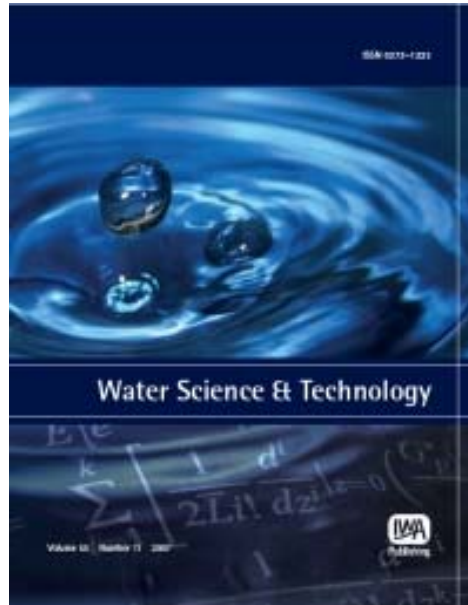


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Photocatalytic reduction of Cr(VI) in a fully illuminated fluidized bed reactor

R. L. Pozzo, L. O. Conte, J. L. Giombi and M. A. Baltanás

ABSTRACT

The potential of a fluidized bed reactor for the UV-A photocatalytic reduction of Cr(VI), a priority water pollutant, by utilizing a TiO₂/quartz sand composite, was explored. The effects of oxalic acid (OA) as a sacrificial agent in the heterogeneous system was also investigated and compared with the homogeneous photoreduction by the same dicarboxylic acid under both oxygenated or anoxic conditions of the reacting media. The performance of the 'preconditioned' photocatalyst, either by pretreating it with the OA solution (at dark or under UV-A illumination) or by letting the catalyst stand wet with the OA solution, during designated time intervals (1–5 weeks) prior to its reuse, was assessed. Then, up to 95% reduction of Cr(VI) to Cr(III) was achieved in less than 100 min.

Key words | chromium reduction, fluidized bed, oxalic acid, supported photocatalysts

R. L. Pozzo

L. O. Conte

J. L. Giombi

M. A. Baltanás (corresponding author)

INTEC (Instituto de Desarrollo Tecnológico para la

Industria Química – UNL/CONICET),

Güemes 3450,

S3000GLN Santa Fe,

Argentina

E-mail: tderliq@santafe-conicet.gov.ar

INTRODUCTION

The Cr(VI) ion is an inorganic pollutant present in natural waters and in many industrial effluents, such as those from leather tanning, or electrochemical processing of metals, among many others. It is highly toxic for the majority of living organisms, and a carcinogenic and mutagenic agent as well. The most commonly proposed approaches to eliminating this noxious waste from natural and/or man-modified waters are based on its reduction to Cr(III), a non-toxic and even essential substance in human nutrition. Cr(III) can then be easily removed as solid waste, by precipitation of chromium hydroxide. Current reduction methods usually employ chemical and/or biological agents (Shing *et al.* 2002; Baig *et al.* 2003; Cheung & Gu 2007; Yoon *et al.* 2011). These methods are, in general, quite expensive.

More recently, Cr(VI) reduction by photocatalysis has emerged as a promising alternative, with lower economic and environmental costs. In a comprehensive review published by Litter (1999) a thorough analysis of the state-of-the-art for this approach, applied to the transformation of dangerous transition metal ions into more harmless substances was done. With regard to the Cr(VI) ion, this report concluded that the reduction is quite slow if hole scavengers and/or hydroxyl radicals are absent, because the oxidation process of water is not kinetically favoured and, also, because the oxidation–reduction process becomes more feasible whenever some oxidizable organics are

present in the media. A similar conclusion was reported by Wang *et al.* (2008) in a study where a variety of thermally treated anatase, in combination with several organic compounds (mono- and dicarboxylic acids, and phenol), was investigated for the photocatalytic reduction of Cr(VI). At the time of the abovementioned review, the deleterious effect of oxygen as a competitor for the photogenerated electrons appeared as a controversial item. A few years later, upon studying the reduction of the Cr(VI) ion in the presence of oxalate, Testa *et al.* (2004) reported that oxalate had a synergistic effect on the photocatalytic reduction at pH 2, either in the presence or absence of oxygen, but no effect at all at pH 3.

