Conference paper

Marta I. Litter*

Mechanisms of removal of heavy metals and arsenic from water by TiO$_2$-heterogeneous photocatalysis

Abstract: This article is an overview of recent work performed in our laboratory on TiO$_2$ heterogeneous photocatalysis of aqueous systems containing toxic forms of chromium, arsenic, lead, uranium and mercury. The cases of chromium and arsenic are treated in profundity. Photocatalytic treatments can convert the ionic species into their metallic solid form and deposit them over the semiconductor surface, or transform them into less toxic soluble species. When a transformation to the zerovalent state is possible, this allows the recovery of the metal from the waters, with an important economical return. Three types of mechanisms can be considered, all of them taking place through successive thermodynamically allowed monoelectronic electron transfer steps: (a) direct reduction by photogenerated electrons; (b) indirect reduction by intermediates generated by hole or hydroxyl radical oxidation of electron donors (reducing radicals); (c) oxidative removal by holes or hydroxyl radicals. Fundamentals of oxidative or reductive heterogeneous photocatalysis are described, with special emphasis on the role of organic donors present in the medium acting as synergists. This indicates the possibility of simultaneous treatment of pollutants of different chemical structure and properties present in the same medium.

Keywords: arsenic; chromium; heavy metals; metalloids; photocatalysis; XXV photochemistry.

Introduction

Metal are ubiquitous on the earth, present in soils and natural waters. Many tons of these chemical species originate yearly from anthropic activities such as hydrometallurgy, metallization of surfaces, photography or come in effluent treatments (washing, rinsing, surface treatments). It has been estimated that the toxicity of all the metals being released annually into the environment far exceeds the combined total toxicity of all the radioactive and organic wastes [1]. The presence of metals or metalloids (chromium, mercury, lead, copper, nickel, cadmium or arsenic) in water can produce dramatic effects on health, very significant economic losses, and perturbation of ecological and geological equilibrium because they are not easily transformed and have generally infinite lifetimes.

Conventional methods for water treatment such as biological methods, ozonation, activated carbon, etc. are not completely suitable to reduce the concentration of metal and metalloids in water to levels within the

*Corresponding author: Marta I. Litter, Gerencia Química, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, 1650 San Martín, Prov. de Buenos Aires, Argentina; Instituto de Investigación e Ingeniería Ambiental, Universidad de General San Martín, Campus Miguelete, Av. 25 de Mayo y Martín de Irigoyen, 1650 San Martín, Prov. de Buenos Aires, Argentina; and Consejo Nacional de Investigaciones Científicas y Técnicas, Av. Rivadavia 1917, 1033, Buenos Aires, Argentina, e-mail: marta.litter@gmail.com

regulations. A relatively new alternative for the treatment of these chemical species are advanced oxidative or reductive processes (AOPs/ARPs). One of the most extensively investigated AOPs/ARPs is heterogeneous photocatalysis (HP), where a broadband semiconductor (SC) is irradiated by UV or visible light leading to oxidation-reduction reactions and to the transformation of pollutants present in aqueous or gaseous systems. HP can lead to the eventual mineralization of organic contaminants and to the transformation of metallic ions and metalloids to less toxic species or species easier to be separated from the system in a subsequent treatment step [2–5].

This article reflects the latest results of our laboratory on the photocatalytic treatment of metal and metalloids, with emphasis on hexavalent chromium and arsenic, known for their high toxicity and environmental damage. Previous reviews have been published treating the state of art on this subject, and the reader can consult them for earlier references [6–9].

Basic principles of heterogeneous photocatalysis

In HP, the SC is excited in a primary process by absorption of photons of energy equal or higher than the SC bandgap (E_g), leading to the promotion of an electron from the valence band (VB) to the conduction band (CB), with creation of a hole:

$$SC + h\nu \rightarrow e_{CB}^{-} + h_{VB}^{+} \tag{1}$$

The electron-hole recombination is a unproductive process, detrimental for the photocatalytic efficiency, that should be avoided. In the absence of electron transfer processes, electrons and holes recombine in <100 ns in a TiO_2 nanoparticle (size: ca. 10 nm) [2, 4]. The productive processes are electron transfer reactions between electrons or holes and organic or inorganic species adsorbed on the SC surface or close to it. Electron acceptors (A) can be reduced by e_{CB}^{-}, and donor species (D) can give electrons to holes, being oxidized. The probability of these transfer processes depend on the relative redox positions of the CB and VB in the SC in relation with the redox potential of the species to be transformed and of the rate of competitive processes. HP carried out under normal illumination (e.g., black light or xenon lamps) leads to redox processes that take place through monoelectronic step reactions (due to the low frequency of photon absorption).

