

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

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Abstract

Uranyl ions can interact with amino-ligands and polymers such as chitin and chitosan by complexation and adsorption. This reaction can be affected by certain circumstances, such as a direct exposure to visible 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 solution is significantly affected by the photoreaction, depending on the experimental procedure, and a precipitate appears after a duration. Elemental analysis and infra-red studies enable the 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 Tubertini, 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(β -(1-4)-2-acetamido-2-deoxy-D-glucose, treated with concentrated sodium hydroxide, at boiling point, with reflux, gives a partially deacetylated form: chitosan, poly(β -(1-4)-2-amino-2-deoxy-D-glucose. Chitin and chitosan are polyacetylglucosamine 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 to describe 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): the case for cooperative 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. Sorption capacity can reach around 250 mg U·g⁻¹, for chitosan. The ability of glucosamine and acetylglucosamine 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

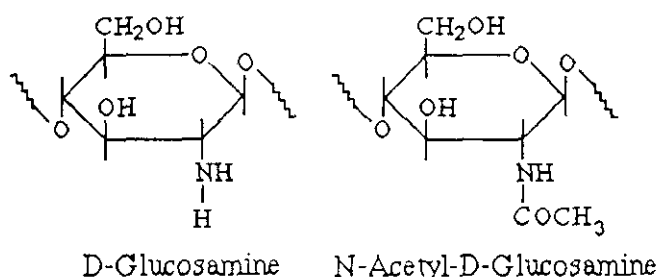


Figure 1
Glucosamine and acetylglucosamine structures
(respectively monomer units of chitosan and chitin)

uranium-glucosamine mix solutions. The effect of solar exposure disappears when the uranium sorption 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; Heckler et al., 1963; Rabinowitch and Belford, 1964; Sakuraba 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).

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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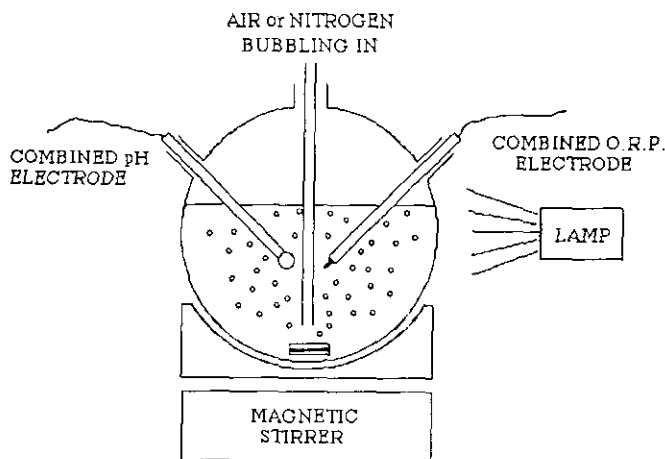


Figure 2
The photodegradation apparatus for the absolute oxidation-reduction potential study

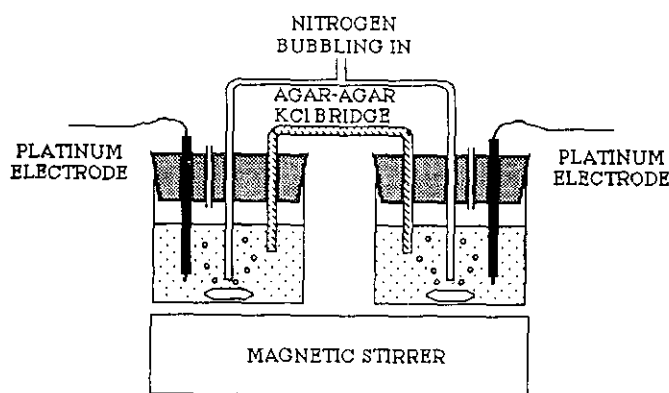


Figure 3
The photodegradation apparatus for the relative oxidation-reduction potential study

Houwink method enable the molecular mass of chitosan to be estimated at around 6×10^5 (Guibal et al., 1995 a). The deacetylation percentage of around 85% was estimated by infra-red analysis. Acetylglucosamine and glucosamine were supplied by Riedel-de-Haen.

The preparation of uranyl media (0.01 M, initial pH: 4) was carried out in a dark room. Solutions were deaerated, for corresponding experiments, with N₂ gas and then sealed. The addition of amino-ligands gives 1: 1 stoichiometric solutions. For chitin and chitosan experiments, the final concentration was 2 g.l⁻¹.

