Uranium sorption by glutamate glucan: A modified chitosan Part II: Kinetic studies

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Abstract

The kinetics of uranium sorption by glutamate glucan, a modified chitosan polymer, were studied. The effects of the particle size of sorbent, pH, metal concentration, temperature and agitation were investigated. Diffusion mechanisms were predominant in rate-controlling steps: external mass transfer seemed to have a restricted effect on kinetic behaviour, on the other hand intraparticle diffusion was the main resistance model. Metal concentration, pH and particle size of the polymer were the major parameters, showing a great effect on the rate ratio of the intraparticle diffusion model and on diffusion coefficient D'_i, whose value varied between 1,5 and 36 x 10^{-12} m^2/min.

Introduction

Many studies have been done in the last 20 years concerning the treatment of waste water with a low metal content. Various mechanisms, including biological techniques, were investigated with the aim of treating heavy metals in solution: the use of adsorbents of biological origin, and particularly fungal biomass, demonstrates good efficiency in this field (Tsezos and Volesky, 1981). The large amount of chitin and chitosan in the cell walls of these fungi and the exclusive sorption of metal in this part of micro-organisms, suggested that these natural polymers are efficient in metal uptake (Guibal, 1990). Nowadays many studies deal with chitin and chitosan in metal removal (Muzzarelli and Zattoni, 1986, Eiden et al., 1980). The modification of these polymers (Muzzarelli et al., 1984; Muzzarelli et al., 1985) improves the efficiency of these materials in waste-water treatment, regarding sorption performances and facility of application. Various processes are possible for the modification of chitosan structure (Nishi et al., 1986;1987), Muzzarelli and co-workers (1984) proposed a simple method of synthesis of organic acid-chitosan polymers. A previous paper on this issue (Saucedo et al., 1993), used this technique to synthetise a glutamate glucan polymer and to study its properties in the uptake of uranium, and the effect of various parameters on sorption capacity was investigated. Sorption kinetics, thus, constitute a major criterion in the determination of the interest of sorption processes. The purpose of this research was to study the kinetic controlling mechanisms: a resistance external mass transfer model and a resistance intraparticle diffusion model. These models were examined according to the main sorption parameters such as temperature, agitation speed, metal concentration, pH and particle size of adsorbent.

Theory

The kinetics can be controlled by various mechanisms and steps in adsorption phenomena. Four major rate-limiting steps are generally cited:

- Mass transfer of solute from solution to the boundary film
- Mass transfer of metal ions from boundary film to polymer surface
- Sorption of ions onto sites
- Internal diffusion of solute.

The third step is assumed to be very rapid and non-limiting in this kinetic analysis: sorption is a rapid phenomenon. The first and the second steps are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. The fourth one is an intraparticle diffusion resistance step.

Approach of models

The main parameters influencing metal sorption were investigated: particle size of sorbent, agitation speed, pH and metal concentration, and temperature. Each of these parameters was studied beyond the range of the 2 major resistance models: external mass transfer resistance, and intraparticle diffusion resistance, which are briefly described in this paper.

External mass transfer resistance model

The model used to calculate the external mass transfer rate is described by the following equation:

$$\frac{dC_t}{dt} = -\beta_L S (C_t - C_s) \tag{1}$$

where β_L is the external mass transfer coefficient and S the specific surface. According to complementary hypotheses such as a surface concentration of solute on the sorbent ($C_s \rightarrow 0$) negligible at time t=0, and the intraparticle diffusion rate also negligible (McKay and Poots, 1980, McKay et al., 1986), Eq. (1) can be simplified to:

$$\frac{d\left(\frac{C_t}{C_o}\right)}{dt} = -\beta_L S \tag{2}$$

according to boundary conditions and the hypothesis formulated: $C_t \rightarrow C_o$ when $t \rightarrow 0$.

So the external mass transfer rate, $-\beta_L S$, is approximated by the initial slope of the C_t/C_o graph and is obtained by the derivative (at t=0) of the polynomial linearisation of $C_t/C_o=f(t)$.

Intraparticle diffusion resistance model

Fick's laws of diffusion through solids are expressed by Eqs. (3) and (4). Theoretical treatments of intraparticle diffusion rates yield rather complex equations differing in form for different shapes of particle (Crank, 1965). All of them show that for batch experiments the evolution of the concentration in solution or in solid is a preferred function of $t^{0.5}$.

$$J = -D \frac{dC}{dX} \tag{3}$$

$$\frac{dC}{dt} = D \frac{d^2C}{dX^2} \tag{4}$$

where J is the rate of transfer per unit area of the section, X the space co-ordinate and D the diffusion coefficient. The assumptions are: diffusion occurs on a single axis, and adsorption happens without reaction.

