

Uranium sorption by glutamate glucan: A modified chitosan Part I: Equilibrium studies

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Abstract

Chitosan, a natural polymer, is modified by an oxo-2-glutaric acid substitution and a subsequent reduction to form glutamate glucan. This modified chitosan is then used to examine uranium sorption. The main parameters that play an important part in sorption mechanisms are the pH and the total metal concentration. Other parameters such as temperature, agitation and particle size of the sorbent show a restricted effect on the sorption equilibrium. The maximum uptake capacity, obtained at pH 5 to 6, reaches approximately 500 mgU/g. At pH 5, a sorption monolayer is predominant; at higher pH, the sorption becomes more complicated. A surface precipitation model of uranium sorption is proposed.

Introduction

Mining and refining industries produce large amounts of aqueous waste streams containing low metal concentrations. These concentrations are too high to allow a direct discharge to the environment, but they are too low to treat with classical physico-chemical processes. Various technologies using biological materials such as bacterial biomass have been tested to treat metal ion waste waters (Strandberg and Shumate, 1982; Tsezos and Volesky, 1981; Horikoshi et al., 1986; Guibal et al., 1993; and Guibal, 1990). Fungal biomass shows a great ability to remove metal ions present in dilute solutions. This sorption ability is shown by the efficient removal of uranium in the semi-industrial biomass treatment of mining waste waters (Guibal and Roulph, 1991). Difficulty is experienced with the application of fungal biomass in a fixed bed process. Other applications, such as the treatment of electroplating waste waters, were evaluated by Coughlin et al. (1990). Coughlin et al. (1990) evaluated the economic and technical feasibility of electroplating waste-water treatment by sorption on chitosan using fixed bed columns.

The studies of Muzzarelli (1985; 1990), Eiden et al. (1980), Maruca et al. (1982) and McKay et al. (1986; 1989) on chitin or chitosan (natural polymers constituting the major part of crab shells or fungal cell wall), show that these polymers are efficient in the sorption of metals such as copper, mercury and uranium. A new trend appears in waste-water technologies: natural polymers, such as chitosan, are being modified by functional group substitutions (Holme and Hall, 1991). Muzzarelli et al. (1984) experimented with a chitosan that had been modified by the substitution of organic acid into a keto-imine intermediary and subsequently reduced to synthesise glutamate glucan. The substituted organic acids investigated are ascorbic acid (Muzzarelli et al., 1984; Muzzarelli, 1985; Saucedo et al., 1992), glyoxylic acid and oxo-2-glutaric acid (Muzzarelli and Zattoni, 1986).

The purpose was to study the sorption of uranium by a chitosan modified by substitution with oxo-2-glutaric acid. This part of the paper in 2 parts deals with equilibrium studies and in

particular sorption isotherms. The classical parameters of sorption mechanisms, such as particle size of adsorbents, pH of metal ion solution, concentration of solute, temperature and degree of agitation, are also investigated.

Experimental

Products

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

Polymer synthesis

Glutamate glucan was synthesised according to a procedure quite similar to the one performed by Muzzarelli et al. (1984). It involved 2 steps: the first one led to the formation of a keto-imine, the second one consisted of reducing this keto-imine with the reducing agent, sodium cyanoborohydride.

70 g of chitosan (representing 0,4 mol of monomeric unit: glucosamine) was dissolved in 3,5 l of deionised water containing 87 g of oxo-2-glutaric acid (0,6 mol, molar ratio between organic acid and chitosan = 1,5). The dissolution took 3 h. The keto-imine was agitated for 48 h; during this time, the pH stabilised at 1,8. Before reduction, the pH was adjusted to 4,5 with a molar solution of NaOH. Sodium cyanoborohydride (40 g dissolved in 100 ml of deionised water) was added step by step. Using NaOH, the pH was adjusted to 6,5 and the solution was agitated for 24 h. Next, the solution was left to settle and a slightly viscous, white product was obtained: the glutamate glucan. The polymer was dried at ambient temperature, screened and washed by soxhlet (with acetone as solvent) for 3 h. After this extraction, the polymer was dried and screened in 4 fractions: G1: particle diameter $d_p < 125 \mu\text{m}$; G2: $125 \mu\text{m} < d_p < 250 \mu\text{m}$; G3: $250 \mu\text{m} < d_p < 500 \mu\text{m}$ and G4: $500 \mu\text{m} < d_p < 1\,000 \mu\text{m}$.