$$A + e_{CB}^{-} \rightarrow A^{\bullet -} \tag{2}$$

$$h_{VB}^{+} + D_{ads} \rightarrow D_{ads}^{\bullet +} \tag{3}$$

TiO_2 is so far the most useful semiconductor material for photocatalytic purposes because of its exceptional optical and electronic properties, chemical stability, non-toxicity, and low cost. The energy bandgaps of the most used photocatalytic forms of TiO_2, anatase and rutile, are 3.23 eV and 3.02 eV, corresponding to 384 and 411 nm, respectively [10]. The most popular commercial TiO_2 material for HP was originally produced by the German company Degussa (now Evonik) with the denomination P-25. Some other commercial products, such as Hombikat UV100, and different products of Cristal Global (PC50, PC100, PC500), Fluka, etc. have been tested in several photocatalytic systems [11, 12]. Although the data are divergent in the literature, the redox levels of h_{VB}^{+} and e_{CB}^{-} photogenerated by HP in P-25 taken in this article will be +2.9 and −0.3 V,[1] respectively [13].

In addition to the direct attack of D species adsorbed on or close to TiO_2, holes can attack also adsorbed water molecules/surface hydroxyl groups, generating $HO^{\bullet}$. These radicals are very oxidizing species with a reduction potential of +2.8 V [3]:

$$h_{VB}^{+} + HO_{surf}^{-} \rightarrow HO^{\bullet} \tag{4a}$$

$$h_{VB}^{+} + H_2O_{ads} \rightarrow HO^{\bullet} + H^{+} \tag{4b}$$

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1 All reduction potentials in this work are standard values vs. SHE; therefore, the values correspond to pH 0.

HP oxidative reactions are usually performed in the presence of molecular oxygen, with the objective of enhancing the mineralization of organic compounds; e_{CB}^- reduce O_2 with formation of hydroperoxyl or superoxide radicals ($HO_2^{\bullet}/O_2^{\bullet-}$), in a rather slow but thermodynamically feasible electron transfer reaction, decreasing the probability of electron-hole recombination [2].

$$O_2 + e_{CB}^- \rightarrow O_2^{\bullet-} \tag{5a}$$

$$O_2 + e_{CB}^- + H^+ \rightarrow HO_2^{\bullet} \tag{5b}$$

The value for the reduction potential for the hydroperoxyl/superoxide radical has been reported as $E^0(O_2/HO_2^{\bullet}) = -0.05$ V [14]; the reduction potentials onto the TiO_2 surface are probably less negative. As the following set of equations indicates, this cathodic pathway is an additional source of hydroxyl radicals:

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{6}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow HO^{\bullet} + HO^- + O_2 \tag{7}$$

$$H_2O_2 + e_{CB}^- \rightarrow HO^{\bullet} + HO^- \tag{8}$$

When a metal ion is present in a HP aqueous system solution, it can undergo reduction or oxidation reactions. Figure 1 shows the reduction potential of different couples together with the energy levels for the e_{CB}^- and the h_{VB}^+; the comparison of the redox levels leads to a first approximation of the thermodynamic feasibility of transformation of the species. All couples with redox potentials more positive than the e_{CB}^- level can be directly reduced and all couples with redox potentials less positive than the h_{VB}^+ level can be, in theory, oxidized.
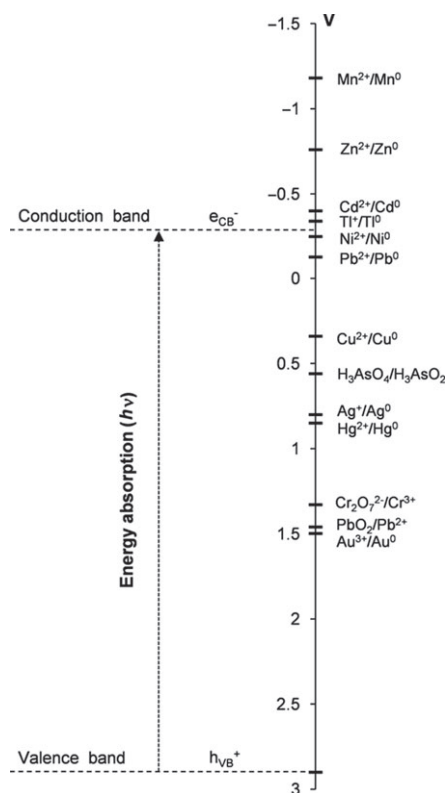
Fig. 1 Position of the reduction potentials of various metallic couples related to the energy levels of the CB and VA of P-25 adapted from reference [8].

