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Removal of Uranium from Solutions and Brines by a Derivative of Chitosan and Ascorbic Acid

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SUMMARY

Dihydroxyethyltetrahydrofuryl chitosan (which is obtained from Euphausia superba *chitosan upon Schiff reaction with dehydroascorbic acid and subsequent reduction of the ketimine obtained) can accumulate uranium from aqueous solutions, including 3% saline waters. By this chemical modification, the characteristic property of the chitosan-glucan complexes of fungal origin which collect uranium by chelation and hydrolysis is conferred to krill and shrimp chitosans. The capacity of dihydroxyethyltetrahydrofuryl chitosan is 1·0 g U/g and is about one order of magnitude higher than that of the cells of* Rhizopus arrhizus *and about two orders of magnitude higher than the mycelia of* Penicillium digitatum.

Although adsorption of uranium on polyaminosaccharides has been well known and documented for more than 15 years (Manskaya & Drozdova, 1968; Muzzarelli, 1972, 1973, 1977; Muzzarelli & Tubertini, 1969; Muzzarelli *et al.*, 1970), our recent discovery of the ability of the ascorbic acid derivative of chitosan to collect uranyl ions (Muzzarelli *et al.*, 1984) permits the attainment of adsorption levels which are orders of magnitude higher than with other biopolymers.

This capability is all the more significant in the light of the additional demonstrations that (i) the modified chitosan can be obtained by simple chemical reactions at room temperature; (ii) uranium is collected to such an extent in terms of capacity that a compound results whose

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inorganic part is predominant by weight over the organic one; and (iii) 30 *N*-substituted chitosans have been unsuccessfully tested for their uranium collection ability (Hirano, 1982).

Our early study on the chelating ability of the mycelia of *Aspergillus niger* as well as those of *Mucor rouxii*, *Choanephora cucurbitarum*, *Phycomyces blakesleeanus* and *Streptomyces* showed that the fungal chitosan-glucan complexes are more effective than chitosan itself in collecting metal ions (Muzzarelli, 1979; Muzzarelli and Tanfani, 1982; Muzzarelli *et al.*, 1980, 1981). Further studies on *Aspergillus terreus*, *Streptomyces niveus*, *Penicillium chrysogenum*, *Pseudomonas fluorescens* and *Rhizopus arrhizus* showed that the last of these has a capacity for uranium of 180 mg/g (Tsezos and Voleski, 1981, 1982), whilst the data reported by Galun *et al.* (1983) on *Penicillium digitatum* are limited to capacity values as low as 3–9 mg/g for equilibrium concentrations of 51–58 mg/litre.

Our study on chitosan and its derivatives obtained from *Euphausia superba* and *Pandalus borealis* shells indicates that uranium uptake by chitosan preparations can be greatly enhanced by reacting the amino groups of chitosan with the ketone groups of dehydroascorbic acid to produce a chitosan ketimine that is further reduced to *N*-[2-(1,2-dihydroxyethyl)tetrahydrofuryl]chitosan (NDTC) with sodium cyanoborohydride.

Ascorbic acid, besides being a suitable acid for the formation of a water-soluble chitosan salt (chitosan ascorbate), can also react with chitosan to form chitosan derivatives *via* a Schiff reaction. Mild oxidising agents such as iodine and air easily convert ascorbic acid to dehydroascorbic acid, whose carbonyl groups are able to react with amines. For example, one of the most widely accepted methods for the quantitative determination of ascorbic acid involves oxidation followed by a reaction with 1,2-phenylenediamine to produce a fluorophor. The preparation of the uranium absorber followed the description already published (Muzzarelli *et al.*, 1984).

The reaction of chitosan with dehydroascorbic acid can be followed by infrared spectrometry (bands at 1710 and 1760 cm^{-1} due to α,β-unsaturated cyclic ketones), by alkalimetry (through the typical shape of the alkalimetric curve), by viscometry (viscosity decrease from 108 to 77 cP within 6 h and to 25 cP within 24 h, for a 1% solution), and by circular dichroism spectropolarimetry (negative band shifted from 194 to 213 nm, positive band at 244 nm, new negative band at 310–

320 nm and positive at 272 nm). The water-soluble ketimine is reduced to NDTC, an insoluble, fibrous and white product.

The presence of the 1,2-dihydroxyethyl group is important for certain uses of chitosan, and this group is found, for instance, in glycol chitosan, a partially *O*-2-hydroxyethylated chitosan, and hydroxypropyl chitin. NDTC apparently possesses extremely high capacity for uranium because it is a polysaccharide carrying aliphatic chains with both dihydroxyethyl and secondary amino groups.

For the batch measurements, the initial uranium concentration ranged from 10 to 1000 mg U/litre, all below the solubility limits set by the solution pH values. Most of the measurements were carried out at pH 4·5; it was noticed, however, that initial higher pH values were lowered to 4·7–5·1 after the period of time allowed for contact. The amounts of NDTC contacted with uranyl acetate solution were weighed quantities between 10 and 100 mg. The solution volume was 25 ml. Following the contact period of 16 h, the NDTC mass was separated from the solution. Separation was accomplished by vacuum filtration on 0·45 μm Sartorius membrane filters; the equilibrium uranium concentration of the filtrate (C_{eq}) was determined by spectrophotometry on 8-hydroxyquinoline extracts.

