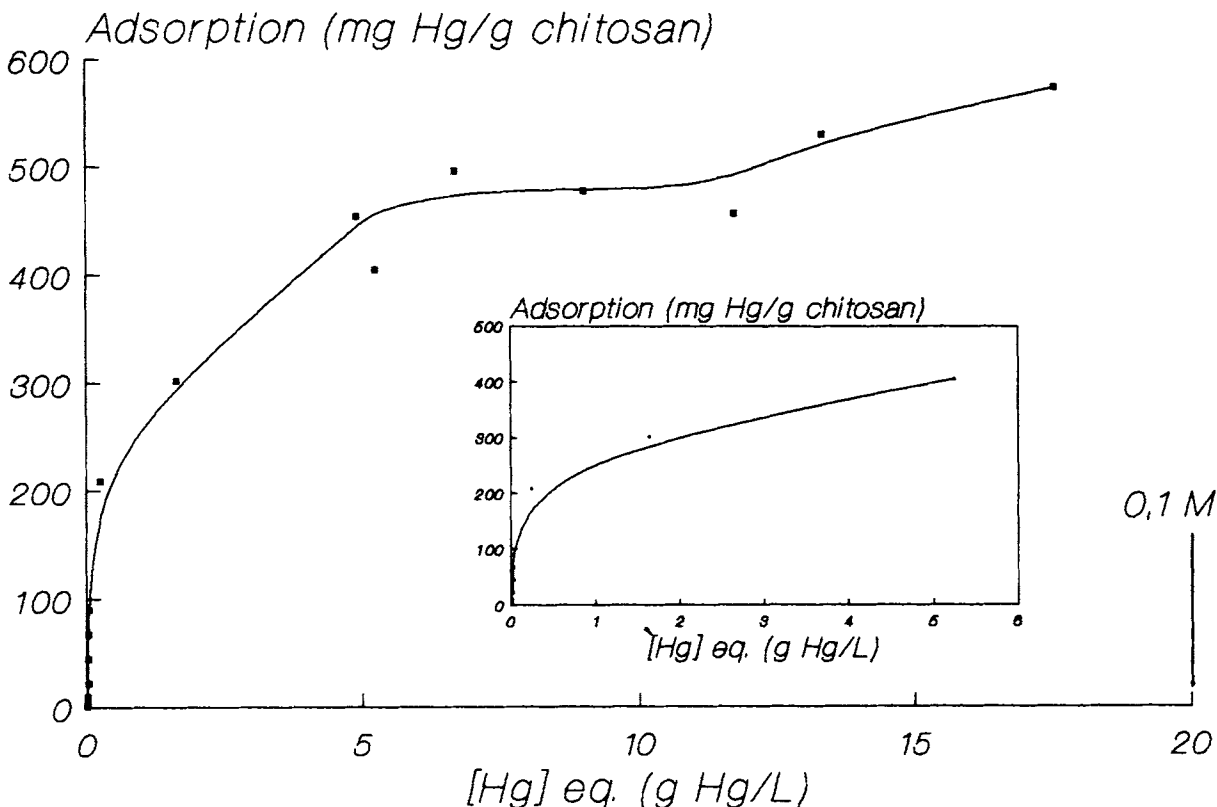


Figure 2 Rate of adsorption plotted on  $t^{1/2}$  scale ( $C_1$  is the residual concentration of solute in solution).

particle diffusion treatments is that the uptake varies almost proportionately with the half-power of time. The data in Figure 1 have been replotted in Figure 2 in terms of the solute concentration remaining in solution on a  $t^{1/2}$  scale. The linearity obtained indicates that intraparticle diffusion is the rate-determining step. It must be recognized that diffusion of the solute in the solution phase could produce this kind of time dependence where this step is controlling the rate of uptake. To eliminate this possibility, mechanical agitation in the experiments was high enough so as to ensure independence of the rate of uptake on stirring rate.

The adsorption rate constant was evaluated for the initial slope and turned out to be  $1.01 \text{ mmolHg}^{2+} \text{ g}^{-1} \text{ h}^{-1/2}$ , which is very similar to the rate constants found by Yang and Zall<sup>10</sup> for chitosan with other metal ions, even though they employed smaller particle sizes (0.315 mm).

The adsorption capacity of chitosan for mercuric ions from solutions in the initial concentration range from 10 to  $24 \cdot 10^3 \text{ mgHg}^{2+} \text{ L}^{-1}$  (0.05–120 mM) was studied. In Figure 3, it can be seen that the adsorption capacity increases as the concentration of mercuric chloride increases until an equilibrium concentration of approximately  $5 \cdot 10^3 \text{ mgHg}^{2+} \text{ L}^{-1}$  is reached. For equilibrium concentrations above  $12 \cdot 10^3 \text{ mgHg}^{2+} \text{ L}^{-1}$  (60 mM), there is a further increase in the amount of mercury retained. The first part of this curve, which is shown enhanced inside the figure, exhibits the form of a Langmuir isotherm. It has been suggested that the adsorption in this stage is due mainly to complexation of the metal ion with the amino groups of the polysaccharide and, to a certain measure, to physical adsorption.<sup>11</sup> On the other side, at the last part of the isotherm, physical deposition phenomena must play a



