

## Photochemical reduction of U(VI) in aqueous solution in the presence of 2-propanol



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### ABSTRACT

The efficiency of the photochemical reduction of uranyl ( $\text{UO}_2^{2+}$ ) (0.25 mM, pH 3) was analyzed in the absence and in the presence of 2-propanol (2-PrOH), evaluating the effect of anions (nitrate, acetate and perchlorate) and the use of quartz and glass photoreactors. A higher removal was observed under all conditions with the quartz photoreactor; the best system was that starting from uranyl nitrate, where a 90%  $\text{UO}_2^{2+}$  removal was attained after 15 min irradiation. In the absence of 2-PrOH, the acetate system was the only one where some U(VI) removal was observed (15% after 15 min in the quartz photoreactor) but, in the presence of the alcohol, the acetate system was the least reactive. Under irradiation, nitrate and acetate were consumed during the reaction, causing important effects on the uranyl conversion, while perchlorate was inactive. Uranium was removed from the system as a solid residue in the case of nitrate- (as U(IV)) and perchlorate-containing systems (as U(VI)), while it remained in solution in the case of the acetate systems. Mechanisms are proposed for the different conditions. The importance of nitrate as a reducing agent of uranium species has not been previously reported. The use of uranyl nitrate and short-near UV–vis light seems to be the most advisable way of removing uranyl from solutions, in the form of a stable precipitate.

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### 1. Introduction

Uranium is used mainly as nuclear fuel, in catalysts and in pigments. Contamination by uranium is common in waters and soils of mining areas and geological deposits, hydrometallurgical plants, wastes and reprocessing products of nuclear power plants, being highly toxic to humans [1,2].

Conventional and emergent methods for uranium removal from water [2], e.g. biotransformation, ion exchange, oxidation processes, coagulation, adsorption [3–5], phytoaccumulation [6], micro- and nanofiltration [7], zerovalent iron [8,9], etc. are expensive or generate toxic wastes. Therefore, low cost procedures for U(VI) removal and waste minimization technologies are imperative.

Photochemical reactions of uranyl for environmental purposes have been widely studied [10–15], including  $\text{TiO}_2$  heterogeneous photocatalysis [16]. The possible application of U(IV) formed by

photoreduction in the reprocessing of spent fuel elements has also been discussed [11]. However, uranium recovery schemes are scarce and reprocessing technologies are very complicated [17]. Direct low-temperature reduction of uranyl to solid  $\text{UO}_2$  represents, therefore, an attractive and simple alternative for minimizing nuclear waste.

Our initial goal was the thorough study of the  $\text{TiO}_2$  photocatalytic transformation of uranyl; however, during the research, it was found that both the nature of the uranyl counterion (or anions present in the system) and the irradiation conditions had an enormous influence on the reaction rate. Therefore, it was decided to analyze profoundly the photochemical reaction of uranyl salts under different irradiation conditions without  $\text{TiO}_2$ , in the absence and in the presence of 2-PrOH. This important system has received poor attention in the last decades and very few references are found in the literature in this century.

### 2. Materials and methods

#### 2.1. Materials

Uranyl acetate ( $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , Fluka), uranyl nitrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Lopal) and 2-PrOH (99%, Biopack) were

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used. Uranyl perchlorate was prepared following the procedure described in [18] from uranyl nitrate and  $\text{HClO}_4(\text{c})$  (Merck). All other chemicals were reagent grade and used without further purification. Water was purified with a Millipore Milli-Q equipment (resistivity = 18 M $\Omega$  cm).

## 2.2. Irradiation experiments

The experiments were performed using a commercial quartz (Q) photoreactor immersion well (Photochemical Reactors Ltd.) provided with a medium pressure mercury lamp (125 W,  $\lambda > 230$  nm,  $\lambda_{\text{max}} = 365$  nm), surrounded by a water jacket set at 25 °C, acting simultaneously as IR filter. Other emissions of the lamp were at 245, 254, 265, 280, 302, 313, 408, 436 and 546 nm. The incident photon flux per unit volume ( $q_{n,p}^0/V$ ) in the irradiated solution, measured by potassium ferrioxalate, was 121  $\mu\text{einstein s}^{-1} \text{L}^{-1}$ . In selected experiments, a glass well was used (G photoreactor,  $\lambda > 310$  nm,  $\lambda_{\text{max}} = 365$  nm,  $q_{n,p}^0/V = 44 \mu\text{einstein s}^{-1} \text{L}^{-1}$ ).

$\text{UO}_2^{2+}$  solutions (1000 mg  $\text{UL}^{-1} \equiv 4.2$  mM) were prepared by dissolving uranyl nitrate in 1%  $\text{HNO}_3$  and uranyl acetate in 1% acetic acid; a strongly concentrated solution (14,100 mg  $\text{UL}^{-1} \equiv 59$  mM) of uranyl perchlorate was prepared in water. From the concentrated solutions, 0.25 mM ( $\equiv 59$  mg  $\text{UL}^{-1}$ ) solutions were prepared. When indicated, the corresponding volume of pure 2-PrOH was added to reach 1 M. pH was adjusted to 3 with 2 M NaOH, except in the case of uranyl perchlorate, where pH was adjusted with concentrated  $\text{HClO}_4$  (70%). No significant pH changes during the runs were observed ( $\Delta\text{pH} < 0.3$ ).