During the last decade, our research work has been focused on the photocatalytic degradation of water pollutants by using granular titania-quartz sand composites in fluidized beds (FB). This approach represents a suitable alternative to the decontamination processes that resort to slurries of finely powdered photocatalysts, which in most cases require additional, and costly, downstream separation steps. Most of our previous efforts were aimed towards determining the optical parameters of the reacting media, to duly model the performance of a UV-A fully illuminated FB photocatalytic reactor from a chemical reaction engineering perspective. The degradation of organic substances, as model reactants, allowed a precise assessment of the

quantum efficiency of these FBs. In particular, oxalic acid (OA) was employed, in oxygenated solutions, given its relatively simple decomposition chemistry to CO₂ (Pozzo *et al.* 2005, 2006, 2010).

Hereinafter, the aptitude of the fully illuminated FB reactor to eliminate an inorganic pollutant such as Cr(VI) ion from contaminated water streams is analyzed and discussed. Oxalic acid, which is usually present together with Cr(VI) as an accompanying contaminant, was evaluated as a sacrificial agent (hole scavenger), using different aeration conditions of the reacting media. It was also of interest to assess the behavior of the photocatalyst upon previous exposure to OA and/or reuse in consecutive runs, as FB reactors are distinctly suited for this approach. In this regard, a recent study of Suwanchawalit & Wongnawa (2008) reported that the photocatalytic activity of titania improved after modifying it with oxalate during the sol-gel TiO₂ generation process, followed by calcination. They attributed this beneficial effect to an increment in the specific surface area of the 'modified' catalyst, as a result of the framework structure generated by the oxalate adsorption.

Therefore, we have also investigated whether these activating catalytic properties of OA would be also attained *via* the 'intimate' contact of OA with our TiO₂-coated quartz sand. This could be in addition, a further motivation in favour of employing OA as the sacrificial agent in the photocatalytic reduction of metal ions with titania, because (via the continuously replenished titanium oxalate) it would readily allow for photocatalyst reuse.

METHODS

Experimental set-up

A slender planar reactor/cell comprising a pair of optically clear 3.0 mm thick borosilicate glass walls attached to a hollow 316SS frame (7.0 mm optical gap) was employed. The cell was vertically divided into two compartments by a grid of Teflon[®], in such a way that a fluidized bed of 20 g of TiO₂-quartz sand catalyst composite was allowed to expand to seven times its unexpanded volume (final volume, 88 cm³; height, 21 cm) in the upper compartment, in each FB experiment. The catalytic composite was prepared by low-temperature CVD-plasma coating of Aldrich white quartz sand ($\rho_s = 2.4 \text{ g cm}^{-3}$; $D_p = 250 \mu\text{m}$) with a thin, compact nanofilm of TiO₂ (by using Ti *t*-butoxide as precursor). The film thickness, measured by TEM, was

about 30 nm. The TiO₂ loading was $\approx 1 \text{ mgTiO}_2/\text{g}$ composite, as determined by elemental analysis. Details about the preparation method and catalyst characterization are given by Karches *et al.* (2002).

A schematic representation of the reaction equipment is shown in Figure 1. The FB was stabilized by means of a constant hydrostatic pressure generation device that included a pair of recirculating loops and two reservoir tanks labeled tank 2 (80 cm³) and tank 3 (200 cm³) in Figure 1. Liquid flow rate was set at about $2.2 \text{ cm}^3 \text{ s}^{-1}$. Mechanical agitation ensured a uniform concentration of the solutes in the recirculating system. Additional information about the FB set up is included in Pozzo *et al.* (2005).