Morris and Weber (1962) and McKay et al. (1980) demonstrate that in diffusion studies rate processes are usually expressed in terms of square root of time. So q_t or fraction metal adsorbed (1 - C_t/C_o) is plotted against $t^{0.5}$. Initial slope is determined by the derivative (at t=0) of the polynomial linearisation of 1 - C_t/C_o versus $t^{0.5}$. Following 1 - C_t/C_o determination, the sorption rate (slope of q_t versus $t^{0.5}$) is calculated according to the conversion:

$$q_t = (C_o - C_t) \, V/m = (1 - C_t/C_o) \, VC_o/m \tag{5}$$

The slope of (1 - C_t/C_o) plot, multiplied by VC_o/m gives the intraparticle diffusion rate.

Urano and Tachikawa (1991) and Urano et al. (1991) proposed an intraparticle diffusion coefficient D'_i based on the concentration in solids. This model, deduced from classical laws of diffusion, assumes that the adsorption rate is very slow and does not change with the stirring speed. So the external mass transfer rate is negligible and intraparticle diffusion is the rate-controlling step. Kinetic results are plotted according to:

$$f(q_t/q_m) = \log [1 - (q_t/q_m)^2] = -4 \, \pi^2 \, D'_i \, t / 2.3 \, d^2 \tag{6}$$

where d is the average diameter of sorbent particle and q_t/q_m is the fractional approach to equilibrium. A linear distribution of experimental points would confirm the adequacy of the model.

McKay et al. (1980) suggested a model which assumes that the concentration is uniform and equal to C_o in the solution and equal to 0 in the adsorbent at t=0, that external resistance is reduced and that diffusion in the adsorbent is radial. So for small times they plotted 1 - $(C_o-Ct)/(C_o-C_{eq})$ against the dimensionless parameter Dt/d^2, where C_{eq} is the metal concentration in solution at equilibrium and D a diffusion rate coefficient approximated by slope of [1 - $(C_o-C_t)/(C_o-C_{eq})$] plotting versus t.

Other models

Numerous more sophisticated models were investigated. In the models presented above, the external mass transfer resistance coefficients and the intraparticle diffusion (pore and/or solid diffusions) constants were examined separately. McKay and

Allen (1991) compared sorption kinetics and rate analysis by a simultaneous contribution of the various mechanisms. Liapis and Rippin (1977) proposed a numerical approach for the simulation of multi-component adsorption from a finite bath. By superposition of the results of model simulations onto data obtained from batch experiments pore and solid diffusion coefficients were estimated. Their estimation of sorption isotherm parameters was deduced from the Fritz and Schlüender model. An approach quite similar to the above was used by Glover et al. (1990) to describe and create a model for the binary adsorption of gold and zinc cyanides onto resins. Van Vliet et al. (1980) proposed another kind of isotherm, which clearly expresses the evolution of metal concentration in solution as a function of the metal concentration in the solid. They used this model to estimate the external mass transfer coefficients, and the intraparticle diffusivities of phenol on various adsorbents. The numerical solution was obtained by an iterative method for the resolution of a system of partial differential equations, applied to specific boundary conditions (batch or column experiments).
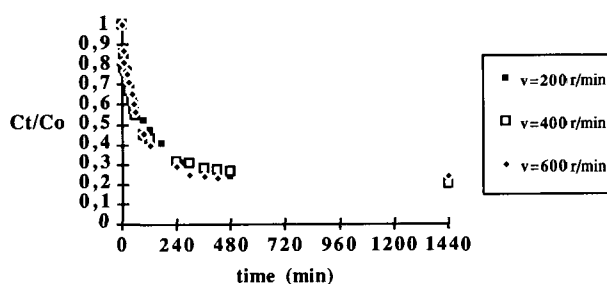

Figure 1
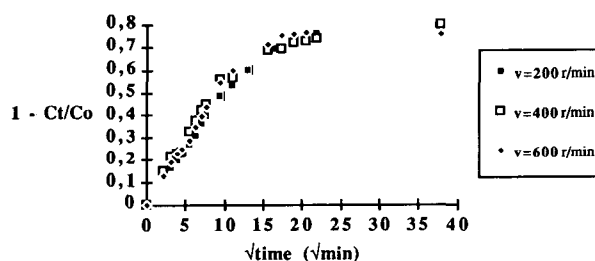*Effect of agitation on sorption kinetics*
Evolution of C/C_o versus t

Figure 2
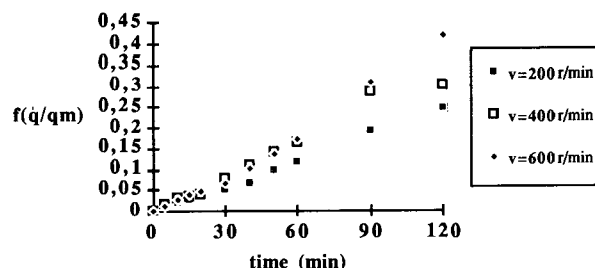*Effect of agitation on sorption kinetics*
Evolution of 1 - C/C_o versus $t^{0.5}$