The following conditions were used in the irradiation experiments: (i) uranyl nitrate in nitric acid in the quartz photoreactor, thereafter named QN, (ii) uranyl acetate in acetic acid, quartz photoreactor, QA, and (iii) uranyl perchlorate with perchloric acid, quartz photoreactor, QP. For experiments with the glass photoreactor, the system will be named G (e.g. GN for the uranyl nitrate salt in the glass photoreactor).

Uranyl solutions (200 mL) were irradiated under nitrogen bubbling (0.5  $\text{L min}^{-1}$ ) all throughout the experiment, prior a 30 min bubbling in the dark. Aliquots (250  $\mu\text{L}$ ) were periodically taken and filtered through 0.2  $\mu\text{m}$  Millipore membranes before analysis. Deposits found on the membranes were carefully conserved under vacuum before analysis.

All the experiments were performed at least twice and results averaged. The experimental error for the averaged experiments was never higher than 10%, as calculated by standard deviation among the replicate experiments; error bars for the averaged experiments are shown in the corresponding figures. ANOVA statistical analysis at a 0.05 significance level was performed at different irradiation times to compare between different experimental conditions; the Fisher LSD test was used to evaluate if the results were significantly different.

## 2.3. Analytical determinations

U(VI) concentration was followed by the spectrophotometric PAR technique [19]. Anions were measured by IC using a Dionex ICS-5000 ion chromatograph, with an Ion Pack AS19-Analytical-4  $\times$  250 mm column and an Ion Pack AG19 Guard-4  $\times$  50 mm pre-column. The detection was suppressed conductivity, using an Anion Self-Regenerating Suppressor (ASRS 300–4 mm), and a carbonate suppressor (CRD 200–4 mm). The eluent was KOH, 1  $\text{mL min}^{-1}$  isocratic flux. For the measurement of perchlorate, chloride, chlorite and chlorate, the following linear concentration gradient was used: 10 mM KOH (0–6 min), 10–80 mM KOH (6–9 min), 80 mM KOH (9–21 min), 80–10 mM KOH (21.0–21.1 min), 10 mM KOH (21.1–24 min). Nitrate and acetate were measured with the following linear concentration gradient: 10 mM KOH (0–10 min),

10–45 mM KOH (10–25 min), 45 mM KOH (25–27 min), 45–10 mM KOH (27.0–27.1 min), 10 mM KOH (27–30 min). Column and detector temperature were 30 and 35 °C, respectively, and the injection loop was 100  $\mu\text{L}$ . 500  $\mu\text{L}$  of the solution were taken at different irradiation times, filtered, taken to 5 mL with water and measured before 48 h. Ammonium [20] and nitrite [21] were determined spectrophotometrically. For the analytical spectrophotometric measurements, a T80+ PG Instruments Ltd. spectrophotometer was used, while the UV–vis spectra of the filtered solutions were obtained using a Hewlett Packard 8453 spectrophotometer. The solid deposits were analyzed by X-ray diffraction (XRD) using a Philips PW-3710 equipment.

## 3. Results

### 3.1. Photochemical experiments in the absence of 2-PrOH

Fig. 1 shows the temporal evolution of normalized uranyl concentration during irradiation experiments in the absence of 2-PrOH starting from different uranium salts and using the Q or the G photoreactor. According to the Fisher test (see Section 2.2), significant removal was observed only for the QA condition, where a 16% removal was observed after 120 min. In QN, a small removal (4%) was observed from the first stages, which indicates that a small U(VI) reduction may take place, while for QP the removal was not statistically relevant. Experiments with the G photoreactor and uranyl perchlorate gave negligible results, and no other experiments in the absence of 2-PrOH with the G photoreactor were then performed.

As QA showed an appreciable U(VI) removal, the temporal variation of acetate concentration was measured (not shown), and a decrease of around 10% in 120 min (from 42 to 38 mM) was found. As the acetate/U(VI) molar ratio is 168, more than 80% of U(VI) is present as the  $\text{UO}_2(\text{CH}_3\text{COO})_3^-$  complex [22–24], with minor amounts of  $\text{UO}_2(\text{CH}_3\text{COO})_2$ ,  $\text{UO}_2\text{CH}_3\text{COO}^+$  and  $\text{UO}_2^{2+}$ . The changes in the UV–vis spectrum during the experiment are shown in Fig. 2. As known, uranyl absorbs strongly in the short UV range [25], with lower absorption peaks from 340 nm to the visible, and a characteristic manifold in the range 350–500 nm [14], clearly seen in the initial spectrum. In the final spectrum, a decrease of these signals is evident together with the appearance of a well-defined peak of high intensity at 962 nm and two lower signals at 736 and 845 nm, which can be associated to U(V), reported to be stable at pH 2–3 [15,26–33]. The 962 nm signal is much more intense than those

