TiO$_2$ Photocatalytic Removal of Hexavalent Chromium and Arsenic
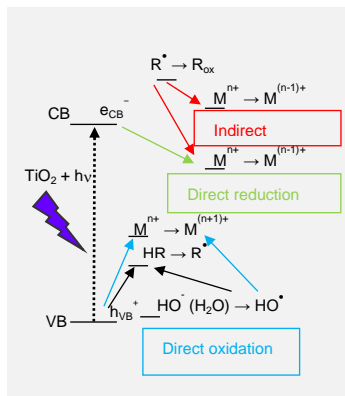
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This presentation is an overview of the work performed in our laboratories on the use of heterogeneous photocatalysis with TiO$_2$ for the treatment of hexavalent chromium and arsenic in water. In the case of hexavalent chromium, direct reductive photocatalysis and indirect reduction by intermediates coming from ethylenediaminetetraacetic acid (EDTA) or citric acid added as electron donors are the main processes governing the removal of Cr(VI) by TiO$_2$ photocatalysis. In the case of arsenic, removal can proceed by oxidation of As(III) to As(V), a very much studied process. However, reductive photocatalysis has been less studied and can take place under specific conditions, leading to the removal of As species by the formation of As(0) on the surface of the photocatalyst. While for As(III) direct reduction by photogenerated electrons is possible, As(V) reduction only proceeds in the presence of an electron donor such as methanol.

Introduction

The presence of metals or metalloids in water can produce dramatic effects on health, very significant economic losses, and perturbation of ecological and geological equilibrium as they are not easily transformed and have infinite lifetimes [1].

Conventional methods for water treatment are not completely suitable to reduce the concentration of these species in water to levels within the regulations. An alternative are Advanced Oxidative or Reductive Processes (AOPs/ARPs), being heterogeneous photocatalysis (HP) one of the most investigated process.

In HP, a broadband semiconductor (SC, the most popular commercial being TiO$_2$ P-25I, is irradiated by UV or visible light leading to the transformation of organic and inorganic pollutants in aqueous or gaseous systems (e.g., [2]). In HP, the SC is excited by absorption of photons of energy equal or higher than the bandgap, leading to the promotion of an electron from the valence band (VB) to the conduction band (CB), with creation of a hole.

$$SC + h\nu \rightarrow e_{CB}^- + h_{VB}^+ \tag{1}$$
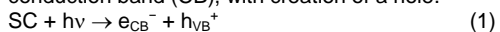
Electron acceptors (A) can be reduced by e_{CB}^-, and donor species (D) can be oxidized by h_{VB}^+.

$$A + e_{CB}^- \rightarrow A^{\bullet-} \tag{2}$$
$$h_{VB}^+ + D_{ads} \rightarrow D_{ads}^{\bullet+} \tag{3}$$

In addition, h_{VB}^+ can attack also surface hydroxyl groups or adsorbed water, generating HO$^\bullet$, a highly oxidizing species.

$$h_{VB}^+ + HO_{surf}^- \ (H_2O_{ads}) \rightarrow HO^\bullet \ (+ H^+) \tag{4}$$
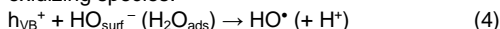
HP oxidative reactions are usually performed in the presence of O$_2$ to enhance the mineralization of organics; e_{CB}^- reduce O$_2$ with formation of Reactive Oxygen Species (ROS) such as H$_2$O$_2$, hydroperoxyl or superoxide radicals (HO$_2^\bullet$/O$_2^{\bullet-}$), and additional HO$^\bullet$.

We postulate that, in general, HP carried out under normal illumination (e.g., black light or xenon lamps) leads to monoelectronic redox processes.
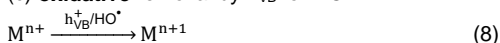
When a metal ion is present in a HP aqueous system, three types of mechanisms can take place through successive monoelectronic electron transfer steps: (a) **direct reduction** by e_{CB}^-, if the reduction potential the M^{n+}/M$^{(n-1)+}$ pair is less negative than that of e_{CB}^-:

$$M^{n+} + e_{CB}^- \rightarrow M^{(n-1)+} \tag{5}$$

(b) **indirect reduction** by reducing radicals generated from electron donors:

$$RH + HO^\bullet \rightarrow R^\bullet + H_2O \tag{6}$$
$$M^{n+} + R^\bullet \rightarrow M^{(n-1)+} + R_{ox} \tag{7}$$
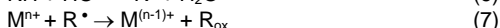
(c) **oxidative** removal by h_{VB}^+ or HO$^\bullet$:

$$M^{n+} \xrightarrow{h_{VB}^+/HO^\bullet} M^{n+1} \tag{8}$$

This presentation reflects the latest results of our laboratory on the HP treatment of hexavalent chromium and arsenic.

Chromium

Chromium is a metal with multiple industrial and technological applications, frequently found in wastewaters, mainly in the Cr(III) and Cr(VI) forms; Cr(VI) is toxic and carcinogenic while Cr(III) is considered nontoxic. The World Health Organization (WHO) [3] recommends a maximum value of 0.05 mg L^{-1} of total Cr in drinking water. The conventional treatment for removal of Cr(VI) from water involves its reduction to Cr(III) with the use of reducing chemicals, and the subsequent economical costs and generation of residues.

Cr(VI) reduction is enhanced in acid solutions, and the net reaction can be written as:

$$2 \ Cr_2O_7^{2-} + 16 \ H^+ \rightarrow 4 \ Cr^{3+} + 8 \ H_2O + 3 \ O_2 \tag{9}$$
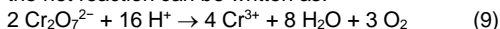
Although the process is thermodynamically feasible, Cr$_2$O$_7^{2-}$ is stable at room temperature in acidic solutions. Therefore, strategies for improving the reduction reaction should be implemented.