Photochemical reaction

Photoreactions were performed using two sets of apparatus. The apparatus described in Fig. 2 enabled the absolute oxidation reduction potential to be measured and the pH to be controlled during the photolysis step. The parameters were varied (Table 1). Figure 3 illustrates the system used to determine the potential difference between two reactors (one exposed to a lamp, the other kept dark by means of a black coating), the platinum electrodes being connected to a potentiometer. The experiments were

performed at least in duplicate or triplicate to ensure reproducible data (data variations lower than 8%). Table 2 summarises the runs for this experimental part. The Prolabo RP VL-206BL lamp provided radiation characterised by a wave number above 365 nm and a 24 W power, with two tubes of 6 W (black light). The distance between the lamp and the reactors was 15 cm. For experiments involving air bubbling, carbon dioxide was removed from the gas by bubbling it into a baryte solution (Ba(OH)₂). The gas flow rate was 2 l.h⁻¹. The system was kept in a dark incubator and the interior faces were covered by aluminium foil in order to reflect light energy.

Infra-red spectrometry

Infra-red spectrometry analysis was used to identify the precipitate obtained during the photolysis process when soluble amino-ligands were being used. The sample was ground with infra-red grade potassium bromide, KBr, in an agate mortar, an aliquot of 400 mg of this taken with an 0.1% m/m sample content. The translucent discs, obtained by compressing the ground material with the aid of a Specac press (pressure 6.6×10^{11} Pa) for 5 min were analysed by transmission with a Nicolet FITR spectrophotometer 510 (50 scans, background: air, resolution 2 cm⁻¹).

Run	Ligand or sorbent	Gas
1	None	Air
2	None	Nitrogen
3	Acetylglucosamine	Air
4	Acetylglucosamine	Nitrogen
5	Glucosamine	Air
6	Glucosamine	Nitrogen
7	Chitin	Nitrogen
8	Chitosan	Nitrogen

Results

The influence of experimental parameters on the oxidation reduction potential and pH

Figure 4 shows the evolution of the oxidation-reduction potential (ORP) in the reactor until equilibrium is reached. Figure 5, under the same experimental conditions, presents the evolution of this potential in the first 5 min and indicates a rapid decrease in the oxidation reduction potential. The experiments were carried out with uranyl acetate solutions.

This figure clearly shows that experimental results can be divided into two groups because of the effect of the bubbling. An air atmosphere produces a reduction of the ORP variation, whatever the ligand. After 7 h exposure to light, equilibrium potential stabilised itself between 540 and 620 mV. Acetylglucosamine (Run 3) displayed a larger variation in the first minutes of exposure but a subsequent increase in potential was observed before it finally reached an equilibrium value consistent with those obtained with glucosamine (Run 5) or in the absence of the ligand (Run 1). The

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reference solution, without ligand and exposed to a nitrogen atmosphere (Run 2), reached, at equilibrium, a 260 mV potential. A comparison of these curves reveals that in nitrogen, light exposure brings about a photoreduction of uranyl acetate, but the introduction of air, and oxygen, produces a partial re-oxidation of the sub-products of the photochemical reaction. Similar results were cited by Dodge and Francis (1994) about the photodegradation of the uranium citrate complex: in the presence of oxygen, U(IV) and citric acid are completely reoxidised to U(VI) and by-products. The nature of these products depends on the pH of the solution: at an acidic pH, acetic, acetoacetic, 3-oxoglutaric and malonic acids, carbon dioxide and acetone are obtained, therefore at a medium pH (i.e. pH 6) malonic and 3-oxoglutaric acids are the sole molecules identified. Obviously chitin produces a similar trend in potential evolution (for both equilibrium and kinetics). The influence of chitin on the photoreduction of uranyl ions is restricted by the low uptake of this metal ion onto poly-acetylglucosamine. Much more significant is the photochemical reaction, in a nitrogen atmosphere, between uranyl ions and acetylglucosamine, glucosamine or chitosan. The final absolute ORP is between 120 and 230 mV. For the first 30 min the ORP evolution is quite similar for both chitosan and acetylglucosamine. Beyond this time, potential of the solution increases for the chitosan and the curve resembles that of glucosamine: a partial re-oxidation occurs, possibly due to a depolymerisation of chitosan, a partial dissolution and further oxidation.

Figure 5 shows the initial decrease in the ORP, the kinetics of reduction follow the same trend observed for equilibrium potentials. Table 2 shows the initial reduction rate, calculated by linearisation of the ORP vs. time, and the subsequent derivative at $t = 0$.

