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URANIUM AND VANADIUM SORPTION BY CHITOSAN AND DERIVATIVES

E. Guibal, I. Saucedo*, M. Jansson-Charrier, B. Delanghe
and P. Le Cloirec

*Laboratoire Génie de l'Environnement, Industriel Ecole des mines d'Alès,
30319 Ales Cedex, France*

ABSTRACT

The modification of chitosan, by grafting of oxo-2-glutaric acid, allows its sorption performance to be increased. This enhancement of uptake ability is observed in overall sorption capacity and specificity in sorbing particular metals. This work focuses on the sorption of uranium (VI) and vanadium (V). The sorption isotherms are studied. The experimental results are described according to the Langmuir and Freundlich models. It was shown that uranium sorption is best described by the Freundlich model, while vanadium sorption is difficult to model. The influence of the particle size, significant in the case of uranium, but not for vanadium, shows that the sorption mechanism is not the same for the two metals : surface control is predominant in the case of uranium, due to the poor porosity of the sorbents. The control of overall sorption capacity is related to the chemistry of the metal and polymer : the appearance of hydrolyzed species and protonation of the polymer.

KEYWORDS

Chitosan; modified chitosan; sorption; uranium; vanadium; wastewater treatment.

INTRODUCTION

In order to propose new wastewater treatments as alternatives to physico-chemical techniques or membrane processes, which are limited by technical or economic criteria, biosorption by materials of biological origin has been studied (Tsezos and Volesky, 1982; Guibal, 1990; Sautel *et al.*, 1991; Deans and Dixon, 1992; Guibal *et al.*, 1992; Orhan and Büyükgüngör, 1993; Sharma and Forster, 1993). Various sorbents were used, chosen according to availability and taking economic constraints into account.

In fungal biomasses metal ion sorption is mainly located in the cell wall, which consists of a network of amino-polymers and glucans. The influence of amino-functions in the complexation and adsorption of metal ions is a well known phenomenon, although other groups such as phosphate or carboxylate could react. Chitin is partially acetylated and is the polymerization of chitin, the cell walls of fungi, yeasts and crustacean shells : lobsters, shrimps or crabs are common sources of chitin. This polymer is a well known sorbent, effective in the uptake of metal ions (Yang and Zall, 1984). This ability for complexation and adsorption is due to the high content of amino functions (Muzzarelli, 1973; Eiden *et al.*, 1980. McKay *et al.*,

* Present address: Instituto de Investigaciones Cientificas, Universidad de Guanajuato, L. de Retana N°5, Guanajuato, Gto 36000, Mexico.

1986, Coughlin *et al.*, 1990). Sorption performances are enhanced by simple modifications of the original chitosan (Ohga *et al.*, 1987; Muzzarelli, 1989; Holme and Hall, 1991). Muzzarelli *et al.* (1984) proposed substituting organic acids onto a chitosan backbone : ascorbic acid or oxo-2-glutaric acid for example.

The mechanisms involved in the metal sorption, depending on the nature and chemistry of the metal considered, include adsorption, complexation and/or precipitation (hydrolysis). This study deals with the sorption of uranium and vanadium, taking into account the effect of pH and initial metal concentration. A possible mechanism is suggested according to the metal chemistry and biopolymer structure.

MATERIAL AND METHODS

Chitosan is an 80 % deacetylated product, uranium is used in the form of uranyl nitrate and vanadium in the form of ammonium vanadate. The modification of chitosan is carried out according to the method previously described by Muzzarelli *et al.* (1984) and Saucedo *et al.* (1992). These modifications take place in two steps. Firstly, the chitosan is dissolved in an organic acid (oxo-2-glutaric acid in the present study) allowing an intermediary ketoimine to be obtained. The pH is adjusted to 4.5 after 6 hours of mixing time. Sodium cyanoborohydride is added to the solution to hydrogenate the ketoimine and the final pH adjusted to 6.5 with a sodium hydroxide solution. The white, fibrous, lightly viscous solid obtained is called glutamate glucan. The raw and modified chitosans are sieved into four fractions of the following diameters, as d_p : G1 < 125 μm , 125 μm < G2 < 250 μm , 250 μm < G3 < 500 μm , 500 μm < G4 < 1000 μm .