**Figure 3** Adsorption isotherm of  $Hg^{2+}$  on chitosan. The first part of the curve is shown enhanced inside the figure.

fundamental role, analogously as reported for other ions.<sup>12</sup>

As it can be seen in Figure 4, the experimental values of the first part of the isotherm adjusted satisfactory to the Langmuir equation in the form

$$\frac{c}{a} = \frac{c}{a_{max}} + \frac{1}{a_{max} \cdot K} \quad (1)$$

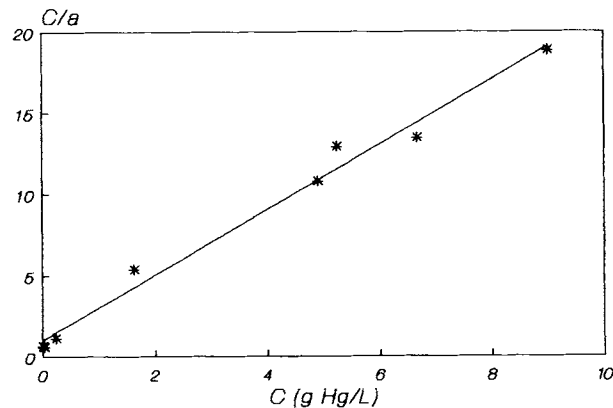
where  $a$  is the amount of  $Hg^{2+}$  adsorbed,  $c$  is the equilibrium concentration, and  $K$  is the adsorption equilibrium constant. The maximum adsorption,  $a_{max}$ , calculated from this model is 430 mgHg<sup>2+</sup> per gram of chitosan.

Taking into account the deacetylation degree of the chitosan employed, it can be estimated that there are 2.5 mol of  $-NH_2$  per gram ion of  $Hg^{2+}$ . This high accessibility of amino groups of chitosan to mercuric ions can be explained in terms of a microporous structure in which pore dimensions are comparable to the thickness of the polymer chains.

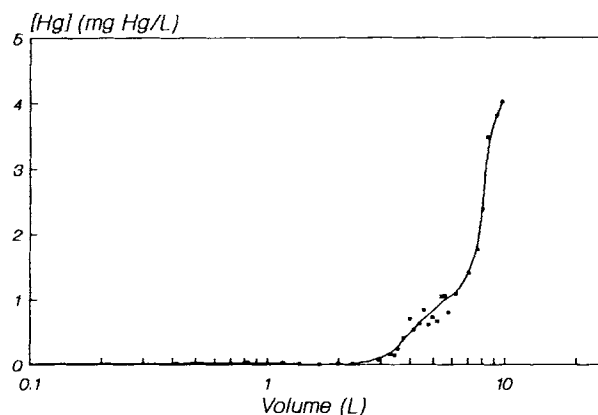
This result, although very different from the one obtained for Cr and Pb by Eiden et al.,<sup>12</sup> is very similar to that reported for silver<sup>11</sup> and is in agree-

ment with the coordination model proposed for different metal ions including mercury, in which one metal ion is bound to one amino group of the D-glucosamine dimmer.<sup>13</sup>

Although the adsorption capacity data registered in this isotherm are in agreement with those found under similar conditions for chitosans obtained from



**Figure 4** Adsorption isotherm of  $Hg^{2+}$  on chitosan, linearized according to the Langmuir equation.



**Figure 5** Breakthrough curve for mercuric chloride solution ( $8\text{--}10\text{ mgHg}^{2+}\text{ L}^{-1}$ ) delivered at a flow rate of  $0.55\text{ mL min}^{-1}$  to a chitosan column ( $4 \times 1.4\text{ cm}$ ) at  $25^\circ\text{C}$ .

other sources,<sup>1</sup> they are considerably lower than the values previously reported for the same type of chitosan.<sup>3</sup> This difference can be explained if one considers that in this latter work the adsorption capacity seems to have been determined in the multilayer adsorption zone (see the indicative arrow in Fig. 3). Furthermore, in the Ref. 3, a smaller particle size was employed (less than  $0.4\text{ mm}$ ).

The collection capacity of chitosan for mercuric ions was also evaluated under dynamic conditions. In this case, the particle sizes of chitosan ranged from  $0.5$  to  $1.25\text{ mm}$ . The results are shown in Figure 5.

There is a notorious similarity in the form of the elution curve obtained with that previously found by Muzzarelli.<sup>2</sup> The adsorption capacity obtained was  $80\text{ mgHg}^{2+}$  per gram of chitosan, which represents 20% of the maximum capacity evaluated under equilibrium conditions. The concentration in the effluent was lower than  $20\text{ }\mu\text{gHg}^{2+}\text{ L}^{-1}$ , the same as reported by Muzzarelli,<sup>2</sup> and although the retention capacity is somewhat higher than that reported by this author, it is of the same order of magnitude.

This result is particularly important for the separation or concentration of  $\text{Hg}^{2+}$  in the absence of a high concentration of chlorides, particularly taking into account that the retention of the metal ion can be improved by appropriately varying the diameter-to-height ratio of the resin in the column.<sup>2</sup>

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