Heterogeneous photocatalytic removal of U(VI) in the presence of formic acid: U(III) formation

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GRAPHICAL ABSTRACT
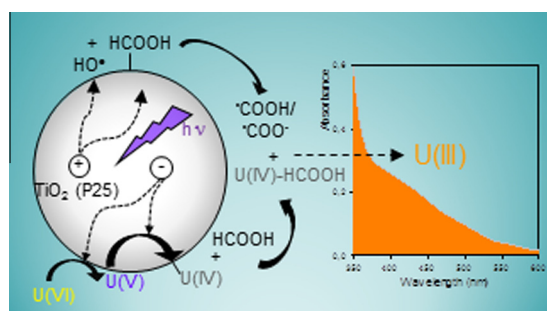
ARTICLE INFO

ABSTRACT

The efficiency of TiO_2 heterogeneous photocatalysis under UV–visible light for removal of uranyl (UO_2^{2+}) (0.25 mM, pH 3) in the presence of formic acid (HCOOH) was investigated. The effect of the counterion of the uranium salt (perchlorate and acetate–nitrate) and the use of quartz and glass photoreactors were analyzed. The transformation of U(VI) in the presence of HCOOH was significantly high and the best removal conditions have been established. The highest efficiency was observed for uranyl perchlorate in the quartz photoreactor with 0.001 M HCOOH, while uranyl acetate yielded a lower removal. HCOOH concentrations >0.01 M provoked uranium reoxidation. U(VI) photocatalytic transformation was also studied by direct spectrophotometry using TiO_2 nanoparticles in the presence of 1 M HCOOH at pH < 2. U(V), U(IV) and U(III) were detected. U(III) formation was also apparent in the absence of the photocatalyst. This is the first time that formation of U(III) in a photochemical U(VI) system is reported.

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1. Introduction

Heterogeneous photocatalysis (HP) of aqueous U(VI) systems has been rather well studied [1–5] as an economical and simple alternative to conventional removal methods [6–8]. This technological approach can solve not only environmental problems but also those related to actinide valence state control for waste minimization in nuclear fuel processing. However, studies on the effect of several variables such as the nature of electron donors or the presence of some ions in the system should be completed because they have profound effects on the efficiency of the transformation. In a similar previous paper [9], the uranyl HP system has been studied in the presence of 2-propanol (2-PrOH). High

U(VI) removal efficiencies were obtained, with complete removal for uranyl nitrate and uranyl perchlorate with 1 M 2-PrOH in a quartz photoreactor. The acetate salt showed a lower U(VI) removal. It was proposed that U(VI) reduction is mediated by conduction band electrons (e_{CB}^-) and not by the organic radicals formed by hole/HO· attack to 2-PrOH [9]. The homogeneous photochemical uranyl system (absence of TiO_2) has also been revisited in a previous work [10]. Although the photochemical reaction under the same conditions to those of the photocatalytic one attained a similar efficiency, the HP treatment exhibited a better performance.

The uranyl HP transformation in the presence of different organic compounds, formic acid (HCOOH) among them, has been studied by Amadelli et al. in an early work with TiO_2 P25, and it was found that the photoelectrochemical conversion rate followed the order formate > acetate > 2-PrOH [1].

The present work aimed to revisit the uranyl HP system in the presence of HCOOH with P25 at pH 3, analyzing the effects of the counterion of the uranyl salt (perchlorate and acetate-nitrate) and the use of quartz and glass photoreactors. Taking into account that in the presence of 2-PrOH [9] uranyl perchlorate and nitrate reacted similarly, the nitrate salt was not tested in the present work. Experiments with transparent TiO_2 nanoparticles (pH < 2) were also performed to shed light on the involved mechanisms.

2. Experimental

2.1. Materials and chemicals

Uranyl acetate ($UO_2(CH_3COO)_2 \cdot 2H_2O$, Fluka), uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$, Lopal) and HCOOH (99%, Carlo Erba) were used. Uranyl perchlorate was prepared from uranyl nitrate and $HClO_4(c)$ (Merck), following a previous procedure [4]. Uranyl acetate solutions were prepared by dissolving uranyl acetate in 1% HNO_3. TiO_2 (now AEROXIDE®TiO_2 P25, Evonik) was provided by Degussa (Germany) and used as received. All other chemicals were reagent grade and used without further purification. Water was purified with a Millipore Milli-Q equipment (resistivity = 18 MΩ cm).

TiO_2 nanoparticles were synthesized in the laboratory, according to a literature procedure [11]. Briefly, 200 mL of water at pH 1.5 ($HClO_4$) were placed in an ice bath and a solution of 1 mL of titanium isopropoxide in 20 mL of 2-PrOH was slowly added with constant stirring. The final mixture was stirred for 2–3 days in the ice bath until a clear solution was obtained. TiO_2 concentration (0.012 M, 1 g L^{-1}) was calculated from the used quantity of titanium isopropoxide.

2.2. Irradiation experiments

Photocatalytic experiments with TiO_2 suspensions were carried out with an irradiation setup consisting of a commercial quartz (Q) photoreactor immersion well (Photochemical Reactors Ltd.) provided with a medium pressure mercury lamp (125 W, $\lambda > 230$ nm, $\lambda_{max} = 365$ nm), surrounded by a thermostatic jacket, set at 25 °C and acting as IR filter (setup I). 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 ($q^0_{n,p}/V$), measured by actinometry with potassium ferrioxalate, was 121 µeinstein s^{-1} L^{-1}. In selected experiments, a glass well was used (G photoreactor, $\lambda > 310$ nm, $\lambda_{max} = 365$ nm, $q^0_{n,p}/V = 44$ µeinstein s^{-1} L^{-1}).

TiO_2 suspensions (200 mL, 1 g L^{-1}) containing 0.25 mM uranyl were irradiated under nitrogen bubbling (0.5 L min^{-1}). When indicated, the corresponding volume of HCOOH was added to reach the corresponding concentration (0.00025–1 M). pH was adjusted to 3 with 2 M NaOH or with concentrated $HClO_4$ (70%). The following conditions were used in the irradiation experiments: (i) uranyl perchlorate with perchloric acid, quartz photoreactor, hereafter named QP and (ii) uranyl acetate in nitric acid, quartz photoreactor, QAN. The experiments with uranyl perchlorate and the glass photoreactor system will be named GP. In QAN, initial nitrate and acetate concentrations were 22.0 and 0.5 mM, respectively; in QP and GP, initial perchlorate concentration was 1.5 mM. Some experiments were carried out with the reactor open to the air or under air bubbling (0.5 L min^{-1}). Before switching on the lamp, the suspension was carefully stirred in the dark during 30 min to ensure the adsorption equilibrium of U(VI) and HCOOH onto TiO_2, and to evaluate concentration changes only under irradiation. Aliquots (250 µL) were periodically taken during the runs, filtered through Millipore membranes (0.2 µm) or centrifuged (see below) before analysis. Deposits were carefully conserved under vacuum before analysis. In the first experiments, the samples were filtered using only one membrane for all samples of the run; in this case, leaching of U(VI) to the solution was observed in samples taken at 10 min and later, detected by an increase of the U(VI) concentration in solution due to oxidation of the formed U(IV) under air contact. To avoid this leaching, in further runs, one membrane per each sample was used or, alternatively, the sample was rapidly centrifuged. Changes of pH in all runs were negligible (ΔpH < 0.3). Reactions in the absence of TiO_2 were performed under identical conditions.

All the experiments were performed at least twice and the results were averaged. The experimental error 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. The fitting of experimental points was performed with Origin 8.0 software.

