CHAPTER 2

Treatment of Chromium, Mercury, Lead, Uranium, and Arsenic in Water by Heterogeneous Photocatalysis

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Contents

1. INTRODUCTION

Presence of heavy metals and metalloids in water nowadays represents one of the most important environmental problems because the yearly total toxicity of mobilized species overcomes the total toxicity of anthropogenically generated organic and radioactive wastes. In addition to natural sources, anthropic activities introduce hundreds of billions of tons per year of heavy metals in the terrestrial ambient. The accumulation of metals and metalloids in effluents and in industrial wastes represents significant losses in raw materials and causes perturbation of the ecological equilibrium. Precious and common metals enter waters through washing, rinsing, pickling, and surface treatment procedures of industrial processes such as

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hydrometallurgy, plating, or photography. Metal and metalloid species such as chromium, mercury, uranium, and arsenic are considered priority pollutants by several environmental agencies, and the allowed amount of these species in drinking water is becoming more and more stringent.

Although removal of organic and microbiological pollutants from waters has been thoroughly studied, less attention has been paid to the transformation of metal or metalloid ions in species of lower toxicity or more easily isolated. Metals in their various oxidation states have infinite lifetimes, and chemical or biological treatments present severe restrictions or are economically prohibitive. Removal of these species is carried out, generally, by precipitation, electrolysis, chemical oxidation, adsorption, or chelation, all of them presenting drawbacks.

Heterogeneous photocatalysis is a very well-known technology, valuable for purification and remediation of water and air. Several excellent revisions exist on the subject, with different approaches (Bahnemann et al., 1994; Emeline et al., 2005; Fujishima and Zhang, 2006; Hoffmann et al., 1995; Legrini et al., 1993; Linsebigler et al., 1995; Mills and Le Hunte, 1997; Rajeshwar, 1995; Serpone, 1997).

In heterogeneous photocatalysis, after excitation of semiconductors with light of energy equal to or higher than the bandgap (E_g), conduction band electrons (e^-_{cb}) and valence band holes (h^+_{vb}) are created. TiO_2 is so far the most useful semiconductor material for photocatalytic purposes because of its exceptional optical and electronic properties, chemical stability, nontoxicity, and low cost. The energy bandgaps of the photocatalytic forms of TiO_2, anatase and rutile, are 3.23 eV (corresponding to 384 nm) and 3.02 eV (corresponding to 411 nm) (Rajeshwar, 1995). The German company Degussa produces the most popular commercial form of TiO_2 under the name P-25. For Degussa P-25, the values of the edges of conduction and valence bands at pH 0 have been calculated as –0.3 and +2.9 V[1], respectively (Martin et al., 1994). Photogenerated holes and electrons can recombine or migrate to the surface where they can react with donor (D) or acceptor (A) species (Figure 1). The energy level at the bottom of the conduction band is actually the reduction potential of photoelectrons and the energy level at the top of the valence band determines the oxidizing ability of photoholes, each value reflecting the ability of the system to promote reductions and oxidations. Valence band holes are strong oxidants that may attack directly oxidizable species D or form hydroxyl radicals ($HO^•$) from water or surface hydroxide ions, while conduction band electrons are mild reducing acceptors. From a thermodynamic point of view, couples can be photocatalytically reduced by conduction band electrons if they have redox potentials more positive than the flatband potential (V_{fb}) of the conduction band and can be

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[1] All standard reduction potentials given in this work are vs. NHE.

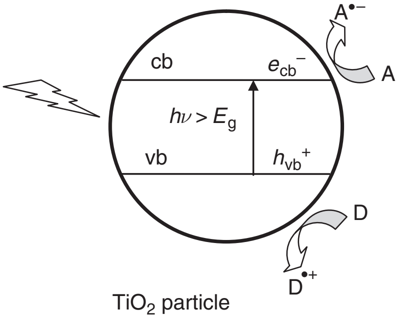

Figure 1 Simplified diagram of the heterogeneous photocatalytic processes occurring at an illuminated TiO_2 particle.

oxidized by valence band holes if they have redox potentials more negative than the V_{fb} (Bahnemann et al., 1994; Hoffmann et al., 1995; Linsebigler et al., 1995; Mills and Le Hunte, 1997; Serpone, 1997).

The above-described scheme is completed by the following basic equations where e_{cb}^{-}, h_{vb}^{+}, and $HO^{\bullet}$ are involved as follows:

$$TiO_2 + h\nu \rightarrow e_{cb}^{-} + h_{vb}^{+} \tag{1}$$

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

$$h_{vb}^{-} + H_2O \rightarrow HO^{\bullet} + H^{\ +} \tag{3}$$

$$h_{vb}^{+} + D \rightarrow D^{\bullet+} \tag{4}$$

In particular, O_2 adsorbed to TiO_2 can be reduced by e_{cb}^{-}, generating $O_2^{\bullet-}$ in a thermodynamically feasible but rather slow electron transfer reaction (Hoffmann et al., 1995). Values of $E^0(O_2/O_2^{\bullet-}) = -0.3\ V$ and $E^0(O_2/HO_2^{\bullet}) = -0.05\ V$ have been reported for homogeneous solutions; 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:

$$O_{2(ads)} + e_{cb}^{-}(+H^{+}) \rightarrow O_2^{\bullet-}\,(HO_2^{\bullet}) \tag{5}$$

$$2O_2^{\bullet-} + 2H_2O \rightarrow 2HO_2^{\bullet} + 2OH^{-} \tag{6}$$

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \tag{7}$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow HO^- + HO^{\bullet} + O_2 \tag{8}$$

In anoxic conditions, protons are the strongest electron acceptors, being reduced to hydrogen atoms, which combine then in hydrogen molecules (Bahnemann et al., 1987):

$$H^+ + e_{cb}^- \rightarrow H^{\bullet} \tag{9}$$

$$2H^{\bullet} \rightarrow H_2 \tag{10}$$

If in solution there is a metal ion of convenient redox potential, conduction band electrons can reduce the species to a lower oxidation state:

$$M^{n+} + e_{cb}^- \rightarrow M^{(n-1)+} \tag{11}$$

Alternatively, the metal can be oxidized by holes or hydroxyl radicals:

$$M^{n+} + h_{vb}^+/HO^{\bullet} \rightarrow M^{(n+1)+} \tag{12}$$

Photocatalytic treatments can convert the ionic species into their metallic solid forms and deposit them over the semiconductor surface or transform them in less toxic soluble species. When a transformation to the zerovalent state is possible, this allows the recovery of the metal by mechanical or chemical procedures, with an important economical return. From the beginning of the development of heterogeneous photocatalysis, transformation and deposit of metals – principally the most noble, expensive, and toxic ones – was visualized as one of the potential applications of the technology in view of the involved economical and environmental aspects. Various semiconductors have been applied in the photocatalytic transformation or deposition of metals such as chromium, gold, silver, platinum, palladium, rhodium, mercury, lead, manganese, thallium, and copper, among others (Serpone et al., 1988). Other applications of heterogeneous photocatalysis related to metal ions are light energy storage, photographic imaging, prevention of semiconductor corrosion, and preparation of modified semiconductors, but these topics will not be treated here.

In view of the enormous literature published on the subject, only the cases of chromium, mercury, lead, uranium, and arsenic are reviewed here. In 1999, we published an extensive review on metal treatment by heterogeneous photocatalysis in which the early literature is mentioned (Litter, 1999). In this chapter, we will remind the most important issues and update the most recent information.