The type of ligand and gas both influenced reduction rates: air atmosphere reduced the kinetics except when acetylglucosamine was present. The oxidation of intermediate products explained this rate decrease. With deaerated solutions, the presence of ligands or sorbents significantly increased the reduction rates compared with a reference solution free of ligand, except with chitin: with chitosan, the rate was multiplied by 2.5, and by 4 with soluble ligands. The interaction of ligands with uranyl ions promoted the potential decrease rate. The accessibility of sorbing sites seemed to be important as soon as the polymers produced a restrictive reduction in both equilibrium and kinetics compared with monomers. This difference could also be related to the nature of the interactions established between metal ions and sites: complexation with glucosamine and acetylglucosamine, sorption and complexation with chitin and chitosan. This second hypothesis was also consistent with the restricted influence of

Run	Ligand	Bubbling	Reduction rate (mV min ⁻¹)	Final decrease in ORP (mV)
1	None	Air	12.5	70
2	None	N ₂	30.7	435
3	Acetylglucosamine	Air	136.8	110
4	Acetylglucosamine	N ₂	130.3	565
5	Glucosamine	Air	49.7	140
6	Glucosamine	N ₂	118.5	505
7	Chitin	N ₂	30.3	420
8	Chitosan	N ₂	70.8	470

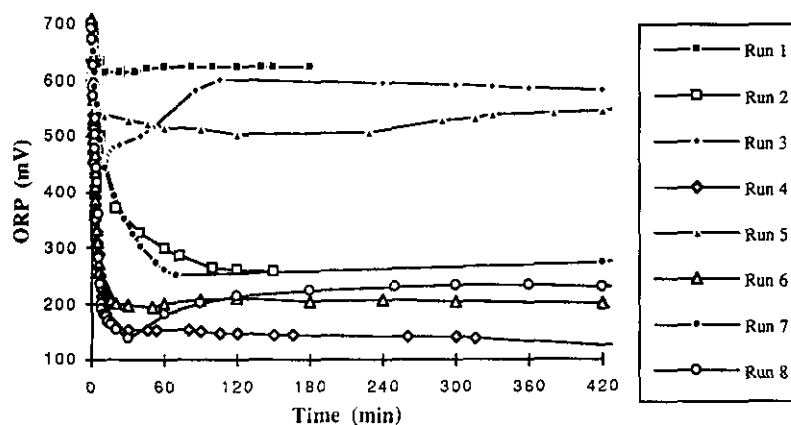


Figure 4
The oxidation-reduction potential decay vs. time for experimental conditions

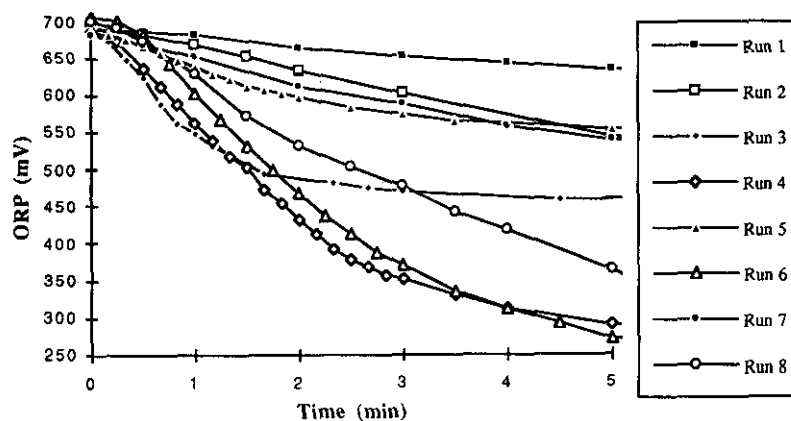


Figure 5
The oxidation-reduction potential decay vs. time for experimental conditions (first 5 min)

chitin, the low metal ion sorbent, on photochemical reaction kinetics. Dodge and Francis (1994) show that uranium-citrate complex degradation kinetics are slightly favoured by anaerobic conditions.

pH is also affected by such photochemical reactions as shown by Fig. 6. Polymers produce an increase in pH mainly due to natural proton exchange. This pH increase appeared mainly significant with chitosan, whose pKa is around 6.2 (Guibal et al., 1995a). pKa value is considered an indicative parameter as it varies