A pair of tubular black light lamps (Philips TLD 18W/08; superficial emission peak at 365 nm) was employed as the UV-A irradiation system. The lamps were disposed lengthwise, one at each side of the cell, concurrent with the focal axis of two parabolic reflectors made of a specularly finished aluminum sheet, to collimate the rays. In this way, both reactor windows were 'quasi uniformly' irradiated (Figure 1). Within the lamp radiation spectral span, the calculated specific scattering and absorption coefficients were practically constant; i.e.: the FB behaves practically as a grey body with respect to both parameters (Pozzo

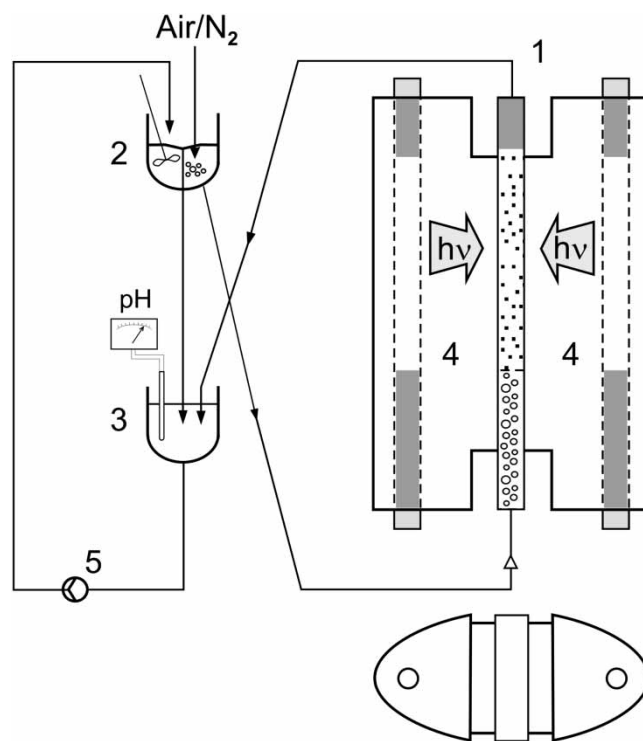


Figure 1 | Experimental set-up: (1) plane photoreactor; (2) and (3), reservoir tanks; (4) lamp-reflector illumination device; (5) peristaltic pump.

et al. 2005). The incident radiation power from the lamps to the reactor windows was determined *via* actinometry with potassium ferrioxalate. More details on the actinometric procedures, together with the radiation field profiles inside the FB of the titania–quartz composite can be found in a previous report (Pozzo *et al.* 2006).

Experimental procedures

Aliquots of 500 cm³ of a K₂Cr₂O₇ solution in ultra pure water [4×10^{-7} gmol K/cm⁻³; 20 mg/L of Cr(VI)], alone or in combination with an excess of OA: 20×10^{-7} gmol/cm⁻³ (180 mg/L), both reagents Carlo Erba RSE 99.9%, and different oxygenation conditions (by the continuous bubbling of either nitrogen or air into tank 2), were alternatively used in the experimental runs. The working pH of the solution was maintained between 1.95 and 2.05, by adding perchloric acid, 70 % v/v. A standard spectrophotometric technique (ASTM 1996) was used to monitor the dichromate degradation by measuring light absorbance at 540 nm, in a Cary 100 UV–vis–NIR spectrophotometer. The colorimetric determinations were performed in triplicate and averaged. Steady state temperature (22–24 °C) and lamp operation conditions were set prior to initiating any experimental run.

RESULTS AND DISCUSSION

A first series of degradation tests of the Cr(VI) model contaminant was conducted in the FB set-up, under UV irradiation, without or with photocatalyst into the photoreactor, the catalyst being ‘fresh’ (i.e. used for the first time) or reused once, in the absence or in presence of OA, and under either N₂ or O₂ bubbling, as summarized in the inset of Figure 2. A blank test, with photocatalyst and without irradiation, was also performed to determine the adsorption of dichromate onto the photocatalytic composite in the dark.

A few runs carried out right after the completion of the first stage of our degradation tests indicated that, by adding OA, and under anoxic conditions, the photoreduction rate of Cr(VI) could be increased whenever a batch of the reused photocatalyst was employed. This was in apparent contradiction with the deleterious impact of sacrificial agents on ‘catalyst recycling’ formerly reported by Papadama and coworkers (Papadama *et al.* 2007), albeit they had used an azo dye as reductant instead of oxalic acid. Hence, it was judged of utmost interest to address this issue.