Figure 3
Effect of agitation on sorption kinetics
Evolution of $f(q/q_m)$ versus t

TABLE 1 EFFECT OF AGITATION ON SORPTION RATE					
	External mass transfer model	Intraparticle diffusion model			
Agitation (r/min)	$B_L S$ (min⁻¹)	$1-C_i/C_0$ slope	k (mg/g·min)	$f(q_t/q_m)$ slope	D'_i (m²/min)
200	$2,6 \times 10^{-2}$	$4,92 \times 10^{-2}$	12,3	$-1,92 \times 10^{-3}$	$3,94 \times 10^{-12}$
400	$3,4 \times 10^{-2}$	$5,73 \times 10^{-2}$	14,3	$-2,76 \times 10^{-3}$	$5,66 \times 10^{-12}$
600	$2,7 \times 10^{-2}$	$5,51 \times 10^{-2}$	13,8	$-2,80 \times 10^{-3}$	$5,73 \times 10^{-12}$

$$\frac{D_s}{r^2} \frac{\partial}{\partial r} [r^2 \frac{\partial q}{\partial r}] = \frac{dq}{dt} \quad (7)$$

$$\frac{v_i \partial C}{\partial z} + \frac{\partial C}{\partial t} + \rho_p \frac{(1-\epsilon)}{\epsilon} \frac{\partial q}{\partial t} = 0 \quad (8)$$

where:

Ds   -   intraparticle diffusion coefficient

ρ_p, ϵ -   particle density and void fraction

C, C_i,q   -   solute concentration in the solution, at the interface and in the solid

r, z   -   solid radial and longitudinal coordinates

v_i, t   -   interstitial fluid velocity and time.

The external mass transfer coefficient (k_f) is found by an equation deduced from Fick's laws, applied to the boundary limits (r = R).

$$\rho_p \frac{\partial q}{\partial r} (R,t) = \frac{k_f}{D_s} (C - C_i) \quad (9)$$

The iterative resolution of the system allows the best fit of mass transfer coefficients relative to experimental results to be determined.

The approach chosen in this study is restricted to an interpretation and subsequent identification of mass transfer coefficients by separating the 2 mechanisms. The resolution of these simple equations to boundary limits allows the tendencies towards the pre-eminance of one of the mechanisms in the limiting steps to be estimated. The adequacy of correspondence of simplifying hypotheses and models with experimental results will be discussed later.

Experimental

Products

Oxo-2-glutaric acid (purum), sodium cyanoborohydride (purum) chitosan (high molecular weight, M ≈ 2 x 10^6, average deacetylation percentage: 80 %) were supplied by FLUKA AG, and uranyl nitrate hexahydrate by PROLABO RP (France).

Polymer synthesis

Glutamate glucan was synthetised according to a procedure quite similar to the one applied by Muzzarelli et al. (1984). The

experimental procedure has been previously described by Saucedo et al (1992, 1993). The polymer samples were ground and screened in 4 fractions: Gl: particle diameter d_p < 125 μm; G2: 125 μm < d_p < 250 μm; G3: 250 μm < d_p < 500 μm and G4: 500 μm < d_p < 1 000 μm.

Sorption procedure

Sorption isotherm studies were carried out by mixing 50 mg of glutamate glucan with 500 mℓ of metal ion solution, with various pH and metal concentrations. The tank reactor had the following characteristics: beaker = 500 mℓ, diameter = 80 mm; magnetic stirrer length = 35 mm. Samples were regularly withdrawn, filtered on Millipore filters (pore diameter = 0,45 μm) and analysed using the arsenazo III method, by comparing it with a standard linear of between 0 and 30 mg/ℓ. Mixing the polymer with the solution caused a fluctuation of the pH of the solution, so the pH had to be adjusted continuously to the experimental value by the addition of small volumes of molar solutions of HNO_3 and NaOH.

The adsorbate concentration in polymer, q_t or sorption capacity, was calculated by material balance: $q_t = V(C_0-C_t)/m$, where V, m, C_0 and C_t represent respectively volume of solution, mass of sorbent, initial uranium concentration and uranium concentration at time t.

Results

The effect of parameters such as agitation, particle size, uranium concentration, pH and temperature was observed according to models defined above. Determination of diffusion coefficients was achieved by successive representation of:

C_t/C_0 versus t

$1 - C_t/C_0$ versus $t^{0.5}$

$f(q_t/q_m) = \log [1 - (q_t/q_m)]$ versus t.