Sorption isotherms are obtained in a batch reactor with magnetic stirring, at 400 rpm, with a ratio L/S (liquid to solid) of 250 ml / 25mg of polymer. In order to avoid complexation of metals by other anions, all the data are reported for unbuffered solutions. The pH is continuously controlled and adjusted by additions of small volumes of sodium hydroxide or nitric acid (sulphuric acid for chitosan). Sulphuric acid promotes a recrystallization of the chitosan which allows the solid structure of the polymer to be maintained. In a nitric medium, chitosan is partially dissolved. The experimental temperature is set at 20°C. Samples are withdrawn and filtered through a Millipore membrane (pore size 0.45 μm).

The metal content in solution is determined by the arsenazo III colorimetric method for uranium (Guibal, 1990). In the case of vanadium, the analysis is obtained by a spectrophotometric method : complexation in a medium containing H_2O_2 , H_2SO_4 and H_3PO_4 (Roussy, 1990). The residual concentration, C_{eq} , is known and allows the metal concentration in the solid, q , to be estimated, according to mass balance and the formulae $q = (C_0 - C_{eq})V/m$, where C_0 is the metal concentration at initial time, V the volume of the solution and m the mass of sorbent.

RESULTS AND DISCUSSION

The adsorption of uranium and vanadium was studied with respect to pH, initial metal concentration and particle size. The sorption isotherms are characterized according to the Langmuir and the Freundlich models, described by the following equations :

$$\text{Langmuir Model : } q = q_0 \frac{bC_{eq}}{1+bC_{eq}} \quad q_0 \text{ (mg}\cdot\text{g}^{-1}\text{)}, b \text{ (l}\cdot\text{l}^{-1}\cdot\text{g}^{-1}\text{)} \text{ Langmuir's constants} \quad (1)$$

$$\text{Freundlich Model : } q = k C_{eq}^{1/n} \quad k \text{ and } n : \text{ Freundlich's constants} \quad (2)$$

Uranium

Figures 1 and 2 show the effect of pH on the respective uranium sorption isotherms for chitosan and glutamate glucan. Table 1 summarizes the Langmuir and Freundlich coefficients. Several facts can be deduced from these isotherms about the mechanism of interaction between metal and polymer.

The ability of chitosan and glutamate glucan to sorb uranium increases with the pH. At low pH the competition between H_3O^+ and UO_2^{2+} limits the uptake efficiency. Increasing the pH, to around pH 5 or 6, induces a reduction in electrostatic repulsion, a decrease in solubility and a modification of speciation equilibrium between uranyl and hydrolyzed forms (mainly $(UO_2)_3(OH)_5^+$). The appearance of uranyl hydrolyzed species is favourable to metal ion sorption. Various studies, about metal ion sorption on oxide or mineral surfaces, show that a drastic sorption increase is observed within a narrow range of pH (Park and Huang, 1989; Kornicker and Morse, 1991). The efficiency in metal removal varies from 0 to 100 %, over a pH range of almost one unit. This preferred pH range is directly related to the existence of hydrolysed species in the solution (Zouboulis *et al.*, 1993). The hydrolyzed metal species, coating the sorbent surface, tends to acquire an electrokinetic behaviour similar to that observed on metal hydroxide.

The representation of q versus C_{eq} shows, in the case of glutamate glucan, that experimental points are almost aligned : the interactions between glutamate glucan and uranium obey a pseudo-linear isotherm within the experimental concentration range. Table 1 shows a greater correlation coefficient with the Freundlich model than the Langmuir model : mutual interactions between sorbed molecules cannot be denied. The correlation coefficients are better with glutamate glucan than with chitosan, indicating that the uptake is more complex with chitosan. For the Langmuir model, hypotheses predict a homogeneous distribution of sorption energies, as opposed to the exponential distribution predicted by the Freundlich model. The values for the exponent in the Freundlich model indicate the type of isotherm : irreversible, favourable, linear or unfavourable. The greater the Freundlich n coefficient, the more favourable is the metal ion sorption at a given pH.