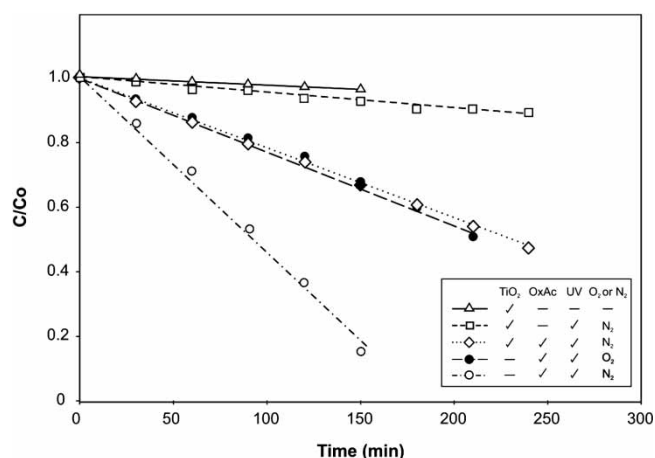


Figure 2 | Fractional chromium ion concentration, referred to the initial concentration value [20 mg/L Cr(VI)] vs. reaction time. Inset: experimental conditions.

Therefore, in order to elucidate whether the performance improvement observed with the reused photocatalyst was a consequence of the interaction of TiO₂ with the dichromate anion or due to some grade of ‘preconditioning’ – or etching – produced by the OA (thereby increasing the specific surface area of the catalyst), a new series of photoreduction tests was carried out by reusing the titania–quartz sand composite under different, deliberately preset conditions.

One type of assessment was carried out by photoreducing Cr(VI) with the catalyst already used (once) in experimental runs where oxalic acid was added neither in the first nor in the second use. In another kind of catalyst preconditioning test, the OA solution (180 mg/L) was recirculated through the FB, either at dark (no irradiation) or under UV-A irradiation for 360 min, before introducing the dichromate into the photoreactor.

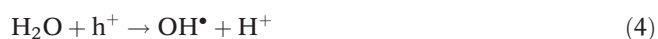
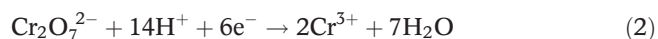
In addition, a set of Cr(VI) photoreduction tests were performed with the catalyst composite that had already been used once (i.e. it was ‘fresh’ in the first run), adding in both cases oxalic acid, according to the following routines: measured quantities (20 g) of the used catalyst composite were put in contact with the 180 mg/L solution of OA during six hours, and then, once drained, were allowed to stand wet in a closed vessel, at room temperature, during different periods of time: (a) 1 week, (b) 2 weeks, and (c) 5 weeks, respectively. All these catalyst reuse or preconditioning tests, were carried out under anoxic conditions; that is, under nitrogen bubbling.

Figure 2 shows the time evolution of the dichromate concentration in the reactor, for the different experimental conditions detailed in the inset. It readily follows from these results that only a negligible sorption of dichromate

took place onto the TiO₂-quartz composite under no irradiation, even though the working pH was below the point of zero charge of TiO₂, which would favor the adsorption of the dichromate ion. This may also be ascribed to a pair of concurrent facts: the relatively low working concentration of TiO₂ in the reacting system, ca. 40 mg/L, and the (expected) low specific surface areas of the compact film of photocatalytic coating in contact with the aqueous solution (Karches *et al.* 2002).

From the figure, the limited, poorer performance of the titania composite for the heterogeneous photoreduction of Cr(VI) in the absence of oxalic acid in anoxic media (N₂ bubbling) can be appreciated, as compared to that under the same aeration conditions but with the dicarboxylic acid present. A similar activating effect by either OA or other sacrificial organic compounds was reported by former research teams (Testa *et al.* 2004; Mytych *et al.* 2005; Wang *et al.* 2008).

According to Wang *et al.* (2008), the photoreduction of Cr(VI) to Cr(III) can be achieved via a photocatalytic pathway that can be succinctly written as follows:



When no hole scavengers are present, the hole–electron pairs generated by UV light illumination on the surface of TiO₂ [reaction (1)] can reduce Cr(VI) to Cr(III) [the electrons, by reaction (2)] and oxidize water [the holes, by reaction (3)] producing oxygen, in a kinetically slow four-electron process (Testa *et al.* 2001). Alternatively, the presence of an organic sacrificial agent such as oxalic acid accelerates the process, by helping to suppress the hole–electron recombination.

