



New insights in the heterogeneous photocatalytic removal of U(VI) in aqueous solution in the presence of 2-propanol



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HIGHLIGHTS

- UV-vis photocatalytic reduction of uranyl is revisited.
- Systems with nitrate and perchlorate are the best for U(VI) removal.
- Acetate plays a negative role in U(VI) removal.
- In the absence and presence of 2-propanol main reduction mechanism is e_{CB}^- attack.
- Photocatalytic removal technologically more advantageous than photochemical removal.

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ABSTRACT

The efficiency of heterogeneous photocatalysis with TiO₂ under UV light (HP) for the removal of uranyl ion from water (0.25 mM, pH 3) in the presence of 2-propanol (2-PrOH) was evaluated. The effects of the counterion of the uranyl salt or anions present in the system and the use of quartz and glass photoreactors were analyzed. High U(VI) removal efficiencies were obtained, reaching 100% when starting from uranyl nitrate and 1 M 2-PrOH after 60 min in a quartz photoreactor. The reaction in the absence of 2-PrOH was rather low, reaching around 50% in 120 min under the same conditions. The photocatalytic reaction yield was similar when the reaction started from uranyl perchlorate, but systems where acetate was present showed less removal, both in the absence and the presence of 2-PrOH. Yields with the quartz photoreactor were always higher than those with the glass reactor.

Kinetic and mechanistic analyses were performed. Comparisons with the photochemical systems in the absence of TiO₂ were made. The results indicated that the uranyl nitrate system in the presence of 2-PrOH gave similar results with and without TiO₂, but the other systems gave higher removal yields when TiO₂ was used. The proposed mechanism suggests that U(VI)/U(V) reduction is mediated by conduction band electrons and not by reducing organic radicals, a distinctive feature of the system. For all studied conditions, the photocatalytic treatment allowed a better recovering of the precipitated uranium.

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1. Introduction

Contamination by uranium is very common in waters and soils of mining areas and geological deposits. Possible sources of

contamination are leaching of deposits, milling of ores, nuclear wastes, carbon combustion, fertilizers, etc. Chemical processes involving the adsorption/desorption, reduction of U(VI) and the oxidation of U(IV) in natural solid and aqueous systems have been the subject of many scientific studies ([1,2] and references therein). Conventional and emergent methods used for uranium removal from water and soils include, among others, biotransformation, ion exchange, oxidation processes, coagulation, adsorption, micro- and nano-filtration, zerovalent iron, etc. [3–12]. However, most of

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them are expensive and involve a high consumption of chemicals, generating in parallel toxic wastes. For this reason, UV–Vis light based methods, either alone or in the presence of TiO_2 (heterogeneous photocatalysis, HP) could be simple, efficient and low cost procedures for U(VI) removal from natural or wastewaters [13–15]. The effect of UV–Vis light on the uranyl system in water has been presented in several papers in the literature, especially in the presence of alcohols or carboxylic acids (see e.g. [16–18]). When the photocatalytic studies on the uranyl system were initiated by us, the importance of the reaction in the absence of TiO_2 was observed, especially in the presence of organic molecules, as noted elsewhere [1]; thus, in a previous paper, we revisited the U(VI) photochemical system in the presence of 2-propanol (2-PrOH) [19], evaluating especially the effect of anions in the system (nitrate, acetate and perchlorate) and the use of quartz (Q) and glass (G) photoreactors. Complete uranyl removal was observed when starting from uranyl nitrate in a Q photoreactor, with transformation of uranium to a solid U(IV) residue and total nitrate depletion. The perchlorate salt yielded a lower removal with production of a solid U(VI) residue and no perchlorate transformation. On the other hand, acetate was detrimental for uranyl removal, and uranium kept dissolved in the system at a large extent at the end of irradiation by formation of uranium acetate soluble complexes. In view of these results, it was expected that the nature of anions present in the system would also have a significant role on uranyl photocatalytic transformation.

As very well known, after the incidence of photons of adequate energy on TiO_2 particles, electrons in the conduction band (e_{CB}^-) and holes in the valence band ($h\nu_{\text{VB}}^+$) are produced, which lead to redox reactions with transformation of the species present in solution [13–15]. Previous studies on uranyl HP reactions are scarce and not conclusive. The experiments were performed in a variety of experimental conditions and the effect of the counterion of the starting uranyl salt (or of other anions present in the system) and of the irradiation wavelength was not clearly analyzed. Among them, the pioneering work of Amadelli et al. [20], who irradiated uranyl nitrate in the presence of TiO_2 particles and electrodes, reports U(IV) formation in the presence of hole scavengers, with formation of a dark gray uranium oxide of stoichiometry close to U_3O_8 , which was reoxidized to UO_3 under air. These authors used a lamp emitting at 360 nm, with narrow band or cut-off filters without specifications. Similar results were reported by Cerrillos and Ollis [21] and by Chen et al. [22], who worked in the presence of EDTA. The first authors used a lamp emitting in the short-near UV (200–400 nm) and visible range, while the latter used a black-light fluorescent bulb (320–400 nm). Evans et al. [23], who worked in the presence of methanol, without details about the uranyl salt employed, used a mercury discharge lamp emitting short UV and visible light. Boxall et al. [24] used SnO_2 as the photocatalyst and reported high yields for the reduction of UO_2^{2+} to U^{4+} at very acid pH and in the presence of hole scavengers, under 312 nm irradiation; the starting uranyl salt was not specified. Bonato et al. [25], starting from uranyl acetate and TiO_2 nanotubes, observed 75% of U(IV) formation in the dark, increasing to 89% with further UV irradiation (indicated as “a direct UV light illumination ($\lambda = 360 \text{ nm}$)”). Two papers [26,27] studied uranyl perchlorate transformation in aqueous TiO_2 suspensions by time-resolved laser induced fluorescence, using a 308 nm laser.

Taking into account that more kinetic and mechanistic analyses were needed on uranyl HP systems, in the present work, we aimed to revisit the system and try to shed light on different aspects still obscure. The reaction with TiO_2 is compared with the previous photochemical results in the absence of the photocatalyst [19], considering the effect of the uranyl counterion or anions present in the system, and the use of Q and G photoreactors.

