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# Cadmium sorption on chitosan sorbents: kinetic and equilibrium studies

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## Abstract

Chitosan is very efficient at removing cadmium through chelation mechanisms involving amine groups of chitosan. The optimum pH is 7, and in acidic solutions, the protonation of the biopolymer reduces the binding of cadmium on amine groups due to electrostatic repulsion. The influence of particle size, temperature and agitation speed on metal sorption is investigated using chitosan flakes and chitosan gel beads. Temperature and agitation speed hardly influence equilibria and kinetics in the selected experimental conditions corresponding to a large sorbent dosage. The major effect on sorption performance is due to sorbent particle size, especially for chitosan flakes. Though intraparticle diffusion represents an important step in the kinetic control, the contribution of external diffusion may not be neglected.

*Keywords:* Chitosan; Cadmium; Isotherms; Kinetics; Sorption; Diffusion; Particle size; Agitation speed; Temperature; Glutaraldehyde crosslinking

## 1. Introduction

Cadmium is widely used in several industries including metallurgy, surface treatment, dye synthesis or battery production. Due to its toxicity, cadmium removal from aqueous effluents has been classified as a priority in the last decade. Industrial wastewaters are usually treated through chemical precipitation. However, these processes involve the production of highly toxic sludges, which must be further treated before being environmentally safe for

disposal [1]. Thus, other treatments have been developed including ion exchange, adsorption, electrodeposition and membrane systems [1]. Though these treatments are adequate for the treatment of medium to high concentration solutions, there is still a need for the development of new materials/processes for the treatment of dilute solutions, including the use of low cost materials of biological origin for the sorption of metals from dilute solutions [2,3].

Chitin is an aminopolysaccharide which is readily found in nature: fungal biomass, crustacean shells, insect cuticles. It is commercially extracted from crustacea shells [4]. This polymer is constituted by acetylglucosamine units. An alkaline treatment at boiling temperature allows the acetylated groups to

be removed and the deacetylation degree to be increased. This chemical treatment leads to the formation of chitosan, a partially deacetylated form of chitin. The amine groups are able to sorb metals through several mechanisms including chemical interactions, such as chelation, electrostatic interactions, such as ion exchange, or the formation of ion pairs [5–7]. The kind of interaction depends on the metal, its chemistry and the pH of the solution [6–11]. Chitosan was also studied for cadmium removal using raw material [12,13] and derivatives produced by physical and/or chemical modifications [14–17].

Owing to the low porosity of chitosan, sorption performances are frequently controlled by mass transfer resistance. The influence of diffusion mechanisms is also controlled by the chemistry of the metal and by the conditioning of the biopolymer. Since chitosan is soluble in acidic solutions, it is necessary to increase its chemical stability in acidic solutions for the sorption of several metal anions whose recovery is only effective at pH lower than 4–5 [6,10,18]. The crosslinking treatment can be carried out using several chemical reagents such as glutaraldehyde [14,19]. Glutaraldehyde crosslinking treatment may affect the sorption efficiency, involving a decrease in the number of free amine groups and a decrease in the accessibility to internal sites. This restricting effect may be decreased using chitosan whose structure has been physically modified: the gel bead formation procedure has been proposed and investigated by several groups [10,14]. This physical modification allows: (i) the polymer network to be expanded: the increase in the polymer network opening enhances the diffusion of large size molecules; and (ii) the crystalline state of the polymer to be reduced. Piron et al. [20] have shown that the dissolving of chitosan followed by a freeze-drying of the resulting solution allows a strong decrease in the crystalline structure of the polymer which can be, in turn correlated to the improvement of sorption kinetics.

This work concentrates on the study of cadmium sorption using gel beads and flakes. The influence of several experimental parameters on sorption kinetics is investigated with both raw and crosslinked materials: particle size, agitation velocity, temperature. The diffusion of cadmium in the gel beads is also studied

using SEM-EDAX analysis (scanning electron microscope coupled with an energy-dispersed analysis of X ray apparatus) for several points of a typical kinetic curve obtained on raw chitosan gel beads put in contact with a cadmium solution.

## 2. Material and methods

### 2.1. Materials

Chitosan was used as received from ABER Technologies (Plouvien, France). Previous characterization performed on the raw material had shown that the deacetylation degree was about 87% and the molecular weight was approximately  $125.000 \text{ g mol}^{-1}$  [10]. Flakes were ground and sieved in four fractions.  $G1 < 125 \mu\text{m} < G2 < 250 \mu\text{m} < G3 < 500 \mu\text{m} < G4 < 710 \mu\text{m}$ . Chitosan gel beads were prepared according to a method which was previously described [10,14]. A chitosan solution prepared by dissolving chitosan flakes in an acetic acid solution (4% w/w) was distributed dropwise into an alkaline (NaOH, 2.5 M) solution using a peristaltic pump through a hypodermic nozzle. The size of the beads may be controlled by blowing air at the base of the nozzle in order to force the bead to fall down into the coagulating bath before it reaches its critical volume and weight. The size of the beads was B1: 0.95 mm, B2: 1.6 mm (results not shown) and B3: 2.75 mm [10]. The dry weight percentage was  $5.2 \pm 0.2\%$ .

The crosslinking was performed by mixing a known amount of chitosan with aqueous glutaraldehyde solutions: the molar ratio between amine groups of chitosan and glutaraldehyde was fixed at 1:2. The large molar excess of glutaraldehyde induces a strong reaction of amine moieties with aldehyde ends. With such a large molar excess of glutaraldehyde, a complete saturation of amine groups is suspected.

Cadmium was used in its  $\text{CdCl}_2$  form and was purchased from Merck (Germany), phosphoric acid (for buffer solutions) was supplied by Mallinckrodt (USA), sodium hydroxide solutions were from Industrial KEM de Leon (Mexico). Solutions were prepared by dissolving cadmium chloride in phosphate-buffered solutions at pH 7 (unless specified) prepared from phosphoric acid and sodium hydrox-

ide concentrated solutions: the buffer concentration was 0.1 M in the solutions.