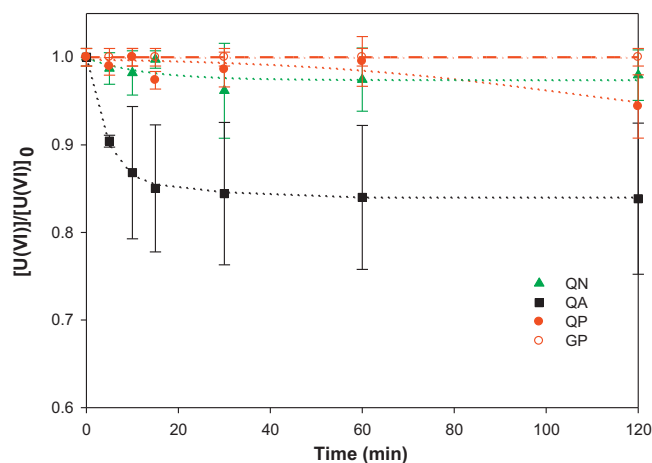


Fig. 1. Temporal evolution of normalized U(VI) concentration in the absence of 2-PrOH under irradiation for QP, QN, QA and GP.  $[\text{U(VI)}]_0 = 0.25$  mM, pH 3,  $q_{n,p}^0/V = 121 \mu\text{einstein s}^{-1} \text{L}^{-1}$  for Q and  $44 \mu\text{einstein s}^{-1} \text{L}^{-1}$  for G. Dotted lines are only indicative for a better visualization of the experimental points.

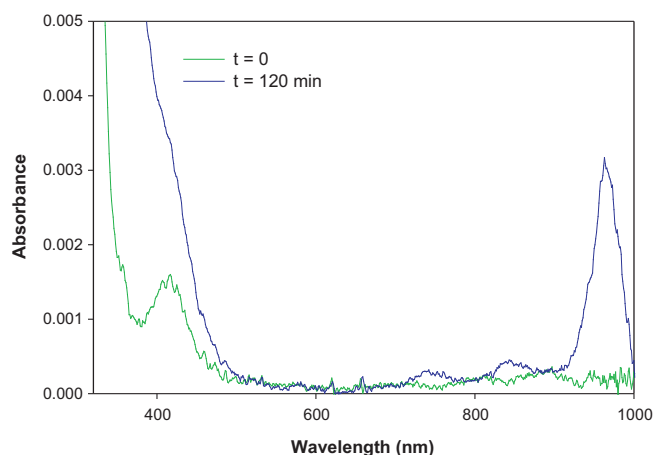


Fig. 2. Initial and final spectra of a photochemical experiment of QA in conditions of Fig. 1.

reported, suggesting a peculiar U(V) species. The U(V) signal at 255 nm [26,30] was not detected here, and only a slight increase of the absorbance in this region is seen, explained by the superimposition with the important absorbance of U(VI), remaining still at 84% in the solution. The absorption increase at 300–450 nm was observed previously, but not assigned [34,35]. The characteristic U(IV) peak around 650 nm [36] was not observed here and, as no precipitate was obtained either at the end of the experiment, it was concluded that U(IV) was not formed in this system.

### 3.2. Photochemical experiments in the presence of 2-PrOH

Fig. 3(a) and (b) show the temporal U(VI) decay in the presence of 1 M 2-PrOH using the Q and the G photoreactors. Due to the high 2-PrOH concentration, it can be assumed that the alcohol is negligibly consumed during the runs.

A fast decrease of the U(VI) concentration in the initial stages took place for QN and QP, with rather similar initial decay rates. In QN, removal was very fast up to 15 min and then a slower decay took place up to 60 min, reaching 98%. A similar behavior was observed for QP, but removal at 15 min was only 50%, followed by a slower decay and reaching 70% at 120 min. Regarding QA, a steadily slow uranyl removal all throughout the run was observed, reaching 32%. Removal in the G photoreactor was always lower, with GN yielding the best results.

### 3.3. Analysis of the components of the photochemical systems

#### 3.3.1. QN condition

Fig. 4 shows the temporal evolution of species during QN. The high initial amount of nitrate is due to the excess of HNO<sub>3</sub> used to prepare the stock U(VI) solutions. At the working concentrations, free U(VI) and nitrate species are the main species, U(VI)–nitrate complexes representing only 0.1% of the total U(VI) [22,37].

Nitrate evolution matched that of uranyl, and both species were almost totally depleted in 30 min, with similar decay profiles, indicating that both transformations are related. Nitrite was identified as a product, at a low concentration. Ammonium was not detected. As the nitrogen balance (NB):

$$NB = [\text{NO}_3^-]_0 - ([\text{NO}_3^-]_t + [\text{NO}_2^-]_t) \quad (1)$$

was not nil, it was concluded that non-identified nitrogen-containing products (NINP), most probably gaseous, have been formed in high amounts with a maximal concentration attained at 15 min, when nitrate was practically depleted. No nitrate transformation was observed in the absence of U(VI).