TABLE 1. Application of Sorption Models to Uranium Uptake by Chitosan and Glutamate Glucan

Polymer	pH	Freundlich Model			Langmuir Model		
		k	n	R ²	q ₀	b	R ²
Chitosan	4	108.3	5.6	0.93	202.9	0.49	0.79
"	5	169.4	6.2	0.88	317.2	0.54	0.79
"	6	154.5	4.0	0.91	344.1	0.72	0.94
Glutamate glucan	5	105.7	3.1	0.98	363.7	0.57	0.82
"	6	43.2	1.8	0.95	363.0	0.16	0.76

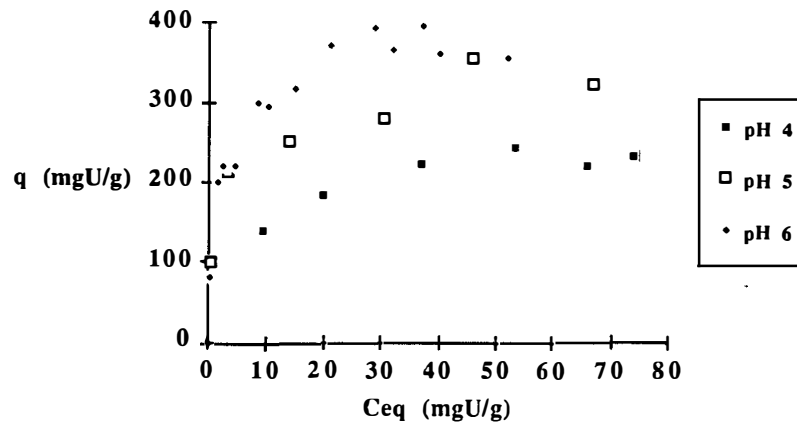


Fig. 1. Effect of pH on the uranium sorption by chitosan (G2).

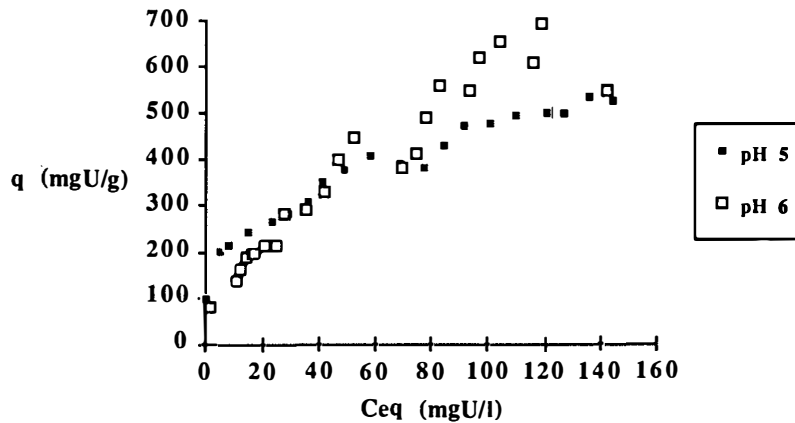


Fig. 2. Effect of pH on the uranium sorption by glutamate glucan (G2).