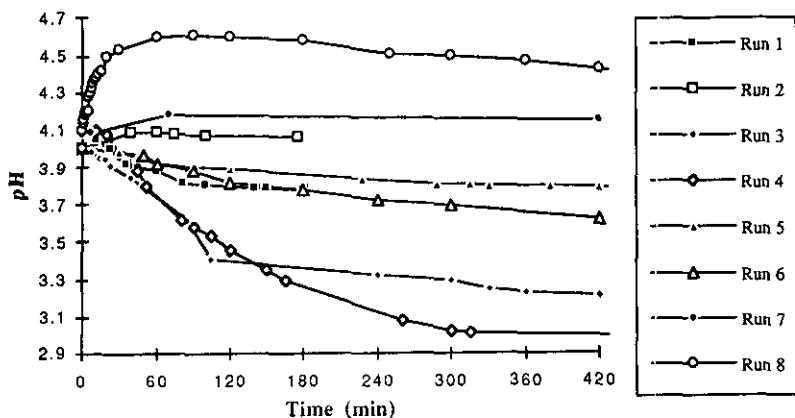


Figure 6
pH decay vs. time for the experimental conditions

with charge density and with external parameters such as pH and ionic strength of the media, according to Katchalsky's equation (Domard, 1987) or the Dubin and Strauss equation (Delben et al., 1989). In an acidic medium (pH: 4), chitin and chitosan are protonated and the residual proton concentration decreases, producing this pH increase. The pH increase reached a value of 4.6 after 1 to 2 h and later a slight decrease in pH gave a final value equal to 4.5. Chitin and the reference sample, exposed to light, showed a variation below 0.2 pH unit, in a nitrogen atmosphere. In an aerated medium, the reference sample and glucosamine (also under nitrogen atmosphere) exhibited a slight decrease in pH, lower than 0.2 units. A third group of experiments included acetylglucosamine, in both air and nitrogen, which produced a great variation reaching 3.0 to 3.2 pH units. It should be noted that variations in pH were rather less rapid than those obtained for the redox potential. The delay between the beginning of the photochemical reaction and the appearance of precipitates clearly indicated that such precipitation was related to the formation of intermediary products. The precipitation took place in the pH and ORP ranges observed after the stabilisation of the initial reductive step, or when the ORP was re-increasing. From Pourbaix (1963) a simplified ORP-pH diagram is drawn taking into account only major constituents (Fig. 7). Such a diagram is only applicable to a ligand-free solution, but enabled the range of predominance of several precipitate products and metal ions to be approached. Experimental conditions, pH and ORP, in the present study are consistent with

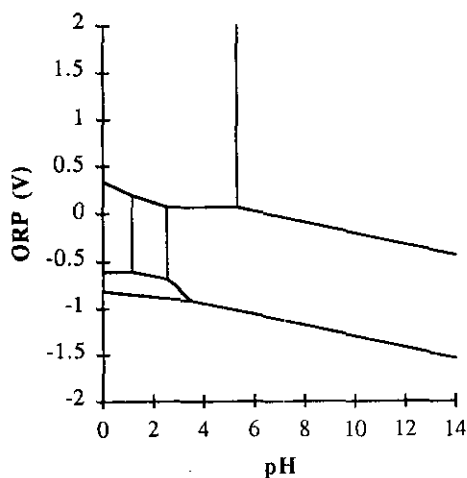


Figure 7
The ORP-pH diagram of uranium/water (total metal concentration 10^{-5} M)

the appearance of a uranate precipitate.

The pH variations are contradictory to observations made by Dodge and Francis (1994), who obtained a great increase in pH, whatever the initial pH, for the photodegradation of the uranium-citrate complex. The non-instantaneous variation in pH correlated with the appearance of precipitate particles in the solution whose composition was presented in Table 3 (elemental analysis). In an aerated medium, particles displayed a typical yellow tinge, while the precipitate was brown-black in a nitrogen atmosphere. Similar products were obtained by Dodge and Francis (1994) for aerobic conditions but in an aerobic medium they referred to a dark brown colloidal material, rather than a precipitate. Various methods, such as X-ray diffraction, X-ray absorption near-edge spectroscopy, and X-ray photoelectron spectroscopy enabled the precipitate to be identified as a hydrated uranium oxide, $UO_3 \cdot 2H_2O$, with traces of a synthetic form of the mineral schoepite, $UO_2(OH)_2 \cdot H_2O$. It is suggested that these products were generated during the re-oxidation phase of the intermediate by-products. The precipitate did not appear instantaneously, a latent time was required and this phase corresponded to the reduction step between acetate, ligands and uranyl ions. Dodge and Francis (1994) also reported that precipitation was totally or partially avoided by an excess of ligand.