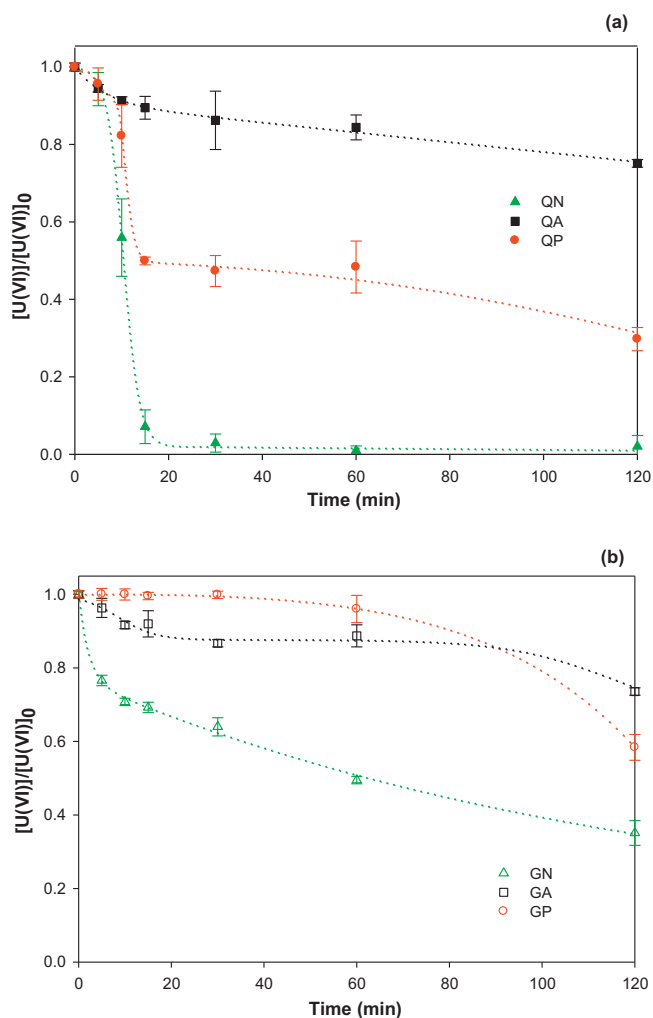


Fig. 3. Temporal evolution of normalized U(VI) concentration in the presence of 1 M 2-PrOH under irradiation for (a) QP, QN, QA and (b) GP, GN and GA under N<sub>2</sub>. [U(VI)]<sub>0</sub> = 0.25 mM, pH 3, q<sup>0</sup><sub>n,p</sub>/V = 121 μeinstein s<sup>-1</sup> L<sup>-1</sup> for Q and 44 μeinstein s<sup>-1</sup> L<sup>-1</sup> for G. Dotted lines are only indicative for a better visualization of the experimental points.

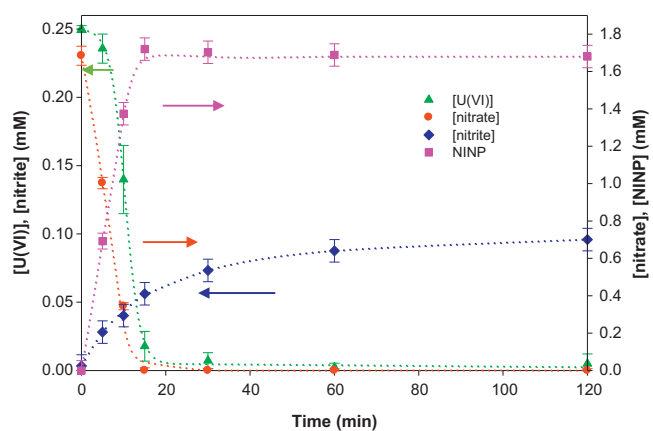
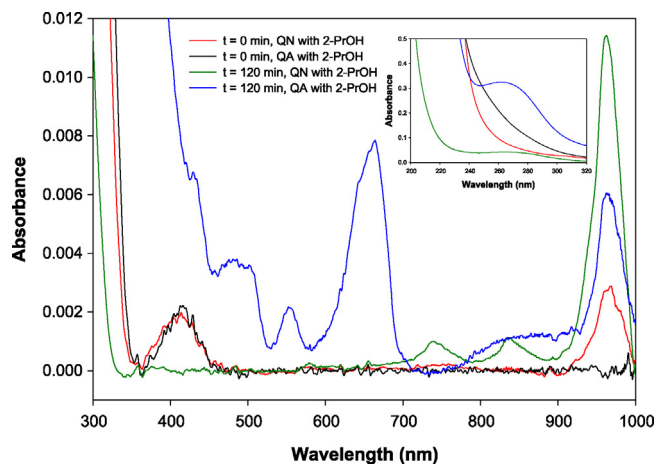


Fig. 4. Initial and final spectra of photochemical experiments for QN and QA in the presence of 2-PrOH. Conditions of Fig. 3(a). The small peak at 963 nm in the initial spectrum of QN can be associated to some U(V) formed by exposure of the sample to the environmental light.