## 2.2. Sorption experiments

The study of the influence of pH was performed by adding 50 mg of chitosan (dry weight) to 50 mL of cadmium solution (initial concentration: 10 mg L<sup>-1</sup>) for 24 h using a Variomag magnetic agitator HD. The pH was regularly controlled and adjusted to the fixed pH value adding microvolumes of either phosphoric acid or sodium hydroxide. Unless specified, experiments were performed at 25°C, using a thermostatically controlled water bath (VWR Scientific 1166). When relevant, the temperature was controlled to 10°C and 40°C. The influence of the temperature and the agitation speed (60, 200 and 340 rpm, controlled by a Caframo Wiarion equipment, Ont.) on sorption kinetics was analyzed by mixing 500 mg of sorbent with 500 mL of a metal ion solution containing cadmium (initial concentration: 10 mg L<sup>-1</sup>) at pH 7 (in a phosphate buffer, 0.1 M). Samples were regularly collected, filtered and analyzed for cadmium content using an Atomic Absorption Spectrometer (AAS Perkin Elmer 3110, wavelength: 288.8 nm, slit width: 0.7).

Sorption isotherms were obtained by mixing varying volumes of cadmium solutions (buffered at pH 7 with a 0.1 molar phosphate buffer, initial concentration: 20 mg L<sup>-1</sup>) with varying amounts of sorbent for 24 h on a reciprocal shaker (Cole Parmer 51502). After reaching the equilibrium, samples were filtered and analyzed for cadmium content using the AAS. The cadmium concentration in the sorbent was determined by mass balance between liquid and solid phases.

## 2.3. SEM-EDAX analysis

These experiments were performed on chitosan gel beads (diameter 2.75 mm) using a buffered cadmium solution ( $C_0$ : 20 mg L<sup>-1</sup>) at pH 7 with phosphate buffer and a sorbent dosage of 26 mg L<sup>-1</sup> (dry weight) or 500 mg L<sup>-1</sup> (wet weight). The preparation of the samples included drying them, embedding the sorbent, polishing and coating the sections, and further analysis using a scanning electron microscope. Samples were dried using a solvent

exchange procedure (samples were contacted with several solvent mixtures: ethanol/water followed by ethanol/ethanol:propylene oxide with increasing percentages of ethanol and propylene oxide, respectively).

The embedding of the samples was performed using a Resicrom resin (Fibras y Resinas de Irapuato Mexico): samples were mixed with increasing percentages of embedding resin in the mixture resin/propylene oxide. Then, the mixture (resin + sample) was polymerized at 60°C for 72 h.

The sections were polished with several abrasive silica discs of decreasing grain size (Buehler No. 600 and 240), alumina pulp 1–0.3 and 0.05 μm (Buehler Micropolish) and a diamond pulp (1/4 μm Buehler Metadi II). The carbon coating was performed with a Cold Sputter Each Unit Carbon Evaporation Accessory (Denton Vacuum DESK II).

The SEM-EDAX analyses were performed on a LEICA S-420 s with an X-ray Dispersive Micro-Analyzer Kevex Superdry (FISONS) with an accelerating voltage of 25 kV. The growing power was 150 X and the current intensity was 268.1 nA. The L<sub>α2</sub> and L<sub>β1</sub> bands of cadmium were detected at 3.2 and 3.8 keV, respectively: the L<sub>α2</sub> band was used for cadmium quantitative analysis.

## 2.4. Modeling of sorption kinetics

Sorption kinetics may be controlled by several processes including diffusion steps: (i) bulk diffusion, (ii) film diffusion, and (iii) intraparticle diffusion. The adsorption reaction and the bulk diffusion are usually considered instantaneous, and sorption kinetics is controlled by either external or intraparticle diffusion or by both diffusion mechanisms at the same time [21]. In this study, the diffusion mechanisms were considered independently in accordance with the assumptions that (i) kinetics is controlled by external diffusion at the beginning of the experiment (within the first 15–20 min) and (ii) then controlled by intraparticle diffusion.

The external diffusion is modeled using the simplified approach described by Findon et al. [22] and McKay et al. [23] who assumes that, at early times of contact, the concentration at the sorbent surface tends to zero and the intraparticle diffusion is negligible.

Thus, the following equation describes external diffusion:

$$\ln \frac{C(t)}{C_0} = -k_f \frac{A}{V} t \quad (1)$$

By plotting  $\ln C(t)/C_0$  against  $t$  (min), the initial external mass transfer coefficient,  $k_f$  ( $\text{m min}^{-1}$ ) may be determined.  $C(t)$  is the solution concentration,  $C_0$  the initial sorbate concentration ( $\text{mg L}^{-1}$ ),  $A$  the sorbent exchange surface ( $\text{m}^2$ ), and  $V$  the volume of solution (L). In standard kinetic experimental conditions,  $A/V$  equals 81.4, 27.1, 13.6, 8.4, 123.8 and  $42.8 \text{ m}^{-1}$  for G1, G2, G3, G4, B1 and B3, respectively, using the following equation:

$$\frac{A}{V} = \frac{6m}{d\rho_a} \quad (2)$$

where  $m$  is the sorbent dosage ( $\text{kg m}^{-3}$ ),  $d$  is the mean particle diameter (m),  $\rho_a$  the apparent density of the sorbent ( $\text{kg m}^{-3}$ ), 1180 and  $1050 \text{ kg m}^{-3}$  for flakes and beads, respectively.