Figure 1 shows an optic micrograph (x 100) of crushed polymer (particle size: G1) which illustrates the dispersion in particle shape. Figure 2, with a greater magnifying power (x 400), illustrates the polymer particles in more detail.

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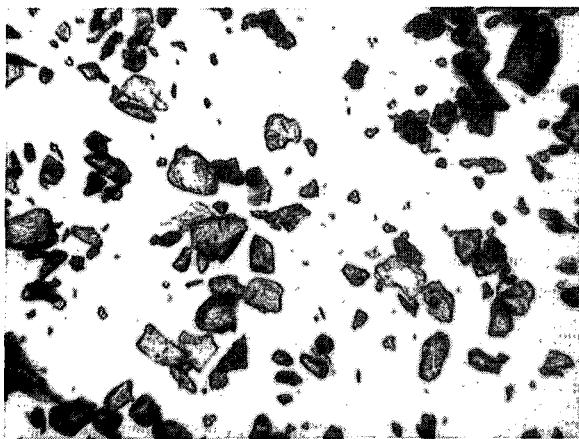


Figure 1
Dispersion of shape and size in G1 polymer fraction



Figure 2
Detailed shapes of polymer grains with sharp edges

The optic micrographs were obtained with a LEITZ LABORLUX D microscope, equipped with a PROLABO vision camera module CCD MACCC71, a SONY trinitron colour video monitor PVM 1442 QM, and a MITSUBISHI colour video copy processor.

The real density of each polymer was determined by an air pycnometer BECKMAN 930. The average measure obtained on each particle size class gives a value equal to $1,45 \pm 0,1 \text{ g/cm}^3$.

Sorption procedure

Sorption isotherm studies were carried out by mixing 25 mg of glutamate glucan with 250 mL of a metal ion solution. The pH and metal concentrations varied. Samples were withdrawn and filtered on Millipore membrane filters (pore diameter = 0,45 μm). The samples were analysed according to the arsenazo III method that is linear between 0 and 30 mg/L. The pH of the solution was adjusted by the addition of small amounts of molar HNO_3 and NaOH solutions. X/M, the adsorbate concentration, or sorption capacity of the polymer, was calculated by a mass balance:

$$X/M = V(C_0 - C_{eq})/m$$

where:

V = volume of solution

m = mass of sorbent

C_0 = initial uranium concentration

C_{eq} = uranium concentration at equilibrium.

Results

The main parameters influencing metal sorption were investigated: particle size of adsorbent, agitator speed, pH, metal concentration and temperature. This study dealt with the effect of these parameters on the equilibrium. Sorption isotherms were also determined as functions of temperature and of pH in terms of the Freundlich and Langmuir models of adsorption (De Rome and Gadd, 1987).

Equilibrium studies

Influence of the particle size

A 24-h contact time between the polymer and the solution was selected. However, the state of equilibrium was reached after various contact times (Guibal et al., 1993). The equilibrium concentration in solution and the resulting sorption capacity were not markedly influenced by the sorbent particle size. This is shown in Table 1. The variations obtained are not significant, taking analytical and experimental uncertainties into account.

The following experimental conditions pertained: $T = 20 \text{ }^\circ\text{C} \pm 1^\circ\text{C}$, $\text{pH} = 5$ (pH controlled and adjusted), stirrer speed = 600 r/min, uranium concentration = 25 mg/L.