The micro-elemental analysis showed that the composition of precipitates was not consistent with the suggested mineral precipitate compositions. The relative proportion of uranium was smaller, while the oxygen proportion was higher than the predicted value. Therefore the elemental analysis of precipitates revealed a cumulative percentage $\neq 100$. A rapid correction, taking into account only U, O and H, of the relative percentage gave in a nitrogen atmosphere the following ratio: $U/O/H = 73.97/24.80/1.22$ for glucosamine and $74.62/23.99/1.39$ for acetylglucosamine, results much more consistent with the composition of the predicted dehydrated UO_3 form. In an oxidative atmosphere, the analysis percentage correction was not enough to predict the actual structure of the precipitate, indicating obviously a different molecule. In air, precipitates had a molar O/U ratio of between 7 and 8, while in a nitrogen atmosphere, this ratio was about 5, consistent with the stoichiometric ratio. The predicted molecule was obtained in the non-oxidative medium, while in the aerated solution a much greater proportion of oxygen was observed. The U/N ratio varied between 15 and 30 for glucosamine, too high to enable such a product to be identified in the precipitate of a complexed uranyl. A partial coprecipitation of by-products could explain such results. In order to confirm the nature of the precipitated species an infra-red spectrophotometric analysis was carried out. Spectra of by-products produced by photoreduction of uranyl acetate in the presence of acetylglucosamine, with either air or nitrogen bubbling through, were realised. A typical uranyl hydroxide peak appeared

Element	Gas					
			Air		Nitrogen	
	[A]	[B]	GlcN	AcGlcN	GlcN	AcGlcN
U	73.9	78.3	57.5	60.1	67.7	67.8
N	-	-	0.1	< 0.1	0.3	< 0.1
O	24.8	21.1	30.1	29.2	22.7	21.8
H	1.2	0.7	2.2	1.7	1.1	1.3
C	-	-	0.9	1.0	1.4	1.3 -

	pH 2	pH 4	pH 6
Uranyl hydroxide	962	942	940
Uranium + GlcN	961	929	911
Uranium + AcGlcN	961	939 and 924	918

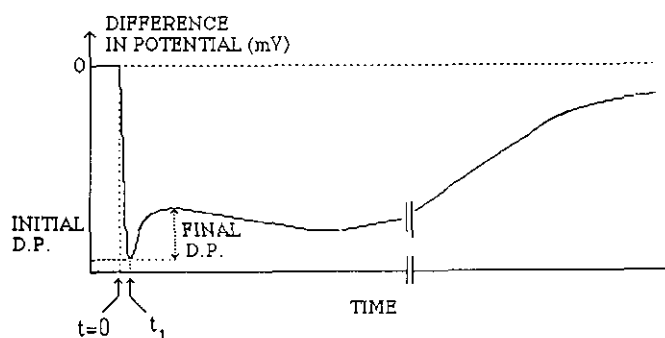


Figure 8
Profile of the difference in potential between the two reactors

at around 908 cm⁻¹. This band corresponded to the V3 deformation vibration, whose wave number, V, (cm⁻¹), is related to the U-O length, R, (Å), by Veal's formula (Tsezos, 1980):

$$R (\text{Å}) = 0.895 + 81.2 V^{-2/3}$$

The location of this uranium hydroxide was not consistent with corresponding wavenumbers observed in an infra-red study of uranyl complexation (Guibal et al., 1995b) (see also Table 4).

The wave number of the uranium band was different from that of uranium hydroxide but not quite identical to those of complexed forms. The precipitate was not obtained in the form of a uranium complex. Other bands, appearing between 1 200 and 1 000 cm⁻¹, indicated the presence of a glucose ring and another band, around 1 500 cm⁻¹, indicated an amide band. Traces of acetylglucosamine could have a similar spectrum. Much more interesting was the appearance of a band around 1 750 to 1 700 cm⁻¹. This wave number range is commonly attributed to carbonyl or carboxylic groups, not reported in the initial spectrum, certainly due to the low acetyl proportion. The photoreduction brought about the formation of such intermediary or by-product groups.