Crank has proposed a model whereby diffusion is controlled only by intraparticle mass transfer for well-stirred solution of limited volume ( $V$ ), assuming the solute concentration is always uniform (initially  $C_0$ ), and the sorbent sphere free from solute [24]. In these conditions, the total amount of solute  $M_t$  ( $\text{mg g}^{-1}$ ) in a spherical particle after time  $t$ , expressed as a fraction of the corresponding quantity after infinite time ( $M_{\text{infin}}$ ,  $\text{mg g}^{-1}$ ) is given by:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)\exp(-Dq_n^2 t/d^2)}{9+9\alpha+q_n^2\alpha^2} \quad (3)$$

where  $D$  is the intraparticle diffusion coefficient ( $\text{m}^2 \text{ min}^{-1}$ ). The fractional approach to equilibrium, FATE, may be used to estimate  $D$ , when the external diffusion coefficient is neglected.  $\alpha$  is the effective volume ratio, expressed as a function of the equilibrium partition coefficient (solid/liquid concentration ratio) and is obtained by the ratio  $C_\infty/(C_0 - C_\infty)$ .  $q_n$  represents the non-zero solutions of equations:

$$\tan q_n = \frac{3q_n}{3+\alpha q_n^2} \quad \text{and} \quad \frac{M_\infty}{VC_0} = \frac{1}{1+\alpha} \quad (4)$$

The infinite sum terms are summed until the summation does not vary. In this study, Eq. (3) was

used to determine the overall intraparticle diffusivity, which best fit the experimental data. A trial and error procedure (on intraparticle diffusion coefficient) was adopted by minimizing the sum of the square of the differences between experimental results and calculated data.

The surface diffusion modified Biot number,  $Bi_s$ , has been defined to give a criterion for the predominance of surface diffusion against external diffusion [26]:

$$Bi_s = \frac{k_f d C_0}{2\rho_a D_s q_0} \quad (5)$$

where  $C_0$  is the initial concentration and  $q_0$  the solid phase concentration in the sorbent in equilibrium with a residual hypothetical liquid concentration  $C_{\text{eq}} = C_0$ . External diffusion predominates when  $Bi_s \ll 1$ , while surface diffusion controls diffusion when  $Bi_s \gg 1$ .

### 3. Results and discussion

#### 3.1. Influence of pH

Fig. 1 shows the influence of pH on the sorption of cadmium using chitosan gel beads for pH ranging between 4 and 7. Sorption efficiency increased with increasing the pH of the solution. In acidic solutions, a strong competition existed between cadmium ions and protons for sorption sites and the sorption efficiency was decreased. Moreover, the protonation of

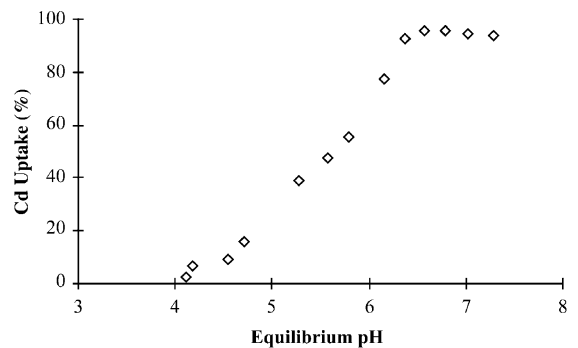


Fig. 1. Influence of pH on cadmium sorption using chitosan gel beads B1 ( $C_0$ :  $10 \text{ mg L}^{-1}$ ; sorbent dosage:  $1 \text{ g L}^{-1}$ , temperature:  $25^\circ\text{C}$ ).

amine groups induced an electrostatic repulsion of cadmium cations. The degree of protonation of the amine groups depends on both the degree of acetylation and the  $pK_a$  of chitosan [7]. Jha et al. [12] established that the zero point of charge ( $pH_{zpc}$ ) for chitosan is about 8.6. Though this zero point of charge depends on the characteristics of the polymer (degree of dissociation of amine groups, degree of deacetylation), this information indicates that the polymer conserves its cationic behaviour in the pH range investigated in this study. When the pH of the solution increased, the competitor effect decreased as well as the electrostatic repulsion. Kawamura et al. [25] obtained a similar trend but with an increase in sorption efficiency beginning at a lower pH (around pH 4). The differences may be explained by the different sorbents used: in their study polyethyleneimine was grafted on the chitosan backbone and the coexistence of several kinds of amine (primary, secondary, and tertiary) may affect the influence of the pH on the sorption. Similarly, Jha et al. [12] showed that the sorption increased strongly above pH 4 but their work was performed with a large excess of sorbent with a low concentration of cadmium. It is difficult to compare the results: chitosan characteristics were not given, especially the percentage of deacetylation. Taking into account the possible occurrence of precipitation mechanisms above pH 7, the optimum pH for cadmium appeared at pH 7, the pH level that was used for further studies (blank experiments showed that precipitation did not occur in the selected concentration range).

### 3.2. Influence of agitation speed

Fig. 2 shows that for both flakes and gel beads, cadmium sorption was independent of the agitation speed in the range 60–340 rpm. The impeller Reynolds number,  $N_{Re}$ , was found at 2400, 8000 and 13,600, for 60, 200 and 340 rpm agitation velocities,  $N$ , respectively using the following equation:

$$N_{Re} = \frac{D_a^2 N \rho}{\mu} \quad (6)$$

where  $\rho$  and  $\mu$  are the fluid density ( $\text{kg m}^{-3}$ ) and viscosity (Pa s), respectively.  $D_a$  is the impeller diameter (m). At high agitation speed (and high

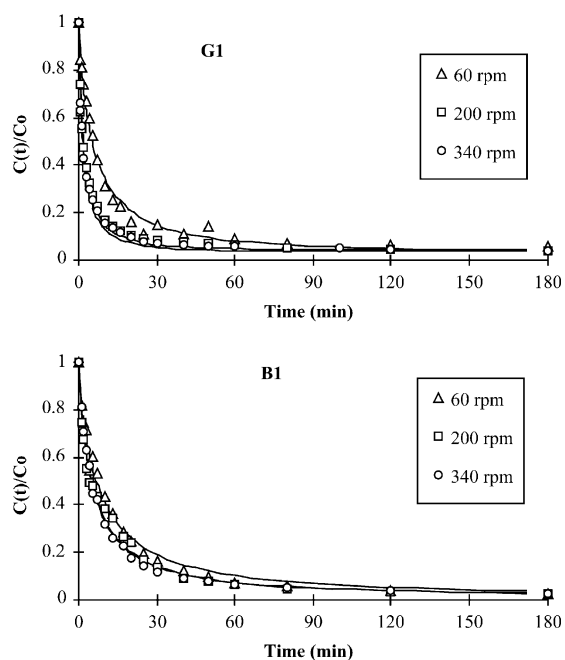


Fig. 2. Influence of agitation speed on cadmium sorption kinetics using chitosan flakes G1 and gel beads B1 ( $C_0$ :  $10 \text{ mg L}^{-1}$ ; sorbent dosage:  $1 \text{ g L}^{-1}$ ; temperature:  $25^\circ\text{C}$ ; pH 7).