These experiments are performed with particle size of the G2 class. Previous work on glutamate glucan shows that increasing the diameter of the particles has no influence on the final concentration of uranium in the polymer (Saucedo *et al.*, 1993), therefore the kinetics of sorption are drastically affected by this parameter (Guibal *et al.*, 1993) as seen in Figure 3. This conclusion is not verified with chitosan : an increase in the particle size leads to a large decrease in the sorption capacity at equilibrium (Figure 4). Moreover the time required to reach the equilibrium is drastically increased for chitosan compared with glutamate glucan : kinetics and equilibrium are affected by the low porosity of the polymer. It should be pointed out that vanadium (IV) sorption is less affected by the particle size, as revealed by previous studies (Jansson-Charrier *et al.*, 1994) : vanadium speciation plays an important part in sorption and diffusion mechanisms. It can possibly be inferred that there is external surface control of the sorption, related to the specific area of sorbent for both uranium and vanadium (V). This polymer has a low porosity which limits the diffusion of metal ions within the structure, so the overall capacity is a function of the developed external surface. The modification of the polymer promotes an increase in the porosity of the polymer and enhances the ability of the solute to diffuse. The recrystallization of chitosan according to the procedure described by Struszczyk (1987) includes dissolving the chitosan in acetic acid at a controlled temperature (70°C), followed by a rapid freezing and a precipitation with sodium hydroxide solution at ambient temperature. This technique improves diffusion within the polymer structure, which allows the maximum uptake to be increased independent of particle size (Saucedo, 1993). Scanning Electron Microscopy and X-ray Energy Dispersed Analysis show a concentration gradient in both polymers which corroborates the previous conclusions (Guibal *et al.*, 1995).

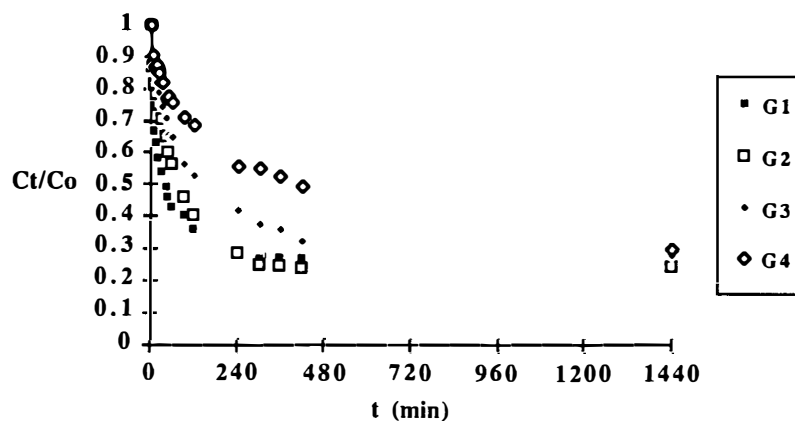


Fig. 3. Influence of the particle size of glutamate glucan on uranium sorption kinetics and equilibrium (pH 5, $C_0=25$ mg.l⁻¹).

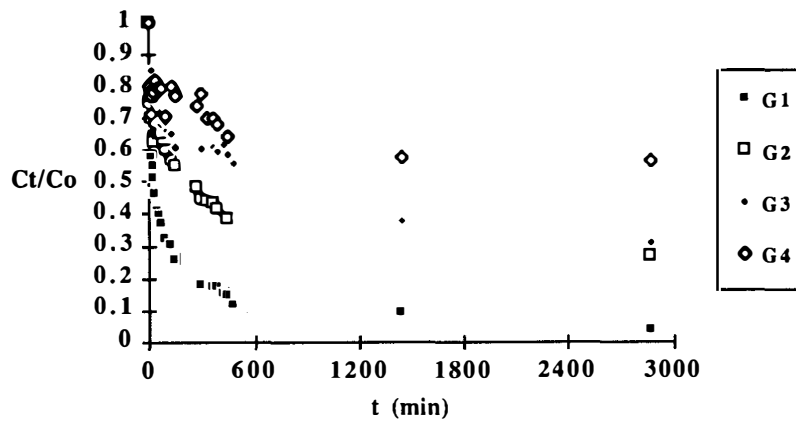


Fig. 4. Influence of the particle size of chitosan on uranium sorption kinetics and equilibrium (pH 5, $C_0=25 \text{ mg.l}^{-1}$).