2. THERMODYNAMICAL CONSIDERATIONS AND MECHANISTIC PATHWAYS

The redox level of the metallic couples related to the levels of the conduction and valence bands can be considered as the most important parameter to predict the feasibility of transformation of the species, and it is possible to take these values for a first approach. Figure 2 shows the redox levels of

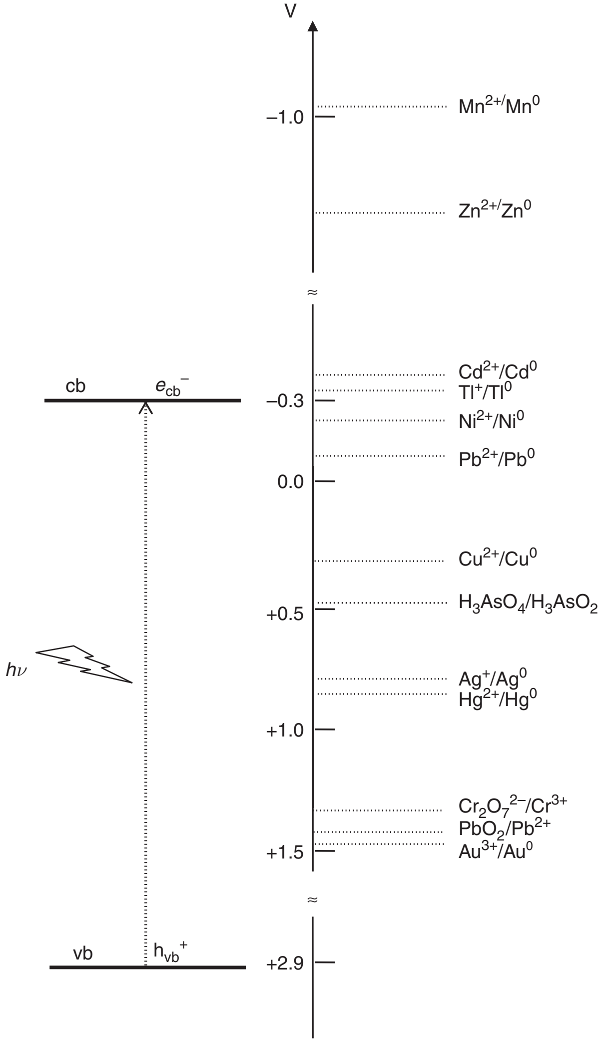

Figure 2 Position of the reduction potentials of various metallic couples (vs. NHE) related to the energy levels of the conduction and valence bands of Degussa P-25 TiO_2 at pH 0. Reduction potentials are taken from Bard et al. (1985).

couples and the thermodynamic ability of the TiO_2 photocatalytic system to reduce or oxidize the corresponding species. According to this, metals have been separated into two groups: those as Cu^{2+}, As^{5+}, Ag^{+}, Hg^{2+}, Cr^{6+}, and Au^{3+}, which show a strong tendency to undergo photocatalytic reduction, and those as Mn^{2+}, Zn^{2+}, Cd^{2+}, Tl^{+}, Ni^{2+} and Pb^{2+}, which show essentially no or a very weak tendency to accept photogenerated electrons from TiO_2 (Rajeshwar et al., 2002).

However, in this chapter, it will be emphasized that the above concepts – generally used when describing heterogeneous photocatalysis applied to metal systems – only express the feasibility of the overall process to occur, implicitly assuming a global multielectronic transfer reaction in many of the cases. Nevertheless, under the working conditions of ordinary photocatalytic reactions, that is, under nonintense irradiation, multielectronic reactions are rather unlikely, considering the frequency of photon absorption (Grela and Colussi, 1996). Recent experiments of our research group (see sections 3, 4 and 5) led to the conclusion that most photocatalytic processes on metal ions occur through successive one-electron pathways that produce unstable intermediates until the most stable species is formed.

Three types of mechanisms can be considered for the photocatalytic removal of metal ions: (a) direct reduction by photogenerated electrons, (b) indirect reduction by intermediates generated by hole or hydroxyl radical oxidation of electron donors present in the media, and (c) oxidative removal by holes or hydroxyl radicals (Lin and Rajeshwar, 1997), all of them represented in Figure 3.

In the direct reduction (a), the initial electron transfer step, reaction (11), is usually considered as the rate determining one (Mills and Valenzuela, 2004). For predicting the feasibility of the transformation, the reduction potential of the first step related to the energy of the conduction band has to be considered. The conjugate anodic reaction of Equation (11) is oxidation of water by holes or $HO^{\bullet}$, initiated by reaction (3) and ending in protons and oxygen:

$$4h_{vb}{}^{+}/HO^{\bullet} + 2H_2O \rightarrow O_2 + 4H^{+} \tag{13}$$

The photogenerated holes or $HO^{\bullet}$ radicals can reoxidize also the species to the original one, causing a nonproductive short-circuiting of the overall process:

$$M^{(n-1)+} + h_{vb}^{+}/HO^{\bullet} \rightarrow M^{n+} \tag{14}$$

As the water oxidation reaction (13) is a very slow four-electron process, metal reductive transformation can be generally improved by addition of sacrificial organic agents (Prairie and Stange, 1993; Prairie et al., 1993a). The process can be improved even more if a strong reducing species is formed

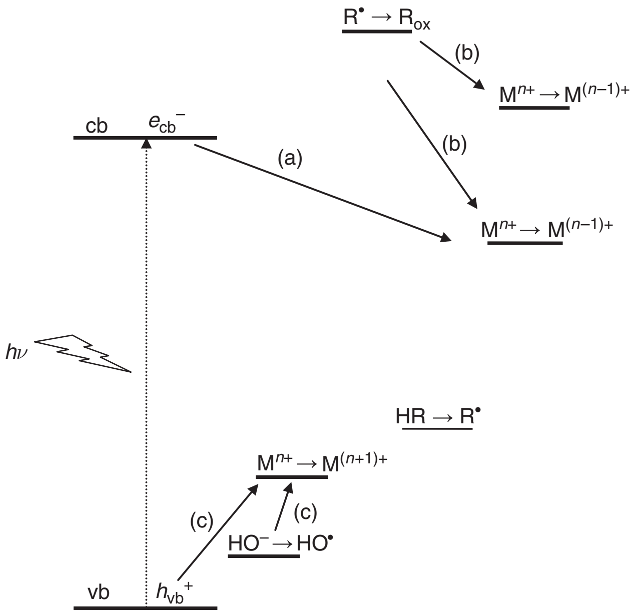

Figure 3 Schematic diagram for the photocatalytic transformation of metal ions on TiO_2. Different pathways (a), (b), and (c) are indicated (see text). The diagram of energy levels is only qualitative.

from the sacrificial agent, giving rise to an indirect pathway (type (b) reaction), as we will see later. The process will be very dependent on the nature of the added agent: low-molecular-weight acids, alcohols, and aldehydes do not cause any effect, while easily oxidizable organics such as EDTA, salicylic acid, and citric acid provide very fast reduction rates. These organic compounds are oxidized by holes or hydroxyl radicals in irreversible reactions, avoiding recombination of electron–hole pairs and enhancing reduction of metal ions:

$$\mathrm{RCOO^-} + h^+_{\mathrm{vb}}/\mathrm{HO}^\bullet \rightarrow \mathrm{R}^\bullet + \mathrm{CO_2} \qquad (15)$$

In addition, this process hinders the short-circuiting depicted by reaction (14).

Indirect reduction (mechanism (b)) was suggested by Baba et al. (1986), who analyzed the photodeposition of Pt, Ag, and Au on an anodically biased TiO_2 electrode in a solution containing alcohols (MeOH, EtOH, or 2-PrOH). As no metal deposition was observed in the absence of alcohols, these authors proposed that photogenerated conduction band TiO_2 electrons do not take part directly in the deposition. As a result, the reduction is then assumed to be driven by intermediates generated by attack of h^+_{vb} or

$HO^{\bullet}$ to alcohols or carboxylic acids (HR), with the generation of highly energetic species ($R^{\bullet}$) (Figure 3):

$$HR + h^{+}_{vb}/HO^{\bullet} \rightarrow R^{\bullet} + H^{+}/H_2O \qquad (16)$$

For the cases of methanol, ethanol, or 2-propanol, $R^{\bullet}$ are 1-hydroxyalkyl radicals, while for formic or oxalic acids the strong reducing $CO_2^{\bullet -}$ is formed, with other carboxylic acid generating similar reducing species. Concurrently, reaction (14) is hindered if HR is added at relatively high concentrations because reaction (16) will predominate. The conjugated cathodic reaction in anoxic conditions will be H^+ reduction by conduction band electrons, with H_2 formation (reactions (9) and (10)). Once produced, $R^{\bullet}$ would be the effective reducing species of M^{n+}:

$$R^{\bullet} + M^{n+} \rightarrow R_{ox} + M^{(n-1)+} \qquad (17)$$

where R_{ox} is an aldehyde, a ketone, or CO_2 depending on the compound. In Figure 3, a simplified diagram of this process is presented.