	G1	G2	G3	G4
C_{eq}/C_0	0,28	0,24	0,28	0,30
X/M (mg/g)	180-185	190-195	180-185	178-183

Influence of the initial uranium concentration

The experimental conditions for this section were: $T = 20 \text{ }^\circ\text{C}$, $\text{pH} = 5$ (pH controlled and adjusted), particle size: G2, stirrer speed = 600 r/min.

The sorption efficiency, represented by $1 - C_{eq}/C_0$, decreased when initial metal concentration increased. On the other hand, an increase in initial metal concentration is followed by an increase in sorption capacity, as shown in Table 2.

	10	25	50	100
C_{eq}/C_0	0,05-0,09	0,24	0,49	0,62
X/M (mg/g)	92-96	190-195	250-255	370-375

Influence of the degree of agitation

In this study, the experimental conditions were: T = 20 °C, pH = 5, uranium concentration = 25 mg/L, particle size: G2.

No significant effect was observed on the uranium sorption efficiency when the agitation speed varied. Although agitation played an important part in diffusion mechanisms, it had little influence on the equilibrium state.

	200	400	600
v (r/min)	200	400	600
C _{eq} /C _o	0,20	0,20	0,24
X/M (mg/g)	198-202	195-200	190-195

Influence of the pH

The influence of the pH was evaluated under the following conditions: T = 20 °C, uranium concentration = 50 mg/L, particle size: G2, stirrer speed = 600 r/min. The pH was held constant at the initial experimental value by the addition of molar acid or basic solutions.

Table 4 shows that the pH influenced the sorption efficiency and the uptake capacity. Previous studies on polymers, obtained by the substitution of ascorbic acid on chitosan (Saucedo et al., 1992) had demonstrated that the uptake capacity reached an equilibrium at an acidic pH (approximate to pH 4). After a few hours, desorption occurred. Equilibrium studies are therefore more uncertain under such acidic conditions. The time necessary to reach equilibrium changes under these specific experimental conditions. The work previously cited also demonstrated that in an acidic medium, the sorption performance is significantly reduced. At pH 4, the pseudo-equilibrium reached after 2 h corresponded to an uptake capacity 3 times lower than the one obtained at a higher pH.

	pH5	pH6
C _{eq} /C _o	0,49	0,44
X/M (mg/g)	250-255	270-280

Influence of the temperature

The experimental conditions were: pH = 5, stirrer speed = 600 r/min, particle size: G2, uranium concentration = 25 and 50 mg/L.

In the experimental range investigated (20 °C to 50 °C), varying temperature seemed to have a negligible effect on the sorption efficiency, as shown in Table 5.

T (°C)	20		30	
C _{eq} (mg/L)	25	50	25	50
C _{eq} /C _o	0,76	0,52	0,78	0,54
X/M (mg/g)	193	254	190	256

Sorption isotherms

Sorption isotherms were carried out against two major parameters: pH (2 values: 5 and 6) and temperature (ranging from 20°C to 50°C). The adsorption data can be interpreted using several mathematical relationships which describe the distribution of the solute between the liquid phase and the solid phase. The Langmuir and the Freundlich isotherms are shown below in Eqs. 1 and 2 respectively.

The Langmuir model equation is described by the following form:

$$\frac{X}{M} = \frac{q_m b C_{eq}}{1 + b C_{eq}} \quad (1)$$

The Freundlich model equation is shown below:

$$\frac{X}{M} = k C_{eq}^{1/n} \quad (2)$$

where:

- X/M = uptake capacity (mgU/g polymer)
- C_{eq} = equilibrium metal concentration in solution (mgU/L)
- q_m = maximum adsorption capacity (mgU/g polymer)
- b = ratio of the kinetic constants of adsorption and desorption (L/mg)
- k and n = constants.