Reynolds number), the flow is turbulent everywhere in the reactor ( $N_{Re} > 10,000$ ), while for lower Reynolds number ( $10 < N_{Re} < 10,000$ ), both turbulent and laminar flows may exist in the reactor.

This result contrasts with that cited by Findon et al. [22] on copper sorption on chitosan for which increasing the agitation speed significantly increased the sorption rate. Table 1 summarizes the diffusion coefficients obtained using Eqs. (1) and (3) for selected experimental conditions. The external diffusion coefficient was hardly changed by the agitation speed and varied between  $1.7 \times 10^{-5}$  and  $2.5 \times 10^{-5} \text{ m s}^{-1}$  for flakes G1, and between  $0.8 \times 10^{-5}$  and  $1 \times 10^{-5} \text{ m s}^{-1}$  for gel beads B1. The intraparticle diffusion coefficients varied between  $0.1 \times 10^{-12}$  and  $0.4 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  for flakes G1 and between  $8 \times 10^{-12}$  and  $15 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  for gel beads B1 in such experimental conditions. The Biot number was slightly lower to 1 for flakes (between 0.07 and 0.24) and beads (between 0.3 and 0.6). It is thus possible to conclude that both external and intraparticle diffusion mechanisms controlled sorption kinet-

Table 1

Influence of experimental conditions on diffusion coefficients for cadmium sorption on chitosan flakes (F) and beads (B) (raw materials—without glutaraldehyde crosslinking)

Condition	Size ( $\mu\text{m}$ )	Speed (rpm)	$T$ ( $^{\circ}\text{C}$ )	$k_f \cdot 10^5$ ( $\text{m s}^{-1}$ )	$R^2$	$D_s \cdot 10^{12}$ ( $\text{m}^2 \text{s}^{-1}$ )	MSR	$Bi_s$
F	G1: 0–125	200	25	1.83	0.887	0.393	0.0218	0.07
F	G2: 125–250	200	25	3.44	0.985	0.560	0.0154	0.46
F	G3: 250–500	200	25	4.68	0.982	0.842	0.0044	1.15
F	G4: 500–710	200	25	5.34	0.966	1.69	0.0118	1.05
F	G4: 500–710	200	10	3.93	0.977	0.740	0.0068	1.76
F	G4: 500–710	200	40	5.56	0.965	7.72	0.0092	0.24
F	G1: 0–125	60	25	1.74	0.984	0.108	0.0215	0.24
F	G1: 0–125	340	25	2.50	0.868	0.393	0.0298	0.09
B	B1: 950	200	10	0.86	0.988	5.32	0.0420	1.01
B	B1: 950	200	25	0.78	0.955	14.6	0.0231	0.34
B	B1: 950	200	40	0.86	0.945	55.37	0.0128	0.10
B	B1: 950	60	25	0.79	0.975	7.965	0.0250	0.62
B	B1: 950	340	25	0.93	0.956	12.48	0.0152	0.47
B	B3: 2750	200	10	0.96	0.986	26.93	0.0053	0.78
B	B3: 2750	200	25	0.84	0.989	22.17	0.0055	0.83
B	B3: 2750	200	40	0.94	0.985	99.03	0.0114	0.20

MSR is the mean square deviation obtained from 
$$\left[ \frac{\sum_{i=1}^n [(X_{\text{exp},i} - X_{\text{calc},i})^2]}{n} \right]^{1/2}$$
.

ics. The equilibrium seemed to be attained within the first 5 h, so the sorption mechanism appeared significantly faster than for the sorption of other metal ions [10,22,23].

### 3.3. Influence of temperature

Fig. 3 shows the sorption kinetics obtained at differing temperatures with both flakes and chitosan gel beads. With chitosan flakes, at equilibrium the residual concentration was the same at  $10^{\circ}\text{C}$  and  $25^{\circ}\text{C}$ , and significantly lower than that at  $40^{\circ}\text{C}$ . The kinetic curves were also slightly different: sorption was faster at  $25^{\circ}\text{C}$ , with a stronger initial decrease in the relative concentration, than at  $10^{\circ}\text{C}$  and  $40^{\circ}\text{C}$ .

However, the curve obtained at  $10^{\circ}\text{C}$  was significantly different than the trend followed by the other curves: the initial sorption rate appeared to be the lowest, but the second step in the sorption process was faster and made it possible to reach the same equilibrium as at  $25^{\circ}\text{C}$ . Considering the fractional approach to equilibrium, it also appeared that the curves at  $25^{\circ}\text{C}$  and  $40^{\circ}\text{C}$  overlapped while the curve at  $10^{\circ}\text{C}$  was significantly different (not shown). This representation of the kinetic curves allowed the ki-

netics to be compared while minimizing the effect of the differences in the equilibrium metal uptake. With chitosan gel beads the differences were less marked than with flakes. Though the kinetics obtained at  $40^{\circ}\text{C}$  was slightly worse than at  $10^{\circ}\text{C}$  and  $25^{\circ}\text{C}$ , the curves drawn using the fractional approach to equilibrium were perfectly overlapped indicating that sorption kinetics is not significantly influenced by temperature. This conclusion was confirmed by the order of magnitude in the intraparticle diffusion coefficients obtained with the selected experimental conditions ( $0.7\text{--}8 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  for the flakes;  $5\text{--}55 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  for beads B1 and  $22\text{--}100 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  for beads B3). These results showed that intraparticle diffusivity increased with the temperature, while the external diffusion was hardly changed: it varied from  $4 \times 10^{-5}$  to  $5.6 \times 10^{-5} \text{ m s}^{-1}$  for flakes G4 and from  $0.8 \times 10^{-5}$  to  $1 \times 10^{-5} \text{ m s}^{-1}$  for gel beads B1 and B3.