The percentage efficiencies of collection from 5 mM uranium solutions on NDTC (100 mg) for various initial pH values were: 87% at pH 4·5; 97% at pH 5·5; 100% at pH 6·8 and 7·4, a few minutes after contact. After reacting with uranyl ions, NDTC had a bright yellow orange colour. In the concentration interval 0·5–5·0 mM, uranium was collected in the batch mode to extents between 90 and 98%.

Figure 1 shows the double logarithmic plot of the uranium adsorption isotherms obtained in this study (curves A and B) and from data derived from *Rhizopus arrhizus* cells, under the same conditions (the only difference being that acetate was used instead of nitrate as the counter-ion). If we compare curves A and C which refer to aqueous solutions with no salt added, we notice that a major portion of curve A employing NDTC is an order of magnitude higher than that of curve C derived from *Rhizopus arrhizus* cells. The capacity of NDTC is so high that equilibrium concentrations higher than 20 mg/litre were not recorded, the slope of the NDTC curve A being steeper than that of curve C (*Rhizopus arrhizus* cells). In practice, when *Rhizopus arrhizus* collects 90 mg/g at an equilibrium concentration of 20 mg/litre, NDTC collects about 700 mg/g at the same equilibrium concentration.

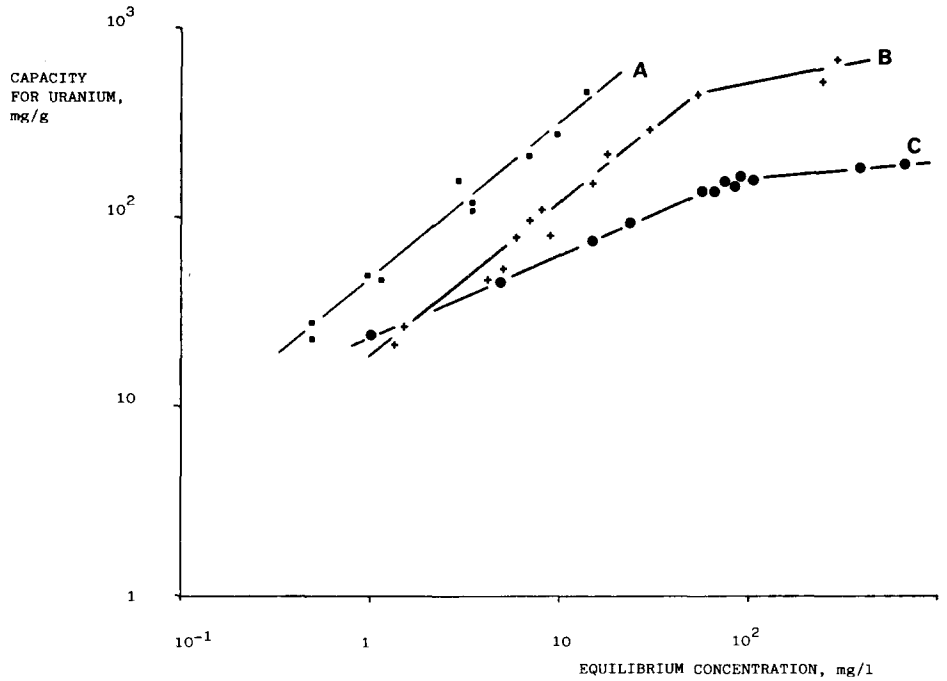

Fig. 1. Uranium collection isotherms from solutions at pH 4·5. (■) NDTC in uranyl acetate solution; (+) NDTC in uranyl acetate solution made to contain 3% sodium chloride; (●) *Rhizopus arrhizus* in uranyl nitrate solution (from Tsezos and Voleski, 1981). Data obtained by spectrophotometry and elaborated according to:

$$q = \frac{V \cdot (C_{in} - C_{eq})}{M}$$

where V is the sample volume (litres), C_{in} is the initial uranium concentration (mg litre^{-1}), C_{eq} is the equilibrium uranium concentration (mg litre^{-1}), M is the powder weight (g) and q is the capacity for uranium (mg g^{-1}).

All the experimental points relevant to uranium collection from sodium chloride solutions on NDTC (curve B) lie above those for *Rhizopus arrhizus* (curve C). While no data have been published for cells of *Rhizopus arrhizus* in brines, it is interesting to note that NDTC in brine performs better than cells of *Rhizopus arrhizus* in solutions with no salt. For instance, the NDTC capacity is 200 mg/g at an equilibrium concentration of 20 mg/litre, against 90 mg/g for *R. arrhizus*,

and it is 800 mg/g for NDTC against 200 mg/g for *R. arrhizus*, both at 300 mg/litre equilibrium concentration. This means that NDTC is superior to cells of *R. arrhizus*, not only under comparable conditions, but even when NDTC is under the adverse effect of high sodium chloride concentration.

Uranium adsorption by NDTC is clearly a physicochemical process with a considerable potential for technical applications.

Under comparable conditions, emulsan, the extracellular bioemulsifier of *Acinetobacter calcoaceticus* has the capacity for uranium (about 200 mg g^{-1}, based on figure 2 of Zosim *et al.*, 1982) similar to the *Rhizopus arrhizus* mycelia capacity.

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