Figure 1 shows global (multielectronic) reactions, and these can be favorable (exergonic) in principle. However, if one-electron steps are considered, only those thermodynamically allowed reactions would occur. Accordingly, the ion could be reduced by e_{CB}^- in a **direct reduction** step, a reaction that requires the e_{CB}^- reduction potential to be more negative than the corresponding to the $M^{n+}/M^{(n-1)+}$ pair:

$$M^{n+} + e_{CB}^- \rightarrow M^{(n-1)+} \tag{9}$$

Alternatively, oxidation of the metal ion can occur by reaction with holes or HO·, reaching a higher oxidation state:

$$M^{n+} \xrightarrow{h_{VB}^+/HO^\bullet} M^{n+1} \tag{10}$$

Some metallic species (such as Cr(VI), Hg(II) or U(VI)) cannot be transformed to a higher oxidation state, but they can be directly reduced by e_{CB}^- [8]. This process can be accelerated and even produced in thermodynamically unfeasible conditions, i.e., when the redox potential of the couple to be reduced is more negative than the level of e_{CB}^-, by the addition of sacrificial donors to the solution. This donor mediated reduction of the metal or metalloid constitutes an **indirect reduction** process. The donors can be separated in two different groups: direct h_{VB}^+ acceptors (as in eq. (3)), e.g., EDTA, citric acid, salicylic acid, or indirect acceptors via HO· reaction, such as methanol, acetic acid or formaldehyde [e.g., eq. (11) for an alcohol].

$$RCH_2OH + HO^\bullet \rightarrow {}^\bullet RCHOH + H_2O \tag{11}$$

$$M^{n+} + {}^\bullet RCHOH \rightarrow M^{(n-1)+} + RCHO \tag{12}$$

The reaction with h_{VB}^+ or HO· reduces the electron-hole recombination probability and generates very strong reducing radicals which allow formation of reducing species that are not likely to be reduced directly by e_{CB}^-. A synergetic effect exists generally between oxidative and reductive processes, especially in the presence of organic compounds that can undergo oxidation [3, 6, 7].

Photocatalytic based treatments can take advantage of these transformations in order to obtain a metallic solid form deposited on the photocatalyst surface; in this way, the species is removed from the solution. This procedure could also be applied for metal recovery (copper, platinum, silver, gold). Another possibility is the formation of a less toxic soluble species [Cr(VI) to Cr(III), As(III) to As(V)], which are also easier to be removed by a ulterior treatment.

Chromium

Chromium is a metal with multiple industrial and technological applications including metallurgy, electroplating, textile industry, leather tanning and wood preservation. As a consequence of its uses, Cr is frequently found in wastewaters, mainly in the Cr(III) and Cr(VI) forms. Cr(VI) presents the highest environmental threat due to its toxicity for biological organisms together with its high solubility and mobility. The World Health Organization (WHO) [15] has established the maximum contaminant level of Cr(VI) in drinking water to be 0.05 mg L^{-1}. Cr(III) is considered non toxic or of very low toxicity [16], and its mobility is lower than that of Cr(VI). The conventional treatment for removal of Cr(VI) dissolved in water involves its reduction to Cr(III) with the use of sodium thiosulfate, ferrous sulfate, sodium metabisulfite, sulfur dioxide or other chemicals, with the subsequent economical costs and generation of residues.

Figure 2 shows the redox potentials for chromium in acid conditions taken from reference [17].