Influence of experimental parameters on the difference in ORP

In order to confirm the hypotheses put forward, a second series of experiments was carried out with the apparatus shown in Fig. 3. The variation of the difference in the ORP between the two reactors, with different compositions and subjected to different conditions (air bubbling through, light exposure) was observed vs. time. Similar trends were observed and are shown in Fig. 8. A rapid and quasi-instantaneous variation in potential was observed between the reactors, followed by a rapid and partial reduction of this

difference. A third stage took place with a lower rate and produced another increase in potential variation and after quite a long time, in a fourth stage, after a stabilisation period of 45 to 60 min, the difference in potential tended to decrease: a re-oxidation of the medium took place. Such variations demonstrated the complexity of the reductive mechanisms involved. The fact that there were several stages producing the reduction and oxidation of the reactive intermediates explained this behaviour.

The variations between the initial and the final differences in potential (ΔE_i , ΔE_f) and the time required (t_1) are presented in Tables 5 and 6. More significant results are obtained for monomer ligands and the effect of the uranyl salt is examined: Difference between acetate and nitrate uranyl is considered.

The differences observed between the two sets of experiments were connected with the pre-equilibrium established before the introduction of the ligand (sorbent) or the exposure to light: the formation of the complex between the uranyl ions and the ligand (sorbent), or the stabilisation of the ORP on exposure to light before the addition of the ligand. For acetylglucosamine and chitosan, in a nitrogen atmosphere, both the initial and the final differences in ORP and t_1 were equal, indicating that a pre-conditioning, for example by a complexation of uranium or by light activation, was not needed to bring about a high reduction, with uranyl acetate. With chitin and glucosamine, an initial light activation brought about a greater reduction than a pre-complexation. Consequently the pre-complexation or the pre-activation seemed to be of great importance in reduction control. In order to confirm the importance of these parameters in reduction kinetics, another experiment was

TABLE 5 THE INITIAL AND FINAL DIFFERENCE IN POTENTIAL BETWEEN THE TWO REACTORS: THE EFFECT OF EXPOSURE TO LIGHT (DARKEN REACTOR AS REFERENCE, LIGAND OR SORBENT IN BOTH REACTORS, GlcN: GLUCOSAMINE, AcGlcN: ACETYLGLUCOSAMINE)				
Uranyl	Ligand or sorbent	ΔE_i (mV)	t_1 (min)	ΔE_f (mV)
Acetate	AcGlcN	- 159	1	+ 23
Acetate	GlcN	- 123	1.5	+ 17
Acetate	Chitin	- 88	3.5	+ 6
Acetate	Chitosan	- 143	3	+ 37
Nitrate	AcGlcN	- 164	1	+ 37
Nitrate	GlcN	- 66	2	+ 8

TABLE 6 THE INITIAL AND FINAL DIFFERENCE IN POTENTIAL BETWEEN THE TWO REACTORS: THE EFFECT OF LIGAND (LIGAND OR SORBENT-FREE REACTOR AS REFERENCE, BOTH REACTORS EXPOSED TO LIGHT, GlcN: GLUCOSAMINE, AcGlcN: ACETYLGLUCOSAMINE)				
Uranyl	Ligand or sorbent	ΔE_i (mV)	t_1 (min)	ΔE_f (mV)
Acetate	AcGlcN	- 140	1	+ 29
Acetate	GlcN	- 90	2	+ 20
Acetate	Chitin	- 49	3.5	0
Acetate	Chitosan	- 149	2	+ 38
Nitrate	AcGlcN	- 117	1	+ 37
Nitrate	GlcN	- 116	2	+ 8

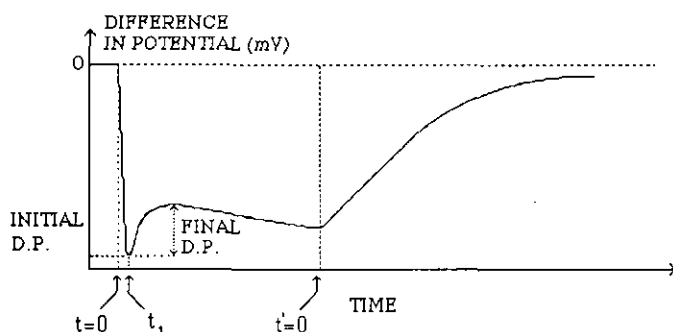


Figure 9

Profile of the difference in potential between the two reactors - the effect of the addition of ligand in the reference reactor at the steady state