The weak effect of this parameter on kinetic curves did not deserve the study of its influence on sorption isotherms. Several studies had previously shown that the differences were not very marked for usual temperatures (in the range  $5\text{--}55^{\circ}\text{C}$ ) for copper, zinc or mercury sorption [27]. Yang and Zall [28]

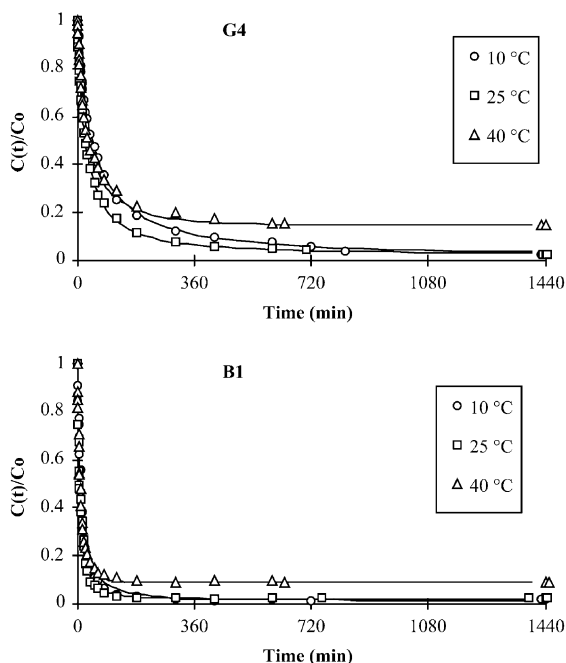


Fig. 3. Influence of temperature on cadmium sorption kinetics using chitosan flakes G4 and gel beads B1 ( $C_0$ :  $10 \text{ mg L}^{-1}$ ; sorbent dosage:  $1 \text{ g L}^{-1}$ ; pH 7; agitation speed: 200 rpm).

obtained a low apparent activity energy for the adsorption of copper on chitosan (about  $400 \text{ cal mol}^{-1}$ ), lower than that obtained by McKay et al. [27]. The endo- or exo-thermal type of sorption depended on the metal [27], but the enthalpy was not very strong in comparison to other sorbent/sorbate systems [26].

### 3.4. Influence of sorbent particle size on sorption kinetics

The particle size and the conditioning of the sorbent have been shown to control sorption performance for chitosan and derivatives [10,18,29]. The influence of these parameters was attributed to diffusion restrictions due to (a) the low porosity of the raw material, and (b) the crystallinity of the material [9,20,30]. To avoid such limiting effects the raw material can be modified (a) through a dissolving/precipitation procedure in order to reduce the crystallinity of the biopolymer, or through (b) the production of chitosan gels [10,14,25]. An increase in the accessibility to internal sites is expected because

of the formation of the gel (as the result of the expansion of the polymer network).

Fig. 4 presents the influence of the particle size on cadmium sorption on chitosan flakes. As expected, increasing the size of the sorbent increased the time required to reach equilibrium. However, the differences were not as marked as they were with some chitosan derivatives [10]. The diffusion coefficient increased with the diameter of the sorbent, but it remained between  $0.4 \times 10^{-12}$  and  $1.7 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ . The external diffusion coefficient also increased with particle size, varying between  $1.8 \times 10^{-5}$  and  $5.4 \times 10^{-5} \text{ m s}^{-1}$ .

Fig. 5 shows the influence of the beads size on the sorption of cadmium. In this case, increasing the size of the beads resulted in an increase in the time required to reach equilibrium. This figure also compares the kinetics for beads with that obtained with the largest flakes. It appeared that cadmium sorption kinetics was comparable for flakes whose diameters ranged between 500 and 710  $\mu\text{m}$  and gel beads B3 with a diameter of 2.75 mm. The external diffusion

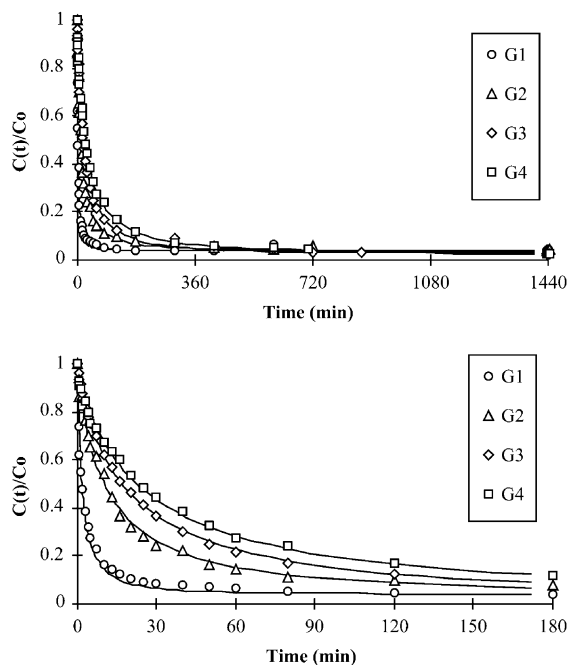


Fig. 4. Influence of particle size on cadmium sorption kinetics using chitosan flakes ( $C_0$ :  $10 \text{ mg L}^{-1}$ ; sorbent dosage:  $1 \text{ g L}^{-1}$ ; temperature:  $25^\circ\text{C}$ ; agitation speed: 200 rpm; pH 7).