2. Experimental

2.1. Materials and preparation of uranyl solution

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 used. Uranyl perchlorate was prepared following the procedure described in [26] from uranyl nitrate and $\text{HClO}_4(\text{c})$ (Merck). TiO_2 (now AEROXIDE TiO_2 P25, Evonik), the model photocatalyst, was provided by Degussa (Germany) and used as received. According to the providers, P25 is a mixture of anatase and rutile ($\cong 80:20$), BET surface area of $35\text{--}65 \text{ m}^2 \text{ g}^{-1}$ and aggregated nanoparticles of around 21 nm.

All other chemicals were reagent grade and used without further purification. Water was purified with a Millipore Milli-Q equipment (resistivity = $18 \text{ M}\Omega \text{ cm}$).

UO_2^{2+} solutions ($1000 \text{ mg U L}^{-1} \cong 4.2 \text{ mM}$) were prepared by dissolving uranyl acetate or uranyl nitrate in 1% HNO_3 ; a strongly concentrated solution ($14,100 \text{ mg U L}^{-1} \cong 59 \text{ mM}$) of uranyl perchlorate was prepared in water. From the concentrated solutions, $0.25 \text{ mM} (\cong 59 \text{ mg U L}^{-1})$ solutions were prepared.

2.2. Irradiation experiments

The experiments were carried out using a commercial quartz photoreactor immersion well (Q photoreactor, Photochemical Reactors Ltd.) provided with a medium pressure mercury lamp (125 W, $\lambda > 230 \text{ nm}$, $\lambda_{\text{max}} = 365 \text{ nm}$), surrounded by a thermostatic jacket set at $25 \text{ }^\circ\text{C}$, acting 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 ($q_{\text{n,p}}^0/V$) in the irradiated solution, measured by actinometry with potassium ferrioxalate, was $121 \mu\text{einstein s}^{-1} \text{ L}^{-1}$. In selected experiments, a glass well was used with the same lamp (G photoreactor, $\lambda > 310 \text{ nm}$, $q_{\text{n,p}}^0/V = 44 \mu\text{einstein s}^{-1} \text{ L}^{-1}$).

TiO_2 suspensions (200 mL , 1 g L^{-1}) containing 0.25 mM uranyl were irradiated under nitrogen bubbling (0.5 L min^{-1}) all throughout the experiment. When indicated, the corresponding volume of pure 2-PrOH was added to reach the corresponding concentration ($0.1\text{--}10 \text{ M}$). pH was adjusted to 3 with 2 M NaOH , except in the case of uranyl perchlorate, where pH was adjusted with concentrated HClO_4 (70%). The following conditions were used in the irradiation experiments: (i) uranyl nitrate in nitric acid in the quartz photoreactor, thereafter named QN (nitrate initial concentration = 2.1 mM), (ii) uranyl acetate in nitric acid in the quartz photoreactor, QAN (nitrate initial concentration = 22.0 mM , acetate initial concentration = 0.5 mM), and (iii) uranyl perchlorate with perchloric acid, quartz photoreactor, QP (perchlorate initial concentration = 1.5 mM). For experiments with the glass photoreactor, the system will be named G (e.g. GP for the uranyl perchlorate salt with perchloric acid in the G photoreactor). Some experiments were carried out with the reactor open to air or under air bubbling. 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 2-PrOH onto TiO_2 . Aliquots ($250 \mu\text{L}$) were periodically taken during the experiment, filtered through Millipore membranes ($0.2 \mu\text{m}$) 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, an increase of the U(VI) concentration in solution (due to reoxidation of U(IV) deposited on the photocatalyst by air contact) was observed in samples taken after 10 min of irradiation and later. To avoid this redissolution, in further runs, one membrane per each sample was used, or the sample was rapidly centrifuged, with complete removal of TiO_2 .

and/or other solids. Changes of pH at the end of all runs were negligible ($\Delta\text{pH} < 0.3$). Reactions in the absence of TiO_2 were performed under identical conditions.

All the experiments were performed at least twice and the results averaged. The experimental error was never higher than 10% of the initial value, 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. The fitting of experimental points was performed with Origin 7.5 software. The procedure for statistical and computational treatment was similar to the one employed in the previous paper [19].

2.3. Analytical determinations

U(VI) concentration was followed by the spectrophotometric PAR technique [28]. Nitrate concentrations were measured by IC using a Dionex ICS-5000 ion chromatograph, with an Ion Pack AS19-Analytical – 4×250 mm column and an Ion Pack AG19 Guard – 4×50 mm precolumn, as reported in [19].

X-ray photoelectron spectroscopy (XPS) was performed with a hemispherical electrostatic energy analyzer ($r = 10$ cm) using Al K_{α} radiation ($h\nu = 1486.6$ eV). The binding-energy (BE) scale was calibrated with the position of the $\text{Ti}2\text{p}_{3/2}$ peak in TiO_2 , located at 458.5 eV [29].

3. Results

3.1. HP experiments in the absence of 2-PrOH

Fig. 1(a) shows the decay of normalized U(VI) concentration (0.25 mM, pH 3) during UV irradiation experiments in the absence of 2-PrOH and in the presence of TiO_2 under different conditions and N_2 bubbling. No U(VI) removal was observed in the dark, showing that uranyl adsorption over TiO_2 at the working pH is negligible, an expected result due to the positive charges of the semiconductor and uranyl at this pH, and in agreement with previous results [20–23] and theoretical calculations ([30–32] and references therein). The examined systems were QN, QP, GP and QAN. The analysis of QAN instead of QA (i.e. the use of the acetate salt dissolved in acetic acid) was preferred here, to ascertain the effect of nitrate and acetate together, based on the results of Ref. [19], where the negative effect of acetate on the photochemical transformation of U(VI) was recognized. Results in the absence of TiO_2 taken from Ref. [19] are shown in Fig. 1(b), which includes the QAN system, non-reported there.

U(VI) removal was rather higher in the presence than in the absence of TiO_2 under the same conditions. The order for the HP removal at 120 min was $\text{GP} < \text{QAN} < \text{QP} < \text{QN}$. Although QAN showed a more marked initial removal compared with QN, the reaction stopped after 30 min, indicating a detrimental effect of acetate. No deposit was observed onto the photocatalyst in any case at the end of the reaction.