Cr(VI) reduction is enhanced in acid solutions, and the net reaction can be written as:
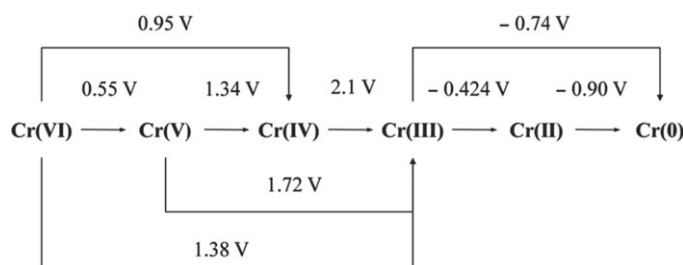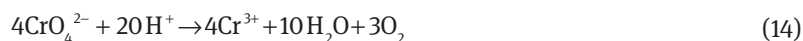
$$2Cr_2O_7^{2-} + 16H^+ \rightarrow 4Cr^{3+} + 8H_2O + 3O_2 \qquad \Delta G_{298}^0 = -115.8\,kJ \tag{13}$$

Fig. 2 Latimer diagram connecting the different Cr species [17].

At neutral pH:
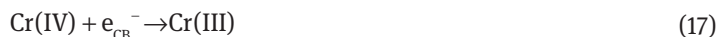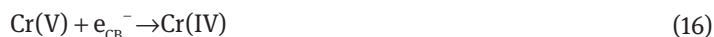
$$4CrO_4^{2-} + 20H^+ \rightarrow 4Cr^{3+} + 10H_2O + 3O_2 \tag{14}$$

Although the process is thermodynamically feasible, $Cr_2O_7^{2-}$ is stable at room temperature in acidic solutions due to the high overpotential of the conjugate reaction of water oxidation. Therefore, strategies for improving the reduction reaction should be implemented.

Numerous works have been published on the photocatalytic reduction of Cr(VI) employing TiO_2, Fe/TiO_2, Pt/TiO_2, and other SCs such as ZnO, CdS, ZnS and WO_3 and many examples have already been described in our previous reviews [6–9] including reactors for technological applications, microparticles used in slurries or conveniently supported, nanoparticles and nanotubes. The major conclusions that emerge from the past publications can be summarized in the following points:

- Cr(VI) HP reduction depends upon pH. Low pH favors the net reaction [eq. (13)]; however, neutral or alkaline conditions favors precipitation and immobilization of Cr(III) as the oxides or hydroxides, facilitating a further separation;
- Cr(VI) reduction can be accelerated by addition of organic compounds acting as hole or HO· scavengers;
- molecular oxygen does not affect Cr(VI) HP reduction, at least at acid pH, as will be explained in detail later.

From a thermodynamic point of view, e_{CB}^- have the appropriate potential to directly reduce Cr(VI), Cr(V) and Cr(IV) (see Figs 1 and 2), and the HP mechanism of Cr(VI) reduction to Cr(III) is proposed to occur through three monoelectronic steps [18–20]:

$$Cr(VI) + e_{CB}^- \rightarrow Cr(V) \tag{15}$$

$$Cr(V) + e_{CB}^- \rightarrow Cr(IV) \tag{16}$$

$$Cr(IV) + e_{CB}^- \rightarrow Cr(III) \tag{17}$$

This was proven by our group through electron paramagnetic resonance spectroscopic studies (EPR), which allowed the identification of paramagnetic Cr(V) species [18–20].

Detrimental reoxidation of reduced Cr species by holes or hydroxyl radicals is however possible:

$$Cr(V/IV/III) \xrightarrow{h_{VB}^+/HO^\bullet} Cr(VI/V/IV) \tag{18}$$

An enhancement of the reaction takes place if convenient electron donors are present, either by reducing the probability of recombination or through the indirect reduction driven by radicals formed by hole/HO· attack [eqs. (3) and (11)], which, at high concentrations, hinder reaction and contribute to the reduction of chromium species.