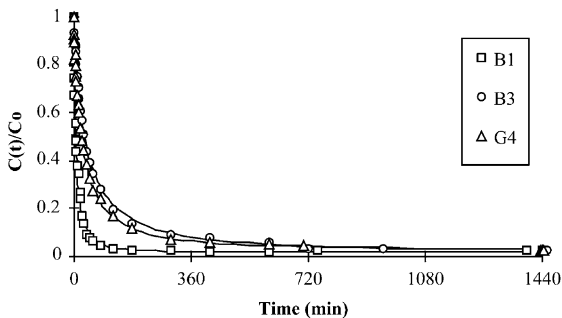


Fig. 5. Influence of chitosan conditioning on cadmium sorption kinetics ( $C_0$ :  $10 \text{ mg L}^{-1}$ ; sorbent dosage:  $1 \text{ g L}^{-1}$ , temperature:  $25^\circ\text{C}$ ; pH 7).

coefficient was hardly influenced by their size, and the coefficients ranged between  $0.8 \times 10^{-5}$  and  $1 \times 10^{-5} \text{ m s}^{-1}$ . The intraparticle diffusion coefficient was more significantly changed by an increase in the particle size: when the particle size was increased from 0.95 to 2.75 mm the intraparticle diffusivity was multiplied by 2–5 depending on the experimental temperature. It was about 1 order of magnitude higher (or more) than the diffusion coefficients obtained with flakes. The expansion of the polymer network increased the accessibility to internal sites and the sorption rates. However, the diffusion coefficient remained several orders of magnitude lower than the molecular diffusivity of cadmium in water ( $7.19 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) [31].

### 3.5. Influence of sorbent particle size on sorption isotherms

Sorption isotherms may be affected by particle size, especially in the case of the sorption of large molecules on compact sorbents characterized by low porosity. In this case, the sorption is restricted to the external layers of the sorbent [29]. In the case of several metal ions such as copper, zinc or mercury, McKay et al. [27] had shown that this parameter did not control the sorption equilibrium. A contrary trend has been observed in the case of cadmium (Fig. 6). It was possible to see that sorption levels were comparable for flakes G1 and beads B1, for B3 they were intermediary between flakes G1 and G2. For the largest flake particles, the decrease in sorption capacities was significant. However, the conclusion may

be moderated taking into account the possible occurrence of diffusion restrictions. Experiments performed on cadmium sorption kinetics with flakes of different diameter had shown that with high sorbent dosage and low cadmium concentration the equilibrium concentration was not affected by the size of the sorbent and that the time required to reach the equilibrium decreased as the diameter of sorbent particle decreased. However, in more unfavorable conditions such as low sorbent dosage and higher metal concentration, a greater effect of diffusion is expected as observed with other metal ions: molybdate, vanadate, and uranium [10,29]. In such conditions, which correspond to the sorption isotherm experiments, the time required to reach the equilibrium should be increased and the influence of particle size is expected to be less pronounced. Jha et al. [12] found a similar link between sorption capacity and particle size; however, they also worked with a large molar excess of sorbent and at low cadmium concentration with a short contact time (about 24 h).

Glutaraldehyde crosslinking strongly reduced cadmium sorption (not shown), the chemical reaction between aldehyde and amine groups diminished the availability of chelating sites. For chitosan flakes the sorption capacity was decreased to 0, and for gel beads it did not exceed  $0.2 \text{ mg g}^{-1}$ . While gel bead conditioning strongly decreased the influence of crosslinking treatment for molybdate sorption, in the case of cadmium this physical modification hardly changed sorption behaviour. The difference may be explained by the difference in the sorption mechanism (ion exchange for molybdate vs. chelation for cadmium).

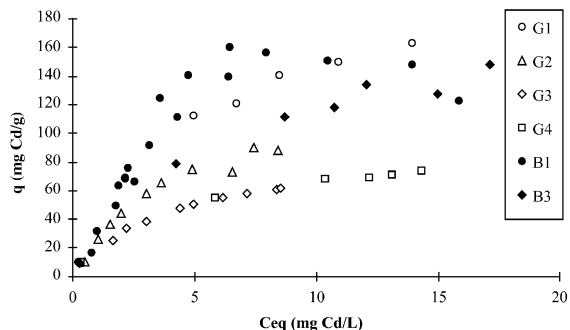


Fig. 6. Influence of particle size and chitosan conditioning on cadmium sorption isotherms (temperature:  $25^\circ\text{C}$ ; pH 7).

### 3.6. SEM-EDAX study of sorption

Fig. 7 shows the diffusion profiles of cadmium in chitosan gel beads (diameter: 2.75 mm) at three selected times of contact: 1, 4 and 24 h. Cadmium diffusion appears both on SEM images (a clear external ring represents the diffusion of cadmium in the external layers) and micro-analysis profiles. After 1 h of contact, a very thin external layer seemed to be partially loaded with cadmium, after 4 h of contact the diffusion thickness increased, a gradient appeared but the intensity of the signal did not reach the maximum level reached after 24 h. At equilibrium, the intensity was maximum, and it was not

possible to detect a gradient between the external layers and the center of the particle: the distribution of cadmium across the particle was homogeneous. This result contrasts with previous results obtained on uranium sorption using chitosan flakes for which the sorption was located in the outer layers of the sorbent [29], but similar observations were recently made with mercury sorption on polyaminated chitosan beads [32] and with platinum sorption on modified chitosan [33]. The differences in the behaviour of these metals for sorption on chitosan derivatives may be attributed to the differences in their chemical speciation in solution. In the experimental conditions selected in these studies, uranium was present under