**Fig. 5.** Temporal evolution of [U(VI)], [nitrate] and [NINP] during the photochemical reaction of QN in the presence of 2-PrOH. Conditions of Fig. 3(a). Dotted lines are only for visualization of experimental points.

The initial spectrum of the filtered solution showed the U(VI) peaks [14], which disappeared in the final spectrum (Fig. 5), in agreement with U(VI) depletion. Here, higher U(V) signals compared with those in the absence of 2-PrOH (Fig. 2) were observed at 737, 845 and 963 nm [14,24,29]; also, the plateau between 240 and 270 nm can be attributed to this species [26,29] (Fig. 5, inset). No U(IV) peaks were observed.

At the end of the run, a dark gray precipitate was obtained by filtration of the irradiated solution. The XRD pattern of this solid (Fig. S1) is in perfect agreement with that of  $\text{UO}_{2+x}$  ( $x = 0\text{--}0.25$ ) [38,39], where  $x$  can be ascribed to the oxidation of  $\text{UO}_2$  in air, a rather fast process for very small particles [40].

### 3.3.2. QA condition

Fig. S2 shows the comparative temporal variation of [U(VI)] and [acetate] for QA under conditions of Fig. 3(a). While uranyl was steadily transformed (32%), acetate (initially 14.4 mM) showed a rapid degradation in the first 15 min, followed by an arrest, decaying to 7.8 mM (54% final removal). The acetate/U(VI) molar ratio was here 48, and U(VI) was also present mainly as  $\text{UO}_2(\text{CH}_3\text{COO})_3^-$ . The initial and final spectra are shown also in Fig. 5 above, and these spectra show the disappearance of the uranyl peaks at 350–500 nm, with new signals of U(IV) clearly seen at 435, 490, 554 and 663 nm [36], together with a broad band at 800–900 nm [41–43]. The important bands at 255 and 963 nm suggest the presence of U(V) [26,30], although the peaks at 745 and 845 nm cannot be here clearly appreciated, probably due to the U(V) low concentration and to overlap with the U(IV) bands. An increase of the absorbance between 280 and 450 nm is noticed, similar to that observed in Fig. 2, but more pronounced, due to the higher U(VI) conversion.

No solid residue was observed after filtration, demonstrating, together with the results of Fig. 5, that the produced U(IV) remained in solution. This can be attributed to the formation of a soluble U(IV)–acetate species; related to this, it has been reported that the U(IV) tetraacetate ( $\text{U}(\text{OAc})_4$ ) is easily hydrolyzable [44].

### 3.3.3. QP condition

Although U(VI) was rapidly removed from solution in the first 15 min (Fig. 3(a)), perchlorate concentration (initially 1.52 mM) did not present any variations during the whole run (not shown), and possible perchlorate degradation products, e.g. chloride, chlorate and chlorite [45], were not detected. In the final spectra (not shown), neither U(V) nor U(IV) bands were observed, with only a decrease of the U(VI) peaks in comparison with the initial sample.

The final product was a yellow solid, suggesting a mixed oxide with predominance of  $\text{UO}_3$  [46].

### 3.3.4. GN condition

Results of temporal evolution of uranyl, nitrate and nitrite concentrations during the photochemical reaction are shown in Fig. S3. Nitrate concentration decreased only 50% after 120 min, in contrast to the total depletion in the QN system in 15 min (Fig. 3(a)). Nitrite was detected at very low concentrations, indicating that most nitrate is converted into NINP; ammonium was not detected. U(VI) was only eliminated up to 62%, suggesting that total elimination of nitrate is necessary to obtain complete U(VI) removal, as took place in QN (Fig. 3).

The spectra of the initial and final solutions (not shown) were not very different, indicating only a decrease of the uranyl concentration, without peaks of dissolved U(V) or U(IV). An amorphous gray precipitate of uranium (IV) oxides was obtained after filtration, but of a lighter color than the one obtained in QN; when exposed to air, the color changed rapidly to yellow, indicating easy oxidation.

### 3.3.5. GA condition

The temporal variation of acetate concentration (not shown) indicated a transformation of only 15% in 120 min, significantly smaller than the 54% obtained in QA (Fig. S2). This contrasts with the amount of removed U(VI) (26%), only slightly lower than that obtained in QA (32%).

At the end of the experiment, no solid residue was obtained. The final spectrum (not shown) presented U(IV) signals at 426, 490, 554 and 663 nm, indicating that uranium was reduced and stayed in solution, similarly to that obtained for QA (Fig. 5).