The role of O_2 in photocatalytic Cr(VI) systems is noteworthy due to its unique behavior compared with other metal cations, because it appears to be independent of the presence of O_2, at least at acid pH. This process was explained by a very strong association between Cr(VI) and TiO_2 through the formation of a charge-transfer

complex, identified by an absorption band at 380 nm [21]. Due to the fast capture of electrons by Cr(VI) as a result of the formation of this complex, no competition of O_2 by e_{CB}^- [eq. (5)] takes place, and consequently, no inhibition by O_2 was observed neither in the absence of organic donors nor in the presence of EDTA, oxalic or citric acid [18–20, 22, 23]. Experiments on platinized photocatalysts supported this independency, the same temporal evolution of Cr(VI) concentration being obtained using Pt/TiO$_2$ or bare TiO$_2$ either in the presence or in the absence of O_2 [21–23]. As Pt decreases the overpotential for electron transfer from the CB to O_2, the presence of O_2 when using Pt/TiO$_2$ should have affected the Cr(VI) decay in two opposite ways: a) either enhancing the reaction rate, with $O_2^{\cdot-}$ being a mediator for Cr(VI) reduction or b) decreasing the rate by competition with e_{CB}^-.

Cr(VI) photocatalytic reduction continues to be a very rich and interesting study system, and extensive work has been done in the latest years, either with the aim of water treatment or as a practical system for the evaluation of the photocatalytic activity of several semiconductor samples in aqueous phase. For example, the behavior of different commercial photocatalysts in the Cr(VI) heterogeneous photocatalytic system in the presence of EDTA was analyzed, in particular, the influence of the type of photocatalyst on the yield, the progressive inactivation of the photocatalyst during the reduction and the effect of adsorbed species. In this work, studies by TRMC (time resolved microwave conductivity) were performed, being the first time that these studies have been applied to a HP reaction of a metal system [24]. The decrease of the TRMC signal of the electrons in the presence of Cr(VI) reinforced the theory that the Cr(VI) reduction proceeds through the e_{BC}^- of TiO$_2$. A further work using P-25 [25] indicates that TiO$_2$ is inactivated after the photocatalysis of Cr(VI) in the absence of EDTA due to deposition of Cr(III) species on the photocatalyst surface, but the organic compound preserves the activity of the photocatalyst forming soluble Cr(III) complexes; these results were also confirmed by TRMC. Another paper of our group evaluated the activity of anatase TiO$_2$ films deposited by cathodic arc (CA) films on glass substrates for Cr(VI) reduction in the presence of EDTA and compared the new films with P-25 films obtained by dip-coating immersion (DC films). Despite of DC films showing higher photoactivity, its adhesion properties were very poor in contrast with CA films, making the latter more promising materials for photocatalytic applications that require immobilized catalysts [26].

Photocatalytic Cr(VI) reduction is also possible under visible irradiation and, in our previous review [9], several examples were described. Dye photosensitized TiO$_2$ samples were proved to be able to reduce Cr(VI) under visible light. For example, Di Iorio et al. [21] studied alizarin red chelated to TiO$_2$, and the results indicate a high efficiency for Cr(VI) reduction, almost independent of the photon flux and of the irradiation wavelength, and slightly dependent on the Cr(VI) concentration in the explored range (40–200 μM), with similar results in air or nitrogen atmosphere. EPR experiments confirmed Cr(V) formation, pointing out to three one-electron consecutive steps for Cr(VI) reduction. Another work [27] using TiO$_2$ coated with hydroxoaluminiumtricarboxymonoamide phthalocyanine (AlTCPc) irradiated under visible-light in the presence of 4-chlorophenol (4-CP) as sacrificial donor showed a very rapid Cr(VI) reduction to Cr(III). In the presence of dyes, the photocatalytic mechanism is different from that taking place under UV light, according to the scheme shown in Fig. 3; after excitation of the dye, electron injection into the CB promotes Cr(VI) reduction:
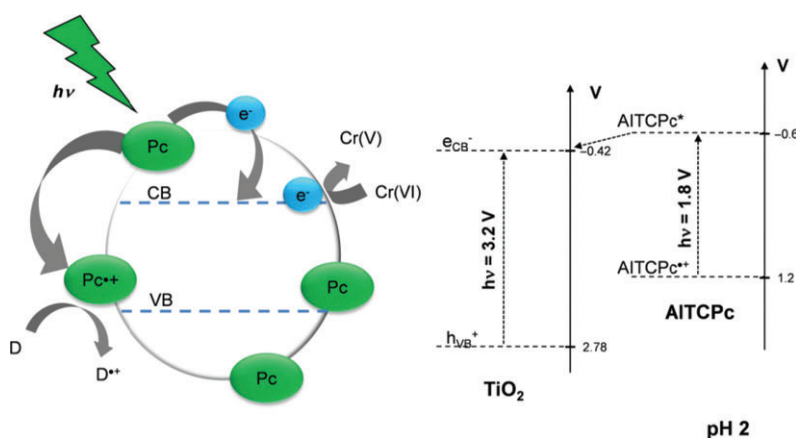