Influence of the agitation

Figures 1, 2 and 3 plot various representations concerning the stirrer speed. The experimental conditions, in this section, are T = 20°C, pH = 5, uranium concentration = 25 mg/ℓ and particle size: G2. As shown the agitation seems to have no effect on the rate of adsorption, except at 200 r/min. In this last case, a slight difference is noticed at 200 r/min, compared to 400 or 600 r/min. Tank reactor and particle size used with a low agitator speed result in a non-uniform distribution of the adsorbent through the
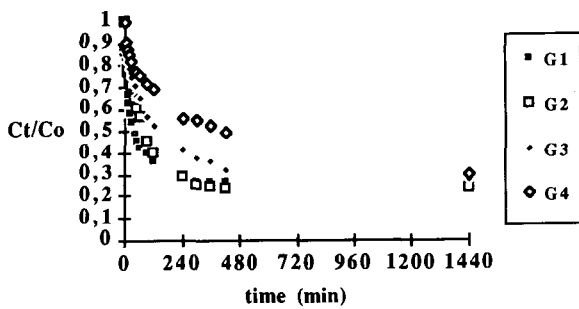
Figure 4
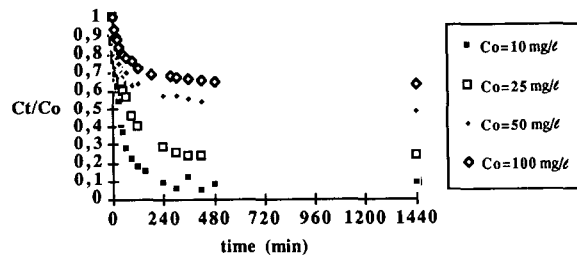*Effect of particle size on sorption kinetics*
Evolution of C_t/C_o versus t

Figure 7
Effect of concentration on sorption kinetics
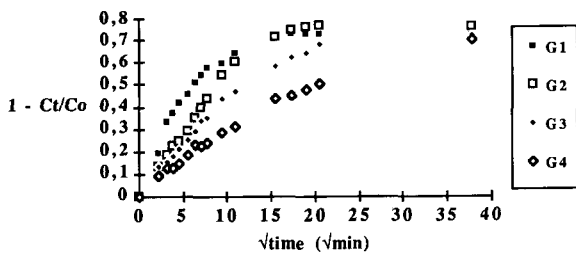*Evolution of C_t/C_o versus t*

Figure 5
Effect of particle size on sorption kinetics
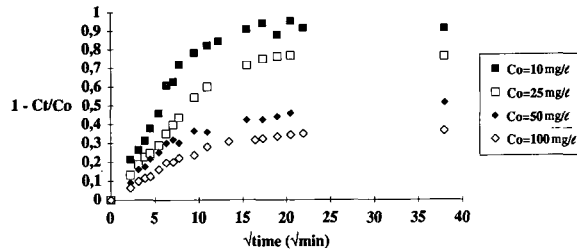*Evolution of $1- C_t/C_o$ versus $t^{0.5}$*

Figure 8
Effect of initial concentration on sorption kinetics
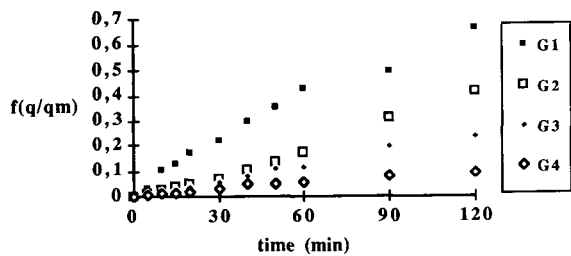*Evolution of $1- C_t/C_o$ versus $t^{0.5}$*

Figure 6
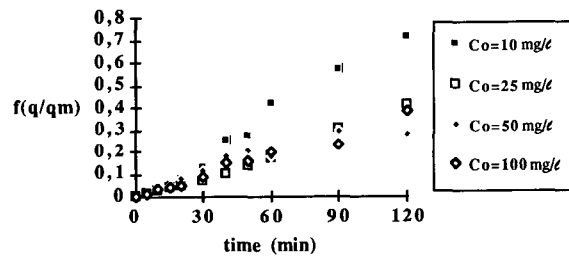*Effect of particle size on sorption kinetics*
Evolution of $f(q/q_m)$ versus t

Figure 9
Effect of concentration on sorption kinetics
Evolution of $f(q/q_m)$ versus t