Obviously, if the potential for the one-electron reduction of the metal is adequate, as described for M^{n+} in Figure 3, the direct reaction (a) can take place. This will not be the case for Pb(II), Ni(II), or Tl(I), which will only react through the indirect mechanism (b), reaction (12). After this first stage, other reducing steps driven by $R^{\bullet}$ or e^{-}_{cb} may take place until a stable metal species is formed. It has been pointed out that direct reduction of metal ions to the zerovalent state by reducing radicals is rather slow, but once some metal nuclei are formed, they serve as cathodic site to facilitate further reduction (Baba et al., 1986).

In mechanism (c), oxidative transformation of the metal species takes place by holes or hydroxyl radicals (or other reactive oxygen species, ROS) attack (Figure 3). This occurs according to reaction (12) when the oxidation of the metal or metalloid to a higher oxidation state is thermodynamically possible (cases of Pb(II), Mn(II), Tl(I), and As(III)).

3. CHROMIUM

Chromium (VI) is a frequent contaminant in wastewaters arising from industrial processes such as electroplating, leather tanning, or paints due to its carcinogenic properties, its concentration in drinking waters has been regulated in many countries. The World Health Organization (WHO) recommends a limit of 0.05 mg L^{-1} in drinking waters (World Health Organization, 2006), value adopted by several national environmental agencies. The preferred treatment is reduction to the less harmful Cr(III), nontoxic and less mobile. This process is performed generally with chemical reagents such as sodium thiosulfate, ferrous sulfate, sodium meta-bisulfite, or sulfur dioxide; in this way, the ion can be precipitated in neutral or alkaline solutions as $Cr(OH)_3$ and removed from the aqueous phase.

The net reaction for Cr(VI) reduction in acid aqueous solutions is:

$$2Cr_2O_7^{2-} + 16H^+ \rightarrow 4Cr^{3+} + 8H_2O + 3O_2 \tag{18}$$

and at neutral pH:

$$4CrO_4^{2-} + 20H^+ \rightarrow 4Cr^{3+} + 10H_2O + 3O_2 \tag{19}$$

The process is thermodynamically feasible ($\Delta G^0_{298} = -115.8\,\text{kJ}$), but dichromate is stable in aqueous acidic solutions due to the high overpotential of the reaction of water oxidation. Cr(VI) photocatalytic reduction has been found effective over several semiconductors (in form of powders or electrodes) such as TiO_2, ZnO, CdS, ZnS, and WO_3. Several examples, all of them investigated before 1999, have already been described in our previous review (Litter, 1999), including reactors for technological applications (Aguado et al., 1991, 1992; Domènech, 1993; Domènech and Muñoz, 1987a, b, 1990; Domènech et al., 1986; Giménez et al., 1996; Lin et al., 1993; Miyake et al., 1977; Muñoz and Domènech, 1990; Prairie and Stange, 1993; Prairie et al., 1992, 1993a; Sabaté et al., 1992; Selli et al., 1996; Wang et al., 1992; Xu and Chen, 1990; Yoneyama et al., 1979). Other papers appeared later (Aarthi and Madras, 2008; Cappelletti et al., 2008; Chenthamarakshan and Rajeshwar, 2000; Chen and Ray, 2001; Colón et al., 2001a, b; Das et al., 2006; Fu et al., 1998; Hidalgo et al., 2007; Horváth et al., 2005; Jiang et al., 2006; Kajitvichyanukul et al., 2005; Kanki et al., 2004; Khalil et al., 1998; Ku and Jung, 2001; Mohapatra et al., 2005; Papadam et al., 2007; Rengaraj et al., 2007; Ryu and Choi, 2008; Schrank et al., 2002; Shim et al., 2008; Tuprakay and Liengcharernsit, 2005; Tzou et al., 2005; Wang et al., 2008; Xu et al., 2006; Yang and Lee, 2006; Zheng et al., 2000). The list includes microparticles used in slurries or conveniently supported, mixed, and modified semiconductors and even nanomaterials (nanoparticles, nanotubes).

The photocatalytic Cr(VI) reduction is more feasible at low pH because the net reaction consumes protons (Equations (18) and (19)), but use of neutral or alkaline conditions can be more convenient because Cr(III) can be precipitated as the hydroxide and immobilized, avoiding expensive separation steps; after the photocatalytic process, an adequate acid or strong basic treatment easily separates Cr(III) from the catalyst (Lin et al., 1993).

Cr(VI) photocatalytic reaction is very slow in the absence of scavengers of holes or $HO^\bullet$, because, as said, reaction (13) is kinetically sluggish. The reaction can be accelerated by the addition of organic compounds (Colón et al., 2001a, b; Fu et al., 1998; Ku and Jung, 2001; Miyake et al., 1977; Papadam et al., 2007; Prairie and Stange, 1993; Rajeshwar et al., 2002; Shrank et al., 2002; Tzou et al., 2005; Wang et al., 2008); even humic acids (Selli et al., 1996; Yang and

Lee, 2006) and MTBE (Xu et al., 2006) were found to be efficient donors. Prairie and Stange (1993) and Wang et al. (2008) found that Cr(VI) removal rate in the presence of different organics increases in the order: *p*-hydroxybenzoic acid < phenol < formic acid < salicylic acid < citric acid. In many cases, these organic compounds can be present simultaneously with Cr(VI) in the wastewaters of different industrial processes. Sometimes, the agent is not able to enhance markedly Cr(VI) reduction but the opposite is true: Cr(VI) acts as a very strong oxidant for organic species, as in the cases of the photoinduced oxidative degradation of anionic (sodium dodecyl sulfate, SDS) and cationic (cetyltrimethylammonium bromide, CTAB) surfactants (Horváth et al., 2005).

Cappelletti et al. (2008), using nanocrystalline TiO_2 samples and different sacrificial molecules (formic acid, isopropyl alcohol and sodium sulfite), found Cr(0) formation at the TiO_2 surface. Since the reduction potential for Cr(III) to Cr(II) is –0.42 V and the global reduction potential from Cr(III) to Cr(0) is –0.74 V (Bard et al., 1985), these processes cannot be driven by TiO_2 conduction band electrons. In contrast, Cr(0) should have been formed by reducing radicals coming from the oxidation of the sacrificial molecules, according to reactions (16) and (17).

A different type of synergy was found in a binary Cu(II)/Cr(VI) system: under N_2 and UV light, acceleration of both Cr(VI) and Cu(II) reduction was observed (Goeringer et al., 2001). While no explanations were provided concerning this behavior, it can be proposed that the enhancement may be due to the formation of a layer or spots of metallic copper that promote photocatalysis.

Our research group (Botta et al., 1999; Di Iorio et al., 2008; Meichtry et al., 2007, 2008b; Navío et al., 1998, 1999; San Román et al., 1998; Siemon et al., 2002; Testa et al., 2001, 2004) reported several studies on Cr(VI) photocatalytic reduction using TiO_2, ZrO_2, and Fe-doped samples and gained insight about the processes taking place in the system. The standard reduction potentials of Cr(VI)/Cr(V), Cr(V)/Cr(IV), and Cr(IV)/Cr(III) couples are +0.55, +1.34, and +2.10 V, respectively (Bard et al., 1985). All of them are positive enough to be reduced by TiO_2 conduction band electrons (Figure 3). Therefore, working with Cr(VI) in pure water TiO_2 suspensions or in the presence of donor agents such as EDTA, oxalic acid, and citric acid, our team proposed for the first time that Cr(VI) photocatalytic reduction over TiO_2 takes place by successive one-electron transfer reducing steps leading to Cr(III), the stable final product (Meichtry et al., 2007; Testa et al., 2001, 2004):

$$\mathrm{Cr(VI)} + e^-_{\mathrm{cb}} \rightarrow \mathrm{Cr(V)} \tag{20}$$

$$\mathrm{Cr(V)} + e^-_{\mathrm{cb}} \rightarrow \mathrm{Cr(IV)} \tag{21}$$

$$\mathrm{Cr(IV)} + e^-_{\mathrm{cb}} \rightarrow \mathrm{Cr(III)} \tag{22}$$

These assumptions were validated, at least for the initial one-electron process (20), by EPR experiments in which Cr(V) species were detected. While the fate of Cr(V) and Cr(IV) is not clear, it is hypothesized that they are probably reduced by conduction band electrons or can suffer disproportionation to other species. As the anodic reaction in the absence of donors is sluggish (reaction (13)), an arrest of Cr(VI) reduction is observed after some time of reaction, because of the reoxidation of Cr(V)/(IV)/(III) species by holes or $HO^{\bullet}$. On the contrary, Cr(VI) removal in the presence of the donors is total in a very short time, as the short-circuiting process is hindered.