3.2. HP experiments in the presence of 2-PrOH

HP experiments with 1 M 2-PrOH were run for the four experimental conditions QN, QP, QAN and GP and compared with similar runs without TiO_2 (Fig. 2). In all cases, U(VI) removal was higher and faster compared with the systems without 2-PrOH.

Reactions in the presence of TiO_2 under N_2 (Fig. 2(a)) revealed a fast decrease of the U(VI) concentration in the initial stages of

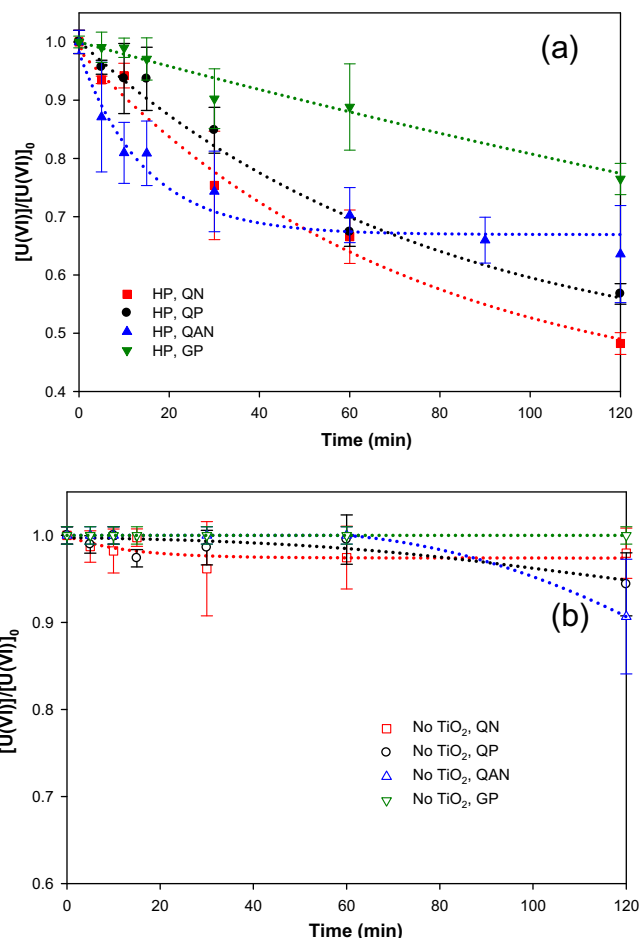


Fig. 1. Temporal evolution of normalized U(VI) concentration in the absence of 2-PrOH during (a) experiments with TiO_2 , (b) in the absence of TiO_2 . Conditions: QN, QP, QAN, GP, $[\text{TiO}_2] = 1 \text{ g L}^{-1}$, N_2 (0.5 L min^{-1}), pH 3, $T = 25^\circ\text{C}$, $\lambda > 230 \text{ nm}$, $\lambda_{\text{max}} = 365 \text{ nm}$, $q_{\text{hp}}^0/V = 121$ and $12.5 \mu\text{einstein s}^{-1} \text{ L}^{-1}$ for the Q and G conditions, respectively. Data for experiments in the absence of TiO_2 were extracted from Ref. [19]. Dotted lines in Fig. 1(a) are fittings of experimental points to Eq. (1); in Fig. 1(b), dotted lines are only for visualization of the points.

reaction, reaching high removal values (in the order $\text{QAN} < \text{GP} < \text{QP} \approx \text{QN}$) compared with similar reactions in the absence of the photocatalyst (Fig. 2(b)). For QN, the yield was similar in the presence as well as in the absence of TiO_2 and, under both conditions, a gray deposit was observed at the end of the reaction time, identified as UO_{2+x} ($x = 0-0.25$) [19]. Interestingly, for QAN in the absence of TiO_2 , after a rapid uranyl removal, a reoxidation began to take place at around 25 min, and the reaction stopped at ca. 60 min (54% removal) without precipitate formation. Measurement of nitrate concentration in this system (not shown) indicated complete depletion in 30 min, while acetate could not be quantified because of its low concentration. In the presence of TiO_2 , in addition to a more efficient uranyl removal (80%), redissolution was not observed, but an arrest of the reaction at 30 min took place. A light gray precipitate was observed in this case.

For the perchlorate system, in contrast with the results in the absence of 2-PrOH, removal was important with both Q and G photoreactors, indicating the relevance of TiO_2 in the system. For QP and GP in the absence of TiO_2 , as indicated in Ref. [19], a yellow solid was obtained after irradiation; in contrast, in the HP experiments, a gray deposit on the TiO_2 surface was observed.

A HP run for QAN was performed in the presence of O_2 (air bubbling, 0.5 L min^{-1}) to test inhibition by oxygen. A U(VI) decay of