	External mass transfer model	Intraparticle diffusion model			
Particle size	**$\beta_L S$ (min^{-1})**	**$1-C_t/C_o$ slope**	**k (mg/g·min$^{0.5}$)**	**$f(q_t/q_m)$ slope**	**D'_i (m^2/min)**
G1	$4,3 \times 10^{-2}$	$7,45 \times 10^{-2}$	18,6	$-6,98 \times 10^{-3}$	$1,59 \times 10^{-12}$
G2	$2,7 \times 10^{-2}$	$5,51 \times 10^{-2}$	13,8	$-2,80 \times 10^{-3}$	$5,73 \times 10^{-12}$
G3	$2,5 \times 10^{-2}$	$4,48 \times 10^{-2}$	11,2	$-1,97 \times 10^{-3}$	$16,16 \times 10^{-12}$
G4	$2,0 \times 10^{-2}$	$3,08 \times 10^{-2}$	7,7	$-0,92 \times 10^{-3}$	$30,25 \times 10^{-12}$

TABLE 2
EFFECT OF PARTICLE SIZE ON SORPTION RATE

TABLE 3
EFFECT OF INITIAL METAL CONCENTRATION ON SORPTION RATE

C_0 (mg/ℓ)	External mass transfer model	Intraparticle diffusion model			
	$\beta_L S$ (min^{-1})	$1-C_t/C_0$ slope	k (mg/g·min$^{0.5}$)	$f(q_t/q_m)$ slope	D'_i (m^2/min)
10	$3,9 \times 10^{-2}$	$9,22 \times 10^{-2}$	9,2	$-6,76 \times 10^{-3}$	$13,85 \times 10^{-12}$
25	$2,7 \times 10^{-2}$	$5,51 \times 10^{-2}$	13,8	$-2,80 \times 10^{-3}$	$5,73 \times 10^{-12}$
50	$2,1 \times 10^{-2}$	$4,62 \times 10^{-2}$	23,1	$-4,30 \times 10^{-3}$	$8,80 \times 10^{-12}$
100	$1,4 \times 10^{-2}$	$2,88 \times 10^{-2}$	28,8	$-3,39 \times 10^{-3}$	$6,95 \times 10^{-12}$

solution. External mass transfer and bulk mass transfer therefore have a limited effect on this adsorption rate. Table 1 shows the mass transfer coefficient corresponding to these diffusion models.

Influence of the particle size

The effect of the particle size was ascertained according to the following experimental conditions: T = 20 °C, pH = 5, stirrer speed = 600 r/min, uranium concentration = 25 mg/ℓ. Figures 4, 5 and 6 represent the various plots: each one of these demonstrates that particle size greatly influences diffusion mechanisms and sorption rates. The time necessary to reach equilibrium is increased by an increase in particle size. Table 2 represents the diffusion coefficients for the various models used in this part as a function of particle size.

Influence of the uranium concentration

Figures 7, 8 and 9 show that the initial uranium concentration strongly influences rates of metal ion adsorption. The experimental conditions were as follows: T = 20°C, pH = 5, particle size: G2, stirrer speed = 600 r/min. C_t/C_0 versus t and $1 - C_t/C_0$ versus $t^{0.5}$ plots demonstrate that the slope decreases with an increase in dissolved uranium concentration. Figure 9, however, shows that $f(q_t/q_m)$ versus time does not exhibit the same behaviour, the slope of the plot varies randomly between 10 and 100 mg/ℓ. Table 3 summarises the mass transfer coefficients for the 2 kinds of transfer resistance, relative to the metal concentration parameter.

Influence of the pH

Uranium concentration and pH are 2 interdependent parameters, as regards hydrolysis phenomena. Baes and Mesmer (1976), studying the hydrolysis of cations, proposed various reactions of equilibrium between UO_2^{2+}, $(UO_2)OH^+$, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$. So the rearrangement of these ionic species depends conjointly on total metal concentration and pH. The main species are UO_2^{2+} in acidic medium, and $(UO_2)_3(OH)_5^+$ when the pH approximates to a neutral value. Consequently the pH corresponding to the first appearance of hydrolysed species decreases when the total uranyl concentration increases. Subsequently when the pH and the total metal concentration are high, $(UO_2)_3(OH)_5^+$ predominates and metal is present in solution in the form of a molecule with an ionic radius greater than those of free metal ions (non-hydrolysed).

The effect of pH was studied according to the conditions: T =

20°C, uranium concentration = 50 mg/ℓ, particle size: G2, stirrer speed = 600 r/min. Figure 11 shows an evolution of $1 - C_t/C_0$ versus $t^{0.5}$ quite similar between pH 5 and pH 6. In contrast sorption kinetics at pH 4 are significantly different. An optimum sorption is obtained at around 2 h of contact. After this first equilibrium, the amount of metal adsorbed on the polymer decreases. So at pH 4, metal removed is desorbed and the metal concentration in the solution increases. The same results are presented in Fig. 10. The model of Urano and Tachikawa (1991) cannot be applied to results at pH 4 (Fig. 12). Table 4 represents the effect of the pH on the values of mass transfer coefficients according to external and intraparticle resistance models.