The irradiation setup for the experiments with TiO_2 nanoparticles consisted of a cylindrical cell (10 mL, 1 cm pathlength) with quartz walls irradiated with a 150 W ozone-free xenon lamp (Newport) (setup II). Continuous wavelengths from the UV-C up to the IR were emitted from the lamp. The UV-A irradiance, measured with a Spectroline DM-365 XA radiometer placed at 10 cm from the lamp, was $E^0 = 3700$ µW cm^{-2}. These photocatalytic runs were performed with uranyl perchlorate dissolved in 0.88% perchloric acid, the corresponding amount of HCOOH, and 0.010 M TiO_2 nanoparticles. N_2 was bubbled for 10 min (0.1 L min^{-1}) before the irradiation and then the cell was closed. Experiments in the absence of TiO_2 were performed under the same conditions.

2.3. Analytical determinations

U(VI) concentration was followed by the spectrophotometric PAR technique [12], with a detection limit of 0.25 µM uranyl. The solid deposits were analyzed by total reflection X-ray fluorescence (TXRF, modular equipment, Seifert X-ray generator, with a Canberra detector). For XRD analyses, a Philips PW-3710 diffractometer was used.

In the experiments with nanoparticles, the temporal evolution of uranium signals was followed by direct UV spectroscopy using a Hewlett-Packard 8453 spectrophotometer.

3. Results

3.1. Heterogeneous photocatalytic experiments

The temporal evolution of normalized U(VI) concentration during HP experiments in anoxic conditions starting from uranyl perchlorate and two HCOOH concentrations (0.001 and 1 M) up to 120 min irradiation is shown in Fig. 1. In the absence of HCOOH, final uranyl removal values were 43% and 24% for the Q and G photoreactors, respectively, and no precipitates were observed on the TiO_2 surface. In the presence of 0.001 M HCOOH, removal was

higher, reaching percentages above 90% without significant differences between both photoreactors and with very similar kinetic decay profiles; dark gray precipitates appeared on the photocatalyst surface. At 1 M HCOOH, removal was lower for both photoreactors, especially for G; with this photoreactor, after an initial rapid U(VI) decrease, a significant increase in the concentration of U(VI) in solution took place after 5 min. Interestingly, no precipitates on TiO_2 were formed, but a brick red color was visible in solution at the end of the experiments under both conditions, which could be attributed to U(III) formation, as we will describe later, and which disappeared very fast when the sample was filtered in contact with air. Similar experiments in the absence of the photocatalyst with 1 M HCOOH and both photoreactors indicated a lower removal compared with the HP experiments, with a higher removal with the Q photoreactor (63% and 14%, respectively for QP and GP), similarly to the system with 2-PrOH [10]. However, in contrast with this system, where dark and light yellow precipitates have been observed, no precipitate was formed, suggesting that U(IV) species stay in solution as HCOOH complexes. No U(VI) removal was observed in the dark in any case, showing that uranyl adsorption over TiO_2 is negligible at the working pH, according to previously reported data [9].

Fig. 2 shows results of similar experiments starting from uranyl acetate in nitric acid in the Q photoreactor (QAN) and various HCOOH concentrations (0.00025–1 M). Experiments were run up to 120 min but no changes were observed after 30 min. A significant and rapid removal (60% and 80%) in the first 7 min took place for all conditions with the exception of the lowest HCOOH concentration (0.00025 M), which presented a slower initial decay. In the experiments without HCOOH and with HCOOH up to 0.01 M, after this rapid decay, uranyl removal stopped without changes up to the end of the run. In the runs at the highest HCOOH concentrations (0.1 and 1 M), an increase in the U(VI) concentration took place after 7 min. Similarly as observed for QP and GP at 1 M HCOOH, no precipitate was formed over TiO_2, and a brick red color was observed in the solution at the end of the experiment, which disappeared by contact with O_2. No uranyl decay was observed in a run with 0.1 M HCOOH in the absence of light. A run under air bubbling (0.1 M HCOOH) yielded a U(VI) decay of only 10% at 30 min, followed by an arrest; a similar run with the reactor open to air gave a somewhat higher decay, 50% in 30 min.

Results of all kinetic profiles for the HP experiments could be adjusted to monoexponential decays, according to Eq. (1):

$$\frac{[U(VI)]_t}{[U(VI)]_0} = A \times \exp^{-k \times t} + (1 - A) \tag{1}$$

where A is the fraction of U(VI) removed by the photocatalytic process and k is the pseudo first order kinetic constant. In the experiments at the highest HCOOH concentrations, where a redissolution of U(VI) was observed and, only for comparison, an adjustment with Eq. (1) was made for the first 5 min.

Table 1 presents the comparative results of all experiments indicating the extent of uranyl removal at 120 min (at 30 min for experiments for QAN), the type of precipitate and the values of kinetic parameters with their errors (obtained from the fittings). The fittings to the monoexponential regime were very good in all cases ($R^2 \geqslant 0.90$) and reflect the profiles of Figs. 1 and 2. The discussion of the values in the absence of donors has been already reported [9], with A decreasing in the order QP > GP > QAN and k indicating a very slow initial removal, with a higher value for QAN. In the presence of HCOOH, both A and k increased under all conditions, except for QAN/0.00025 M HCOOH, where A was similar to the experiment without HCOOH. For the perchlorate system, the highest removal and A values were obtained at [HCOOH] = 0.001 M in both photoreactors, but a higher k value was obtained at [HCOOH] = 1 M. The use of the quartz photoreactor gave better results than the use of the glass one, with the exception of 0.001 M HCOOH, where A and k were similar. For the QAN system, the optimal HCOOH concentration was 0.01 M, where the higher removal was reached. An increasing HCOOH concentration caused a decrease in U(VI) removal, ascribed to the formation of soluble formate complexes [13], followed by U(IV) reoxidation during filtration [9]. The values of A and k were almost constant for all QAN systems at [HCOOH] $\geqslant$ 0.01 M. Except for GP at 1 M HCOOH, the percentage of removal and A were equal or smaller for QAN, indicating a detrimental effect of acetate, as previously observed with 2-PrOH [9]. A decrease of A and k was observed in QAN experiments with the reactor open to air or under air bubbling. The kinetic parameters point out that a smaller fraction of U(VI) was removed at a reduced rate, the results being much more noticeable under air bubbling due to the higher O_2 concentration.

Remarkably, the formation of precipitates was observed only at 0.001 and 0.01 M HCOOH, either with QP or with QAN. At lower HCOOH concentrations, not enough U removal was probably achieved, and, as said, at higher HCOOH concentrations, soluble

Table 1

Percentage of uranyl removal at 120 min, type of precipitate obtained at the end of the run and kinetic parameters obtained from the fitting of the experimental points of Figs. 1 and 2 with Eq. (1).

Condition/[HCOOH] (M)	% U(VI) removal	Precipitate	A	k (min^{-1})	R^2
TiO_2, QP, 0	43	No	0.56 ± 0.08	0.013 ± 0.003	0.98
TiO_2, GP/0	24	No	0.45 ± 0.04	0.006 ± 0.002	0.90
TiO_2, QAN/0	26[a]	No	0.32 ± 0.03	0.068 ± 0.005	0.95
TiO_2, QP/0.001	94	Yes (dark gray)	0.90 ± 0.03	0.19 ± 0.02	0.99
TiO_2, GP/0.001	90	Yes (dark gray)	0.87 ± 0.05	0.17 ± 0.01	0.98
TiO_2, QP/1	78	No	0.78 ± 0.09	0.37 ± 0.08	0.91
TiO_2, GP/1[b]	29	No	0.47 ± 0.04	0.4 ± 0.1	0.97
No TiO_2, QP/1	63	No	ND	ND	ND
No TiO_2, GP/1	14	No	ND	ND	ND
TiO_2, QAN/0.00025	44[a]	No	0.40 ± 0.03	0.26 ± 0.02	0.96
TiO_2, QAN/0.001	75[a]	Yes (light gray)	0.74 ± 0.07	0.34 ± 0.01	0.99
TiO_2, QAN/0.01	79[a]	Yes (light gray)	0.81 ± 0.02	0.50 ± 0.08	0.99
TiO_2, QAN/0.1[b]	49[a]	No	0.81 ± 0.02	0.5 ± 0.1	0.99
TiO_2, QAN/1[b]	43[a]	No	0.75 ± 0.02	0.50 ± 0.04	0.99
TiO_2, no light, QAN/0.1	≈0[a]	No	ND	ND	ND
TiO_2, open to air, QAN/0.1	51[a]	No	0.53 ± 0.02	0.10 ± 0.01	0.99
TiO_2, with O_2, QAN/0.1	11[a]	No	0.11 ± 0.03	0.10 ± 0.01	0.90

