

Uranium sorption by glutamate glucan: A modified chitosan

Part I: Equilibrium studies

I Saucedo, E Guibal*, J Roussy, Ch Roulph and P Le Cloirec

Ecole des Mines d'Ales - ENSTIMA Centre de VEnvironnement Industriel, Laboratoire Genie de l'Environnement, 6, avenue de clavieres, 30319 ALES cedex - FRANCE

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, $M = 2 \times 10^6$, 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: $500 \mu\text{m} < d_p < 1000 \mu\text{m}$.

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.

*To whom all correspondence should be addressed.

Received 14 January 1992; accepted in revised form 26 August 1992.