Photochemical reaction of uranium with glucosamine, acetylglucosamine and related polymers: Chitin and chitosan

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Abstract

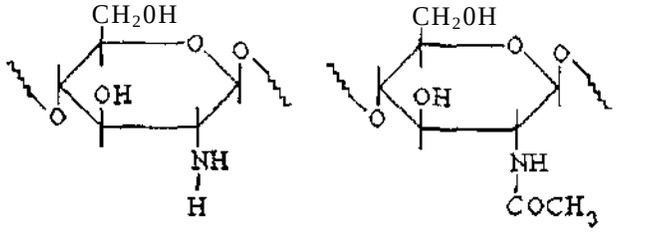
Uranylions can interact with amino-Ugands and polymers such aschitivt and chiiosan by complexalion and adsorption. This reaction can be affected by certain circumstances, such as a direct exposure to visibie light, to give photoreactions. Among the main photoreduction mechanisms, sensitised photoactivation (SP) and charge transfer to mass (CTTM) are thought to explain the various responses obtained under several experimental conditions, where the nature of the ligand and the aerobic or anaerobic media are all changed. It seems that a preliminary complexation of uranium by ligand is required to optimise the reduction rate. The pH of the solulion is significantly affected by the photoreaction, depending on the experimental procedure, and a precipltate appears after a duration. Elemental analysis and infra-red studies enable she structure of the precipitates to be determined as dihydrated uranate forms.

Introduction

The development of new processes for the treatment of low-metal concentration effluents, required for pollution control, involves the use of new sorbents. Bacterial and fungal biomass is useful for the recovery of metal ions in such dilute effluents (Tsezos and Volesky, 1981; De Rome and Gadd. 1987; Guibal et al., 1992; Guibal et al., 1993; Saucedo et al., 1993). Other polymers are also used to remove copper, lead, chromium and uranium from aqueous media (Muzzarelli and Tubertirti, 1969; Eiden et al., 1980; Deans and Dixon. 1992;. Guibal et al.. 1994). Chitin, a widely available natural material, obtained from shrimps, crustaceans, lobsters and also from fungal cell walls, is characterised by a high nitrogen content. This polymer, poly(P-(l-4)-2-acetamido -2-deoxy-D-glucose, treated with concentrated sodium hydroxide, at boiling point, with reflux, gives a partially deacetylated form: chitosan, poly(B-(l-4)-2-amino-2-dcoxy-D-glucose. Chitin and chitosan are polyacetyl glucosamine and polyglucosamine respectively. The related monomer units are presented in Fig. 1.

Glucosamine and acetylglucosamine are also reported to be metal-ion ligands. Several mechanisms are put forward todescribe the interaction of such molecules with copper ions (Park and Park. 1984; Micera et al., 1985) . The stoichiometry between amino-ligands or chitosan and metal ions is still highly controversial (Muzzarelli et al.. 1980; Domard, 1987; Lopez de Alba et al., 1989):thecaseforcooperative 1:1 linking is proposed and contested. Some of these studies show a precipitation phase of metal ions into the polymer network and in particular into the pores (Eiden et al.. 1980; Park and Park. 1984),

These ligands and sorbents are effective in uranium collection from dilute effluents. Sorplion capacity can reach around 250 mg $U\text{-}g^{1}$, forchitosan. The ability of glucosamine and acetylglucos-amine is examined according to pH (Guibal, 1990; Guibal et al., 1995b). In a continuous mixed tank reactor or in a column continuously fed with solutions, no significant change in the aspect of the polymers or the solutions is noticed. But in a confined medium with natural UV-visible irradiation a noticeable change in colour is observed both in chitosan-saturated particles and in uranium-glucosamine mix solutions. The effect of solar exposure disappears when the uranium sorplion or complexation occurs under aerobic conditions. These observations suggest the photodegradation of complexes formed between uranyl ions and ligands or sorbents. Several works deal with similar observations in terms of the photoreduction of uranium in a complex medium exposed to radiation (Heidt and Moon, 1953; Adams and Smith. 1960;Heckleretal., 1963;RahinowitchandBelford. 1964;Sakwaba and Matsushima, 1970). Several approaches suggest charge transfer to mass (CTTM) or sensitised photo-activation (SP) mechanisms to interpret such phenomena (Ohyoshi and Ueno, 1974; Bhatt et al., 1986; Sandhu et al., 1987; Zuo and Holgne, 1992; Dodge and Francis, 1994).



D-Glucosamine N-Aceryl-D-Glucosamine

Figure 1
Glucosamine and acetylglucosamine structures (respectively monomer units of chitosan and chitin)

The aim of this work is to show the influence of photochemical reactions on uranium/amino-ligands interactions, and to identify the main parameters. The influence of the atmosphere (air or nitrogen) and of the ligand (e.g. glucosamine, acetylglucosamine, chitin or chitosan) is estimated in turn, together with the effect of exposure to a visible lamp.

Materials and methods

Reagents

Uranyl ions were used (in the nitrate or acetate form, Prolabo RP). Chitin and chitosan polymers are obtained from Fluka products. A viscometric study and a further application of the Sakurada-Mark-

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