Fig. 3 Visible light HP Cr(VI) reduction with TiO$_2$ modified with AlTCPc at pH 2 (from reference [9], with permission).

A very good protecting effect of 4-CP preventing AlTCPc photobleaching was observed, as reactive oxygen species (ROS, e.g., $O_2^{\cdot-}$, $HO_2^{\cdot}$), which could oxidize the dye, cannot be formed due to the fast reaction of e_{CB}^- with Cr(VI). Further studies on photocurrent and absorption spectra of AlTCPc/TiO$_2$ films, and of absorption and fluorescence of the dye in solution in function of the dye concentration demonstrated that the photoactive species is the monomeric dye electronically coupled to TiO$_2$ [28].

The scientific community have been successful in the generation of knowledge about fundamental mechanisms, mechanistic pathways, role of O_2 and electron donors, etc., related with the very rich reductive photocatalytic Cr(VI) system. More studies and efforts should be made to transfer the knowledge on this promising technology into practical applications.

Arsenic

Arsenic contamination in water can be anthropogenic (mining, use of biocides, wood preservers), but it mainly comes from natural sources due to dissolution of minerals in surface or groundwaters, or to volcanic processes [29, 30]. Chronic ingestion of arsenic for prolonged periods of time results in arsenicosis, a hydric disease, which causes severe skin lesions including pigmentation changes, palmoplantar keratosis and other syndromes, ending generally in cancer. Arsenic in drinking water constitutes a serious problem, affecting several million people all over the world. The World Health Organization (WHO) [31] recommends 10 µg L^{-1} as the maximum allowable As concentration in drinking water, a value which is taken by most national regulatory agencies.

Conventional water treatments used to remove As are oxidation/coagulation/adsorption processes on iron or aluminum hydroxides, ionic interchange, activated alumina, lime softening, and reverse electrodialysis and osmosis. Transformation to As(V) makes easier the application of conventional technologies, e.g. ion exchange and adsorption. However, new emerging techniques have to be investigated to offer low-cost solutions to the arsenic problem, especially for low-income populations, as mentioned in some references [29].

Photocatalysis of arsenical systems was most studied for the oxidative system, and mechanisms for As(III) oxidation were reported in studies that spanned concentrations from the micro- to the millimolar range, showing in every case very fast oxidation in 10 – 100 min. Our previous reviews describe the latest advances [8, 9]. On the other hand, multielectronic reduction of As(V) to As(III) or As(0) is thermodynamically favored even with mild reductants, as can be inferred from the Latimer diagram (Fig. 4). Further reduction to arsine [As(−3)] is more difficult. All the reductive steps are less favored at higher pH values.

Oxidative TiO$_2$ HP has been shown as a good alternative for As(III) oxidation. In an effort to explain the mechanism of oxidation, monoelectronic steps with formation of As(IV) that could involve either the reaction with HO$\cdot$ [eq. (19)], with VB holes [eq. (20)], or with $O_2^{\cdot-}$ [eq. (21)] have been suggested:

$$As(III) + HO_{ads}^{\cdot}(HO_{free}^{\cdot}) \rightarrow As(IV) + OH^- \tag{19}$$

$$As(III) + h_{VB}^+ \rightarrow As(IV) \tag{20}$$

$$As(III) + HO_2^{\cdot}/O_2^{\cdot-} \rightarrow As(IV) + HO_2^-/O_2 \tag{21}$$
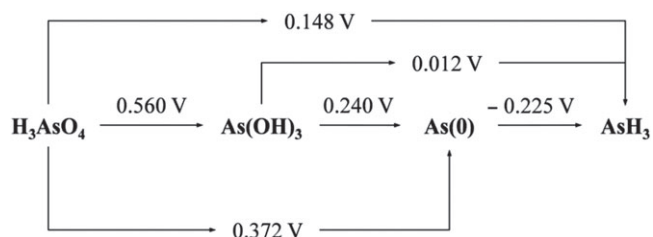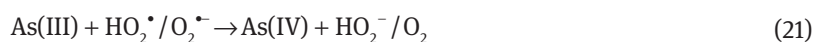

Fig. 4 Latimer diagram connecting the different As species [32].