Our research group also reached to very important conclusions concerning the role of dissolved molecular oxygen in the photocatalytic reduction of Cr(VI), which was the object of controversy for many years. In fact, it can be possible to think that O_2 inhibits Cr(VI) reduction, given the likelihood that conduction band electrons are consumed via reaction (5). However, research of our team and some other investigations show no particular effect of O_2 (Domènech and Muñoz, 1987a; Domènech et al., 1986; Navío et al., 1998; Siemon et al., 2002; Testa et al., 2004). There is in this respect important evidence supporting this lack of effect of oxygen:

1. There is no difference in the Cr(VI) photocatalytic reduction efficiency while working under nitrogen or under oxygen (or air) (Siemon et al., 2002; Testa et al., 2004).
2. There is no variation in Cr(VI) photocatalytic reduction efficiency while measured over pure or platinized TiO_2 (Siemon et al., 2002). If O_2 competes with Cr(VI) for conduction band electrons, a faster Cr(VI) reduction should have been obtained over Pt/TiO_2, as platinum reduces the overpotential for oxygen reduction. Experimental results suggest that electron transfer to metallic ion from the conduction band or from Pt is rapid and there is no oxygen mediation requirement.
3. Spectroscopic evidences (an absorption band at 375 nm) of the formation of a charge-transfer complex between Cr(VI) and TiO_2 nanoparticles, showing a strong interaction of the metal ion with the semiconductor surface, were reported in a recent paper (Di Iorio et al., 2008).

The behavior of Cr(VI) contrasts strongly with that of other metal ions such as Hg(II) (see section 4), whose reduction is greatly inhibited by dissolved oxygen. In this sense, it is a unique system and the fact that its photocatalytic reduction can be made in air represents an important technological advantage.

The photocatalytic Cr(VI) reduction has been reported to take place also under visible irradiation. Kyung et al. (2005) found simultaneous and synergistic conversion of Cr(VI) and Acid Orange 7 over TiO_2 using light of $\lambda > 420$ nm, explained by internal light-induced electron transfer in a complex formed between both Cr(VI) and the dye. A similar behavior was observed in the presence of the nonionic surfactant Brij (Cho et al., 2004). Sun et al. (2005) found the simultaneous visible-light Cr(VI) reduction and oxidation of 4-chlorophenol (4-CP) or salicylic acid by TiO_2 irradiation at $\lambda > 400$ nm; the effect was attributed to visible-light excitation of electrons from the valence band to oxygen vacancy states located around 2 eV above the valence band, followed by electron transfer to Cr(VI); alternatively, the transfer could be to surface defects or trap states present at ca. 0.5 eV below the conduction band, from where Cr(VI) may capture electrons.

In the presence of dyes, it is widely accepted that the photocatalytic process under visible light is different from that under UV light. As it can be seen in Figure 4, the dye is excited to a singlet state from which it can inject electrons to the TiO_2 conduction band, leaving behind a radical cation that replaces h^+_{vb} or $HO^\bullet$ as usual oxidant entities, lowering the oxidizing ability of the system in comparison with that under UV irradiation (Hodak et al., 1996; Meichtry et al., 2008b). However, the reducing power remains intact, making possible Cr(VI) reduction.

In a recent paper, our research group showed that alizarin red chelated to TiO_2 nanoparticles promotes reduction of Cr(VI) to Cr(V) under visible light; Cr(V) formation was confirmed by EPR measurements (Di Iorio et al., 2008).

Another dye, hydroxoaluminiumtricarboxymonoamide phthalocyanine (AlTCPc), adsorbed on TiO_2 particles at different loadings was tested for Cr(VI) photocatalytic reduction under visible irradiation in the presence of 4-CP as sacrificial donor. Direct evidence of the one-electron reduction of Cr(VI) to Cr(V) was also obtained by EPR experiments. The inhibition

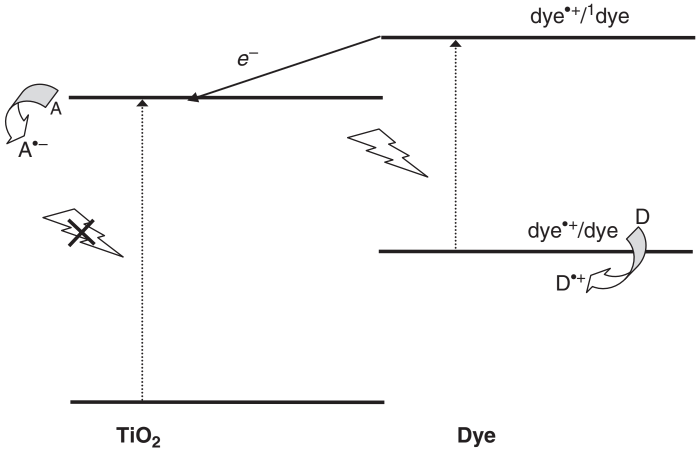

Figure 4 Simplified diagram of the heterogeneous photocatalytic processes occurring under visible irradiation when a dye is attached to a semiconductor.

of formation of ROS in a photocatalytic reductive pathway by the fast trapping of electrons by Cr(VI) and the easier oxidability of 4-CP compared to AlTCPc protects the dye and avoids its photobleaching, making feasible Cr(VI) reduction by the use of solar radiation (Meichtry et al., 2008b).

In conclusion, much experimental work has been done on Cr(VI) photocatalytic reduction since 1999. The advances are related to the elucidation of mechanistic pathways, detection of intermediary species, kinetic calculations, role of dissolved oxygen, and potential use of visible light. However, several interesting points are still worthy of investigation with the aim of optimizing the technology for real use in wastewaters; the presence of synergetic organic compounds such as carboxylic acids or phenols, common constituents of real wastes, makes the process even more attractive.

4. MERCURY

Mercury (II) is a frequent component of industrial wastewaters, remarkably toxic at concentrations higher than 0.005 mg L^{-1}. The World Health Organization (2006) and national environmental agencies recommend a limit of 0.006 mg L^{-1} of inorganic mercury in drinking water. The health hazards due to the toxic effect of mercury at Minamata, Japan, and Iraq are very well known (Bockris, 1997).

The major use of mercury compounds is as agricultural pesticides. It is also used in the chlorine-alkali industry, in paints, as a catalyst in chemical and petrochemical industries, in electrical apparatus, cosmetics, thermometers, gauges, batteries, and dental materials. For this reason, it is a very common pollutant in wastewaters.

Removal of mercuric species in aqueous solutions is difficult because they are hard to be bio- or chemically degraded. At high concentrations, mercury can be removed from the solution by membrane filtration, precipitation with chemicals, ion exchange, adsorption, and reduction (Botta et al., 2002). However, these methods are much less efficient and very expensive for concentrations lower than 100 mg L^{-1} (Manohar et al., 2002).

Mercury transformation by heterogeneous photocatalysis with semiconductors (including electrodes, micro- and nanoparticles) such as ZnO, TiO_2, WO_3 under UV, visible irradiation, and even solar light has been reported in a series of papers. Some of them have been detailed in our previous review (Aguado, et al., 1995; Chen et al., 1997; Clechet et al., 1978; Domènech and Andrés, 1987a, b; Kaluza and Boehm, 1971; Lin et al., 1993; Litter, 1999; Prairie and Stange, 1993; Prairie et al., 1993a, b; Rajeshwar et al., 2002; Serpone et al., 1987, 1988; Tanaka et al., 1986; Tennakone, 1984; Tennakone and Ketipearachchi, 1995; Tennakone and Wickramanayake, 1986; Tennakone et al., 1993; Wang and Zhuang, 1993), and some others appeared later (Bussi et al., 2002; Horváth and Hegyi, 2001, 2004; Khalil et al., 2002;

Lau et al., 1998; Rader et al., 1994; Skubal and Meshkov, 2002; Wang et al., 2004). It was concluded that the removal efficiency depends strongly on pH, that the reaction is inhibited by oxygen and that there is an enhancement by organic donors.