The Scatchard model assumes that linear plots of (X/M)/C_{eq} versus X/M result when a single type of binding site is present (Tobin, 1986). Consequently, non-linear plots suggest that multiple, non-equivalent binding sites participate in the uptake. Therefore, linear Scatchard plots support the Langmuir model.

pH effect

Figures 3 and 4 show the effect of pH on Freundlich and Langmuir sorption isotherm models respectively. As can be seen, experimental results fit the Freundlich model. The 2 Freundlich plots (pH 5 and pH 6) are quite similar, with a slight difference in the slope of each isotherm. The Scatchard model (Fig. 5) is in accordance with this observation.

Temperature effect

Figure 6 indicates that the temperature did not significantly influence the equilibrium in the range of temperatures

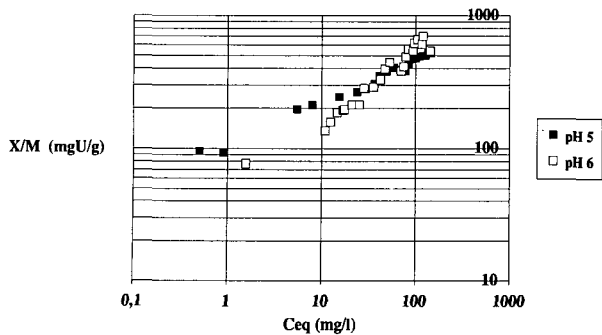


Figure 3
Effect of pH on sorption isotherm – Freundlich model

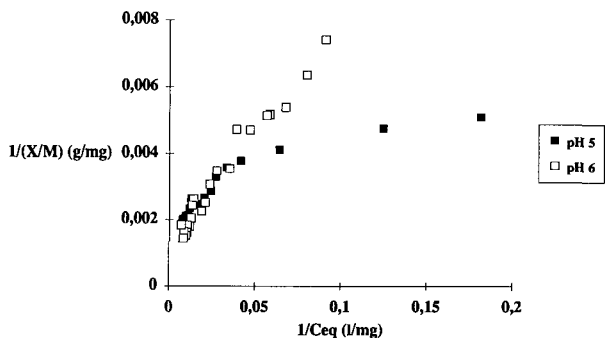


Figure 4
Effect of pH on sorption isotherm – Langmuir model ($1/C_{eq}$ values are restricted to C_{eq} corresponding to $C_o \geq 25$ mg/l)

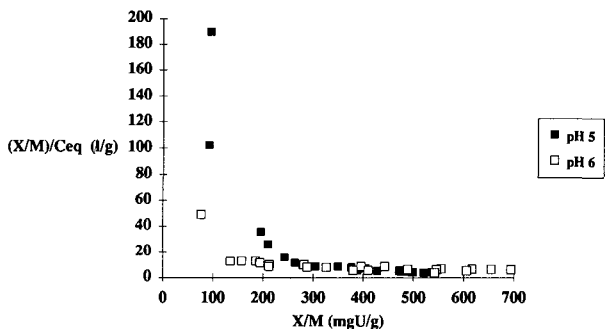


Figure 5
Effect on pH on sorption isotherm – Scatchard model

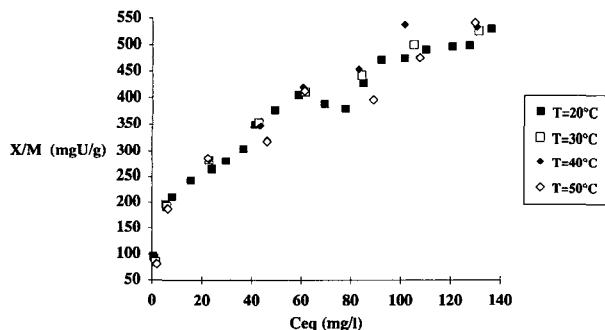


Figure 6
Effect of temperature on sorption isotherm

investigated. The slight differences noticed between each plot are possibly due to experimental and analytical uncertainties.