ND: not determined.
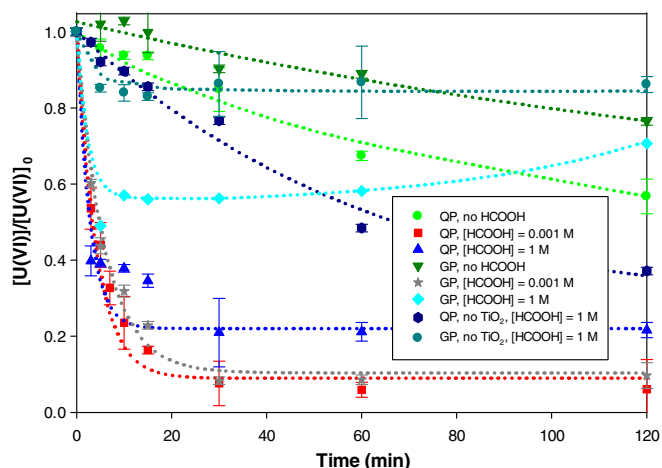[a] At 30 min.
[b] Adjustment only up to the first 5 min.

Fig. 1. Temporal evolution of normalized U(VI) concentration in the presence of HCOOH during HP experiments with uranyl perchlorate. Conditions: setup I, QP and GP, $[U(VI)]_0 = 0.25$ mM, $[TiO_2] = 1$ g L^{-1}, N_2 (0.5 L min^{-1}), pH 3, $T = 25$ °C. Q photoreactor: $\lambda > 230$ nm, $\lambda_{max} = 365$ nm, $q^0_{n,p}/V = 121$ µeinstein s^{-1} L^{-1}. G photoreactor: $\lambda > 310$ nm, $\lambda_{max} = 365$ nm, $q^0_{n,p}/V = 44$ µeinstein s^{-1} L^{-1}. Dotted lines are fittings of experimental points to Eq. (1), with the exception of GP with 1 M HCOOH, which was fitted up to 5 min, and experiments without TiO_2, where dotted lines are only for a better visualization of the experimental points.

Fig. 2. Temporal evolution of normalized U(VI) concentration in the presence of HCOOH during experiments with TiO_2 with uranyl acetate (QAN conditions). Experiments were run up to 120 min but no changes were observed after 30 min. Conditions of Fig. 1. Dotted lines are fittings of experimental points to Eq. (1) with the exception of the curves with 0.1 and 1 M HCOOH, which were fitted up to 5 min.

complexes are formed [13]. Dark gray precipitates were observed for QP/0.001 and GP/0.001, while for QAN/0.001 and QAN/0.01, precipitates were light gray, in agreement with the lower U(VI) removal. The color suggested the formation of oxides of stoichiometry UO_{2+x} ($x = 0$–0.25) [1,9], with a predominance of U(IV). Although TXRF analysis of these deposits (not shown) confirmed the presence of uranium, XRD analysis reported only signals of TiO_2, probably due to the low uranium concentration or to the lack of crystallinity of deposits. Thus, these analyses did not allow the identification of the uranium oxides.

A comparison of the absorbance spectra of the filtered suspensions before and after a HP experiment for QAN with 1 M HCOOH is presented in Fig. 3. The initial spectrum showed the characteristic U(VI) signals in the region 350–500 nm (see inset) [14–16], while the final one showed U(IV) signals at 435, 490, 554 and 663 nm together with a broad band at 800–900 nm [17–21]. This result confirms that uranium remains in solution in the form of a U(IV)-formate complex [13], being reoxidized to U(VI) by O_2 during the filtration and increasing U(VI) concentration in solution after approximately 7 min (Fig. 2). The peak at 963 nm indicates that U(V) is also formed [22–24].

3.2. Irradiation experiments at pH < 2 in the presence of TiO_2 nanoparticles

Irradiation experiments of 1 mM uranyl perchlorate solutions with 0.010 M TiO_2 nanoparticles in the absence and in the presence of 1 M HCOOH at very acid pH (<2) under N_2 were performed using setup II. Higher initial U(VI) concentrations than in the experiments with P25 suspensions were used to clearly observe changes. Fig. 4 shows the evolution of the UV–Vis spectra of the uranyl perchlorate solution with the TiO_2 nanoparticles and absence of HCOOH after 120 min irradiation. After this time, no more spectral changes were observed.

The spectrum of the initial solution shows the characteristic U(VI) signals (see inset) [14–16] overlapped with the spectrum of the TiO_2 nanoparticles. The signals of U(VI) disappeared after irradiation, indicating a complete reduction, and three new signals at 737, 836 and 963 nm appeared, corresponding to U(V) [22–24]. The spectrum of the nanoparticles in the absence of U(VI) is
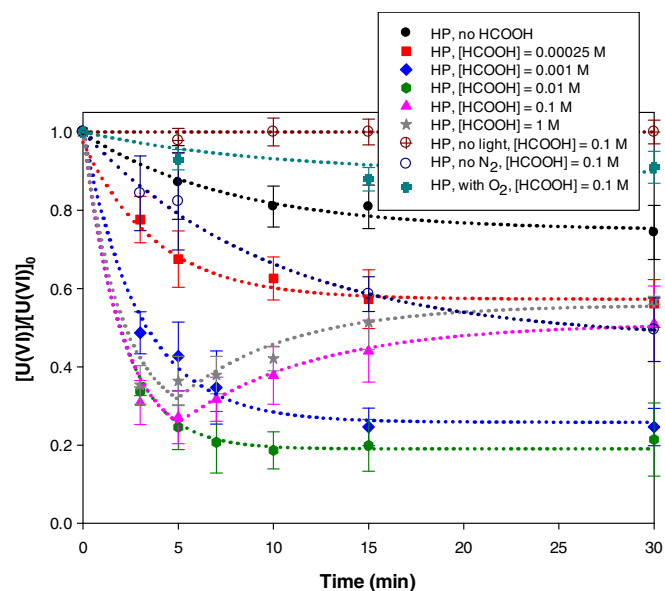
included, showing only the TiO_2 absorbance in the 250–400 nm range [25].

Fig. 5 shows the initial and final spectra of a HP run under the same conditions of Fig. 4 but in the presence of 1 M HCOOH. The initial spectrum shows signals of U(VI) [15]. After 120 min, peaks of U(IV) at 663 and 800–900 nm [17–21], and of U(V) at 737 and 963 nm [22–24] can be seen; the peak at 836 nm visible in Fig. 4 was surely overlapped by the broad U(IV) band. Remarkably, an important increase in the absorbance in the 350–600 nm range was observed (see inset), together with a change of color in the suspension, from transparent to deep orange, which coincides with the reported absorbance of U(III) species [19,20,26,27], corresponding probably to a U(III)-HCOOH complex [28–30]. Other peaks corresponding to U(III) were not observed, surely due to a masking by the strong U(IV) signals [19,20].