Recent studies of our research team on TiO_2-photocatalysis of three inorganic mercuric salts, $Hg(NO_3)_2$, $HgCl_2$ and $Hg(ClO_4)_2$, shed light on this complex system (Botta et al., 2002). Depending on the conditions, different products are formed on the photocatalyst surface: Hg(0), HgO, or calomel. Time profiles of Hg(II) concentration with time were characterized by a relatively rapid initial conversion followed by a decrease or an arrest of the rate. Three pH values (3, 7, and 11) were tested, finding that the faster transformation takes place at pH 11 for all salts. Inhibition by oxygen was observed in acid and neutral media but not at basic pH.

The global reaction for metallic mercury deposition is

$$\mathrm{Hg(II)} + \mathrm{H_2O} \rightarrow 2\mathrm{H}^+ + {}^1/_2\,\mathrm{O_2} + \mathrm{Hg(0)} \tag{23}$$

Accordingly, the photocatalytic reaction was found to occur with proton release (Serpone et al., 1987).

In line with the fact that photocatalytic reactions under nonintense photon fluxes take place through monoelectronic steps, a direct reductive mechanism (pathway (a) in Figure 3) involving successive one-electron charge-transfer reactions was postulated (Botta et al., 2002; Custo et al., 2006):

$$\mathrm{Hg(II)} + e^-_{\mathrm{cb}} \rightarrow \mathrm{Hg(I)} \tag{24}$$

$$\mathrm{Hg(I)} + e^-_{\mathrm{cb}} \rightarrow \mathrm{Hg(0)} \tag{25}$$

This reaction sequence explains the formation of calomel when the photocatalytic reaction starts from mercuric chloride. At pH 11, however, calomel was not observed, as it disproportionates to Hg(0) and HgO.

On the other hand, reduced mercury species can be reoxidized by holes or $HO^\bullet$ as follows (Botta et al., 2002; Custo et al., 2006):

$$\mathrm{Hg(0)/(I)} + h^+_{\mathrm{vb}}/\mathrm{HO}^\bullet \rightarrow \mathrm{Hg(I)/(II)} \tag{26}$$

This reoxidation can be hindered by synergistic electron donors. In these cases, mechanism (a) or (b) can take place, according to Figure 3. EDTA was found to be one of the best reductants (Chen and Ray, 2001; Custo et al., 2006), probably because it forms stable complexes with Hg(II). Complexation with citrate also proved to be a very good alternative for Hg(II) removal from water through metallic mercury deposition (Tennakone and Ketipearachchi, 1995). Ethanol enhanced Hg(II) removal dramatically (Horváth and Hegyi, 2001, 2004); SDS was an even better hole scavenger (Horváth and Hegyi, 2004; Horváth et al., 2005). This could have important environmental results for treating domestic and industrial laundry wastewaters containing both Hg(II) and SDS. On the contrary, the cationic CTAB surfactant promoted only slight photoreduction of Hg(II) because repulsion due to its positive charge hinders an efficient reaction (Horváth and Hegyi, 2004; Horváth et al., 2005). Formic acid also enhanced Hg(II) removal, the effect increasing with the organic donor concentration until a limiting value (Wang et al., 2004).

An interesting application of Hg(II) photocatalysis is the use of an activated carbon developed from municipal sewage sludge using $ZnCl_2$ as chemical activation reagent combined with TiO_2. Hg(II) was first photoreduced to Hg(0) and then adsorbed on the carbon and TiO_2 surfaces, with a final recovery of the metal on a silver trap by heating (Zhang et al., 2004).

Another remarkable example is the separation of Cr(VI)/Hg(II) mixtures, which are present in dental office wastewaters (Wang et al., 2004). When Cr(VI) is added to TiO_2 suspensions at pH 4, there is an inhibition of the initial Hg(II) reduction rate. This phenomenon was attributed to catalyst deactivation by Cr(III) species deposited on the TiO_2 surface.

Another interesting application of the photocatalytic technology is the removal (more than 99%) of mercury from hazardous wastes of a chloralkali plant. The process begins by acid attack of the solid wastes and treatment of the acid solution under UV irradiation in the presence of TiO_2 and citric acid. The selective precipitation of reduced mercury took place, while the other metal compounds remained in the solution. It was claimed that the final effluents reached a quality close to that of the standards imposed by international environmental agencies (Bussi et al., 2002).

The toxicity of organic mercury compounds, for example, methyl- or phenylmercury, is considerably higher than that of the inorganic species. For example, the massive case of poisoning in Japan, the Minamata Bay incident, was attributed to industrial discharge of organomercurials, and declining bird populations in Sweden was blamed on the use of phenyl- and methylmercurial pesticides as seed dressings (Baughman et al., 1973). Phenylmercury chloride (PMC) and phenylmercury acetate (PMA) were commonly used as pesticides; in particular, PMA was widely used in Argentina until 1971, when it was forbidden.

TiO_2-photocatalytic treatment of methylmercury was tested. It was found that metallic mercury can be deposited only in the presence of methanol and absence of oxygen, according to an indirect photocatalytic reduction (Serpone et al., 1987, 1988).

Interesting applications for treatment of dicyanomercury (II) and tetracyanomercurate (II) ion, high-toxic pollutants coming from precious metal cyanidation processes, were also studied (Rader et al., 1994). Both compounds underwent over 99% removal by TiO_2-photocatalysis in alkaline solutions with deposition of Hg and HgO and oxidation of cyanide to nitrate.

Complete mineralization of the dye mercurochrome (merbromin) by TiO_2 photocatalytic oxidation was found to occur in oxygenated solutions in the presence of citrate, with the corresponding deposition of metallic mercury (Tennakone et al., 1993).

UV/TiO_2 photocatalysis of PMC and PMA in acid aqueous solutions was studied recently by our research group (de la Fournière et al., 2007). Previous work of Prairie et al. (1993b) reports fast PMC mineralization with simultaneous Hg immobilization onto the catalyst. Removal of Hg(II) took place in both cases, with Hg(0) deposition when starting from PMA, and mixtures of Hg(0) and Hg_2Cl_2 when starting from PMC. The reaction was faster at pH 11, with formation of mixtures of Hg and HgO. Oxygen inhibited the reaction. Phenol was detected as a product of both PMA and PMC. It was found that, fortunately, no dangerous methyl- or ethylmercury species were formed in the case of PMA. Calomel formation from PMC under nitrogen reinforces the two successive one-electron transfer reactions, as in the case of inorganic salts. As a result, it can be proposed that the organic moiety plays the role of an electron donor, according to the following sequence of simplified reactions:

$$\begin{aligned} &C_6H_5Hg^{+}(Cl^{-}\ \text{or}\ CH_3COO^{-}) + h^{+}_{vb}/HO^{\bullet} \\ &\quad \rightarrow C_6H_5OH + Hg^{2+}(Cl^{-}\ \text{or}\ CH_3COO^{-}) \end{aligned} \tag{27}$$

followed by reactions (24) and (25). The anodic pathways would continue through:

$$C_6H_5OH + h^{+}_{vb}(HO^{\bullet}) \rightarrow \ldots \rightarrow CO_2 + H_2O \tag{28}$$

$$CH_3COO^{-} + h^{+}_{vb}(HO^{\bullet}) \rightarrow \ldots \rightarrow CO_2 + H_2O \tag{29}$$

It is also possible to consider a simultaneous Hg(II) reduction and oxidation of the organic moiety, taking place on the initial organomercurial. However, it is not possible to distinguish between simultaneous or consecutive steps.

In closing, important advances have been performed after 1999 on Hg(II) photocatalysis, especially concerning the highly toxic organomercuric compounds. However, and as said in a previous paper (Botta et al., 2002), it is worthwhile to remark that remediation of Hg(II) in aqueous solutions is hard to attain completely, because of the low levels needed to avoid toxicity (in the order of $\mu g\ L^{-1}$). Thus, very sensitive analytical tools must be used to control the concentration of species in the solution. The physicochemical properties of the products derived from the treatment also introduce serious difficulties. Although zerovalent mercury can be carefully distilled off by mild heating, trapped and recondensed, or it can be dissolved with nitric acid or *aqua regia* for confinement or further treatment of smaller volumes of the effluent, metallic Hg is volatile and somewhat water soluble, HgO is also fairly water soluble, and Hg(I) and Hg(II) nitrates and perchlorates are water soluble.

In spite of these potential complexities, it shall be emphasized that it is always better to have the pollutant immobilized as metallic deposit, treating it later on the solid residue as a hazardous species. It must be also reminded that calomel, if formed, is a less toxic species than $HgCl_2$ with all this leading to a less hazardous chemical system.