Discussion

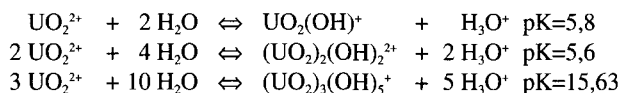
The results obtained show that 2 of the various parameters strongly influence the sorption performance. These parameters are pH and initial uranium concentration. Three other parameters i.e. temperature, particle size, and agitation do not influence the sorption equilibrium but are of interest as they may affect the kinetics of specific mechanisms. For example, temperature could influence the desorption step and consequently the reversibility of the sorption equilibrium. The polymer particle size is also an important parameter for determining the time necessary to reach equilibrium, since intraparticle diffusion is the predominant controlling step in uranium sorption kinetics, as shown by Guibal et al. (1993). Agitation also plays an important role in external mass transfer and as a result, the influence of this parameter is restricted to kinetic studies. The parameters which influence the mechanisms of external or intraparticle diffusion affect the kinetics but not the equilibrium reached. Therefore these parameters are of great interest in industrial application such as decreasing the time needed to reach equilibrium, and consequently the size of industrial plants. However, the total uranium uptake capacity is independent of these parameters.

The measured uranium sorption by glutamate glucan is quite similar to that observed in a chitosan modified by the Schiff reaction. The chitosan was substituted (using ascorbic acid) and reduced by sodium borohydride. Saucedo et al. (1992) presented similar results. The maximum uptake is slightly lower than that obtained by the latter and the one obtained by Muzzarelli (1985). It is difficult to compare the Muzzarelli results and the present results since the chitosan used is not the same. The greater percentage of substitution obtained by Muzzarelli (1989) was due to a higher deacetylation ratio of chitosan: Muzzarelli used a 3% acetylated chitosan, the present work was done with an almost 20% acetylated chitosan. The decrease in deacetylated percentage and substitution ratio in this study explains the decrease in sorption performance.

pH and isotherms

pH induces changes in speciation of metal ions present in solution. Baes and Mesmer (1976) give several equilibria existing between the various species of uranyl ion, depending on pH and uranium concentration.

According to the following equilibria:



it appears that the pH corresponding to the first appearance of hydrolysed species (mainly $(\text{UO}_2)_3(\text{OH})_5^+$) decreases when the total metal concentration increases.

With an acidic pH, the competition between H_3O^+ and UO_2^{2+} for the uptake sites limits the adsorption of the metal ions on the sorbent. The electrostatic repulsion decreases when the pH increases. Another important parameter in adsorption processes is solubility. In the pH range studied, the uranyl solubility reaches a minimum between pH 5 and 6. A medium of this pH favours sorption.

pH	Langmuir model			Freundlich model		
	q _m	b	R ²	k	n	R ²
5	363,7	0,57	0,82	105,7	3,15	0,98
6	363,0	0,155	0,76	43,2	1,81	0,95

Figures 3 and 4 show that an increase of pH is followed by an increase of the saturation capacity (for a high concentration solution, an approximately neutral pH is optimal; but when residual metal ion concentration is low, an acidic pH is optimal). Table 6 clearly demonstrates that the best fit of the experimental results (at T = 20 °C) is obtained with the Freundlich model: the metal adsorbed forms a monolayer with lateral interactions between the molecules adsorbed. The surface presents heterogeneity in structure and in distribution of adsorption energy. The uranium sorption coefficients (for the 2 models), compared to those obtained using the ascorbic acid chitosan (Saucedo et al., 1992), show some differences: at pH 5, the 2 polymers are not significantly different in their sorption coefficients; but, at pH 6, the sorption performance for glutamate glucan is lower and the sorption coefficients strongly decrease.