Results of similar experiments in the absence of TiO_2 nanoparticles are shown in Fig. 6, where the spectra of the initial solution and after 90 min of irradiation can be seen. The spectrum of the initial sample shows the characteristic U(VI) peaks at 350–500 nm (see inset) [15]. After 90 min of irradiation, the spectrum showed signals of U(V) (963 nm) [22–24] and U(IV) (450, 500, 550, 650 and 850 nm) [17–21]; as no further changes were observed and the spectrum was very different from that of U(VI), it will be assumed that U(VI) was almost completely reduced. At 90 min, the cell was opened to air and left in the dark for 30 min more. The spectrum registered the disappearance of the 963 nm peak due certainly to the fast oxidation or disproportionation of U(V) [24,31–35]. Interestingly, a small decrease of the absorbance in the 350–600 nm range can be observed, which cannot be ascribed neither to U(V) [22–24] nor to U(IV) [17–21]. After the reaction with O_2, if this absorbance would have corresponded to U(VI), an increase in the absorbance should have been observed; therefore, the decrease in the absorbance can only be ascribed to U(III) formation. In addition, the U(IV) peak centered at 850 nm was certainly higher, while the peak at 650 nm seemed to be more defined. A very similar change of the U(IV) spectra during U(VI) radiolytic studies was found by Elliot et al., who also ascribed this change
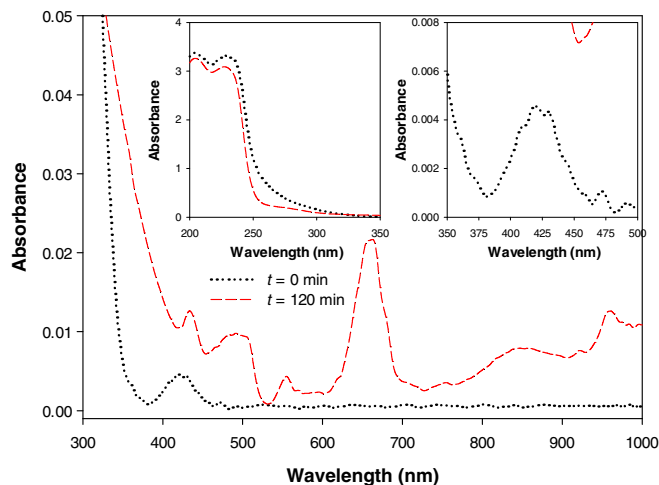
Fig. 3. Spectra of the initial and final filtered solutions of a HP experiment for QAN in the presence of 1 M HCOOH. Conditions of Fig. 2. Spectra of the initial and final filtered solutions of a HP experiment for QAN in the presence of 1 M HCOOH. Conditions of Fig. 1. Insets: detailed views of the 200–350 nm and 350–500 nm regions.
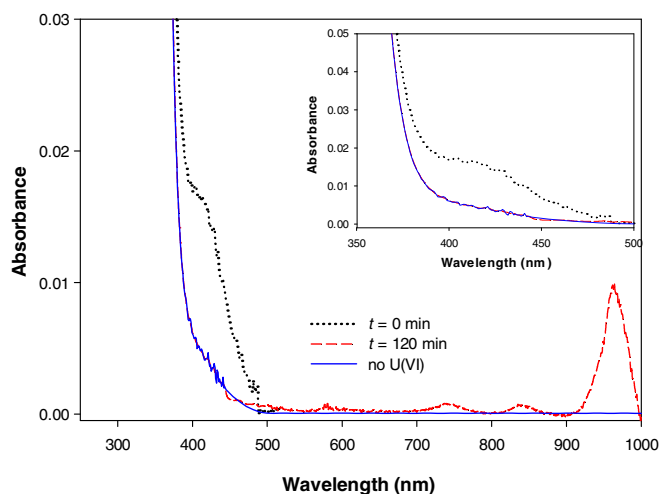

Fig. 4. Temporal evolution of the spectrum of a uranyl perchlorate solution in the presence of TiO$_2$ nanoparticles and absence of HCOOH. Conditions: setup II, [U(VI)]$_0$ = 1 mM, [TiO$_2$] = 0.010 M, pH 1.80, N$_2$ atmosphere, E^0 = 3700 μW cm^{-2}, full emission spectrum. The spectrum in the absence of U(VI) is also included. Inset: detailed view of the 350–500 nm region.

to U(III) [36]. Although U(III) is unstable, its half-life has been reported to be at least 755 h under similar conditions to ours [37], enough to be spectroscopically detected.

4. Discussion

For P25, the values of the edges of conduction band (CB) and valence band (VB) at pH 0 have been calculated as −0.3 and +2.9 V vs. SHE,[†] respectively [38]. Under normal laboratory UV illumination conditions and at pH 3, P25 e$^-_{CB}$ are able to photocatalytically transform UO$_2^{2+}$ into UO$_2^+$ and U(IV) through one-electron consecutive steps (Eq. (2)), while further reduction to other uranium oxidation states is not possible, according to the Latimer diagram (Scheme 1).

The discussion of results in the absence of electron donors can be reviewed in the previous work [9]. Briefly, uranyl removal from
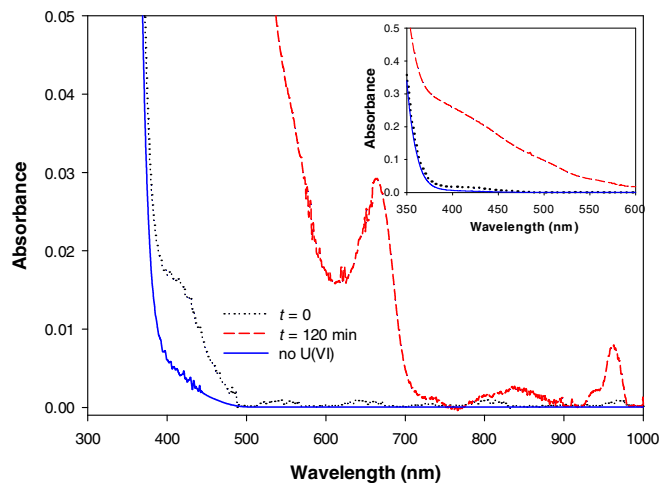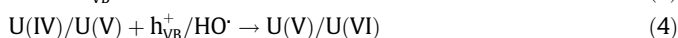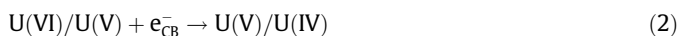

[†] All reduction potentials given in this paper are standard values vs. SHE.

Fig. 5. Temporal evolution of the spectrum of a uranyl perchlorate solution in the presence of TiO$_2$ nanoparticles and HCOOH. Conditions: setup II, [U(VI)]$_0$ = 1 mM, [TiO$_2$] = 0.010 M, [HCOOH] = 1 M, pH 1.3, N$_2$ atmosphere, E^0 = 3700 μW cm^{-2}, full emission spectrum. Inset: detailed view of the 350–600 nm region.

water takes place, but it is low because the conjugate reaction, oxidation of water by h$^+_{VB}$ to give free HO$^·$ (Eq. (3)) is slow (yielding finally H$_2$O$_2$ and O$_2$), and reoxidation to U(V/VI) by h$^+_{VB}$ or HO$^·$ (Eq. (4)) competes, leading to a short-circuit and fast e$^-$/h$^+_{VB}$ recombination, both stopping U(VI) transformation.

$$U(VI)/U(V) + e^-_{CB} \rightarrow U(V)/U(IV) \qquad (2)$$

$$H_2O + h^+_{VB} \rightarrow HO^· + H^+ \qquad (3)$$

$$U(IV)/U(V) + h^+_{VB}/HO^· \rightarrow U(V)/U(VI) \qquad (4)$$

The reported characteristic time for the formation of trapped HO$^·$ on TiO$_2$ according to Eq. (3) is 10 ns [42]. Formation of HO$^·$ is a necessary and well-known reaction in photocatalytic systems, which induces oxidation of different species present in the medium [42].

Although no values were found for the reaction of U(IV) or U(V) with TiO$_2$-h$^+_{VB}$, the reported value for the reaction of U(IV) with free HO$^·$ in aqueous solution ranges between 8 × 10^8 M^{-1} s^{-1} [36] and 8.6 × 10^8 M^{-1} s^{-1} [43,44]. For the UO$_2^+$/HO$^·$ radical pair in water, a lifetime of 20 ns [31 and references therein] was found. This means that both reduced U species are very rapidly oxidized by hydroxyl radicals.