5. LEAD

Lead (II) is a toxic metal ion frequently found in wastewater coming from industrial effluents. Lead pollution is mainly anthropogenic and originates in municipal sewages, mining, refining of Pb-bearing ores, chemical manufacture, and other sources. It is a component of insecticides, batteries, water pipes, paints, alloys, food containers, and so on. It has been extensively used as a gasoline additive (tetramethyl- or other alkyl-lead compounds). Although this application has been fortunately forbidden or reduced in most countries, some dangerous wastes could still be present, and they have to be treated. Lead may also be present naturally in groundwater, soils, plants, and animal tissues (Vohra and Davis, 2000). The World Health Organization (2006) and national agencies recommend a maximum of 0.01 mg L^{-1} in drinking water.

Removal of lead from water is performed generally by precipitation as carbonate or hydroxide with or without coagulation. Chelation with EDTA, nitrilotriacetic acid, or other agents is another usual treatment followed by recovery using precipitation, electrolysis, or chemical oxidation (Borrell-Damián and Ollis, 1999). However, most of these treatments are expensive, and some other ways of lead elimination from wastewater are necessary to be developed.

Heterogeneous photocatalysis of Pb(II) systems has received scarce attention. In our previous review (Litter, 1999), we cited a few early papers (Inoue et al., 1978, 1980a, b; Kobayashi et al., 1983; Lawless et al., 1990; Maillard-Dupuy et al., 1994; Rajh et al., 1996a, b; Tennakone, 1984; Tennakone and Wijayantha, 1998; Thurnauer et al., 1997; Torres and Cervera-March, 1992), and although some new papers appeared later (Aarthi and Madras, 2008; Chen and Ray, 2001; Chenthamarakshan et al., 1999; Kabra et al., 2007, 2008; Kobayashi et al., 1983; Mishra et al., 2007; Rajeshwar et al., 2002), information was and continues to be scant. The mechanisms of transformation of lead (II) in water by UV-TiO_2 are especially attractive because they depend very much on the reaction conditions, related to the nature of the photocatalyst, the effect of oxygen, and the presence of electron donors.

Recent results of our group (Murruni et al., 2007, 2008) using TiO_2 and Pt—TiO_2 under different conditions tried to shed light on the mechanisms related to this complex system. As in previous reported cases (Chen and Ray, 2001; Kobayashi et al., 1983; Tanaka et al., 1986; Torres and Cervera-March, 1992), a low Pb(II) removal was obtained over pure TiO_2 either in the absence or in the presence of oxygen. The efficiency could be enhanced (1) by using platinized TiO_2 in oxygenated suspensions, (2) by bubbling ozone, and (3) by addition of hole/$HO^{\bullet}$ scavengers.

All these results can be explained by the occurrence of oxidative or reductive pathways. The oxidative route to Pb(IV) species through hole or $HO^{\bullet}$ attack (pathway (c), Figure 3) is one possible process. The global reaction is

$$2Pb^{2+} + 2H_2O + O_2 \rightarrow 2PbO_2 + 4H^+ \tag{30}$$

In this route, PbO_2 is formed as the final product, obtained as a dark brown deposit on TiO_2 (Inoue et al., 1980a, b; Murruni et al., 2007; Tennakone, 1984). Considering two consecutive one-electron charge-transfer steps, the first one will be h^+_{vb} or $HO^{\bullet}$ attack leading to the trivalent state (Murruni et al., 2007):

$$h^+_{vb}/HO^{\bullet} + Pb(II) \rightarrow Pb(III) \tag{31}$$

The one-electron reduction potential for the Pb(III)/Pb(II) couple is not reported, but it is not unreasonable to assume that Pb(II) can be easily oxidized. Pb(III) is unstable, forming Pb(IV) by simple oxidation by O_2 or by stronger oxidants (h^+_{vb}, ROS, etc.); disproportionation is also possible:

$$Pb(III) + \text{oxidants} \rightarrow Pb(IV) \tag{32}$$

$$2Pb(III) \rightarrow Pb(II) + Pb(IV) \tag{33}$$

The conjugate cathodic rate-limiting reaction is O_2 reduction to $O_2^{\bullet -}$, reaction (5). Removal is poor over pure TiO_2 in O_2 or air due to the high overpotential of this reaction. In contrast, the reaction is remarkably rapid over platinized TiO_2, because Pt facilitates the reaction (Chenthamarakshan et al., 1999; Lawless et al., 1990; Murruni et al., 2007; Tanaka et al., 1986; Torres and Cervera-March, 1992). In agreement, the concentration of dissolved O_2 was found to decrease on illumination (Tanaka et al., 1986) and a dependence of the removal rate with O_2 concentration was found (Torres and Cervera-March, 1992). Thus, the oxidative route seems to be the preferred photocatalytic pathway in the absence of electron donors.

Bubbling of ozone improves Pb(II) removal over Pt—TiO_2 and allows the oxidation even on pure TiO_2 in comparison with the same reaction under oxygen (Murruni et al., 2007). It is important to note that there is no Pb(II) removal by O_3 in the absence of photocatalyst, even under UV irradiation. The enhancement by ozone is attributed to the production of a higher concentration of ROS (H_2O_2, $HO^\bullet$, $O_2^{\bullet-}$, $O_3^{\bullet-}$) through reactions (34) to (41), including reaction (7), where the ozonide radical ($O_3^{\bullet-}$) is a relevant species:

$$O_3 + H_2O + h\nu(\lambda > 300\,\mathrm{nm}) \rightarrow H_2O_2 + O_2 \tag{34}$$

$$O_3 + H_2O_2 \rightarrow HO^\bullet + HO_2^\bullet + O_2 \tag{35}$$

$$O_3 + OH^- \rightarrow O_2^{\bullet-} + HO_2^\bullet \tag{36}$$

$$O_3 + HO^\bullet \rightarrow O_2 + HO_2^\bullet \leftrightarrow O_2^\bullet + H^+ \tag{37}$$

$$O_3 + HO_2^\bullet \rightarrow 2O_2 + HO^\bullet \tag{38}$$

$$2HO_2^\bullet \rightarrow O_2 + H_2O_2 \tag{7}$$

$$O_{3(\mathrm{ads})} + e_{\mathrm{cb}}^- \rightarrow O_3^{\bullet-} \tag{39}$$

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^\bullet \tag{40}$$

$$HO_3^\bullet \rightarrow HO^\bullet + O_2 \tag{41}$$

In the ozone systems, $PbO_{1.37}$ and PbO_2 are identified as deposits on the catalyst.

It is also possible to propose a direct reductive route driven by TiO_2-conduction band electrons through successive one-electron reduction steps finishing in metallic lead (pathway (a), Figure 3), with oxidation of water by holes or $HO^\bullet$, ending in protons and oxygen, reaction (13):

$$\mathrm{Pb(II)} + e_{\mathrm{cb}}^- \rightarrow \mathrm{Pb(I)} \tag{42}$$

$$\mathrm{Pb(I)} + e_{\mathrm{cb}}^- \rightarrow \mathrm{Pb(0)} \tag{43}$$

$$4h_{\mathrm{vb}}^+/HO^\bullet + 2H_2O \rightarrow O_2 + 4H^+ \tag{13}$$

The global reaction releases protons as follows:

$$2Pb^{2+} + 2H_2O \rightarrow 2\mathrm{Pb(0)} + 4H^+ + O_2 \tag{44}$$

However, the direct reductive route by TiO_2 conduction band electrons is not feasible, considering that the one-electron reduction potential of the couple Pb(II)/Pb(I) is very negative ($E^0 = -1.0$ V, Breitenkamp et al., 1976). Accordingly, Pb shows essentially no or a very weak tendency to accept photogenerated electrons from TiO_2, as said in Section 2. This reduction pathway was not observed even using platinized TiO_2 under nitrogen. (Chenthamarakshan et al., 1999; Lawless et al., 1990; Murruni et al., 2007).

In fact, direct reduction of Pb(II) to Pb(0) by a bielectronic process has been reported under laser irradiation, where due to the high photonic frequency, accumulation of electrons may allow multielectronic injection (Rajh et al., 1996a, b; Thurnauer et al., 1997).