The shapes of the curves obtained at pH 5 and 6 on Langmuir representation are significantly different. As shown in Table 6, the Freundlich model generally gives a better approximation of the experimental results. The Langmuir representation approximates a straight line if the very low residual metal concentration field is neglected. The existence of 2 linear ranges in the Langmuir and Scatchard plots (the Langmuir model proposed an adsorption monolayer without lateral interactions between adsorbed molecules) shows that 2 ranges can be distinguished. Huang et al. (1991) demonstrated that a possible explanation for these different ranges is due to the co-existence of 2 types of sorption sites. The nature of the polymer suggests that the sorption sites can be the amino-groups present in the original chitosan framework and the carboxylate groups cross-linked by substitution of carboxylic acids. The pH of the solution caused a change in the distribution of ionic species present in solution (uranyl hydrolysed species). Some mechanisms of precipitation should co-exist in the total adsorption process. Surface precipitation adsorption has been proposed by Farley et al. (1985) in the case of adsorption of cations on metal oxides; the same mechanisms are suggested in uranyl ion adsorption on fungal biomass (Guibal et al., 1992). It is proposed that uranyl hydrolysed species, initially present in solution, are adsorbed in this form on the polymer. Consequently, the total metal concentration in solution decreases. The hydroxylation equilibrium in solution is modified in favour of the existence of free forms of metal in the liquid phase. The residual metal ions are adsorbed by precipitation on the novel superficial structure of the polymer (external surface plus the hydroxylated metal adsorbed during the first step). The resultant sorption takes place in multilayer form, and it can be described by another model such as the Brunauer Emmet and Teller model (BET isotherm) (De Rome and Gadd, 1987).

Temperature	Langmuir model			Freundlich model		
	q _m	b	R ²	k	n	R ²
20°C	363,7	0,57	0,82	105,7	3,15	0,98
30°C	439,1	0,155	0,98	81,0	2,55	0,98
40°C	455,7	0,13	0,99	74,9	2,40	0,98

Isotherms and temperature

Figure 6 clearly demonstrates that temperature, a classical parameter in sorption mechanisms, has a very restricted effect on uranium sorption isotherms by glutamate glucan at pH 5, in the investigated temperature range. The equilibrium reflects the joint effects of adsorption and desorption. If the temperature increases, the desorption step is favoured. The reported results are contradictory to this hypothesis. McKay et al. (1989) found that temperature dependence in metal sorption by chitosan depends upon the nature of the adsorbed metal: copper and mercury sorption is temperature-dependent whereas zinc and nickel sorption is not influenced by temperature variations. This is consistent with the present results. Table 7 shows that the parameters of the Langmuir and Freundlich models fitted the experimental results. The Freundlich model shows a good agreement between the parameters at each temperature. However, the Langmuir model is more controversial: the correlation coefficients and parameters at 20 °C are strongly different from those obtained at higher temperatures. This difference may be explained by the number of experiments performed at specific conditions: with T = 20 °C, the number of experiments performed at low initial concentrations are greater than those performed at T > 20°C. Since it has already been shown that the Langmuir model does not agree well with the experimental results in the low metal concentration range, this difference is explained by the relative importance of experiments realised with low initial metal concentration. It may be possible that with an increase in temperature, the sorption mechanisms become intermediary between the models proposed by Langmuir and Freundlich.

Increasing the temperature results in a slight increase of q_m, and a decrease of b, k and n. These results could be explained by a dilation of polymer pores with temperature resulting in slight changes in sorption performances and mechanisms.

The variation of the Langmuir and Freundlich constants with temperature is not significant. As a result, conclusions concerning the thermodynamic nature of the adsorption (i.e. exothermic or endothermic sorption) cannot be made.