It can also be observed in Figure 2 that the homogeneous photoreduction of Cr(VI) (i.e. only in presence of dissolved OA with no photocatalyst added), occurs either under oxygenated or anoxic conditions, with a better

performance in the second environment. A similar behavior and a plausible, comprehensive mechanism for the homogeneous photoreduction of Cr(VI) was reported by Mytych *et al.* (2005). According to these researchers, the presence of oxygen would facilitate the reoxidation of Cr(III) to Cr(VI), thus decreasing the net (observable) reduction.

Noteworthy, and against all prospects, the homogeneous photoreduction of Cr(VI) in the anoxic environment was substantially more efficient than the photocatalyzed process. In the second case, both types of reactions (i.e. homogeneous and heterogeneous) were present in the FB reactor. However, extinction of radiation due to light scattering *and* absorption by the catalyst composite reduces significantly the available intensity of radiation at every point of the reacting space and, thus, the performance of the homogeneous photoreduction. Certainly, notwithstanding the fact that our fluidized bed reactor operates as a fully illuminated one (Pozzo *et al.* 2006), the contribution of the heterogeneous photoreaction using the fresh composite could not offset, nor compensate, the attenuated irradiance that was available in the FB, as compared to that in the fully liquid-filled reaction space in the homogeneous photoreduction situation.

Under oxygenated conditions, but in the absence of OA, photocatalyst performance did not show any difference with that conducted under the anoxic environment, as was also observed by Testa *et al.* using a slurry of particulate titania (Testa *et al.* 2004).

Zero order reaction with respect to the Cr(VI) concentration was found for both heterogeneous and homogeneous photoreductions either under oxygenated or anoxic conditions. Thus, given the relative molar concentrations of the model reactants used (i.e. using a significant molar excess of OA) and the hydrodynamic properties of the FB, which make kinetic control by mass transfer highly unlikely, it can be safely assumed that the photoreaction kinetics was always governed by the local volumetric rate of the system's photon absorption (LVRPA).

Effect of catalyst reuse or preconditioning

Figure 3 depicts revealing results about the impact of photocatalyst pretreatments with OA, as well as of catalyst reuse (i.e. after it was used at least once) on catalyst performance under nitrogen bubbling and UV-A illumination. In a preliminary test it was established that reusing the photocatalyst with no OA added to the aqueous solution, did not make any difference to the (poor) performance of the TiO₂-quartz composite. Therefore, any possible impact

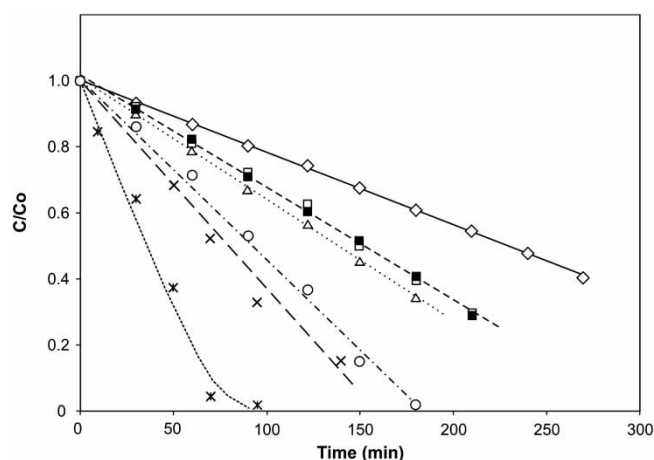


Figure 3 | Impact of photocatalyst pretreatment with OA, or photocatalyst reuse, on Cr(VI) photoreduction (under UV-A illumination and N₂ bubbling): \diamond — 1st time used; \square — Pretreated with oxalic acid (360 min), in the dark; \blacksquare — Pretreated with oxalic acid (360 min), under UV-A illumination; \triangle — Reused, after 1 week of waiting time, wet, together with the (drained) OA solution, at room temperature; \times — Reused, after standing by for 2 weeks, as detailed before; $*$ — Reused, after standing by for 5 weeks, as detailed before; \circ — Homogeneous photoreduction.

on the performance of the reused photocatalyst due solely to preadsorbed dichromate (i.e. from the first run) could be ruled out. However, when the photocatalyst was used for the first time after having being put in contact with oxalic acid for six hours, either with or without UV-A irradiation, it showed in either case a better (and similar between them) performance in the photoreduction of Cr(VI) than the first time used, but ‘non-preconditioned’ catalyst (runs with squares vs. rhombus in Figure 3, respectively).