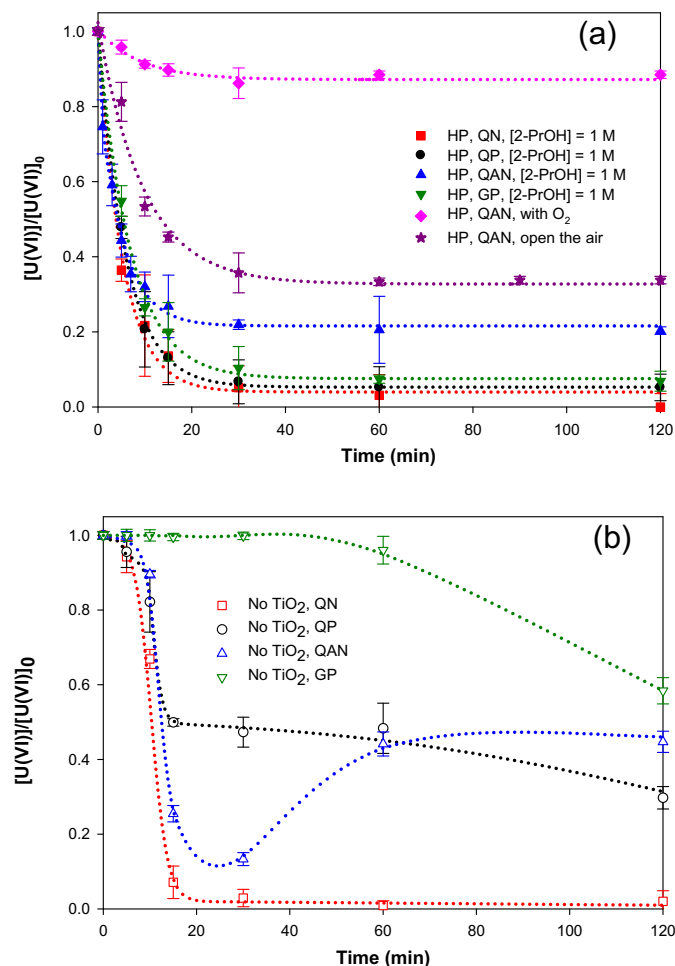


Fig. 2. (a) Temporal evolution of normalized U(VI) concentration in the presence of 2-PrOH during experiments with TiO_2 in QN, QP, QAN and GN conditions, experiments with air included; (b) similar experiments without TiO_2 . Other conditions of Fig. 1. Data for experiments in the absence of TiO_2 for QN, QP and GN were extracted from Ref. [19]. Dotted lines in Fig. 2(a) are fittings of experimental points to Eq. (1); in Fig. 2(b), dotted lines are only for visualization of experimental points.

only 10% at 30 min was observed, followed by an arrest of the reaction and no deposit over TiO_2 . When the run was made with the reactor open to air (without air bubbling), the decay was somewhat higher, reaching 60% in 30 min, with no further decay. Spectra of the filtered solutions before and after a photocatalytic run for the QN system were taken (Fig. 3). The spectrum of the initial solution presents a strong absorption in the short UV range [33], with lower absorption peaks and the characteristic U(VI) manifold in the range 350–500 nm [16]. In the spectrum of the filtered solution after the photocatalytic run, no signals corresponding to reduced uranium species (U(V), U(IV) or U(III)) could be seen, in contrast with the results in the absence of TiO_2 [19], where U(V) in solution was clearly detected at 736, 845 and 963 nm, including a UVC band [16,34,41]. No U(IV) peaks were observed.

Other HP runs were performed with different 2-PrOH concentrations and are presented in Figs. S1 and S2 of the Supplementary Data (SD). As in QP and QN the reactions were too fast to be analyzed properly and similar results were obtained (Fig. S1), experiments with a larger range of 2-PrOH concentrations were performed only with QAN (Fig. S2). All the curves presented a similar shape: a fast decrease in the first minutes, followed by a deceleration and an arrest of the reaction at 10 min.

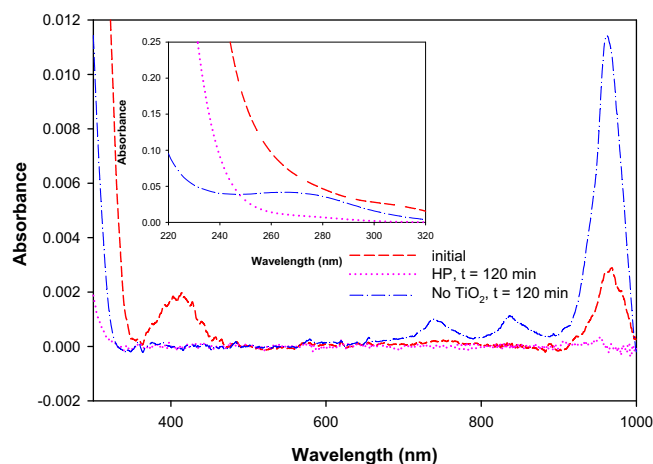


Fig. 3. Initial and final spectra of a photocatalytic and a photochemical experiment for QN in the presence of 2-PrOH. Conditions of Fig. 2. The small peak at 963 nm in the initial spectrum can be associated to some U(V) formed by exposure of the sample to the environmental light.

3.3. Comparison of results

Table 1 presents the comparative results of all experiments indicating the percentage of uranyl removal at 120 min, and the type of precipitate formed.

For QN, QP and GP systems, dark gray precipitates were observed over TiO_2 , with no difference in color within the studied concentration range (1–10 M). For QAN, dark gray deposits were observed only for the highest 2-PrOH concentrations (5 and 10 M), while in the presence of O_2 (O_2 and air) no precipitates were found.

3.4. Fitting of the kinetic plots

Results of all kinetic photocatalytic profiles could be adjusted to monoexponential decays, according to Eq. (1):

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

Table 1

Percentage of uranyl removal at 120 min taken from Figs. 1 and 2, S1 and S2, and type of precipitate obtained at the end.

Condition	% U(VI) removal	Precipitate
TiO_2 , QN no 2-PrOH	52	No
TiO_2 , QP no 2-PrOH	43	No
TiO_2 , GP no 2-PrOH	24	No
TiO_2 , QAN no 2-PrOH	36	No
TiO_2 , QAN [2-PrOH] = 0.1 M	73	Yes (light gray)
TiO_2 , O_2 , QAN [2-PrOH] = 1 M	12	No
TiO_2 , air, QAN [2-PrOH] = 1 M	66	No
TiO_2 , QN [2-PrOH] = 1 M	100	Yes (dark gray)
TiO_2 , QP [2-PrOH] = 1 M	95	Yes (dark gray)
TiO_2 , GP [2-PrOH] = 1 M	93	Yes (dark gray)
TiO_2 , QAN [2-PrOH] = 1 M	80	Yes (light gray)
TiO_2 , QP [2-PrOH] = 10 M	96	Yes (dark gray)
TiO_2 , GP [2-PrOH] = 10 M	95	Yes (dark gray)
TiO_2 , QAN [2-PrOH] = 5 M	81	Yes (dark gray)
TiO_2 , QAN [2-PrOH] = 10 M	84	Yes (dark gray)
no TiO_2 , QN no 2-PrOH	4	No
no TiO_2 , QP no 2-PrOH	5	No
no TiO_2 , QAN no 2-PrOH	9	No
no TiO_2 , GP no 2-PrOH	≈0	No
no TiO_2 , QN [2-PrOH] = 1 M	98	Yes (dark gray)
no TiO_2 , QP [2-PrOH] = 1 M	70	Yes (yellow)
no TiO_2 , QAN [2-PrOH] = 1 M	55	No
no TiO_2 , GP [2-PrOH] = 1 M	42	Yes (light yellow)

Table 2

Kinetic parameters obtained from the fitting of the experimental points of photocatalytic experiments of Figs. 1 and 2, S1 and S2 with Eq. (1).