Weber and Chakravorti (1974) proposed a criterion to define the favourability of an isotherm by noting that the essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor. This factor, called the equilibrium parameter, is defined as:

$$R = \frac{1}{1 + bC_0} \quad (3)$$

where:

- b = the Langmuir constant previously defined
C₀ = the initial concentration observed at the saturation of the adsorbent (near to 200 mg/ℓ)

This parameter R indicates the shape of the isotherm as follows:

Value of R	Type of isotherm
R > 1	Unfavourable
R = 1	Linear
0 < R < 1	Favourable
R = 0	Irreversible

For the experimental temperature conditions, the coefficient b varies between 0,1 and 0,6. As a result, R varies between 0,008 and 0,05. Consequently, at the limit of irreversibility, the uranium sorption isotherm can be described as "very favourable". The same conclusion can be made about the pH effect: at pH 6, the b coefficient increases and hence the R value decreases. The type of isotherm approximates an "irreversible" isotherm.

Conclusion

The equilibrium studies of uranium sorption by glutamate glucan, an oxo-2-glutaric acid substituted chitosan, led to the conclusion that maximum uranium uptake approximates 450 to 550 mgU/g, under specific experimental conditions. According to the Muzzarelli and Zattoni (1986) studies, the high sorption capacity presented by other types of polymers is due to the polymers' porosity and their hydrophilic structure, and also due to the availability of amines and carboxylate functional groups on the glucan framework.

Parameters such as pH and metal ion concentration greatly influence the maximum uranium uptake. Other parameters such as temperature, agitation and particle size of adsorbent show a restricted effect on the equilibrium between the solid and the liquid phase. These 3 parameters mainly influence the kinetic behaviour of the polymer in uranium sorption. The shapes of the isotherms, confirmed by the R separation factor, indicate that isotherms are very favourable. Within the range of temperatures studied, the differences in Langmuir and Freundlich parameters are not significant. As a result, conclusions concerning the exothermic nature of the sorption mechanisms cannot be reached.

At pH 5, the fit of the experimental results to the Langmuir and Freundlich models demonstrates that uranium sorption by glutamate glucan results in the formation of an adsorption monolayer. With a higher pH, the distribution between free non-hydrated and hydrolysed uranyl species results in a slight change in the mechanisms and in the shapes of the isotherms. Surface precipitation adsorption is the probable cause for the adsorption multilayer mechanism (like the Brunauer Emmet and Teller model). This conclusion is consistent with the hypothesis presented by Muzzarelli and Zattoni (1986). The high adsorption capacity is attributed to the chelation process in addition to other mechanisms. The chelates initially formed promote the mechanisms of deposition of inorganic aggregates on polymer flakes. With a lower pH, sorption decreases. In an acidic medium, the desorption step increases and the solubility of uranyl increases. As a result, the sorption performance is strongly reduced.