### 3.3.6. GP condition

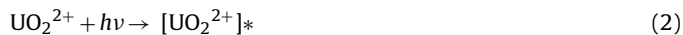
As no changes in perchlorate concentration had been observed for QP (Section 3.3.3), no changes were expected either for GP; the spectrum of the final sample indicated only U(VI) removal, without dissolved U(IV) detection; a small amount of a light yellow solid could be isolated by filtration.

## 3.4. Comparison of results

Table 1 presents the comparative results of all experiments indicating the percentage of uranyl removal at 120 min, the type of precipitate formed and detection of U(IV) and U(V) in the final solution.

## 4. Discussion

Photochemistry of uranyl is unique with respect to other inorganic ions, exhibiting luminescence at room temperature. Although this species is a weak oxidizing agent in the ground state, the excited state,  $[\text{UO}_2^{2+}]^*$ , is a potent oxidant ( $E^0 = +2.6\text{V}^1$  [24]), which allows several redox reactions to take place under UV or visible irradiation through different mechanisms [14,15,17,24,29,33,47–49]. One-electron reduction steps transform sequentially U(VI) into U(V) and U(IV) according to the redox potentials indicated in Scheme S1 of SI. In the absence of electron donors, the excited state decays by luminescence or physical quenching, or reacts with water, with production of U(V) and  $\text{HO}^\bullet$  (Eqs. (2)–(5)). Reformation of uranyl occurs by U(V) reoxidation (6), with no overall photochemical transformation [24,33,50]. This explains why in QP in the absence of 2-PrOH U(VI) removal does not take place (Fig. 1).



<sup>1</sup> All reduction potentials in this paper are standard values vs. NHE.



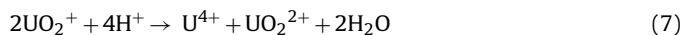
**Table 1**

Percentage of uranyl removal at 120 min, type of precipitate and data on detection of U(IV)/U(V) in the final solution. Conditions of Fig. 3, except for QN and QA without 2-PrOH, taken from Fig. 1.

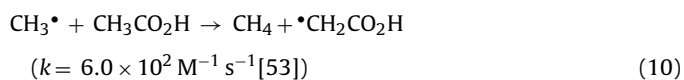
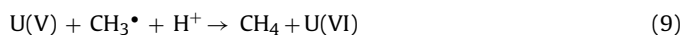
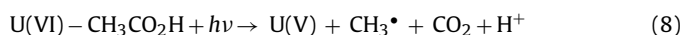
Condition	% U(VI) removal	U(IV) in solution	U(V) in solution	Precipitate
QN no 2-PrOH	4	No	No	No
QP no 2-PrOH	<3	No	No	No
QA no 2-PrOH	16	No	Yes	No
QN	98	No	Yes	Yes (dark gray)
QP	70	No	No	Yes (yellow)
QA	32	Yes	Yes	No
GN	62	No	No	Yes (light gray)
GP	41	No	No	Yes (light yellow)
GA	26	Yes	Yes	No



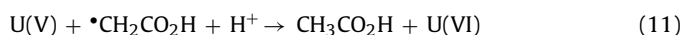
Although  $\text{UO}_2^+$  is prone to disproportionation (Eq. (7) [23,26,29,51]), it is long lived at pH 3 [26,29].



The small (16%) but statistically significant removal in QA in the absence of 2-PrOH can be explained considering that U(VI) is mainly as the  $\text{UO}_2(\text{CH}_3\text{COO})_3^-$  complex and that the ligand acts here as an electron donor. The photochemical transformation is proposed to occur through an oxidative photodecarboxylation (Eq. (8) [14]; the produced methyl radical can be reduced to  $\text{CH}_4$  ( $E^0(\text{CH}_3^\bullet, \text{H}^+/\text{CH}_4) = 1.72 \text{ V}$  [52]) with U(V) reoxidation [14] (Eq. (9)) or can react through a minor step with free acetic acid/acetate [53] (Eq. (10));  $\text{CH}_3^\bullet$  cannot reduce U(VI) ( $E^0(\text{CH}_3^+/\text{CH}_3^\bullet) = 1.5 \text{ V}$  [54]):

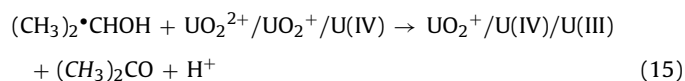
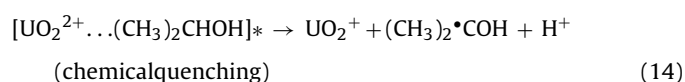
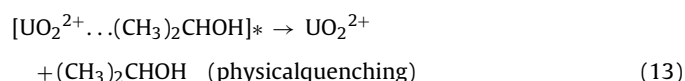
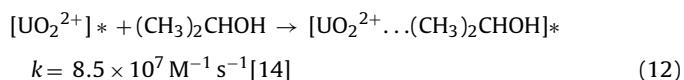