Condition/[2-PrOH] (M)	A	k (min ⁻¹)	R ²
QN/0	0.62 ± 0.09	0.014 ± 0.003	0.98
QP/0	0.56 ± 0.08	0.013 ± 0.003	0.98
GP/0	0.45 ± 0.04	0.010 ± 0.004	0.90
QAN/0	0.32 ± 0.03	0.068 ± 0.005	0.95
QN/1	0.96 ± 0.02	0.19 ± 0.01	0.99
QP/1	0.95 ± 0.03	0.17 ± 0.01	0.99
QP/10	0.96 ± 0.02	0.49 ± 0.02	1
GP/1	0.93 ± 0.02	0.14 ± 0.01	1
GP/10	0.93 ± 0.01	0.27 ± 0.01	1
QAN/0.1	0.72 ± 0.01	0.25 ± 0.01	1
QAN/1	0.74 ± 0.04	0.24 ± 0.04	0.98
QAN/1 (air)	0.15 ± 0.01	0.08 ± 0.003	0.97
QAN/1 (open air)	0.70 ± 0.03	0.10 ± 0.02	0.95
QAN/5	0.73 ± 0.02	0.45 ± 0.07	0.98
QAN/10	0.80 ± 0.04	0.47 ± 0.06	0.98

In Table 2, the values of kinetic parameters and their errors (obtained from the fittings) are shown. It is important to say that experimental points for runs in the absence of TiO₂ could not be fitted and were not taken into account for the kinetic analysis.

The fittings to the monoexponential regime were very good in all cases ($R^2 > 0.90$). In the absence of the alcohol, the fraction of U(VI) removed, given by the value of A, decreases in the order QN > QP > GP > QAN. The values confirm that acetate markedly affects the uranyl transformation, and at 120 min around 70% of uranium remains in solution. The values of the kinetic constants k are similar and low for all the runs, indicating a very slow initial removal, with the exception of QAN, where k was higher, in agreement with that observed in Fig. 1(a).

In the presence of 1 M 2-PrOH, the values of A are higher and similar for all conditions, with the exception of QAN, whose lower value evidences again the detrimental effect of acetate; the values of k are similar for the four conditions and reflect the higher initial removal in the presence of the alcohol.

Results with higher 2-PrOH concentrations indicate that the amount of 2-PrOH affects more significantly the reaction rate (k) than the rate of U(VI) conversion (A).

When air is bubbled into the suspension, a sharp decrease of A and k is observed, indicating that a larger fraction of initial U(VI) is not reduced and remains in solution, as seen in Fig. 2(a). In the experiments with the reactor open to air, the kinetic parameters point out that a larger fraction of U(VI) was removed but at a reduced rate (a k value almost similar to that with bubbled O₂).

Selli et al. [27], when studying the photocatalytic reduction of U(VI) in the presence of humic acids, proposed a general biexponential model for the reaction, with an exponential term assigned to reduction of adsorbed U(VI) by e_{CB}⁻, and another one related to reduction of U(VI) in solution; a constant term in the fitting equation was ascribed to the steady-state U(VI) concentration due to competition between U(VI) reduction and U(IV) reoxidation. Under our experimental conditions, U(VI) adsorption over TiO₂ is negligible (see Section 3.1), and the biexponential equation proposed in [27] becomes a simple exponential of the form of Eq. (1).

3.5. Analysis of solid residues

Table 1 indicates that for HP runs performed in the absence of 2-PrOH, neither change of color nor a solid on the TiO₂ surface was seen. In the presence of the alcohol, for QN, QP and GP, dark gray deposits were obtained over the photocatalyst, suggesting the formation of UO₂ (uraninite) mixed with U₃O₈ [35]. For the QAN photocatalytic systems in the presence of various 2-PrOH concentrations, deposits of different color intensities were

obtained, the darkest one being that obtained with 10 M 2-PrOH; the higher intensities indicate a predominance of the more reduced uranium oxidation state.

Deposits at the end of a HP QAN run (10 M 2-PrOH) were analyzed by XPS. Survey spectra (Fig. S3) show the region of the Ti2p and U4f peaks measured before (bottom) and after the HP treatment (top); the spectra are normalized to the intensity of the Ti2p_{3/2,1/2} core-level peaks at around 460 eV. The presence of uranium in the solid after the treatment is evident from the appearance of new peaks in the region between 380 and 400 eV, corresponding to photoelectrons emitted from the U4f_{7/2,5/2} core levels. The intensity ratio of U4f and Ti2p doublets allows to estimate the amount of U trapped on the surface. The procedure employed for this calculation is indicated in the SD. With the values of estimated parameters and the measured intensities, a U covering $\theta = 0.78$ was calculated, indicating that almost one atom of U for each Ti atom exists on the surface.

To determine the oxidation state of the U atoms, the U4f spectrum was measured with a better energy resolution (Fig. 4). For comparison, the spectra of UO₂ and UO₃ pure samples are also included, showing the 4f_{7/2} peaks centered at 380.4 eV (UO₂) and 381.9 eV (UO₃), in good agreement with published data [25,36], with full-widths at half maximum (fwhm) of 2.8 eV. In the spectrum of the sample, the 4f_{7/2} peak lies in between the positions