Vanadium

The kinetic behaviour of chitosan and glutamate glucan towards vanadium differs significantly from mechanisms observed with uranium : the particle size effect is not significant and equilibrium is independent of the specific area (Saucedo, 1993) as shown by the Figure 5. For the small particles used sorption seems to occur in the whole mass of the sorbent and not only on the external surface or in a thin layer revealed in the case of the uranium sorption.

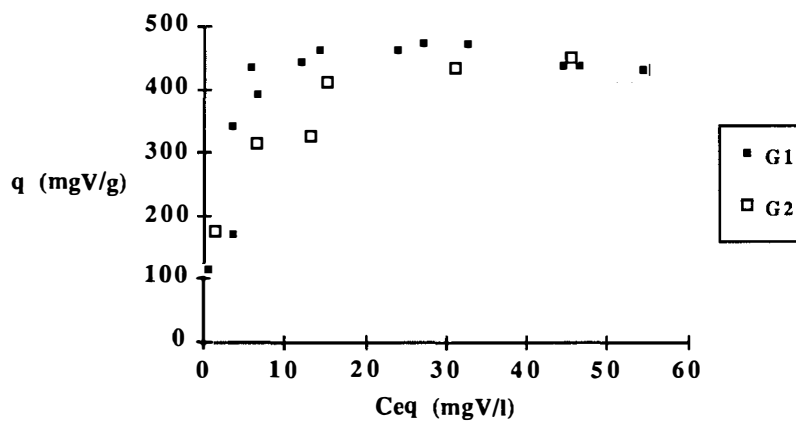


Fig. 5. Effect of the particle size on vanadium sorption by chitosan at pH 3.

The great sensitivity of the aqueous medium to simple variation in pH induces dispersion of experimental results, moreover sorption isotherms quickly reach a plateau, and the application of the Langmuir and Freundlich models would give low correlation coefficients. The shape of the isotherms approximates to a pseudo rectangular isotherm.

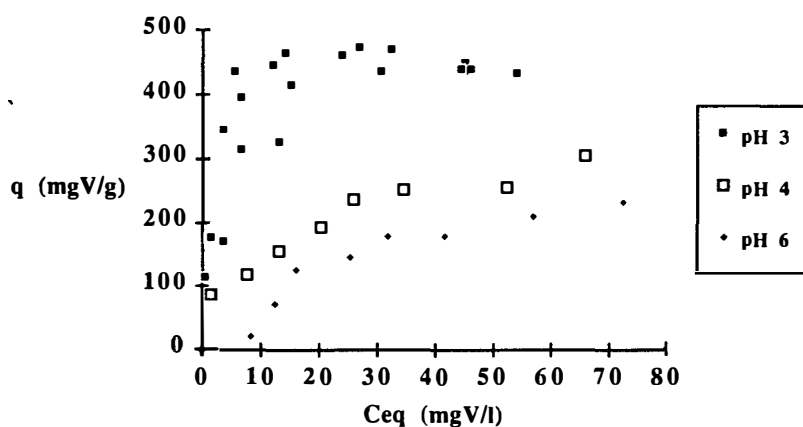


Fig. 6. Effect of pH on vanadium sorption by chitosan (G2).

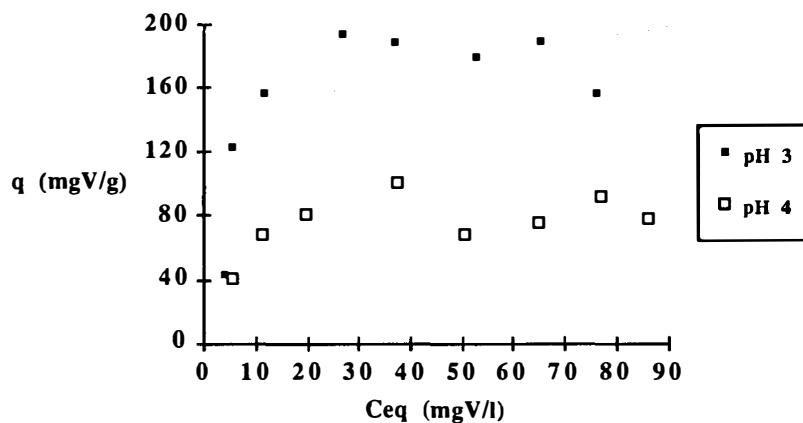


Fig. 7. Effect of pH on vanadium sorption by glutamate glucan (G2).