The faster reaction at initial times for QAN in the absence of donor was explained because acetate acts as a donor, favoring uranyl transformation; however, at longer times, U(VI) concentration in solution increases due to the formation of soluble and oxidizable U(IV)-acetate complexes, as reflected by the smaller value of A (Table 1) [9].

In the presence of electron donors at high concentrations, recombination of e$^-_{CB}$/h$^+_{VB}$ pairs and reoxidation of uranium species is prevented, since these species are oxidized by h$^+_{VB}$ or HO$^·$ in preference to uranium species. Moreover, the sacrificial donor generates highly reactive radicals by attack of h$^+_{VB}$ or HO$^·$ (E^0 = +2.8 V for HO$^·$/H$_2$O) [45], which enhance reductive steps.

Regarding HCOOH addition as electron donor, it is interesting to analyze first the effect of this electron donor in the absence of TiO$_2$. Several authors examined the photochemical reaction of uranyl in the presence of HCOOH [46–53], and some of them [46,50] proposed the following process, with U(IV) and CO$_2$ being the only detectable products and U(V) an intermediate species.

$$UO_2^{2+} + 3H^+ + HCOO^- + h\nu \rightarrow U^{4+} + CO_2 + 2H_2O \qquad (5)$$
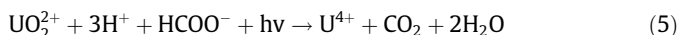
In a recent work, Lucks et al. [54] studied the U(VI) photoreduction in the presence of HCOOH through density functional theory calculations, and concluded that the reaction takes place by
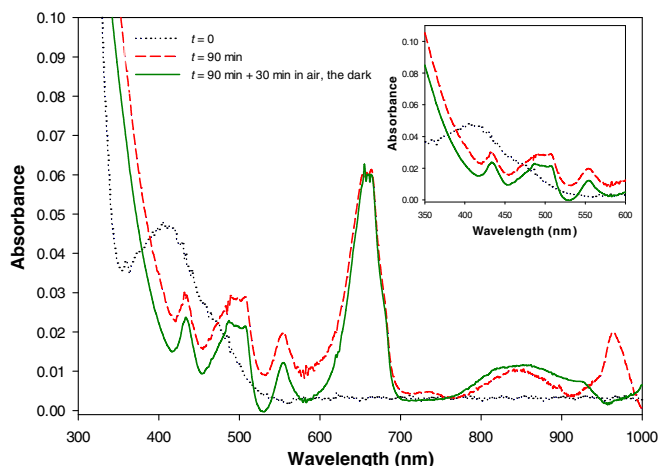
Fig. 6. Temporal evolution of the spectrum of a uranyl perchlorate solution in the presence of HCOOH (no TiO_2 nanoparticles) up to 90 min of UV–Vis irradiation and after 90 min of UV–Vis irradiation plus 30 min of exposure in the dark to the air. Conditions: setup II, $[U(VI)]_0 = 1$ mM, $[HCOOH] = 1$ M, pH 1.9, N_2 atmosphere, $E^0 = 3700$ µW cm^{-2}, full emission spectrum. Inset: detailed view of the 350–600 nm region.

intermolecular hydrogen abstraction only from the protonated acid, as also proposed by McCleskey et al. some years before [53]. According to Lucks et al. [54], the abstracted H is the one linked to the C atom, with generation of ·COOH/·COO$^-$ radicals (as pK$_a$ = 1.4, the ·COO$^-$ anion is the dominant species at the working pH) [55].

$$UO_2^{2+} + hv \rightarrow [UO_2^{2+}]^* \tag{6}$$

$$[UO_2^{2+}]^* + HCOO^- \rightarrow UO_2^+ + \cdot COO^- + H^+ \tag{7}$$

A second order rate constant around 2×10^7 M^{-1} s^{-1} was determined for Eq. (7), while the lifetime of $[UO_2^{2+}]^*$ in the absence of chemical quenchers was 50 µs [53], both in water.

Considering E^0 for ·CO$_2^- \sim -1.9$ V [45], this radical is able to reduce U(VI) to U(V) and U(IV) but also to U(III) (Eq. (8)). Even U(II) might be generated, but its existence is still unclear [27,56] and it will not be considered here.

$$U(VI)/U(V)/U(IV) + \cdot COOH/\cdot COO^-$$
$$\rightarrow U(V)/U(IV)/U(III) + CO_2 \tag{8}$$
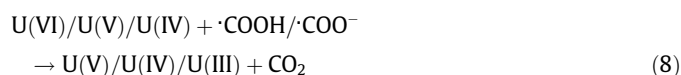
The possible reoxidation of U(V) by ·COO$^-$/·COOH (Eq. (9)), proposed elsewhere [53], cannot be completely discarded, due to the acidic conditions [57]. However, this would cause only consumption of HCOOH without net U(VI) reduction.
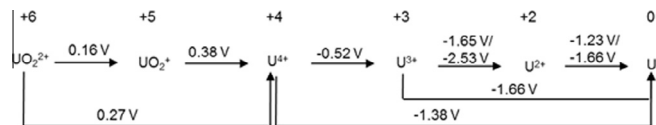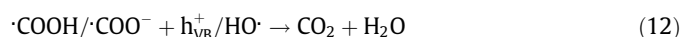
$$U(V) + \cdot COOH/\cdot COO^- \rightarrow U(VI) + CO \tag{9}$$
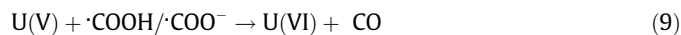
U(III) can be oxidized by h$_{VB}^+$ or HO·:

$$U(III) + h_{VB}^+/HO \cdot \rightarrow U(IV) \tag{10}$$

The rate constant for the reaction of U(III) with h$_{VB}^+$ is unknown, but a value of 4.1×10^8 M^{-1} s^{-1} has been reported for the reaction with HO· [58]. It can be suggested that U(III) can be easily oxidized by h$_{BV}^+$/HO·.

In the presence of TiO_2, the process will be similar but mediated by the semiconductor. First, direct U(VI) reduction by e$_{CB}^-$ (Eq. (2)) takes place up to U(IV). The conjugate reaction is generation of ·COOH/·COO$^-$ by reaction (11), ending in CO_2 through further oxidation (Eq. (12)) [59].

$$HCOOH/HCOO^- + h_{VB}^+/HO \cdot \rightarrow \cdot COOH/\cdot COO^- + H_2O \tag{11}$$

$$\cdot COOH/\cdot COO^- + h_{VB}^+/HO \cdot \rightarrow CO_2 + H_2O \tag{12}$$

Scheme 1. Latimer diagram for different uranium species vs. SHE [27,39–41].