This improving effect of OA further emerged when the catalyst composite was put on hold in a closed vessel at room temperature, still wet with the (drained) oxalic acid solution, for 1, 2 or 5 weeks, in such a way that the longer the contact time had been, the better the beneficial effect on the degradation of Cr(VI) during the second use of the photocatalyst was observed. Moreover, after 2 or 5 weeks of stand-by time, the photocatalyst handled this way rendered a much better degradation of the dichromate than the homogeneous system (i.e. when only OA had been added), thus proving the photocatalytic enhancement of the process.

These results agree with a recent study of Suwanchawalit & Wongnawa (2008), who used TiO₂ powders prepared by the sol-gel method. These authors reported that the photocatalytic activity of titania for decolorizing methylene blue solutions improved by doping the material with oxalate during the catalyst preparation process itself, followed by partial calcination of the solid. We believe that it is highly

likely that a similar, slow growth, of a superficial titanium oxalate ‘adlayer’ was brought about by both the preconditioning treatment and/or the soaking of the photocatalyst with the oxalic acid solution at room temperature, during the elapsed (stand by) time between the first use and the second-use runs of the composite. In this regard, Mendive *et al.* (2007) demonstrated, by ATR-FTIR techniques, that OA readily adsorbs on the anatase surface, following a dynamically evolving process characterized by the formation of at least two different chemisorbed, coexistent complexes: a more stable bidentate structure (named species A) and a more labile one (named species B), with their sigma carbon-carbon bond either parallel or perpendicular to the TiO₂ surface, respectively. Furthermore, they were also able to show that, for longer time windows than those usually employed for adsorption experimental studies on metal oxide surfaces (that is, days instead of minutes or hours), the adsorption equilibria were modified in such a way that the surface coverage of TiO₂ by species B declined with time, whereas the area occupied by species A, as well as the total overall adsorption, increased instead. These effects were observed either when the TiO₂/OA system was allowed to evolve for a relatively long period of time (at least 80 h) in the dark, or for shorter times under UV illumination, but in both cases to the same extent. They attributed these effects to several possible – perhaps concurrent – causes, such as: replacement of surface impurities, exchange of adsorbed water molecules by oxalic acid, increment of surface hydroxylation and augmentation of the catalyst surface area due to desegregation of particle agglomerates. All of them point to an important modification of the catalyst surface which could lead to the positive impact on the photocatalytic activity hereby reported.

We conducted additional AFM tests (available upon request), using an (110) anatase monocrystal immersed in 180 mg/L OA for 6 h, 1, 2 and 4 weeks at room temperature, which showed the absence of titania etching in every case. This strongly suggests that the observed improvement in the photocatalytic performance toward Cr(VI) reduction can plausibly be attributed to surface changes at a local (molecular?) level.

CONCLUSION

The reduction of Cr(VI) in a dilute aqueous solution using a fully-illuminated reactor with a FB of TiO₂/quartz sand composite as photocatalyst, was much more efficient in the presence than in the absence of OA. Under anoxic

conditions, a better performance of the homogeneous photoreduction of Cr(VI) by OA, as compared with the heterogeneous photoreduction upon using the fresh, 'non-conditioned', catalyst composite was also observed. However, when oxygen was present in the solution, the homogeneous reaction rate was notoriously diminished, thus indicating that oxygen was competing with Cr(VI) in oxidizing the (sacrificial) OA. This is in line with previous work reported in the literature.

The catalyst exposure to OA, either by preconditioning it with an aqueous solution of the dicarboxylic acid or by reusing the aged, OA-wetted, composite employed in a previous batch after 2 to 5 weeks, significantly enhanced the photocatalytic process. This improving effect, which increased with the waiting time, is attributed to the activation of the catalyst surface due to structural modifications – at a local level – generated by a strong interaction of the oxalate ion with the titania.

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