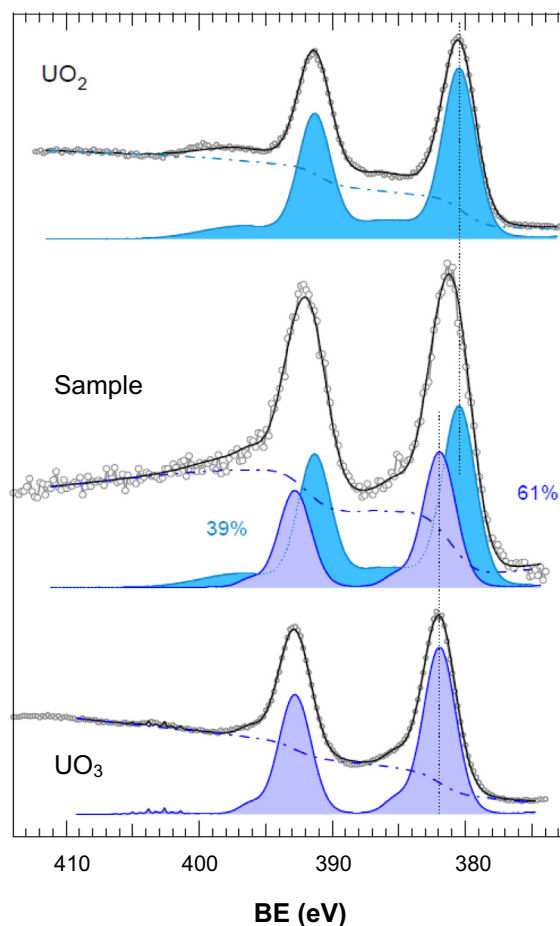


Fig. 4. U4f photoemission spectra of a pure UO₂ sample (upper panel), a sample after a HP experiment (middle panel), and a pure UO₃ sample (lower panel). The spectra of the two reference oxides was fitted with Voigt functions and a Shirley background, and the spectrum of the HP sample was fitted with a linear combination of the two reference spectra plus a Shirley background. Conditions of the HP run: QAN, [U(VI)]₀ = 0.25 mM, TiO₂ (1 g L⁻¹) under N₂ (0.5 L min⁻¹), [2-PrOH] = 10 M, pH 3, T = 25 °C.

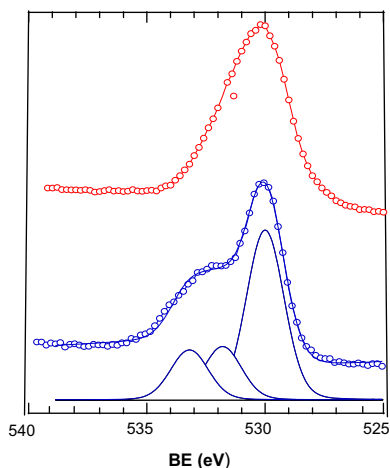


Fig. 5. O1s photoemission spectra of a TiO₂ sample before (lower panel, blue line) and after (red line) the HP treatment. The spectrum of the TiO₂ sample has been fitted with three components representing the oxide, OH and H₂O components (in order of increasing binding energy). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the references, with a considerably larger fwhm (3.5 eV), suggesting that the spectrum may be a superposition of the other two spectra, confirmed by the fitting with a linear combination. According to the best fitting, 39% of the atoms can be assigned to U(VI) and the other 61% to U(IV).

Fig. 5 presents the O1s spectra corresponding to TiO₂ samples before (blue line) and after (red line) the run. Following Ref. [25], the spectrum of the unreacted sample was decomposed into three components representing the oxide component (O1 at 529.9 eV), hydroxyl groups or defect oxides (O2 at 531.7 eV), and adsorbed water or chemisorbed oxygen (O3 at 533.1 eV). After the treatment, the spectrum exhibited two important changes: (i) a broader component at the position of the oxide, denoting the presence of other oxidized species on the surface, and (ii) a loss of intensity in the region of the OH and H₂O components, which indicates that after adsorption on the hydrated TiO₂ surface, U(VI) is reduced on the non-stoichiometric surface phases to form UO_{2+x}.

4. Discussion

4.1. Heterogeneous photocatalysis of uranyl systems in the absence of electron donors

For P25, the values of the edges of conduction (CB) and valence bands (VB) at pH 0 have been calculated as -0.3 and $+2.9$ V vs. NHE, respectively [37]. Under standard laboratory HP illumination conditions, species can be reduced by e_{CB}^- through consecutive one-electron steps until the production of a stable form (Eq. (2)); this mechanism has been proposed in other works [2,26,27].

As seen in Scheme 1, where a simplified energy diagram is shown, uranyl salts can be photocatalytically transformed by e_{CB}^- to UO₂⁺ and to U(IV) at pH 0, the respective couples having redox potentials more positive than the e_{CB}^- redox level¹. Further reduction to other states would not be possible [38].

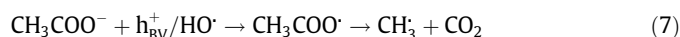
The conjugate reaction is water oxidation by h_{BV}^+ (Eq. (3)) to give HO[•]; a slow process, yielding O₂ as the final stable product (Eq. (4)); reoxidation to U(VI) by h_{VB}^+ or HO[•] (Eq. (5)) would be a competing process leading to a short-circuit that can stop U(VI) transformation, decreasing the efficiency.



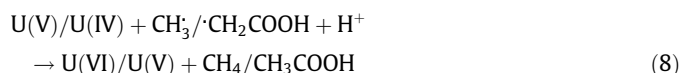
Under UV irradiation in the presence of TiO₂, the appreciable transformation that takes place under all working conditions (Fig. 1(a)) contrasts with the results in the absence of the photocatalyst (Fig. 1(b)) and indicates that the uranyl species can actually react with e_{CB}^- at pH 3. As discussed in Ref. [2], the role of TiO₂ in the reductive immobilization of uranyl complexes appears to be mainly photocatalytic while surface defects play little or no role in the reduction of surface adsorbed U(VI) complexes. In contrast, the photoreduction of U(VI) complexes by organic molecules in the absence of a solid photocatalytic surface is well known from experimental studies.