The rate constant of HCOOH with HO· in water is reported to be 1.3×10^8 M^{-1} s^{-1} [43], while for the formate ion is 3.2×10^9 M^{-1} s^{-1} [43,59]. Similarly to other electron donors, HCOOH (1) accelerates uranyl reduction by reducing the recombination rate of e$_{CB}^-$/h$_{VB}^+$ pairs, and (2) is able to indirectly reduce U(VI) by ·COO$^-$ [36]. Photochemical experiments at acid pH (<2) with TiO_2 nanoparticles in the presence of high HCOOH concentrations (Fig. 5) allowed to elucidate and support the mechanism of HP uranyl reduction by direct detection of species in solution. The anoxic and acidic pH conditions used were appropriate for detection of U(III) [19,37], but this occurred significantly only in the presence of TiO_2 nanoparticles and HCOOH. In this case, all reduced uranium species, i.e., U(V), U(IV) and U(III) could be detected. The change of color of the suspension also confirmed U(III) formation. Interestingly, U(III) seems to have been formed also in the HP experiments with P25 at high HCOOH concentrations (pH 3) in QP, GP and QAN, as suggested by the brick red color developed in the suspension [27] which disappeared in air [19,27,60]. This contrasts with the 2-PrOH system [9], where this change of color was never appreciated, and neither U(IV) nor U(III) in solution was observed. Although U(IV) can be produced by direct e$_{CB}^-$ reduction, it is not detected in solution in the 2-PrOH system due to the fast deposition on the TiO_2 surface as UO_{2+x}. In the previous 2-PrOH study, when starting from uranyl acetate [9], it was shown that even when acetate was able to solubilize U(IV), U(III) was not formed either. In HCOOH, U(IV) stays in solution as a formate complex [13], allowing further reduction to U(III). On the other hand, U(III) was not observed in the 2-PrOH system because $(CH_3)_2$·COH radicals, formed by hole/HO· attack to 2-PrOH and able to produce U(III) (E^0 from –1.8 to –1.39 V) [45] have been proposed not to be directly involved in the U(VI) reduction mechanism, which is mediated only by e$_{CB}^-$. This is a distinctive feature of the 2-PrOH system, probably due to the low reaction rate of U(VI) with organic radicals [18], as proposed also for the homogeneous system [10]. It is necessary to remember that the TiO_2 nanoparticles are synthesized in a large amount of 2-PrOH (around 1 M); when HCOOH is absent (Fig. 4), U(III) was not detected, confirming that, even at low pH, it cannot be formed by $(CH_3)_2$·COH. In contrast, Fig. 5 shows the ability of CO$_2^-$ to reduce U(VI) up to U(III) in the presence of HCOOH. No reports exist on the values of the rate constants of the reaction of U(VI) or U(IV) with ·COO$^-$, but it can be suggested that they are higher than the constants of the reaction of these species with organic radicals (e.g., $(CH_3)_2$·COH), as expected from: (1) the higher reduction potential of ·COO$^-$ compared with that of organic radicals [45], and (2) the higher affinity between the positive U(VI) or U(IV) ions and ·COO$^-$. All this discussion reinforces that, up to now, only HCOOH has proven to be able to promote reduction of U(IV) to U(III).

According to the above reported rate constants for the reactions of HO· in water with HCOOH and U(IV), and the lifetime of U(V), at $[HCOOH] \geqslant 0.01$ M, HCOOH would be oxidized in preference to the uranium reduced species. At smaller $[HCOOH]$, U(V)/U(IV)/U(III) oxidation by HO· would be preferred to HCOOH oxidation; however, HCOOH could be preferentially oxidized by h$_{VB}^+$ due to a higher adsorption on TiO_2 compared with the cationic uranium species. Besides, U(IV)/U(V) oxidation by h$_{VB}^+$/HO· yields U(V)/U(VI), which can then react with e$_{CB}^-$, with no net change.

A possible competition of the reaction of carboxyl radicals with U(IV) is injection of e_{CB}^-; as can be estimated from the values reported in [61], the second order rate constant for the reaction of a carboxyl radical with TiO_2 to give CO_2 plus e_{CB}^- is 4×10^4 M^{-1} s^{-1}, while the combination rate between two carboxyl radicals is around 4–8×10^8 M^{-1} s^{-1} [62]. Given the short lifetime of this radical, this reaction can be discarded. The results of the present work indicate that $\cdot COOH/\cdot COO^-$ would react in preference with U(IV) giving U(III); on the contrary, the blue color of e_{CB}^- should have been observed [63].

Injection of electrons into the TiO_2 CB by U(III) (Eq. (13)) would be thermodynamically possible. However, this reaction does not take place, as the development of the U(III) signal in Fig. 5 was observed without the simultaneous increase of the broad band of trapped electrons around 600 nm (with a characteristic blue color) [11].

$$U(III) \rightarrow U(IV) + e_{CB}^- \tag{13}$$

A much faster reaction of h_{BV}^+ with U(III) than with HCOOH would imply that this species could not be detected, as the remaining e_{CB}^- cannot reduce U(IV) to U(III); the net results would be similar to Eq. (13). As stated before, as the characteristic blue color of trapped e_{CB}^- was not observed, a significant oxidation of U(III) by h_{BV}^+ in the studied conditions can be discarded.

Reduction of H^+ to H_2 by U(III) (Eq. (13)) [27] is also negligible at the working pH, as U(III) half-life for this decay is at least 755 h [37].

$$U(III) + H^+ \rightarrow U(IV) + \frac{1}{2}H_2 \tag{14}$$

U(III), together with all uranium reduced forms, could be spectrophotometrically seen at acid pH also in the system in the presence of HCOOH and absence of TiO_2 (Fig. 6), but the amount of U(III) was very small. U(III) formation during photochemical reactions has not been previously reported and represents a significant contribution to the elucidation of both, homogeneous and heterogeneous photochemical mechanisms.

Comparing now the efficiency of the HP process with 2-PrOH [9] and with HCOOH, despite the negative effect of HCOOH at high concentrations (Figs. 1 and 2), this electron donor seems to be more beneficial; moreover, very small amounts of HCOOH (1 mM, i.e. HCOOH/U(VI) molar ratio = 4) cause a very high removal initial rate, while 2-PrOH needs much higher 2-PrOH/U(VI) molar ratios ($\geqslant 4 \times 10^3$). The higher efficiency of HCOOH can be attributed to the higher adsorption of HCOOH over TiO_2, which promotes a more efficient scavenging of h_{VB}^+ and a faster oxidation by $HO\cdot$ (Eq. (11)), and to the high $\cdot COO^-$ reducing power. These results are in agreement with those found by Amadelli et al. [1].

As expected, a less efficient photocatalytic U(VI) reduction took place in aerated suspensions (Fig. 2) due to the competition between O_2 and uranyl for e_{CB}^- and/or the reducing radicals, and because O_2 can easily reoxidize U(IV)/U(V) to U(VI); this is consistent with previous results [3,4,9]. However, it is important to remark that the effect of O_2 is somewhat counteracted because it is partially used in the oxidation of formic acid. The difference between U(VI) removal under air bubbling (10%) or with the reactor open to air (50%) can be ascribed only to the smaller oxygen concentration present under the last condition. Of course, the efficiency of U(VI) reduction increases considerably when O_2 is totally replaced by direct N_2 bubbling in the suspension.

The lower yield of the HP reaction for QAN compared with QP (*cf.* Figs. 1 and 2) is explained by the formation of soluble U(IV)-acetate complexes. h_{VB}^+ or $HO\cdot$ will preferentially react with HCOOH instead of acetate due to a more suitable reduction potential (*cf.* $E^0(\cdot CH_2 CO_2H, H^+/CH_3CO_2H) = 1.8$ V and $E^0(HCOO\cdot, H^+/HCOOH) = 1.3$ V) [64].

Similarly to the 2-PrOH system either in the absence [10] or in the presence of TiO_2 [9], the yield in the HCOOH system was higher with the Q photoreactor (Fig. 1), and this can be explained by the more energetic radiation transmitted by the material, the higher amount of photons arriving to the solution, and the higher U(VI) absorption. A change in the mechanism due to the different wavelength range is not expected.

Effects of nitrate (QAN) were considered negligible. In the 2-PrOH system, as said, no significant differences were observed using uranyl nitrate or perchlorate. NO_3^- reduction is not possible by e_{CB}^- in the absence of HCOOH and, although it could be reduced by $\cdot COO^-$, our evidences point out that U(VI) is preferentially reduced. Effects of ClO_4^- will be also considered negligible. Although Cohen and Carnall [20] indicate that ClO_4^- can be slowly reduced by U(III), Satô et al. [19] report no reaction and, in any case, ClO_4^- can be considered inert toward U(III) in the timescale of the present experiments. On the other hand, ClO_4^- was found inert in the HP uranyl/2-PrOH system [9].