References

- BAES, CF (Jr) and MESMER, RE (1976) *Hydrolysis of Cations*. New York. John Wiley and Sons. 489 pp.
- COUGHLIN, RW, DESHAIES, MR and DAVIS, EM (1990) Chitosan in crab shell wastes purifies electroplating wastewater. *Environ. Prog.* **9**(1) 35-39.
- DE ROME, L and GADD, GM (1987) Copper adsorption by *Rhizopus arrhizus*, *Chlamydosporium resinae* and *Penicillium italicum*. *Appl. Microbiol. Biotechnol.* **26** 84-90.
- EIDEN, CA, JEWELL, CA and WIGHTMAN, JP (1980) Interaction of lead and chromium with chitin and chitosan. *J. Appl. Polymer Sci.* **25** 1587-1599.
- FARLEY, KJ, DZOMBAK, DA and MOREL, FMM (1985) A surface precipitation model for the sorption of cations on metal oxides. *J. Colloid and Interface Sci.* **106** 226-242.
- GUIBAL, E, ROULPH, C and LE CLOIREC, P (1992) Uranium biosorption by a filamentous fungus *Mucor miehei* - pH effect on mechanisms and performance of uptake. *Water Res.* **26**(8) 1139-1145.
- GUIBAL, E (1990) Contribution à l'étude de la biofixation de l'uranium par un champignon filamenteux: *Mucor miehei*. Thèse de Doctorat, Institut National des Sciences Appliquées de Lyon, Villeurbanne, France, 20 juin 1990. 165 pp.
- GUIBAL, E and ROULPH, C (1991) Fixation de l'uranium par un champignon filamenteux: Application au traitement d'effluents faiblement chargés. *J. Fr. Hydrol.* **21**(2) 229-240.
- GUIBAL, E, SAUCEDO, I, ROUSSY, J, ROULPH, C and LE CLOIREC, P (1993) Uranium sorption by glutamate glucan: A modified chitosan. -Part II: Kinetic studies. *Water SA* **19**(2) 119-126.
- HOLME, KR and HALL, LD (1991) Novel metal chelating chitosan derivative: Attachment of iminodiacetate moieties via a hydrophilic spacer group. *Can. J. Chem.* **69** 585-589.
- HORIKOSHI, T, NAKAJIMA, A and SAKAGUCHI, T (1986) Accumulation of uranium by microorganisms. *Eur. J. Appl. Microbiol. Biotechnol.* **12** 90-96.
- HUANG, C, HUANG, CP and MOREHART, AL (1991) Proton competition in Cu(II) adsorption by fungal mycelia. *Water Res.* **25**(11) 1365-1375.
- MARUCA, R, SUDER, BJ and WIGHTMAN, JP (1982) Interaction of heavy metals with chitin and chitosan. III Chromium. *J. Appl. Polymer Sci.* **27** 4827-4837.
- McKAY, G, BLAIR, HS and FINDON, A (1986) Sorption of metal ions by chitosan. In: Eccles, H and Hunt, S (eds.) *Immobilisation of Ions by Bio-sorption*. Ellis Horwood Limited, Chichester. 59-69.
- McKAY, G, BLAIR, HS and FINDON, A (1989) Equilibrium studies for the sorption of metal ions onto chitosan. *Indian. J. Chem., Sec. A*, May 1989 **28A** 356-360.
- MUZZARELLI, RAA (1985) Removal of uranium from solutions and brines by a derivative of chitosan and ascorbic acid. *Carbohydr. Polymers* **5** 85-89.
- MUZZARELLI, RAA (1989) Carboxymethylated chitins and chitosans. *Carbohydr. Polymers* **8** 1-21.
- MUZZARELLI, RAA (1990) *Chitin and Chitosan: Unique Cationic Polysaccharides*. Techn. Report Review Comm. Europ. Communities Rep. Eur. Towards Carbohydr. Based Chem. 197-232.
- MUZZARELLI, RAA, TANFANI, F and EMANUELLI, M (1984) Chelating derivatives of chitosan obtained by reaction with ascorbic acid. *Carbohydr. Polymers* **4** 137-151.
- MUZZARELLI, RAA and ZATTONI, A (1986) Glutamate glucan and aminogluconate glucan, new chelating ampholytes obtained from chitosan. *Int. J. Biol. Macromol.* **8** 137-141.
- SAUCEDO, I, GUIBAL, E, ROULPH, C and LE CLOIREC, P (1992) Sorption of uranyl ions by a modified chitosan: Kinetic and equilibrium studies. *Environ. Technol.* **13**(12) 1101-1115.
- STRANDBERG, GW and SHUMATE II, SE (1982) *Accumulation of Uranium, Cesium and Radium by Microbial Cells, Bench Scale Studies*. Oak Ridge National Laboratory, juillet 1982, ORNL TM-7599, Contract W. 7405 eng. 26.
- TOBIN, JM (1986) The uptake of metal ions by *Rhizopus arrhizus* biomass. Ph. D. Thesis, McGill University, Montreal, Canada. 172 pp.
- TSEZOS, M and VOLESKY, B (1981) Biosorption of uranium and thorium by *Rhizopus arrhizus*. *Biotechnol. and Bioeng.* **24** 385-401.
- WEBER, TW and CHAKRAVORTI, RK (1974) Pore and solid diffusion models for fixed-bed adsorbers. *AIChE J.* **20** (2) 228-237.