Influence of temperature

Figures 13 and 14 show the effect of temperature on the relative concentration of uranium versus time (initial concentration = 25 mg/ℓ): it is obvious that the temperature hardly changes kinetics and equilibrium concentration. Experimental conditions were: pH = 5, stirrer speed = 600 r/min, particle size: G2, uranium concentration = 25 and 50 mg/ℓ. This parameter seems to have no effect on metal sorption within the range of temperatures investigated. The sorption rate is characterised by a slight increase in the initial rate, even though near the equilibrium, sorption rate tends to level off at an equilibrium approximating to the one reached at a lower temperature. The same results are observed in Figs. 15 and 16 (all other experimental conditions remain unchanged) with a higher initial concentration (50 mg/ℓ). Table 5 describes the evolution of mass transfer coefficients with temperature and metal concentration.

Discussion

Influence of agitation

Varying stirring speed seems to have no effect on sorption phenomena (see Table 1). This means that adsorbate transfer from bulk solution to sorbent surface (through film or boundary) is not a major parameter in this phenomenon. The hypothesis that the external mass transfer is negligible can be assumed. Intraparticle diffusion resistance therefore is the main controlling mechanism. This hypothesis is consistent with the linearisation of $1 - C_t/C_0$ versus $t^{0.5}$. McKay et al. (1980) noticed that the extrapolation of the linear portion of the plots back to the axis provides intercepts which are proportional to the extent of the boundary layer thickness. This linearisation (between 0 and 60 min) allows us to obtain a linear expression: $1 - C_t/C_0 = A - B\ t^{0.5}$, with A negligible against B $t^{0.5}$, in present experiments. Thus it is
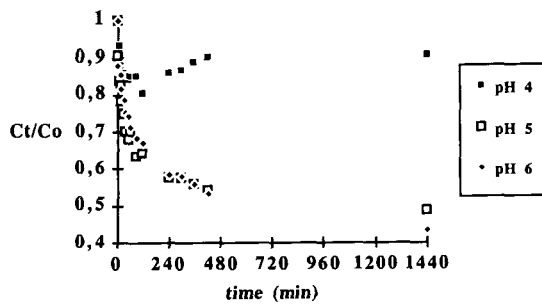
Figure 10
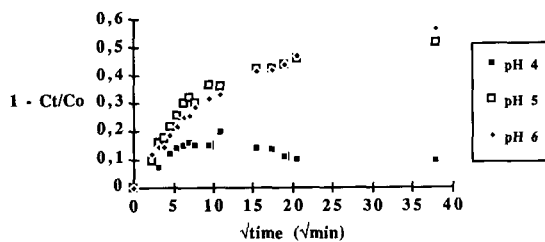*Effect of pH on sorption kinetics*
Evolution of C_t/C_o versus t

Figure 11
Effect of pH on sorption kinetics
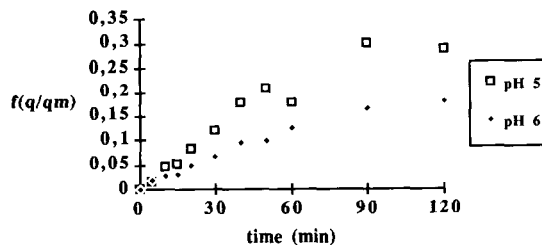*Evolution of $1- C_t/C_o$ versus $t^{0.5}$*

Figure 12
Effect of pH on sorption kinetics
Evolution of $f(q/q_m)$ versus t

possible to conclude that the boundary layer is negligible.

Influence of particle size

Table 2 shows sorption rate according to particle size. If the intraparticle diffusion mechanism plays an important part in the control of metal sorption, increasing particle size will result in a decrease in sorption rate; the metal ion will therefore have a greater intraparticle distance to diffuse before the polymer becomes saturated. Consequently increasing particle size increases the time needed to reach equilibrium.

Weber and Morris (1964) demonstrated in the case of a non-porous sorbent that the sorption rate parameter is proportional to the first power of the diameter of particles. When the adsorbent is porous and when the transport rate is controlled by an external resistance mechanism, such as boundary film resistance to diffusion, the rate parameter is inversely proportional to the diameter. So when the rate parameter is inversely proportional to the particle diameter raised to some power it is concluded that intraparticle diffusion is the controlling phenomenon (Crank, 1965).