5. Conclusions

The UV heterogeneous photocatalysis of the uranyl ion in the presence of HCOOH under anoxic conditions is a very efficient process to remove uranyl from water by conversion to U(IV). However, the counterion of the uranyl salt has effect on the efficiency of the reaction, and the best removal conditions have been established, the perchlorate being the best system (and probably the nitrate, not tested here). However, excess of HCOOH should be avoided because, despite a significant initial conversion, an important reoxidation took place, which prevents U(VI) removal. This can be explained by the formation of the soluble and easily reoxidizable U(IV)-formate complex, and of soluble U(III). Lower HCOOH concentrations than those of 2-PrOH are required to obtain very good removal efficiencies. In addition, CO_2 is the only product of the reaction, in contrast with 2-PrOH, which is transformed into acetone and can be environmentally harmful.

The experiment with nanoparticles at very low pH values (<2) allowed to detect and confirm spectrophotometrically the generation of U(III) in the presence of a high HCOOH concentrations. It was proved that U(III) is formed at a large extent only in the presence of TiO_2 and HCOOH. This is the first time that the formation of U(III) in a photochemical U(VI) system has been reported.

Acknowledgments

References

[1] R. Amadelli, A. Maldotti, S. Sostero, V. Carassiti, Photodeposition of uranium oxides onto TiO_2 from aqueous uranyl solutions, J. Chem. Soc., Faraday Trans. 87 (1991) 3267–3273.

[2] C. Cerrillos, D.F. Ollis, Photocatalytic reduction and removal of uranium from a uranium-EDTA solution, J. Adv. Oxid. Technol. 3 (1998) 167–173.

[3] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, Photocatalyzed deposition and concentration of soluble uranium (VI) from TiO_2 suspensions, Colloids Surf. A 151 (1999) 339–349.

[4] V. Eliet, G. Bidoglio, Kinetics of the laser induced photoreduction of U(VI) in aqueous suspensions of TiO_2 particles, Environ. Sci. Technol. 32 (1998) 3155–3161.

[5] M. Bonato, G.C. Allen, T.B. Scott, Reduction of U(VI) to U(IV) on the surface of TiO_2 anatase nanotubes, Micro Nano Lett. 3 (2008) 57–61.

[6] M.I. Litter, Heterogeneous photocatalysis. Transition metal ions in photocatalytic systems, Appl. Catal. B 23 (1999) 89–114.

[7] M.I. Litter, Treatment of chromium, mercury, lead, uranium and arsenic in water by heterogeneous photocatalysis, Adv. Chem. Eng. 36 (2009) 37–67.

[8] M.I. Litter, N. Quici, New advances of heterogeneous photocatalysis for treatment of toxic metals and arsenic, in: B.I. Kharisov, O.V. Kharissova, H.V. Rasika Dias (Eds.), Nanomaterials for Environmental Protection, John Wiley & Sons, Hoboken, New Jersey, 2014, in press, http://dx.doi.org/10.1002/9781118845530.ch9.

[9] V.N. Salomone, J.M. Meichtry, G. Zampieri, M.I. Litter, New insights in the heterogeneous photocatalytic removal of U(VI) in aqueous solution in the presence of 2-propanol, Chem. Eng. J. 261 (2015) 27–35.

[10] V.N. Salomone, J.M. Meichtry, G. Schinelli, A.G. Leyva, M.I. Litter, Photochemical reduction of U(VI) in aqueous solution in the presence of 2-propanol, J. Photochem. Photobiol. A 277 (2014) 19–25.

[11] C. Kormann, D.W. Bahnemann, M.R. Hoffmann, Preparation and characterization of quantum-size titanium dioxide, J. Phys. Chem. 92 (1988) 5196–5201.

[12] T.M. Florence, Y. Farrar, Spectrophotometric determination of uranium with 4-(2-pyridylazo) resorcinol, Anal. Chem. 35 (1963) 1613–1616.

[13] T. Arai, Y. Wei, M. Kumagai, An efficient elution method of tetravalent uranium from anion exchanger by using formic acid solution, J. Alloys Compd. 451 (2008) 400–402.

[14] H.D. Burrows, T.J. Kemp, The photochemistry of the uranyl ion, Chem. Soc. Rev. 3 (1974) 139–165.

[15] J.T. Bell, R.E. Biggers, The absorption spectrum of the uranyl ion in Perchlorate. Part I. Mathematical resolution of the overlapping band structure and studies of the environmental effects, J. Mol. Spectrosc. 18 (1965) 247–275.

[16] J.T. Bell, R.E. Biggers, The absorption spectrum of the uranyl ion in Perchlorate. Part II. The effect of hydrolysis on the resolved spectral bands, J. Mol. Spectrosc. 22 (1967) 262–271.

[17] L.J. Heidt, K.A. Moon, Evidence for pentavalent uranium as an intermediate in the reaction in water between photoactivated uranyl ions and sucrose and closely related substances, and quantum yields for these reactions, J. Am. Chem. Soc. 75 (1953) 5803–5809.

[18] Y. Katsumura, H. Abe, T. Yotsuyanagi, K. Ishigure, Photochemical reactions of uranyl ion in nitric acid – quantum yields of photoemission and photoreduction with ethanol, J. Photochem. Photobiol. A 50 (1989) 183–197.

[19] A. Satô, S. Suzuki, Studies of the behaviour of trivalent uranium in an aqueous Solution. II. Absorption spectra and ion exchange behaviour in various acid solutions, Bull. Chem. Soc. Japan 41 (1968) 2650–2656.

[20] D. Cohen, W.T. Carnall, Absorption spectra of uranium(III) and uranium(IV) in DClO₄ solution, J. Phys. Chem. 64 (1960) 1933–1936.

[21] S.N. Guha, P.N. Moorthy, K.N. Rao, Radiation induced redox reactions in the U(VI)-U(IV) system in aqueous H₂SO₄ solutions, Radiat. Phys. Chem. 29 (1987) 425–428.

[22] D. Cohen, The preparation and spectrum of U(V) in aqueous solutions, J. Inorg. Nucl. Chem. 32 (1970) 3525–3530.

[23] C. Miyake, T. Kondo, S. Imoto, H. Ohya-Nishiguchi, Direct evidence of uranium(V) intermediates by electron spin resonance in photo- and electrolytic reduction processes of uranyl complexes in organic solutions, J. Less-Common. Met. 122 (1986) 313–317.

[24] J.T. Bell, H.A. Friedman, M.R. Billings, Spectrophotometric studies of dioxouranium(V) in aqueous media I. The perchlorate medium, J. Inorg. Nucl. Chem. 36 (1974) 2563–2567.

[25] Y. Di Iorio, E. San Román, M.I. Litter, M.A. Grela, Photoinduced reactivity of strongly coupled TiO₂ ligands under visible irradiation: an examination of an alizarin Red@TiO₂ nanoparticulate system, J. Phys. Chem. C 112 (2008) 16532–16538.

[26] C.K. Jørgensen, Absorption spectra of red uranium(III) chloro complexes in strong hydrochloric acid, Acta Chem. Scand. 10 (1956) 1503–1505.

[27] S.A. Kulyukhin, N.B. Mikheev, A.N. Kamenskaya, N.A. Konovalova, I.A. Rumer, Physicochemical properties of uranium in lower oxidation states, Radiochemistry 48 (2006) 535–551.

[28] J. Drożdżyński, Tervalent uranium compounds, Coord. Chem. Rev. 249 (2005) 2351–2373.

[29] J. Drożdżyński, K. Schwochau, H.-J. Schenk, Spectroscopic, magnetic and X-ray powder diffraction studies on U(III) and Np(III) formates, J. Inorg. Nucl. Chem. 43 (1981) 1845–1848.

[30] J. Drożdżyński, J.G. Conway, Low-temperature absorption spectrum of uranium (3+) formate energy level scheme of uranium (3+), J. Chem. Phys. 56 (1972) 883–891.