Numerous works have been published on the

photocatalytic reduction of Cr(VI) employing TiO_2, and other SCs [1].

From a thermodynamic point of view, e_{CB}^- have the appropriate potential to directly reduce Cr(VI), Cr(V) and Cr(IV), and the HP mechanism of Cr(VI) reduction to Cr(III) is proposed to occur through three successive monoelectronic steps [4]:

$$Cr(VI/V/IVI) \xrightarrow{3\ e_{CB}^-} Cr(VI/V/IV) \qquad (10)$$
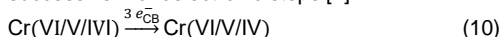
This was proven by our group through electron paramagnetic resonance spectroscopy (EPR), which allowed the identification of Cr(V) species [4], then transformed to Cr(IV) and Cr(III), the final species. Detrimental reoxidation of reduced Cr species by h_{VB}^+ or $HO^\bullet$ is however possible:

$$Cr(V/IV/III) \xrightarrow{h_{VB}^+/HO^\bullet} Cr(VI/V/IV) \qquad (11)$$
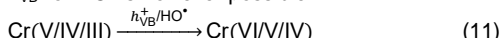
This can be avoided by addition of convenient electron donors, which reduce the recombination or or produce reducing radicals by $h_{VB}^+/HO^\bullet$ attack.
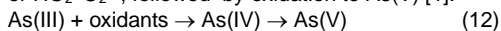
The photocatalytic Cr(VI) system is independent of the presence of O_2, explained by the formation of a charge-transfer complex, identified by an absorption band at 380 nm [5]. Due to the fast capture of electrons by Cr(VI) by the formation of this complex, no competition of O_2 by e_{CB}^- takes place [1].

Arsenic

Arsenic contamination in water can be anthropogenic (mining, biocides, etc.), but it is mainly natural, coming from dissolution of minerals in surface or groundwaters, or volcanic processes [6]. Chronic ingestion of As-containing water for prolonged times results in arsenicosis, a disease causing severe skin lesions and other syndromes, ending generally in cancer. Arsenic in water affecs several million people all over the world. The WHO recommends 10 $\mu g\ L^{-1}$ as the maximum As concentration in drinking water [3].

Although there are several conventional water treatments to remove As, new emerging techniques have to be investigated to offer low-cost solutions, especially for low-income populations [6].

Oxidative TiO_2 HP has been shown as a good alternative for As(III) oxidation, taking place by formation of As(IV) through reaction with h_{VB}^+, $HO^\bullet$, or $HO_2^\bullet/O_2^{\bullet-}$, followed by oxidation to As(V) [1]:

$$As(III) + oxidants \rightarrow As(IV) \rightarrow As(V) \qquad (12)$$

In contrast, reductive HP for As transformation has been scarcely studied. Our group [7] studied the HP reduction of As(V) in the presence of methanol; the As(III) re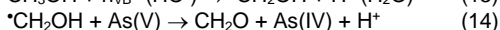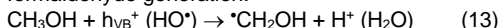duction in the presence and absence of the organic compound was also analyzed. A mechanism based on the formation of a hydroxymethyl radical produced by $h_{VB}^+/HO^\bullet$ attack to methanol, was proposed, which is effective as As(V) reductant, with formaldehyde generation:

$$CH_3OH + h_{VB}^+ (HO^\bullet) \rightarrow {}^\bullet CH_2OH + H^+ (H_2O) \qquad (13)$$
$${}^\bullet CH_2OH + As(V) \rightarrow CH_2O + As(IV) + H^+ \qquad (14)$$

CH_2O can be transformed to formic acid and finally to CO_2 with generation of $CO_2^{\bullet-}$, a strong reducing radical that can contribute to the reducing process:

$$CO_2^{\bullet-} + As(V) \rightarrow CO_2 + As(IV) \qquad (15)$$
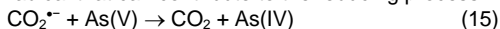
Then, As(IV) is reduced by e_{CB}^-, ${}^\bullet CH_2OH$ or $CO_2^{\bullet-}$ to As(III). Unlike to As(V), the direct HP As(III) reduction in the absence of methanol was also observed for the first time; then, monoelectronic consecutive steps would lead to the formation of As(0) and AsH_3, unambiguously identified through XPS and XANES analyses of the solid residues formed onto the TiO_2 surface after the reaction. Reduction to solid As(0) is a very convenient method for purposes of As removal from water. However, attention must be paid to formation of AsH_3, one of the most toxic forms of As.

Conclusions

✓ **Sequential one-electron processes** may be a general behavior of reduction of metals and other species using TiO_2 under irradiation.

✓ HP Cr(VI) reduction is faster under acid conditions.

✓ HP Cr(VI) reduction can be accelerated by electron donors.

✓ Molecular oxygen does not affect Cr(VI) HP reduction, at least at acid pH.

✓ A Cr(VI)-TiO_2 surface complex has been detected and is responsible for the HP reaction.

✓ Cr(VI) photocatalytic reduction is possible under visible light with a dye adsorbed onto the dye (not presented here).

✓ As(III) HP reduction is possible by e_{CB}^- attack in deoxygenated suspensions (demonstrated for the first time).

✓ No electron donors are required but, with electron donors, reaction is faster by the action of reducing radicals.

✓ As(V) can be also reduced, but only indirectly in the presence of electron donors (e.g., methanol).

✓ More studies and efforts should be made to transfer the knowledge on this promising technology into practical applications.

References

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