The sorption rates as defined in Table 1 can be correlated by the following formulae:

$$\beta_L S = 2,31 \ d_p^{-0,30} \approx A \ d_p^{1/3} \qquad (R^2 = 0,96) \tag{10}$$

$$k = 2,75 \times 10^{-3} d_p^{-0,35} \approx B \ d_p^{-1/3} \ (R^2 = 0,97) \tag{11}$$

These results confirm the hypothesis of a sorption rate controlled by intraparticle diffusion, according to Crank's conclusions.

Influence of the uranium concentration

As seen above (Table 3), an increase in metal concentration induces a change in the redistribution of ionic species and the appearance of hydroxylated forms whose ionic radius is greater than those of free metal ions. Moreover, the comparison of these values with those of ions in the liquid phase. (Perry and Green, 1984) indicates a 4th order of magnitude reduction of diffusion constants. So the diffusion of these molecules is reduced either by steric hindrance or by surface migration resistance; diffusion constants should be an average value governed by 2 mechanisms. Rosen (1952) and Crittenden and Weber (1978) studied the following proposed sequence: adsorption in the outer surface of the adsorbent, followed by diffusion in the adsorbed state. Consequently the rate of the relative decrease in concentration is proportional to the initial concentration of metal in solution. The rate of adsorption, described as the slope of the plot of the amount of metal sorbed as a function of $t^{0.5}$, increases with initial concentration according to:

	External mass transfer model	Intraparticle diffusion model			
pH	$\beta_L S$ (min⁻¹)	$1-C_t/C_0$ slope	k (mg/g·min⁰·⁵)	$f(q_t/q_m)$ slope	D'_i (m²/min)
4					
5	2,1 x 10-2	4,62 x 10-2	23,1	-4,30 x 10-3	8,80 x 10-12
6	2,2 x 10-2	3,56 x 10-2	17,8	-2,80 x 10-3	4,13 x 10-12

TABLE 4
EFFECT OF pH ON SORPTION RATE

$$k = 2{,}78\ C_0^{0{,}52} \approx A\ C_0^{1/2} \qquad (R^2 = 0{,}98) \qquad (12)$$

The concentration decays relatively faster at low concentrations than at higher concentrations, and it takes longer to reach equilibrium at a high uranium content.

External mass transfer resistance, and the corresponding rate $\beta_L S$ are proportional to the initial concentration according to:

$$\beta_L S = 10{,}88\ 10^{-2}\ C_0^{-0{,}44} \qquad (R^2 = 0{,}99) \qquad (13)$$

Influence of the pH

The effect of this parameter is similar to the uranium concentration effect (see Table 4). Increasing the pH results in the formation of uranyl hydroxides, the diffusion of which through the polymer is reduced as a result of its larger ionic size. The differences observed between pH 5 and pH 6 are low, in contrast to those at pH 4 (Figure 11). The other significant difference at pH 4 is that at high contact times, the amount of

sorbed metal decreases. The equilibrium of sorption-desorption is possibly affected by the mobility of the solute. The phenomenon can be simulated assuming a desorption rate greater than the sorption rate after reaching a first equilibrium.

Influence of the temperature

The results presented above demonstrate that temperature is not a parameter which affects kinetic sorption, within the temperature range studied. Figures 13 to 16 and Table 5 show that with varying initial metal concentrations temperature barely affects the sorption rates, whichever diffusion model is used. This conclusion is consistent with that previously observed concerning sorption isotherms (Saucedo et al., 1993). If adsorption is governed only by physical phenomena, an increase in temperature will be followed by a decrease in sorption capacity. Within the temperature range investigated, it is impossible to come to a conclusion. In general an increase in temperature is followed by an increase in the diffusivity of the
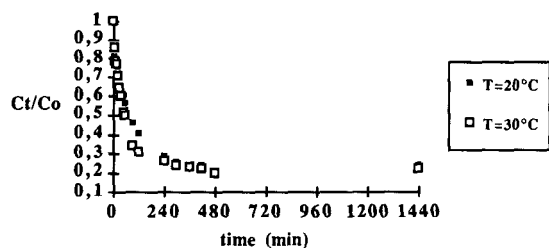

Figure 13
Effect of temperature on sorption kinetics
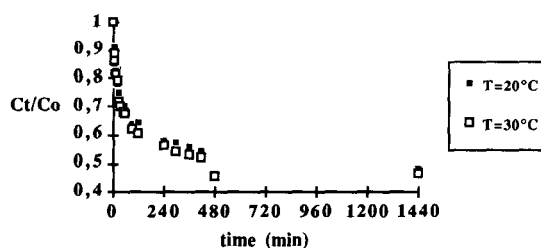Evolution of C_t/C_o versus t $(C_o = 25\ mg/\ell^{-1})$