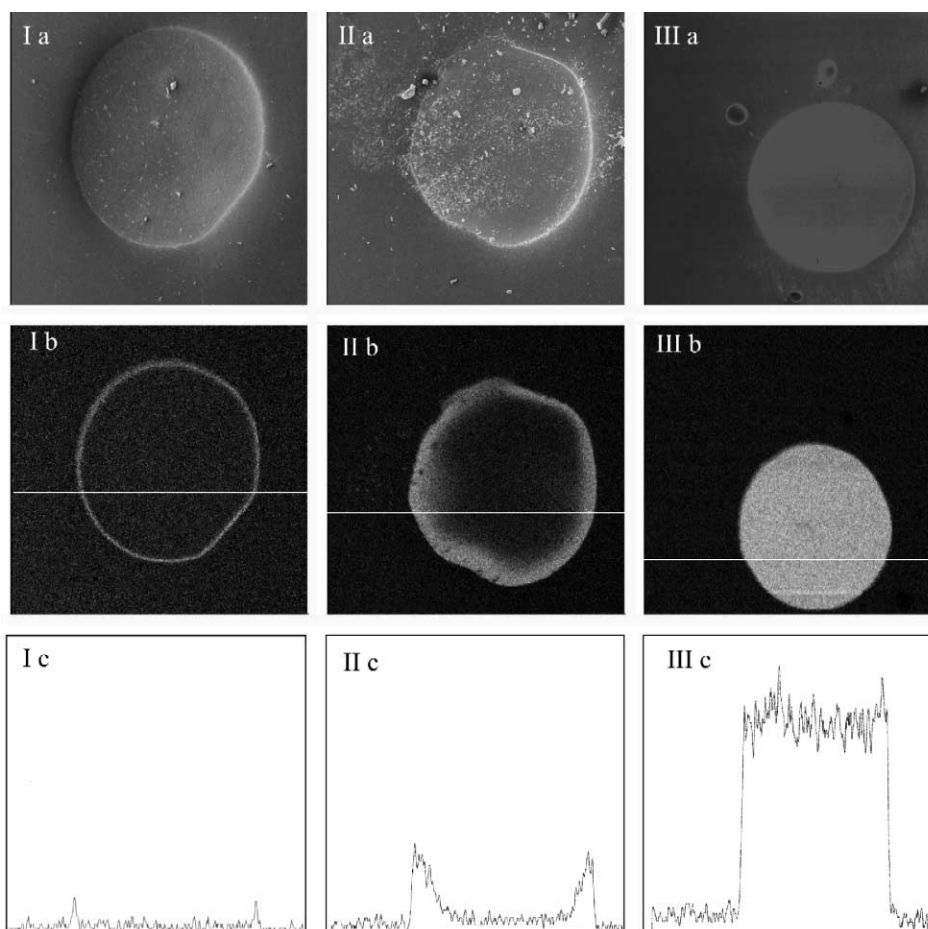


Fig. 7. SEM-EDAX analysis of cadmium sorption kinetics using chitosan gel beads B3—Contact time: 1 h (I), 4 h (II), and 24 h (III)—Secondary electron images ( $150\times$ ) (a), cartography of Cd (b), and distribution of Cd along a cross-section of the particle (c) ( $C_0$ :  $20\text{ mg L}^{-1}$ ; sorbent dosage:  $25\text{ mg L}^{-1}$ , temperature:  $25^\circ\text{C}$ , agitation speed: 200 rpm, pH 7).

polynuclear hydrolyzed species of large ionic size, while the other metal ions (mercuric ions, hexachloroplatinate anions) are mononuclear species whose diffusion was less sterically hindered.

#### 4. Conclusion

Chitosan is very effective at removing cadmium with sorption capacity exceeding  $150 \text{ mg g}^{-1}$  (about  $1.5 \text{ mmol g}^{-1}$ ). Sorption equilibrium and kinetics are hardly affected by temperature in the range  $10\text{--}40^\circ\text{C}$  or agitation speed ( $60\text{--}340 \text{ rpm}$ ;  $N_{Re}$ :  $2400\text{--}13,600$ ). Sorption capacities decrease as particle size increases. Although decreasing the particle size of the sorbent makes it possible to reduce the time required to reach equilibrium, it changes the external and intraparticle diffusion coefficients by less than one order of magnitude. The external mass transfer coefficient ranges between  $0.8 \times 10^{-5}$  and  $5.6 \times 10^{-5} \text{ m s}^{-1}$  under selected experimental conditions. For chitosan flakes, the intraparticle diffusivities range between  $0.1 \times 10^{-12}$  and  $7.7 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ , while for chitosan beads it increases from  $5 \times 10^{-12}$  to  $10^{-10} \text{ m}^2 \text{ s}^{-1}$ . Glutaraldehyde crosslinking diminishes the availability of chelating sites resulting in a strong reduction in cadmium sorption capacity. SEM-EDAX analyses confirm the sorption of cadmium occurs in the whole mass of the sorbent, and that intraparticle diffusion has a significant influence on kinetic control.