The reaction profiles for QN and QP are rather similar, but QN is somewhat more reactive (Table 2). In the homogeneous photochemical uranyl removal studied before by us [19], NO₃⁻ oxidation by the excited state of uranyl ([UO₂²⁺]^{*}, $E^0 = +2.6$ V [41]) was proposed to explain the enhanced reactivity of QN in the absence of 2-PrOH compared with the other tested systems. This effect can be discarded in the HP reaction because U(VI) removal is much smaller in the absence of TiO₂ (Fig. 1(b)) and by the scattering and UV filter effects of the semiconductor. As neither NO₃⁻ [42] nor ClO₄⁻ [43] can be photocatalytically reduced in the absence of a hole scavenger, the small but evident higher efficiency in QN compared with QP can be attributed to a somewhat more efficient trapping of h_{BV}^+ or HO[•] by NO₃⁻ than by ClO₄⁻, as can be expected from the values of the respective one-electron oxidation potentials ($E^0(NO_3^-/NO_2^-) = 2.3-2.6$ V [39,44], $E^0(ClO_4^-/ClO_3^-) = 2.8$ V [45]). The differences between QP and GP will be explained in Section 4.2.

The case of QAN is interesting because it allows to analyze the effect of acetate and nitrate present simultaneously. The higher k value (Table 2) for QAN reflects the higher photocatalytic transformation in the first minutes, probably due to a more efficient trapping of h_{BV}^+ or HO[•] by acetate ($E^0(\cdot CH_2CO_2H, H^+/CH_3CO_2H) = 1.8$ V, $E^0(CH_2CO_2^\bullet, H^+/CH_3CO_2^-) = 2.4$ V [46], Eqs. (6) and (7)), compared with NO₃⁻.



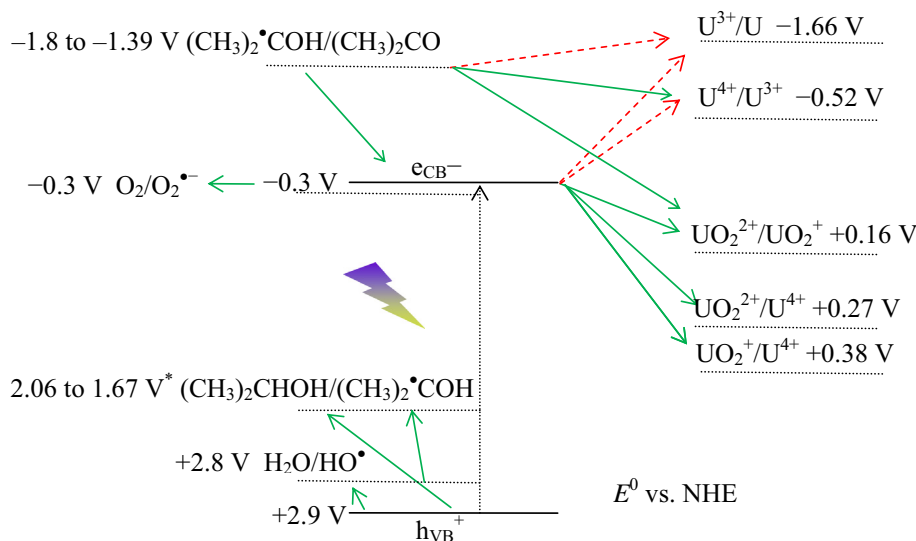
Once the organic radicals are formed (Eqs. (6) and (7)), they might reoxidize reduced uranium species ($E^0(CH_3^\bullet, H^+/CH_4) = 1.72$ V [47]; $E^0(\cdot CH_2CO_2H, H^+/CH_3CO_2H) = 1.8$ V [48], Eq. (8)), or react through non reducing steps like self-recombination or reaction between CH₃[•] and $\cdot CH_2CO_2H$, and other minor mechanisms without net U(VI) reduction [19].



Eq. (8) explains the arrest of the reaction after the rapid initial U(VI) decay, complemented by the formation of soluble U(IV)-acetate complexes, followed by reoxidation of U(IV) to U(VI) when the filtered sample enters in contact with oxygen [49].

As can be noted, U(VI) removal in QAN in the absence of TiO₂ is higher in comparison with the other conditions (Fig. 1(b)), and this can be explained as indicated in Ref. [19] for QA, where 16% uranyl removal was obtained. The lower removal here obtained can be explained just by the smaller initial acetate concentration present in QAN (0.5 vs. 42.0 mM).

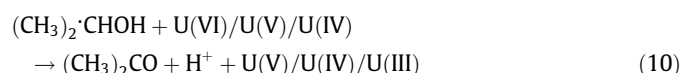
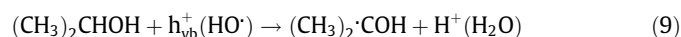
¹ All reduction potentials in this paper are standard values vs. NHE.



Scheme 1. Energy diagram of the uranyl reductive HP system at pH 0. Green (solid) lines: thermodynamically possible processes; red (dashed) lines: non-thermodynamically possible processes. Redox potentials from Refs. [37,38,56,57]; *calculated from Refs. [39] and [40]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.2. Heterogeneous photocatalysis of uranyl systems in the presence of 2-PrOH

As very well known, addition of electron donors such as 2-PrOH causes a synergetic effect in HP reactions, and this has been observed for all our conditions (cf. Figs. 1(a) and 2(a)). The alcohol scavenges $h_{\nu b}^+$ or $HO\cdot$ (Eq. (9)), hindering the short-circuit of Eq. (5) and decreasing recombination of electrons and holes. In addition, the resulting strong reducing $(CH_3)_2\cdot COH$ radical (E^0 ranges from -1.8 to -1.39 V [39]) could be able to reduce successively UO_2^{2+} to UO_2^+ [50,51], U(V) to U(IV) and even U(IV) to U(III) [51] (see Scheme 1).



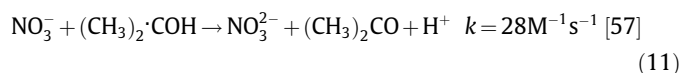
The effect of 2-PrOH in the increase of the photocatalytic efficiency is clearly reflected by the values of k , which are 10 times higher with 1 M 2-PrOH compared with the values in the absence of the alcohol (Table 2). An increase in the amount of U(VI) reduced (A) also takes place and, moreover, the alcohol promotes uranium removal due to the formation of precipitates over TiO_2 .