The reduction potential of the As(IV)/As(III) couple has been reported to be $E^0 \approx +2.4$ V [33]. Therefore, formation of As(IV) by attack of holes, $HO^\bullet$ or $HO_2^{\bullet}/O_2^\bullet$ is thermodynamically possible. Regardless of the first oxidation step, As(IV) goes further to As(V), the stable form:

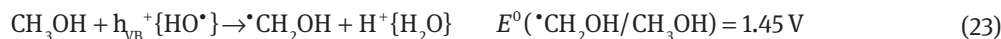$$As(IV) \xrightarrow{O_2/O_2^{\bullet-}/h_{VB}^+/HO^\bullet} As(V) \tag{22}$$

The mechanism of photocatalytic oxidation of As(III) has been a matter of discussion for many years, the controversy being centered on determining the major oxidant in the system, either $O_2^{\bullet-}$ $HO^\bullet$ or h_{VB}^+. However, whatever the oxidant is, it is not possible to deny the efficiency of the HP process to transform As(III) into As(V). The real problem is, however, how to remove later dissolved As(V).

Regarding low-cost applications, several works of our laboratory [29, 34–36] report results of an application to remove arsenic from natural waters of rural areas; to perform HP experiments, walls of PET plastic bottles were impregnated with TiO_2 by a very simple technique [37]. As(III) solutions ($[As(III)]_0 = 1000$ µg L^{-1}, pH 7.8) were placed in these bottles, which were put in a horizontal position and irradiated during 6 h by UV light (366 nm, 800 µW cm^{-2}). After irradiation, non-galvanized packing iron wire pieces (usually employed in agricultural applications) were added. After 24 h settlement in the dark, As removals ranging 80–86 % were obtained. The same bottle could be reused at least three times without loss of efficiency. The HP procedure was proposed to remove As (500–1800 µg L^{-1}, unidentified speciation) from well water samples of Las Hermanas (Santiago del Estero Province, Argentina). In this case, a $FeCl_3$ solution was added at the end of an experiment under solar irradiation, and more than 94 % As removal took place, attaining concentrations below the WHO limits.

The HP oxidation of As(III) in the presence of Hg(II) in equimolar concentration was studied by our group at pH 7. The results indicated that, in the absence of TiO_2, some oxidation of As(III) in air takes place in the dark, without changes by addition of TiO_2. Under UV irradiation in anoxic conditions in the presence of the photocatalyst, the conversion was much higher, with formation of a gray solid (Hg(0) + Hg_2Cl_2) while in the presence of O_2, HP oxidation was produced in a similar way in the presence or in the absence of Hg(II), indicating a competence between O_2 and Hg(II) [38].

In contrast, reductive photocatalytic systems for arsenic transformation are still scarce. Reduction of As(III) by TiO_2 e_{CB}^- is thermodynamically possible either in the presence or the absence of an electron donor in the aqueous system. However, in the case of As(V), the direct reduction seems to be not feasible because the reported reduction potential of the As(V)/As(IV) couple is highly negative ($E^0 \approx -1.2$ V [33]) and thus, the indirect pathway by using sacrificial electron donors is indispensable in this case. Our group [39, 40] studied the reaction starting from As(V) and also from As(III) in the presence of methanol; the As(III) reaction in the absence of the organic compound was also analyzed. A mechanism based on the formation of a hydroxymethyl radical produced by hole/$HO^\bullet$ attack to methanol, was proposed. This radical can donate electrons to the CB or be itself effective as As(V) reductant, with formaldehyde generation in both cases:

$$CH_3OH + h_{VB}^+\{HO^\bullet\} \rightarrow {}^\bullet CH_2OH + H^+\{H_2O\} \qquad E^0({}^\bullet CH_2OH/CH_3OH) = 1.45\,V \tag{23}$$