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#### References

- [1] C.S. Brooks, *Metal Recovery from Industrial Wastes*. Lewis Publishers, Chelsea, MI, 1991.
- [2] P.R. Puranik, J.M. Modak, K.M. Paknikar, A comparative study of the mass transfer kinetics of metal biosorption by microbial biomass. *Hydrometallurgy* 52 (1999) 189–197.
- [3] A.K. Bhattacharya, C. Venkobachar, Removal of cadmium(II) by low cost adsorbents. *J. Environ. Eng.* 110 (1984) 110–122.
- [4] G.A.F. Roberts, *Chitin Chemistry*. MacMillan, London, 1992.
- [5] R.A.A. Muzzarelli, F. Tanfani, *N-(o-carboxybenzyl)chitosan, N-carboxymethyl chitosan and dithiocarbamate chitosan: new chelating derivatives of chitosan*. *Pure Appl. Chem.* 54 (1982) 2141–2150.
- [6] K. Inoue, Y. Baba, K. Yoshizuka, Adsorption of metal ions on chitosan and crosslinked copper(II)-complexed chitosan. *Bull. Chem. Soc. Jpn.* 66 (1993) 2915–2921.
- [7] A. Domard, pH and C.D. measurements on a fully deacetylated chitosan: application to Cu(II)polymer interactions. *Int. J. Biol. Macromol.* 9 (1987) 98–104.
- [8] E. Guibal, C. Milot, J. Roussy, Influence of hydrolysis mechanisms on molybdate sorption isotherms using chitosan. *Sep. Sci. Technol.* 35 (2000) 1021–1038.
- [9] E. Piron, A. Domard, Interaction between chitosan and uranyl ions: Part 1. Role of physicochemical parameters. *Int. J. Biol. Macromol.* 21 (1997) 327–335.
- [10] E. Guibal, C. Milot, J.M. Tobin, Metal–anion sorption by chitosan beads: equilibrium and kinetic studies. *Ind. Eng. Chem. Res.* 37 (1998) 1454–1463.
- [11] R.-S. Juang, C.-Y. Ju, Kinetics of sorption of Cu(II)-ethylenediaminetetraacetic acid chelated anions onto cross-linked polyaminated chitosan beads. *Ind. Eng. Chem. Res.* 37 (1998) 3463–3469.
- [12] I.N. Jha, L. Iyengar, A.V.S. Prabhakara Rao, Removal of cadmium using chitosan. *J. Environ. Eng.* 114 (1988) 962–974.
- [13] M. Gonzalez-Davila, J.M. Santana-Casiano, F.J. Millero, The adsorption of Cd(II) and Pb(II) to chitin in Seawater. *J. Colloid Interface Sci.* 137 (1990) 102–110.
- [14] G.L. Rorrer, T.-Y. Hsien, J.D. Way, Synthesis of porous-magnetic chitosan beads for removal of cadmium ions from waste water. *Ind. Eng. Chem. Res.* 32 (1993) 2170–2178.
- [15] M. Weltrowski, B. Martel, M. Morcellet, Chitosan *N*-benzyl sulfonate derivatives as sorbents for removal of metal ions in an acidic medium. *J. Appl. Polym. Sci.* 59 (1996) 647–654.
- [16] K. Inoue, H. Hirakawa, Y. Ishikawa, T. Yamaguchi, J. Nagata, K. Ohto, K. Yoshizuka, Adsorption of metal ions on gallium(III)-templated oxine type of chemically modified chitosan. *Sep. Sci. Technol.* 31 (1996) 2273–2285.
- [17] W. Kaminski, Z. Modrzejewska, Application of chitosan membranes in separation of heavy metal ions. *Sep. Sci. Technol.* 32 (1997) 2659–2668.
- [18] E. Guibal, A. Larkin, T. Vincent, J.M. Tobin, Chitosan sorbents for platinum sorption from dilute solutions. *Ind. Eng. Chem. Res.* 38 (1999) 401–412.
- [19] T.-Y. Hsien, G.L. Rorrer, Heterogeneous cross-linking of

- chitosan gel beads: kinetics, modeling, and influence on cadmium ion adsorption capacity. *Ind. Eng. Chem. Res.* 36 (1997) 3631–3638.
- [20] E. Piron, M. Accominotti, A. Domard, Interaction between chitosan and uranyl ions. role of physical and physico-chemical parameters on the kinetics of sorption. *Langmuir* 13 (1997) 1653–1658.
- [21] C. Tien, *Adsorption Calculations and Modeling*. Butterworth Heinemann, Newton, MA, 1994, 244 pp.
- [22] A. Findon, G. McKay, H.S. Blair, Transport studies for the sorption of copper ions by chitosan. *J. Environ. Sci. Health, Part A* 28 (1993) 173–185.
- [23] G. McKay, H.S. Blair, A. Findon, Sorption of metal ions by chitosan. in: H. Eccles, S. Hunt (Eds.), *Immobilisation of Ions by Bio-Sorption*. Ellis Horwood, Chichester, UK, 1986, pp. 59–69.
- [24] J. Crank, *The Mathematics of Diffusion*. 2nd edn., Oxford Univ. Press, Oxford, UK, 1975, 414 pp.
- [25] Y. Kawamura, M. Mitsuhashi, H. Tanibe, H. Yoshida, Adsorption of metal ions on polyaminated highly porous chitosan chelating resin. *Ind. Eng. Chem. Res.* 32 (1993) 386–391.
- [26] W.J. Weber Jr., F.A. DiGiano, *Process Dynamics in Environmental Systems*. Wiley, New York, 1995, 943 pp.
- [27] G. McKay, H.S. Blair, A. Findon, Equilibrium studies for the sorption of metal ions onto chitosan. *Ind. J. Chem.* 28A (1989) 356–360.
- [28] T.C. Yang, R.R. Zall, Absorption of metals by natural polymers generated from seafood processing wastes. *Ind. Eng. Chem. Prod. Res. Dev.* 23 (1984) 168–172.
- [29] E. Guibal, M. Jansson-Charrier, I. Saucedo, P. Le Cloirec, Enhancement of sorption performances of chitosan: effect of the structure on the diffusion properties. *Langmuir* 11 (1995) 591–598.
- [30] Y. Koyama, A. Taniguchi, Studies on chitin: X. Homogeneous cross-linking of chitosan for enhanced cupric ion adsorption. *J. Appl. Polym. Sci.* 31 (1986) 1951–1954.
- [31] Y. Marcus, *Ion Properties*. Marcel Dekker, New York, 1997 259 pp.
- [32] Y. Kawamura, H. Yoshida, S. Asai, H. Tanibe, Breakthrough curve for adsorption of mercury(II) on polyaminated highly porous chitosan beads. *Water Sci. Technol.* 35 (1997) 97–105.
- [33] E. Guibal, T. Vincent, R. Navarro-Mendoza, Synthesis and characterization of a thiourea-derivative of chitosan for platinum recovery. *J. Appl. Polym. Sci.* 75 (2000) 119–134.