[31] S.J. Formosinho, H.D. Burrows, M.G. Miguel, M.E.D.G. Azenha, I.M. Saraiva, A.C.D.N. Ribeiro, I.V. Khudyakov, R.G. Gasanov, M. Bolte, M. Sarakha, Deactivation processes of the lowest excited state of [UO₂(H₂O)₅]²⁺ in aqueous solution, Photochem. Photobiol. Sci. 2 (2003) 569–575.

[32] J. Selbin, J.D. Ortego, The chemistry of U(V), Chem. Rev. 69 (1969) 657–671.

[33] D.M.H. Kern, E.F. Orlemann, The potential of the Uranium (V), Uranium (VI) couple and the kinetics of uranium (v) disproportionation in perchlorate media, J. Am. Chem. Soc. 71 (1949) 2102–2106.

[34] A. Ekstrom, Kinetics and mechanism of the disproportionation of Uranium(V), Inorg. Chem. 13 (1974) 2237–2241.

[35] E. Atinault, V. De Waele, J. Belloni, C. Le Naour, M. Fattahi, M. Mostafavi, Radiolytic yield of U^IV oxidation into U^VI: a new mechanism for UV reactivity in acidic solution, J. Phys. Chem. A 114 (2010) 2080–2085.

[36] A.J. Elliot, S. Padamshi, J. Pika, Free-radical redox reactions of uranium ions in sulphuric acid solutions, Can. J. Chem. 64 (1986) 314–320.

[37] Y. Kobayashi, A. Saito, Autoxidation and metal surface catalysed oxidation of uranium(III) in acid solutions, J. Inorg. Nucl. Chem. 41 (1979) 1595–1599.

[38] S.T. Martin, H. Herrmann, M.R. Hoffmann, Time-resolved microwave conductivity. Part 2. — Quantum-sized TiO₂ and the effect of adsorbates and light intensity on charge-carrier dynamics, J. Chem. Soc. Faraday Trans. 90 (1994) 3323–3330.

[39] L. Martinot, J. Fuger, The actinides in Standard potentials in aqueous solution, in: A.J. Bard, R. Parsons, J. Jordan (Eds.), Marcel Dekker, New York, 1985, pp. 631–674.

[40] M. Duflo-Plissonnier, K. Samhoun, Etude de la reduction U/III/-U/O/ en solution aqueuse par polarographie radiochimique, Radiochem. Radioanal. Lett. 12 (1972) 131–138.

[41] C.J. Evans, G.P. Nicholson, D.A. Faith, M.J. Kan, Photochemical removal of uranium from a phosphate waste solution, Green Chem. 6 (2004) 196–197.

[42] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.

[43] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O⁻) in aqueous solution, J. Phys. Chem. Ref. Data 17 (1988) 513–886.

[44] S. Gordon, J.C. Sullivan, A.B. Ross, Rate constants for reactions of radiation-produced transients in aqueous solutions of actinides, J. Phys. Chem. Ref. Data 15 (1986) 1357–1367.

[45] P.J. Wardman, Reduction potentials of one-electron couples involving free radicals in aqueous solution, J. Phys. Chem. Ref. Data 18 (1989) 1637–1755.

[46] E. Rabinowich, Photochemistry of Uranyl Compounds, Pergamon Press, Oxford, U.K., 1954. pp. 2–96.

[47] G.E. Heckler, A.E. Taylor, C. Jensen, D. Percival, R. Jensen, P. Fung, Uranyl sensitized photodecomposition of organic acids in solution, J. Phys. Chem. 67 (1963) 1–6.

[48] D. Greatorex, R.J. Hill, T.J. Kemp, T.J. Stone, Electron spin resonance studies of photo-oxidation by metal ions in rigid media at low temperatures. Part 4. — Survey of photo-oxidation by the uranyl ion, J. Chem. Soc. Faraday Trans. 1 (68) (1972) 2059–2076.

[49] M. Goldstein, J.J. Barker, T. Gangwer, A photochemical technique for reduction of uranium and subsequently plutonium in the Purex process. September 1976, informal report, Department of Applied Science, Brookhaven National laboratory, Associated Universities, Inc.

[50] A.G. Brits, R. Van Eldik, J.A. Van Der Berg, The photolysis of the uranyl formic acid/formate system in acidic aqueous solution, Inorg. Chim. Acta 30 (1978) 17–22.

[51] J. Hu, X. Zhang, D. Yunfu, Z. Zhihong, H. Xu, Studies of the photochemical reduction of uranyl nitrate in aqueous solution, J. Less-Common Met. 122 (1986) 287–294.

[52] D.M. Roundhill, Photochemistry and Photophysics of Lanthanide and Actinide Complexes, in Photochemistry and Photophysics of Metal Complexes, Springer Science + Business Media, New York, 1994. pp. 303–320.

[53] T.M. McCleskey, T.M. Foreman, E.E. Hallman, C.J. Burns, N.N. Sauer, Approaching zero discharge in uranium reprocessing: photochemical reduction of uranyl environ, Sci. Technol. 35 (2001) 547–551.

[54] C. Lucks, A. Rossberg, S. Tsushima, H. Foerstendorf, K. Fahmy, G. Bernhard, Formic acid interaction with the uranyl(VI) ion: structural and photochemical characterization, J. Chem. Soc. Dalton Trans. 42 (2013) 13584–13589.

[55] G.V. Buxton, R.M. Sellers, Acid dissociation constant of the carboxyl radical. Pulse radiolysis studies of aqueous solutions of formic acid and sodium formate, J. Chem. Soc. Faraday Trans. 1 (69) (1973) 555–559.

[56] I. Grenthe, J. Drożdżyński, T. Fujino, E.C. Buck, T.E. Albrecht-Schmitt, S.F. Wolf, Uranium, in: L.R. Morss, N.M. Edelstein, J. Fuger, J.J. Katz (Eds.), The Chemistry of the Actinide and Transactinide Elements, fourth ed., Springer, Dordrecht, 2011.

[57] N.W. Alcock, Uranyl oxalate complexes. Part I. Preparation and crystal and molecular structure of ammonium uranyl trioxalate, J. Chem. Soc. Dalton Trans. (1973) 1614–1620.

[58] D. Golub, H. Cohen, D. Meyerstein, Kinetics and mechanism of single electron oxidations of the tervalent uranium ion, U³⁺ (aq) by free radicals in aqueous solutions, J. Chem. Soc. Dalton Trans. (1985) 641–644.

[59] G.R. Dey, K.N.R. Nair, K.K. Pushpa, Photolysis studies on HCOOH and HCOO⁻ in presence of TiO₂ photocatalyst as suspension in aqueous medium, J. Nat. Gas Chem. 18 (2009) 50–54.

[60] N.L. Banik, B. Brendebach, C.M. Marquardt, Investigations of actinides in the context of final disposal of high-level radioactive waste: trivalent actinides in aqueous solution, J. Radioanal. Nucl. Chem. 300 (2014) 177–183.

[61] L.L. Perissinotti, M.A. Brusa, M.A. Grela, Yield of carboxyl anion radicals in the photocatalytic degradation of formate over TiO₂ particles, Langmuir 17 (2001) 8422–8427.

[62] P. Neta, R.E. Huie, A. Roos, Rate constants of inorganic radicals in aqueous solution, J. Phys. Chem. Ref. Data 17 (1988) 1027–1284.

[63] D. Bahnemann, A. Henglein, J. Lilie, L. Spanhel, Flash photolysis observation of the absorption spectra of trapped positive holes and electrons in colloidal TiO₂, J. Phys. Chem. 88 (1984) 709–711.

[64] D. Yu, A. Rauk, D.A. Armstrong, Radicals and ions of formic and acetic acids: an ab initio study of the structures and gas and solution phase thermochemistry, J. Chem. Soc. Perkin Trans. 2 (1994) 2207–2215.