$$^\bullet CH_2OH \rightarrow CH_2O + H^+ + e_{CB}^- \qquad E^0({}^\bullet CH_2OH/CH_2O) \approx -0.9\ to -1.18\,V \tag{24}$$

$$^\bullet CH_2OH + As(V) \rightarrow CH_2O + As(IV) + H^+ \tag{25}$$

CH_2O can be transformed to formic acid and finally mineralized to CO_2 with generation of $CO_2^{\bullet-}$ ($E^0_{(CO2/CO2^{\bullet-})} \approx -2.0$ V) [14], another strong reducing radical that can contribute to the reducing process:

$$CO_2^{\bullet-} + As(V) \rightarrow CO_2 + As(IV) \tag{26}$$

In a further step, As(IV) is reduced by CB or trapped electrons, or by $^\bullet CH_2OH$ or $CO_2^{\bullet-}$ to As(III). Unlike to As(V), the direct photocatalytic As(III) reduction by e_{CB}^- in the absence of MeOH was also observed for the first time; this indicates that, although the value for the monoelectronic couple As(III)/As(II) is not known, it should be located below the CB level:

$$As(III) + e_{CB}^{-} \rightarrow As(II) \tag{27}$$

Therefore, after As(III) formation, monoelectronic consecutive steps would lead to the formation of stable products such as As(0) and AsH_3, which were unambiguously identified by the authors in all cases through XPS and XANES analyses of the solid residues formed onto the TiO_2 surface after the reaction. In this way, reduction to solid As(0) was achieved, which is a very convenient method for purposes of As removal from water. However, attention must be paid in this kind of reactions to formation of AsH_3, one of the most toxic forms of As. Strategies for AsH_3 treatment were proposed, like adsorption on suitable materials or oxidative treatment by a coupled gas phase photocatalytic system, what are currently under development in our research group.

In a recent paper, it was demonstrated that reduction of As(V), thermodynamically not possible by HP in normal conditions, can be produced in the dark by the action of accumulated electrons by UV irradiation of TiO_2 nanoparticles in alcohol. The accumulation of electrons and their participation in As(V) reduction was followed by UV-vis spectrophotometry and EPR, and detected as Ti(III) [41, 42].

Due to the extensive and good quality work done on photocatalytic systems for As removal and the importance of the problem of As in the environment, research on practical applications of these systems should be reinforced in the future in order to provide cost effective systems.

Conclusions

Heterogeneous photocatalytic treatment of metals and metalloids such as Cr, Pb, U, Hg and As, among others, can be a valuable option for removal of these species from water, which does not require expensive reagents or equipment. Photocatalytic treatments can convert the ionic species into their metallic solid form and deposit them over the semiconductor surface, or transform them into less toxic soluble species. When a transformation to the zerovalent state is possible, this allows the recovery of the metal from the waters, with an important economical return.

In regular photocatalytic reactions under normal illumination, redox reactions take place usually through thermodynamically allowed successive monoelectronic electron transfer steps; three types of mechanisms can be postulated: (a) direct reduction by photogenerated electrons; (b) indirect reduction by intermediates generated by hole or hydroxyl radical oxidation of electron donors (reducing radicals); (c) oxidative removal by holes or hydroxyl radicals.

Organic donors, generally present in polluted waters with the metals are good synergic agents of the treatment and the photocatalytic process allows the simultaneous treatment of pollutants of different chemical structure and properties.

Although several metal and metalloids have been studied, chromium and arsenic systems are interesting examples of how photocatalysis can be addressed from the fundamental background to the implementation of technological applications.

The mechanistic features of the photocatalytic reduction of chromium (VI) to the less toxic Cr(III) form have been thoroughly studied by our group. The Cr(VI) photocatalytic reduction is unique because it is not inhibited by oxygen, at least at acid pH. All these features represent advantages that should be taken into account for the successful application.

Heterogeneous photocatalysis of arsenic species is very promising taking into account that both oxidative and reductive mechanisms may lead to less toxic species [As(V) compared with As(III)] or solid phases [As(0)]. Although the oxidative system has been studied in detail, the reductive pathway is a challenging alternative that should be taken into account and improved.

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