As can be appreciated from Fig. 2, U(VI) removal in the photocatalytic QP and GP systems with 1 M 2-PrOH is much higher than in the homogeneous media, what can be explained by the same reasons given for the systems in the absence of 2-PrOH. Table 1 shows that for QP in the absence of TiO_2 the residue is yellow, indicating the presence of a more oxidized uranium oxide [52], generally more soluble. In contrast, a dark gray solid was obtained for the same reaction in the presence of the photocatalyst, and this is an additional advantage of the photocatalytic systems over the photochemical ones because a stabilization of the deposits is promoted. At a higher 2-PrOH concentration (10 M, Fig. S1), the reaction rate (k) for the perchlorate systems improves; however, the value of A is almost independent of the 2-PrOH concentration (Table 2).

For the homogeneous system, the lower yields with the G photoreactor were explained in Ref. [19] by the less amount of photons arriving to the solution, the less energetic radiation transmitted by the glass and the lower U(VI) absorption. However, in the photocatalytic system, the difference between QP and GP systems is much smaller than in the absence of TiO_2 , as could be appreciated

when comparing Figs. 1(a) and 2(a) with Figs. 1(b) and 2(b), and the values of k (30% lower for GP, without and with 1 M 2-PrOH). In the presence of TiO_2 , the photocatalyst is the main light absorbing species, at least for $\lambda \leq 365$ nm [53] and, in contrast to the homogeneous system, the amount of light absorbed is independent of the degree of U(VI) conversion. On the other hand, the total U(VI) absorbance in the quartz system is much higher than that when using glass [19]; these two facts explain the higher increase in the removal rate of the photocatalytic G system. For 10 M 2-PrOH, the values of k are $\approx 50\%$ higher for QP compared with GP; this increase in the rate with the increasing light intensity at higher concentration of the reactant has been previously observed for phenol [54].

Regarding QN, this is the only system where the efficiencies in the presence and in the absence of TiO_2 are similar. In the homogeneous system [19], the higher rate and conversion for QN with 2-PrOH compared with the other studied conditions were explained by an important photochemical effect of NO_3^- , due to reduction by $(CH_3)_2\cdot COH$ (Eq. (11)), producing NO_3^{2-} species, which were able to reduce U(VI) up to U(III). However, almost no differences in the kinetic parameters were obtained in the photocatalytic systems for QN and QP (Table 2). This can be explained just considering that $(CH_3)_2\cdot COH$ reacts faster through electron injection to the CB (Eq. (12) [55], see Scheme 1) than with NO_3^- . Therefore, uranium attack by e_{CB}^- (Eq. (5)) is the main responsible for the reductive process and explains the similar efficiencies if either NO_3^- or ClO_4^- are present. The fact that U(VI)/U(V) reduction is mediated by conduction band electrons and not by reducing organic radicals is a distinctive feature of the system



The fact that U(V), stable at pH 3, could not be detected in the spectrum of the final solution, observed actually in the absence of TiO_2 (Fig. 3), could be attributed to a rapid photocatalytic reduction of U(V) to U(IV). On the other hand, as Reaction (12) is much faster than Reaction (10), this explains also why U(III) species were never observed in this work.

Turning now to the HP QAN system, the evolution of the reaction is initially similar to those of QP and QN (similar k values,

Table 2); however, the smaller A value can be related to the formation of soluble U(IV)-acetate species. In the homogeneous QAN system (Fig. 2(b)), the highest U(VI) removal ($\approx 90\%$) was found at 30 min, coincident with nitrate depletion (Section 3.2). Then, uranium redissolution by acetate and U^{4+} reoxidation by O_2 , as described for the system in the absence of 2-PrOH, takes place. In the HP system, redissolution does not take place, and partial precipitation could be observed (Table 1). Although Amadelli et al. [20] observed a higher reactivity for HP uranyl removal in the presence of acetate compared with 2-PrOH, this can be explained by the higher U(VI) adsorption over TiO_2 caused by acetate at the pH used by the authors. As indicated before, under our conditions, adsorption of U(VI) is negligible, ruling out a beneficial effect of acetate. The effect of different 2-PrOH concentrations (Fig. S2) in QAN is explained by the same reasons given for QP and GP. As the final removal is similar at all the 2-PrOH concentrations, the higher color intensity of the deposits with the highest alcohol concentrations is attributed here more to a predominance of reduced uranium forms than to a higher amount of oxides deposited over TiO_2 .

As expected and already observed by other authors [22,26], the photocatalytic reaction is inhibited in the presence of oxygen because U(IV) reoxidation is favored and also because oxygen competes with U(VI) for the e_{CB^-} .

5. Conclusions

Heterogeneous photocatalysis with TiO_2 and UV light under N_2 atmosphere is an efficient process to reduce uranyl concentration in water. In the absence of electron donors such as 2-PrOH, the efficiency is low, but high percentages of U(VI) removal were obtained with the alcohol. As expected, uranyl removal is lower (but still possible) in the presence of oxygen, due to the competition for the e_{CB^-} and/or to uranium reoxidation.

In contrast to that observed in the homogeneous photochemical system, similar and very good results were obtained when starting from nitrate and perchlorate salts in the presence of TiO_2 . Oppositely, acetate plays a negative role in U(VI) removal in both the photochemical and the photocatalytic reaction, rendering the lowest removal yields.

As similar results were obtained starting from perchlorate and nitrate, it is proposed that the main mechanism for uranium reduction (either in the absence or in the presence of 2-propanol) is e_{CB^-} attack, and that reducing radicals are not directly involved.

Heterogeneous photocatalysis presents advantages over the photochemical transformation. Higher removals are generally obtained, with the exception of the nitrate system in the presence of 2-PrOH where the removal extent was the same in the presence and in the absence of TiO_2 . In addition, Q or G photoreactors can be used with similar results, and this would allow the use of solar light. In the best cases, uranyl is photocatalytically reduced to U(IV), forming a dark gray precipitate, probably a mixture of UO_2 with U_3O_8 . Uranium oxides deposited on the TiO_2 surface can be easily removed from the system, offering a way of concentrating uranium from diluted solutions. Increasing the 2-PrOH concentration, darker gray deposits were obtained, attributed to the predominance of higher reduced uranium forms on the TiO_2 surface. As the more reduced uranium forms are less soluble, this is an additional advantage of the photocatalytic systems because it favors the stabilization of the deposits.

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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.cej.2014.06.001>.

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