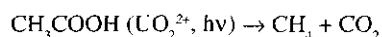
carried out in which acetylglucosamine was added to the reference reactor, in similar ligand concentration, with similar exposure to light, when the difference in potential was stabilised. According to Fig. 9, this addition brought about a reduction in the difference in potential, but the kinetics were significantly reduced against the first stage of the reduction process. The complexation of the uranyl ion prior to exposure to light determined the reduction kinetics, this phase was a limiting stage. Another possible hypothesis is connected with a reduction of the metal complexation due to by-products or intermediary components produced by the photoreaction of the

uranyl acetate in the ligand-free reactor. From Tables 5 and 6, it appears that the uranyl counter-ion is important in the case of glucosamine, when it is exposed to light after the pre-complexation of the uranium. This effect is less important with acetylglucosamine as this ligand is a less effective complexing agent than glucosamine for uranyl ions at this pH (Guibal et al., 1995 b). From these observations it can be deduced that if the effect of acetate cannot be ignored, as proved by Balzani and Carassiti (1970) and Greatorex et al. (1972), ligands and sorbents are also active in the reduction process.

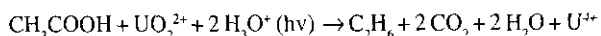
Discussion

These results show that uranyl ions and amino-ligands or their polymerised forms undergo complex interactions when they are exposed to light. This complexity depends on the diversity of molecules able to interact: uranyl ions on one side and both acetate (or nitrate) and glucosamine (or derivative monomers and polymers) on the other.

Acetate and uranyl ions have been reported to interact when exposed to UV-visible light according to several mechanisms: a sensitised photo-oxidation of the counter-ion (SP) or a charge transfer to metal (CTM) as put forward by Greatorex et al. (1972). Balzani and Carassiti (1970) describe a decarboxylation of the acetic acid:

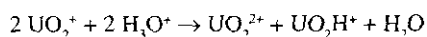
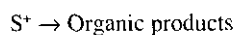
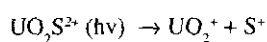
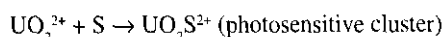


or an effective reduction of the uranium:



The SP mechanism supposes a preliminary photo-activation of the uranyl ion, which interacts with the substrate, or counter-ion, by formation of U^{3+} (UO_2^+), an unstable form in an aqueous medium, which gives U^{4+} and U^{6+} by thermal disproportionation reaction (Sandhu et al., 1987), or which is directly re-oxidised into uranyl by production of molecules similar to those of the decarboxylation process. The CTTM mechanism supposes a preliminary step of metal ion complexation, which is photo-activated. The instability of the complex brings about the formation of by-products and pentavalent uranium ions which gives the same chain products as the SP mechanism. These mechanisms can co-exist in the effective photochemical reaction, the relative importance of both phenomena is conditioned by the excess of ligand. A large excess of ligand displaces the complexation equilibrium and imposes a CTTM stage, therefore in an equimolar distribution, as in the present example, the SP mechanism is predominant.

These mechanisms explain the absolute ORP variations observed in the acetate ligand-free medium, but the great increase in reduction kinetics observed with the addition of ligand (or sorbents) clearly indicates that the contribution of these substrates cannot be ignored. These molecules are constituted by a glucose ring substituted by an amine or amide capable of having photochemical interactions with uranyl ions. Heidt and Moon (1953) and Balzani and Carassiti (1970) put forward the theory of photoreduction of uranyl ions in the presence of carbohydrates such as glucose, gluconic acid or methyl glycosides (S : substrate):



The unstable pentavalent form is then subjected to a disproportionation into uranyl and uranous ions. But amine and amide are also photoreacting groups with uranyl ions as shown by Greatorex et al. (1972): uranyl ions photo-oxidise these components by expulsion of a hydrogen atom, producing active radicals such as activated $\text{CH}_2\text{RCONH}_2$, which reacts with other intermediary components and especially U^{4+} . Bhatt et al. (1986) put forward a theory of SP mechanism for the oxidation of L(-)B-phenylalanine: a photo-activation of uranyl ions which take a proton from the amine function. The pentavalent uranium is reoxidised with oxygen present in the solution. The active radical is successively decomposed into imine, phenylaldehyde and phenylalanic acid.