$\bullet\text{CH}_2\text{CO}_2\text{H}$  might also reoxidize reduced uranium species giving acetic acid ( $E^0(\bullet\text{CH}_2\text{CO}_2\text{H}, \text{H}^+/\text{CH}_3\text{CO}_2\text{H}) = 1.8 \text{ V}$  [55]) without net U(VI) reduction:



or react through non reducing steps, like self-recombination ( $k = 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [56]) or reaction with  $\text{CH}_3^\bullet$  ( $k \approx 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [53]). This explains the small U(VI) reduction observed. Decrease of acetate (4 mM, Section 3.1) was much higher than U(VI) decay (0.04 mM, Fig. 1) indicating that the reaction would take place mainly through (8) and (9) or that  $\bullet\text{CH}_2\text{CO}_2\text{H}$  oxidizes very efficiently reduced uranium. The 4% U(VI) removal in QN (Fig. 1) will be explained later.

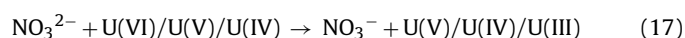
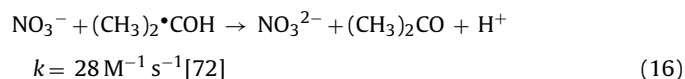
In excess of 2-PrOH (Fig. 3),  $[\text{UO}_2^{2+}]^*$  and the alcohol react through an encounter complex (Eq. (12) [14,29,33,47,57–61]), followed by physical and chemical quenching [33]. Chemical quenching produces  $(\text{CH}_3)_2\bullet\text{COH}$ , a strong reducing radical [57] ( $E^0$  ranges from  $-1.8$  to  $-1.39 \text{ V}$  [62]), which can reduce  $\text{UO}_2^{2+}$  to  $\text{UO}_2^+$ , U(IV) and even to U(III) [41,63] (see however below).



A gray precipitate confirmed U(IV) formation in QN and GN, but U(IV) remained in solution in QA and GA (Table 1). The anions present in the system determine the production of each species and this will be analyzed below. As U(VI) reacts rather slowly with organic radicals [33],  $(\text{CH}_3)_2\bullet\text{COH}$  should react preferentially by recombination ( $k = 1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [64]).

In QP with 2-PrOH, perchlorate demonstrated to be stable and inert, without effect on the photochemical reaction (Section 3.3.3), in agreement with previous results [50,65] and with the fact that perchlorate can be degraded only under VUV irradiation [66]. Thus, the mechanism is simply that of Eqs. (12)–(15). After irradiation, a precipitate was detected, consisting in a mixture of amorphous U(VI)/U(IV) oxides; U(VI) solubilization from these oxides can be related to the rather high U(VI) concentration in solution even at long irradiation times.

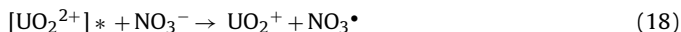
In previous papers, it was proposed that UV photons were detrimental for U(VI) photoreduction, because UV photolysis of  $\text{NO}_3^-$  generates highly oxidizing  $\text{NO}_x$  [67–70], which cause uranium reoxidation [17]. Surprisingly, a faster U(VI) removal was observed in QN in the present work compared with the other conditions (Fig. 3). As  $\text{NO}_3^-$  and 2-PrOH did not react in the Q photoreactor in the absence of uranium (Section 3.3.1), the enhancement of U(VI) reduction can be attributed to  $\text{NO}_3^{2-}$  formation by reaction of  $\text{NO}_3^-$  ( $E^0(\text{NO}_3^-/\text{NO}_3^{2-}) = -0.89 \text{ V}$  [71]) with  $(\text{CH}_3)_2\bullet\text{COH}$  (Eq. (16)).  $\text{NO}_3^{2-}$  is then able to reduce U(VI) up to U(III) (Eq. (17)).



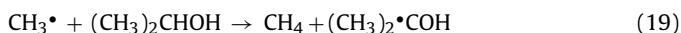
$\text{NO}_3^{2-}$  can react through (S4)–(S12) (see SI) [69,73], forming for example  $\text{NO}_2^\bullet$  (Eq. (S3)), which could oxidize reduced U species (Eq. (S4),  $E^0(\text{NO}_2^\bullet/\text{NO}_2^-) = 1.0 \text{ V}$  [62]). Nitrogen products, like  $(\text{CH}_3)_2\text{C(OH)NO}_2$ ,  $(\text{CH}_3)_2\text{C(OH)NO}$  and  $\text{NO}^\bullet$ , can be some of

the mentioned NINP (Section 3.3.1), explaining the low  $\text{NO}_2^-$  concentration and absence of ammonium (Fig. 4). As Fig. 3 shows that nitrate is photochemically consumed in QN in a few minutes, the participation of a soluble  $\text{U(IV)}-\text{NO}_3^-$  complex (formed at high  $\text{NO}_3^-$  concentrations and acid pH [74–76]), can be ruled out, explaining precipitation of  $\text{U(IV)}$  as a gray oxide (Table 1).