The reductive mechanism may take place, however, through the indirect pathway (b) (Figure 3), in the presence of hole/$HO^•$ scavengers, that is, alcohols or carboxylic acids that form powerful reducing intermediates. Methanol, ethanol, 2-propanol, 1-butanol, *t*-butanol, and citric acid and formic acid were tested successfully under nitrogen and over pure TiO_2 (Chenthamarakshan et al., 1999; Lawless et al., 1990; Murruni et al., 2007, 2008). Reactions (16) and (11) took place, where M^{n+} and $M^{(n-1)+}$ are Pb^{2+} and Pb^+, respectively, while $R^•$ are the reducing species formed from the organics. Once a small amount of Pb^+ is formed, easy reduction (E^0(Pb(I)/Pb(0)) $= +0.75$ V, Breitenkamp et al., 1976) or disproportionation (reaction (45)) takes place:

$$2\mathrm{Pb(I)} \rightarrow \mathrm{Pb(II)} + \mathrm{Pb(0)} \qquad (45)$$

Formic acid and 2-propanol promoted the highest efficiency. However, formic acid is considered a better additive because it can be used at lower concentrations, and it does not introduce toxic degradation products in the system (Murruni et al., 2008). In those cases, no lead deposits on the photocatalyst are obtained, but stains were observed on the lamp surface, composed mainly by colloidal zerovalent Pb, as demonstrated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis.

Reactions in the presence of electron donors are inhibited by oxygen or air, because of the competition of O_2 with Pb(II) for the reducing species (Kabra et al., 2007, 2008). In these conditions, the oxidative mechanism leading to Pb(IV) is not feasible, considering that the donor competes with Pb(II) for the oxidant, leading to a decrease more than to an enhancement of Pb(II) removal.

In conclusion, although an oxidative Pb(II) removal from water could be viable, leading to immobilization by formation of lead oxides, the use of hole/$HO^•$ scavengers can be considered the most effective and economic method. This approach avoids expensive platinization of the catalyst or use of ozone. In addition, reactions can be conducted under air, and lead (II) and organic scavengers (alcohols, carboxylates) may be present together in industrial wastes, with this approach having the potential of providing economical methods for the removal of the very toxic lead-related water pollutants.

6. URANIUM

Uranium occurs naturally in the III, IV, V, and VI oxidation states, but the most common natural form is the hexavalent one, as uranyl ion (UO_2^{2+}). Natural uranium is a mixture of three radionuclides, ^{234}U, ^{235}U, and ^{238}U, with higher proportion of the last one. Uranium is present in the nature in granite and other mineral deposits. In some groundwaters, levels of uranium reach 50 mg L^{-1} (Noubactep et al., 2006) and considerable concentrations of natural uranium and its radionuclide daughters (radium, polonium, and lead) can be present in well waters used for drinking purposes. In oxic waters, U is present as UO_2^{2+} or hydroxycomplexes, although it easily forms complexes with carbonates, phosphates, and sulfates. The main applications of uranium are as fuel for nuclear power plants, in catalysts, and in pigments. Pollution sources are lixiviation of deposits, emissions from the nuclear industry, combustion of coal or other fuels, and U-containing phosphate fertilizers (WHO, 2004).

In human beings, uranium can provoke nephritis, and it is considered carcinogen, causing bone cancer. These consequences are even more noxious than radiological risks (Katsoyiannis, 2007). The World Health Organization (2006) and national regulatory agencies recommend no more than 0.015 mg L^{-1} in drinking water.

Removal methods of uranium from water are ionic exchange, ultrafiltration, adsorption on granular ferric hydroxide, iron oxides (ferrihydrite, hematite, magnetite, and goethite), activated carbon or TiO_2; evaporation, biorreduction, and zerovalent iron have been also tested (Behrends and van Cappellen, 2005; Cantrell et al., 1995, Chen et al. 1999; Charlet et al., 1998; Gu et al., 1998; Kryvoruchko et al., 2004; Liger et al., 1999; Mellah et al., 2006; Naftz et al., 2002; Noubactep et al., 2006; O'Loughlin et al., 2003; Vaaramaa and Lehto, 2003).

There are very few reports in the literature concerning heterogeneous photocatalysis for uranium treatment in water. In our previous review, only one case of photocatalytic reaction on uranium salts was reported (Amadelli et al., 1991). Taking into account the standard reduction potentials, U(VI) can be photocatalytically reduced by TiO_2 conduction band electrons to U(V) and then to U(IV) ($E^0 = +0.16$ V and $+0.58$ V, respectively, Bard et al., 1985). However, more reduced U(III) and U(0) forms cannot be generated because of very negative redox potentials (Bard et al., 1985). In addition, U(V) rapidly disproportionates to U(VI) and U(IV), and its chemistry is very complex (Selbin and Ortego, 1969). For example, uranyl carbonate, which can be easily formed in natural or wastewaters, has a more negative standard redox potential than the aqueous uranyl ($E^0 = -0.69$ V, Grenthe et al., 2004), making unfeasible its reduction to the pentavalent state via conduction band electrons. Accordingly, Amadelli et al. (1991) obtained photoreduction of uranyl solutions on illuminated TiO_2 suspensions and electrodes only in the presence of hole scavengers (2-propanol, acetate, or formate), obtaining an uranium oxide of stoichiometry close to U_3O_8. Complexation of uranyl with the hole scavengers was found to play an essential role in the photoredox process, and, in addition, this indicates the predominance of pathway (b) of Figure 3. Similar results are presented in by Chen et al. (1999). No uranium deposition in the presence of air was observed; however, in the presence of EDTA and absence of oxygen, a reductive deposition took place. Further exposure to air reoxidizes and redissolves the uranium species. Platinization of TiO_2 enhanced the reaction only slightly, confirming the predominance of a reductive process. This method was proposed for recovering uranyl from aqueous solutions of dilute uranium(VI)-EDTA species, which are usually present in wastewaters of nuclear power stations.

Another work indicates the possibility of photocatalytic treatment of the wastes of nuclear fuels with separation of Np, Pu, and U (Boxall et al., 2005).

While mechanistic studies on the photocatalytic removal of uranium-related species are scarce and merit further research, additional investigation is mandatory to clarify major reaction engineering issues following this approach.

7. ARSENIC

The toxicity of the metalloid arsenic is well known. Ingestion of more than 100 mg of the element causes acute poisoning, but ingestion of small amounts during a long period causes the occurrence of chronic regional endemic hydroarsenicism (“hidroarsenicismo crónico regional endémico”, HACRE, in Spanish), which produces skin alterations and cancer (Manahan, 1990; Rajeshwar, 1995). The World Health Organization (2006) and most national regulatory agencies recommend 10 $\mu g\ L^{-1}$ as the maximum allowable arsenic concentration in drinking water.

Arsenic pollution can be originated in anthropic activities (mining, use of biocides, wood preservers). However, most pollution is natural, coming from mineral dissolution in surface or groundwaters (Bundschuh et al., 2000, 2004; Litter, 2002). Predominant As forms in natural ground and surfacewaters (neutral pH) are arsenate (As(V), as $H_2AsO_4^-$ and $HAsO_4^{2-}$) and arsenite (As(III), as neutral $H_3AsO_3^0$). The mobility of arsenical forms in waters is very dependent on pH, Eh conditions, and presence of different chemical species (Smedley et al., 2002). Consequently, removal methods must take into account these physicochemical properties. While As(V) can be easily removed by conventional ion exchange and adsorption techniques, As(III) removal is difficult due to its nonionic form in aqueous solutions at pH $<$ 9. For this reason, treatment includes generally an oxidation step with agents such as chlorine, permanganate, H_2O_2, solid MnO_2, iron chloride, and even microorganisms. Conventional treatments are oxidation–coagulation–adsorption processes on flocs of iron or aluminum hydroxides, ionic interchange, activated alumina, lime softening, and reverse electrodialysis and osmosis (Emett and Khoe, 2001; Ingallinella et al., 2003). There are emergent technologies, such as adsorption on granular iron hydroxides or TiO_2, micro- and nanofiltration, bacteriogenic iron oxides, desalinization by evaporation (see, e.g., Bang et al., 2005; Castro de Esparza, 1999; Cumbal and SenGupta, 2005; Dávila-Jiménez et al., 2008; Driehaus et al., 1998; Guan et al., 2008; Haque et al., 2008; Liu et al., 2008; Sancha, 1996; Zhang et al., 2008).