Dodge and Francis (1994) suggest there are two mechanisms for the photodegradation of the uranium-citrate complex, depending on the pH of the solution. In an acidic medium (i.e. pH 3.5) the protonated binuclear uranyl-citrate is degraded to a mononuclear complex, acetoacetic acid and carbon dioxide by a two-electron transfer. The presence of oxygen enables the residual U^{4+} to be oxidised into $\text{UO}_3 \cdot 2\text{H}_2\text{O}$. In a nitrogen atmosphere the uranous ion is more stable. In the medium pH range (i.e. pH 6) the unprotonated binuclear uranium-citrate complex is transformed into a mononuclear complex, pentavalent uranium, 3-oxoglutaric acid and carbon dioxide, by a one-electron transfer mechanism. The residual complex is then transformed into the same products as the

first phase. The thermal disproportionation of U^{5+} enables uranyl and uranous ions to be obtained. The uranous ion is further oxidised and precipitated as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ in the presence of oxygen.

From these various approaches, two main mechanisms explain the photochemical reactions taking place in the first stage of the process: the photosensitisation and the preliminary complexation. Results presented in this work show, mainly by ORP kinetics and potential difference measurements, that a pre-complexation of uranyl by a ligand (or sorbent) has a predominant effect on the reduction rate. This is proved by the effect of the complexation by ligands and sorbents on the absolute ORP time decay in the presence of such molecules, compared with ligand-free solutions. The measure of the difference in potential confirms this result, taking also into consideration the order of the process stages. Complexing the metal ion before the exposure to light increases variations in potential when compared with the same experimental conditions but with the exposure to light taking place before the introduction of the ligand. The charge transfer to metal mechanism seems to be more apt for the description of the uranium photoreduction by such ligands. The complexation is the limiting stage.

In an acidic medium protonated complexes are more effective at energy transfer (Ohyoshi and Ueno, 1974). The decrease in reduction rate observed with polymers is certainly due to polymerisation and a less efficient electron transfer ability. Air (oxygen) favours the re-oxidation of uranous ions produced during the photoreaction, but a micro-elemental analysis of precipitates shows that those produced in a nitrogen atmosphere have a composition much more typical of uranates than those precipitated with air bubbling through. Furthermore that the precipitation takes longer than the initial reductive stage is consistent with the proposed theory of the transformation of uranous ions into uranate precipitate by late oxidation. The traces of organic compounds observed in both infra-red studies and elemental analysis cannot be attributed to a precipitation of complexed forms but more likely to a co-precipitation of ligand or reaction products onto uranates. Organic materials produced during the photoreaction have not been identified. By analogy with previous works on carbohydrates (Heidt and Moon, 1953; Balzani and Carassiti, 1970) amine, amides (Greatorex et al., 1972; Bhatt et al., 1986), acetate (Balzani and Carassiti, 1970; Greatorex et al., 1972) or citrate (Dodge and Francis, 1994) media, we can put forward a theory of formation of CO_2 , NH_3 , acetic acid and glucose. Some of them can be oxidised to a greater extent by propagation of the photochemical reaction: acetic acid for example can give CO_2 and CH_4 .

Conclusion

Uranium sorption and complexation by ligands and sorbents such as glucosamine, acetylglucosamine, chitin or chitosan are sensitive to exposure to light. A solution containing both uranyl ions and ligands exposed to visible light, in a non-oxidant atmosphere, changes in colour and can form a precipitate. In the same way, the colour of a column of chitosan saturated by uranium, in anaerobic conditions, changes from yellow to brown. These phenomena related to photoreduction, are favoured by nitrogen bubbling through and by the presence of a monomer. Polymers give a lower reduction effect due to the accessibility of sites and to energy charge transfer. The photochemical reaction can involve sensitised photo-activation and activation of the metal-ion-ligand complex. In this study it appears that the reduction rate is increased by a preliminary complexation of the uranyl ions by ligands, prior to the exposure to light. Although a decrease in pH is observed, a

precipitation occurs: a yellow compound is obtained in an aerobic medium, a brown one in an anaerobic solution. Micro-elemental analyses and infra-red characterisation enable the structure of the precipitates to be approximated, a dihydrated uranate is proposed, $UO_2 \cdot 2H_2O$, is the suggestion. This by-product occurs by oxidation and further precipitation of U^{6+} . A first stage produces the main activation of the complex, and also an activation of the uranium, but to a lesser extent. This preliminary step is followed by a reduction of the uranyl ion to pentavalent uranium and the production of compounds such as glucose, acetic acid, methane or carbon dioxide. The instability of U^{5+} leads to a thermal disproportionation into uranous and uranyl ions. The uranous ions are then oxidised and give a precipitate while intermediate compounds undergo a further oxidation into elemental constituents such as CH_4 and CO_2 , if the redox potential is maintained at a low value, in an anaerobic medium only.

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