The small (4%)  $\text{U(VI)}$  removal in QN without 2-PrOH (Fig. 1) can be caused by direct reaction between  $[\text{UO}_2^{2+}]^*$  and  $\text{NO}_3^-$  ( $E^0(\text{NO}_3^*/\text{NO}_3^-) = 2.3\text{--}2.6\text{ V}$  [62,77], Eq. (18)), similarly to the mechanism proposed in the UV photolysis of the  $\text{Ce(IV)}-\text{NO}_3^-$  complex [78].



The QA system with 2-PrOH presented the lowest removal degree compared with the other conditions. Removal was only twice the value obtained in the absence of the alcohol (cf. Figs. 1 and 3 and Table 1), indicating that acetate interferes in uranyl reduction. According to the rate constants [79], acetate cannot compete with 2-PrOH for  $\text{HO}^*$  (see Eqs. (S1)–(S3)); however, acetate degradation is higher in the presence of 2-PrOH (4 against 7.8 mM, respectively). This indicates that  $\text{U(VI)}$  transformation in QA with 2-PrOH is initiated by steps (8) and (9), but including reaction (19) instead of (10) because of a more efficient  $\text{CH}_3^*$  trapping by 2-PrOH than by acetate [80], causing the observed rate increase.



The formed  $\text{U(V)}$  may decay by reactions (7) or (17) to  $\text{U(IV)}$ , which stays, as said, as a soluble uranium(IV) form [44]. It is also possible that, after the photochemical reaction, the uranium species is rapidly oxidized to  $\text{U(VI)}$  during the filtration, rendering a fictitious lower uranyl reduction. In view of these conclusions, the presence of acetate should be avoided in photochemical processes for uranyl removal.

Fig. 3(b) shows that the uranyl removal with the G photoreactor was always lower compared with the Q one, and that the highest removal was produced again in the nitrate system. Similar routes to those presented for the respective Q systems account for the results, reinforced by the analysis of anions. The more energetic radiation transmitted by Q, with a higher  $\text{U(VI)}$  absorption [14] ( $A_{\text{in}} = 3.0 \times 10^{-2}$  at 300 nm,  $A_{\text{in}} = 0.2 \times 10^{-2}$  at 400 nm, Figs. 2 and 5), and a higher amount of incident photons increasing the transformation [58] explain the larger yields. In particular, it was observed that total elimination of nitrate, a crucial requirement to obtain complete  $\text{U(VI)}$  removal, does not take place in GN.

A final point refers to  $\text{U(III)}$ . The characteristic  $\text{U(III)}$  peak at 900 nm [42] was not observed in this work under any conditions. The reason of the lack of detection of this species is not clear and could be attributed to the high instability of  $\text{U(III)}$  in aqueous solution at the working pH [2], or to a low reaction rate between  $\text{U(IV)}$  and  $(\text{CH}_3)_2\text{COH}$ , not reported in the literature.

Finally, it is important to remark that very anoxic conditions are needed for  $\text{U(VI)}$  reduction because  $\text{O}_2$  can directly reoxidize  $\text{U(IV)}$  [58] or compete with photogenerated reducing species formed in the system, hindering uranium reduction processes.

## 5. Conclusions

The photochemical reduction of uranyl in the presence of 2-PrOH, with solid  $\text{U(IV)}$  formation, could be used for uranyl removal from water and in reprocessing technology with minimization of nuclear wastes. The stability of the precipitate and its elimination from the solution depend on the used conditions, particularly of the starting uranium salt and the irradiation conditions.

The highest efficiency was obtained with systems containing nitrate under short-near UV–vis irradiation (98% in 60 min). We do

not agree with the conclusions of a previous paper [17] with respect to the use of visible photons to avoid a detrimental interference of nitrate. In our case, the presence of nitrate not only does not interfere but even enhances  $\text{U(VI)}$  reduction compared with systems where nitrate is not present. The importance of nitrate as a reducing agent of uranium species has not been previously reported. This possibility of simultaneous removal of nitrate and uranyl from aqueous solutions is another technological advantage of the photochemical system and contrasts with other removal methods as, for example, biological treatments with dissimilatory metal-reducing microorganisms, where nitrate is detrimental because the microorganisms reduce more preferentially nitrate than  $\text{U(VI)}$  [81]. The QN system is, therefore, excellent, taking into account that  $\text{U(VI)}$  and nitrate are pollutants usually present together in industrial and nuclear wastes.

The possibility of  $\text{N}_2$  generation, not evaluated here, could be another important advantage of the system. However, as highly oxidizing N-containing products can be generated from nitrate, strategies for their identification and removal should be developed, and they are underway in our laboratories. Nevertheless, it has been reported that reducing radicals such as  $^*\text{CH}_2\text{OH}$ , under anoxic conditions, may act as a reducing agent toward various nitrogen-containing intermediates [67] and this behavior could be extended to  $(\text{CH}_3)_2\text{COH}$ .

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jphotochem.2013.12.006>.

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