Photocatalysis of arsenical systems were not described in our previous review (Litter, 1999). However, in the meantime, together with the increasing relevance of the subject, some papers appeared in the literature. Oxidative TiO_2 heterogeneous photocatalysis through pathway (c) (Figure 3) can be a convenient option for As(III) oxidation. The global reaction at alkaline pH is indicating a pH decrease with the reaction time:

$$HO^- + H_2AsO_3^- + \tfrac{1}{2}\,O_2 \rightarrow HAsO_4^{2-} + H_2O \tag{46}$$

Monoelectronic steps with formation of As(IV) are suggested. The reduction potential of the couple As(IV)/As(III) is $E^0 \approx +2.4\,V$ (Kläning et al., 1989). Therefore, formation of As(IV) by attack of holes or $HO^\bullet$ (reaction (12)) is thermodynamically possible. However, reduction of As(III) or As(V) by TiO_2 conduction band electrons, which could lead to the less mobile elemental As, seems to be not feasible, as judged from the recent stopped-flow experiments developed by our research team (Meichtry et al., 2008a). This is in agreement with the highly negative reduction potential of the As(V)/As(IV) couple ($E^0 \approx -1.2\,V$, Kläning et al., 1989). The values for the subsequent monoelectronic couples until As(0) are not known.

Accordingly to the above conclusions, some examples of oxidative As(III) removal using TiO_2-heterogeneous photocatalysis under UV light are reported (Bissen et al., 2001; Dutta et al., 2005; Jayaweera et al., 2003; Lee and Choi, 2002; Ryu and Choi, 2004; Yang et al., 1999). In all cases, As(III) oxidation was very rapid, taking place in time scales of 10–100 min at various concentrations from the micromolar to the millimolar range. The reaction rate did not depend on pH, at least between 5 and 9. Addition of Fe(III), polyoxometalates, fluoride and humic acids, as well as platinization of TiO_2, increased the oxidation rate. The reaction was very fast in the presence of oxygen but not completely inhibited in its absence.

Mechanisms for As(III) oxidation were analyzed by several authors (Dutta et al., 2005; Ferguson et al., 2005; Ryu and Choi, 2004). In effect, the participation of As(IV) species is proposed, and the possible oxidants are $HO^{\bullet}$, trapped holes, or superoxide radicals. However, by the use of $HO^{\bullet}$ scavengers and superoxide dismutase, participation of $HO^{\bullet}$ is ruled out and superoxide radical is proposed to be the main oxidant, according to the following mechanism (Ferguson et al., 2005; Lee and Choi, 2002; Ryu and Choi, 2004):

$$\mathrm{As(III)} + \mathrm{O_2^{\bullet -}} \rightarrow \mathrm{As(IV)} \tag{47}$$

$$\mathrm{As(IV)} + \mathrm{O_2}/\mathrm{O_2^{\bullet -}}/h^{+}_{\mathrm{vb}}/\mathrm{Fe(III)} \rightarrow \mathrm{As(V)} \tag{48}$$

However, in the presence of Fe(III), the participation of $HO^{\bullet}$ in the oxidative pathway was proved (Lee and Choi, 2002).

Zhang and Itoh (2006) described a low-cost, environmentally friendly adsorbent for As(III) photocatalytic removal, formed by a mixture of TiO_2 and slag-iron oxide obtained from an incinerator of solid wastes. Arsenite is first oxidized to arsenate in a fast process, followed by a slow adsorption of arsenate, although the material shows an adsorbent capacity higher than that of pure anatase.

Ferguson and Hering (2006) reported a method to oxidize As(III) in a fixed-bed, flow-through reactor with TiO_2 immobilized on glass beads. The reactor residence time, the influent As(III) concentration, the number of TiO_2 coatings on the beads, the solution matrix, and the light source were varied to characterize the reaction and determine its feasibility for water treatment. A reactive transport model with rate constants proportional to the incident light at each bead layer fitted reasonably the experimental data. The reaction was also effective under natural sunlight.

Rapid and complete As(III) oxidation was obtained in our laboratory by TiO_2-photocatalysis and further addition of Fe(III) salts (Mateu, 2007). The influence of photocatalyst mass, pH, and As(III) concentration were analyzed. It was found that dissolved oxygen concentration was one of the most important factors for the reproducibility of the experiments. Addition of H_2O_2 increased the rate, while addition of Fe(III) at the beginning of irradiation caused complete As(III) removal from the suspension.

In a recent work (Morgada de Boggio et al., 2006, 2008, 2009), our research group studied the photocatalytic removal of As(III) and As(V) in PET plastic bottles impregnated with TiO_2 and exposed to artificial UV light for 6 h. Before or after irradiation, nongalvanized packing wire was added. After 24 h in the dark, an As removal higher than 80% was obtained. Experiments with well water samples of Las Hermanas (Tucumán Province, Argentina) resulted in As removal higher than 94%. Fostier et al. (2008) obtained similar results.

As already said, As(V) or As(III) transformation by a direct reductive pathway driven by TiO_2 conduction band electrons is not thermodynamically possible. However, complete As(V) removal in the presence of methanol under N_2 at pH 3 was successful, indicating the participation of an indirect reductive mechanism (Yang et al., 1999). As an evidence, XPS measurements revealed the presence of elemental As deposited on the photocatalyst. Then, the authors proposed a viable scheme for TiO_2-photocatalytic As removal in two stages (As(III) → As(V) → As(0)) with only changing pH and methanol addition.

Summarizing, although the photocatalytic mechanisms for As removal have been analyzed, it is felt that application of photocatalysis is still in an early stage and more research studies for the possible application are necessary. The reductive mechanism is promissory in this sense.

8. CONCLUSIONS

Based on the information reported, the following can be concluded:

(a) Heterogeneous photocatalytic treatment of metals and metalloids can be a valuable option for removal of metals and metalloids from water in some especial cases, without use of expensive reagents and with the possibility of employing costless solar light. An overview of the literature on the subject for chromium, mercury, lead, uranium, and arsenic indicates that, in general, much important fundamental and applied research is still missing.

(b) On a thermodynamical basis, three types of mechanisms can take place, depending on the nature of the ion species, all of them involving one-electron charge-transfer processes to initiate the process: (a) a direct reduction driven by conduction band electrons, (b) an indirect reduction promoted by electron donors, or (c) an oxidative process produced by holes or hydroxyl radicals.

(c) For chromium (VI), a large quantity of papers has been published since 20 years ago involving photocatalytic transformation under UV light. The usual mechanism is direct reduction by conduction band electrons, which is very slow in the absence of electron donors but can be accelerated by organic electron donors. In many cases, the organic compounds are present simultaneously with Cr(VI) in wastewaters as a result of different industrial processes. Because Cr(VI) photocatalytic reduction is not inhibited by oxygen, this represents an additional advantage for the application. Recently, some photocatalytic reactions under visible light with good yields were observed, making possible the potential use of costless solar light. Mechanistically, several questions remain unanswered, and investigations merit to be continued.

(d) For mercury (II) photocatalysis, fewer examples are reported. The reaction occurs through direct reduction driven by conduction band electrons; electron donors cause an enhancement of the reaction rate. The features of the reaction are very dependent on the conditions of the medium and the nature of the starting mercuric compound; the final products can be metallic Hg, HgO, or calomel. Interesting and encouraging results have been found in the case of the extremely toxic organomercurial species.

(e) Lead (II) is a very motivating photocatalytic system. Although removal from water can take place by an oxidative pathway, over pure TiO_2 this route is poor and can be enhanced only by platinization or use of ozone, both expensive methodologies. On the other hand, the direct reductive route is unfeasible because reduction of Pb(II) to the monovalent state is highly energetic. The indirect route, driven by reducing species formed in the presence of alcohols or carboxylates is a viable route. These species can be present together with Pb(II) in wastewaters, rendering the technology appropriate for Pb(II) removal.

(f) Photocatalytic removal of uranium salts from water was scarcely studied. Photoreduction was possible only in the presence of hole scavengers in the absence of oxygen with the formation of uranium oxides; however, a rapid reoxidation and redissolution took place after exposure to air. Comprehensive studies should, however, be performed to fully demonstrate the possible application of the technology.

(g) The reaction of arsenic species in photocatalytic systems is also interesting because both oxidative and reductive mechanisms may lead to less toxic or solid phases. Although the oxidative system has been studied rather well, the reductive pathway must be also the goal of new research in order to find a best of application of this alternative route for As removal.

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