For vanadium the best uptake occurs at acid pH. The competition of protons has a restricted effect in comparison with uranium sorption. A pH of 3 to 4 allows vanadium hydrolysis products to appear. In this range of pH, the predominant vanadium species are $V_{10}O_{27}(OH)^{5-}$ or $V_{10}O_{26}(OH)_2^{4-}$, depending on total metal concentration (Baes and Mesmer, 1976).

In an acidic medium the overall charge of the sorbent is positive, favouring the uptake of these vanadium hydrolysis products. A previous study of acid-base behaviour, by titrimetric methods, allows some proton exchange properties of these sorbents to be determined (Muzzarelli and Zattoni, 1986; Saucedo, 1993) : the pK_a of chitosan varies between 6.1 and 6.5. For glutamate glucan the pK_a of the carboxylic grafted function is measured between 4.4 and 5.1, the pK_a of the amino function is set between 8.2 and 8.6, for an isoelectric point of approximately 6.8. So in an acidic medium, the protonation of binding functions promotes the uptake of metal anions such as the above species. This interpretation is consistent with previous work on metal ion sorption by *Rhizopus arrhizus* (Tobin *et al.*, 1984). This behaviour is the opposite of uranium sorption phenomena.

The pseudo-linear isotherm observed with uranyl is not seen with vanadium, for which sorption presents a pseudo-rectangular shape. In contrast with uranium, glutamate glucan is a poorer vanadium sorbent than chitosan. The modification of chitosan promotes selectivity in metal ion sorption.

The differences observed in sorption mechanisms for uranium and vanadium removal seems to indicate that the optimum pH is a result of both metal ion chemistry in solution and sorbent proton exchange properties. The speciation of metal ions in an aqueous medium, and the appearance of hydrolysis forms in the one hand and the protonation of the sorbent surface on the other. Moreover the porosity of the sorbent, and the ability of metal ions to diffuse in the mass of the sorbent by several migration steps (homogeneous, surface or bulk diffusion) can determine overall performances in metal ion sorption.

The ability of the sorbents to be eluted and regenerated is of great interest for a potential industrial application. Previous personal results (unpublished) show that uranium can be desorbed by sodium hydrogenocarbonate, as observed for the elution of uranium saturated fungal cells (Tsezos, 1984; Guibal, 1990), allowing a concentration factor of approximately 1000-5000 between influent concentration and eluate. The metal can be economically removed and recovered. For the vanadium effluents, the saturated sorbent can be eluted by diluted solutions of sulphuric acid.

CONCLUSION

Chitosan and its oxo-2-glutaric acid substituted form are very effective in uranium and vanadium sorption : concentrations as high as 450 mg of metal per gram of adsorbent can be reached in a batch reactor. The sorption occurs preferentially through a monolayer adsorption with lateral interactions between sorbed molecules, as described by the Freundlich model. The best pH range depends on metal and polymer chemistry. An acidic medium brings about a protonation of the polymer favourable to the sorption of vanadate, which is negatively charged. These experimental conditions are unfavourable to uranyl, which is positively charged. So uranium is best accumulated in a lightly acidic medium (between pH 5 and 6). It has been shown that the highest uptake capacity is obtained in a pH range where hydrolyzed metal ions predominate. The particle size of the polymer greatly influences the uranium sorption by chitosan, but has a limited effect on vanadium (V) sorption by the same sorbent. The modification of the chitosan by substituting some functional groups allows both maximum uptake capacity and kinetic behaviour to be increased, generally enhancing the diffusion properties.

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