Figure 15
Effect of temperature on sorption kinetics
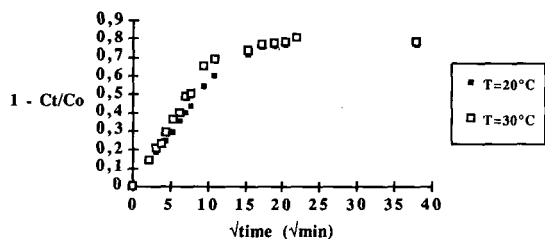Evolution of C_t/C_o versus t $(C_o = 50\ mg/\ell^{-1})$

Figure 14
Effect of temperature on sorption kinetics
Evolution of $1 - C_t/C_o$ versus $t^{0.5}$ $(C_o = 25\ mg/\ell^{-1})$
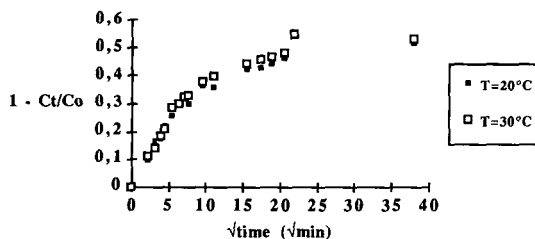

Figure 16
Effect of temperature on sorption kinetics
Evolution of $1 - C_t/C_o$ versus $t^{0.5}$ $(C_o = 50\ mg/\ell^{-1})$

TABLE 5 EFFECT OF TEMPERATURE ON SORPTION RATE					
	External mass transfer model	Intraparticle diffusion model			
C_0 T	$\beta_L S$ (min^{-1})	$1-C_t/C_0$ slope	k $(mg/g \cdot min^{0.5})$	$f(q_t/q_m)$ slope	D'_i (m^2/min)
25 mg/ℓ-20°C	$2{,}7 \times 10^{-2}$	$5{,}51 \times 10^{-2}$	13,8	$-2{,}80 \times 10^{-3}$	$5{,}73 \times 10^{-12}$
25 mg/ℓ-30°C	$2{,}9 \times 10^{-2}$	$6{,}61 \times 10^{-2}$	16,5	$-3{,}30 \times 10^{-3}$	$6{,}76 \times 10^{-12}$
50 mg/ℓ-20°C	$2{,}1 \times 10^{-2}$	$4{,}62 \times 10^{-2}$	23,1	$-4{,}30 \times 10^{-3}$	$8{,}80 \times 10^{-12}$
50 mg/ℓ-30°C	$2{,}0 \times 10^{-2}$	$4{,}45 \times 10^{-2}$	22,2	$-4{,}15 \times 10^{-3}$	$8{,}50 \times 10^{-12}$

solute, and consequently by an increase in sorption rate if diffusion is the rate-controlling step. One possible conclusion is that the diffusivity of the solute in the solid is not affected by temperature under the present experimental conditions.

Conclusion

The various models used for the description of C_t/C_0 versus t, and 1- C_t/C_0 versus $t^{0.5}$, demonstrate that a variation in agitation hardly changes the sorption rate. Moreover, particle size greatly influences the modelling of 1- C_t/C_0 versus $t^{0.5}$. Other parameters, such as pH and uranium concentration, play an important part in the controlling the rate of adsorption. This influence is related to the rearrangement of metal species in the solution and the ionic size of the adsorbate influencing the diffusion through the polymer structure. Diffusion mechanisms, and most importantly intraparticle diffusion, are the controlling steps in the adsorption, compared to external mass transfer, and to the sorption step. Considering intraparticle diffusion as the main resistance mechanism, 2 kinds of diffusion are possible: homogeneous diffusion and pore diffusion followed by surface migration, as defined by Dedrick and Beckmann (1967), and studied by Mathews and Weber (1984). The reduced effect of agitation on the sorption performances confirms the hypothesis that external mass transfer is not the main limiting step.

The present conclusions are consistent with the results obtained by Saucedo et al. (1992) with another type of modified chitosan. The ascorbic substituted chitosan shows great similarities to uranium sorption kinetic behaviour. Metal ion concentration and pH are the main parameters and particle size greatly influences intraparticle diffusion. The glutamate glucan sorption rate constants differ by less than one order of magnitude from the ones obtained with "ascorbic chitosan".

The performances of sorption are significantly higher than those of the pure chitosan ones: maximal uptake is around 3 times higher (other conditions being equal). Muzzarelli and Zattoni (1986) studying glutamate glucan and aminogluconate glucan with other metals focused on the interesting aspects presented by these new chelating polyampholytes. In relation to chromatographic or, more generally, to separation techniques, highly porous and hydrophilic polymers carrying suitable complexing groups (ascorbate functions, amino-acid moieties, oxo-2-glutaric acid...) chelate metal ions fast enough to prevent the deposition of metal hydroxides, this conclusion is only valid in a certain pH range.

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