



## CONFERENCE EQUIPE PHOTOCHEMIE

**Mardi 16 octobre 2012 à 10h30 – Salle Lavoisier (Chimie 6)**

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### **Photocatalytic treatment of Cr(VI) by Heterogeneous Photocatalysis with TiO<sub>2</sub>**

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. The World Health Organization (WHO) recommends a limit of 0.05 mg L<sup>-1</sup> in drinking waters, value adopted by several national environmental agencies.

The preferred treatment is reduction to the less harmful, nontoxic and less mobile Cr(III) species. This process is generally performed with expensive chemical reagents; Cr(III) can be then precipitated in neutral or alkaline solutions as Cr(OH)<sub>3</sub> and removed from the aqueous phase. Reductive heterogeneous photocatalysis (RHP) with TiO<sub>2</sub> has proven to be a valid, economical, simple and environmental friendly treatment alternative for Cr(VI) removal from water, which can take profit of inexpensive UV lamps and even costless solar radiation. The process can be accelerated by the presence of synergetic organic electron donors, such as EDTA or citric acid, which can be present simultaneously with Cr(VI) in the wastewaters of industrial processes, turning the procedure even more attractive.

Cr(VI) RHP has been widely reported in the literature using semiconductors such as TiO<sub>2</sub>, ZnO, CdS, ZnS, and WO<sub>3</sub>. The list includes powders, electrodes, microparticles in slurries or supported, mixed and modified semiconductors and even nanomaterials (nanoparticles, nanotubes). From the point of view of fundamental chemistry, kinetic and mechanistic studies on the Cr(VI)/UV/TiO<sub>2</sub> made the system a very attractive and rich one, which allowed to understand several processes common to heterogeneous photocatalysis of metals and similar chemical species. The advances are related to the elucidation of mechanistic pathways, detection of intermediary species, kinetic calculations, role of dissolved oxygen, time resolved studies and potential use of visible light.

Our research group reported several studies on Cr(VI) RHP using TiO<sub>2</sub>, ZrO<sub>2</sub>, and Fe-TiO<sub>2</sub> and Pt-TiO<sub>2</sub> 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 positive enough to be reduced by TiO<sub>2</sub> conduction band electrons. Therefore, working with Cr(VI) in pure water TiO<sub>2</sub> 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) RHP over TiO<sub>2</sub> takes place by successive one electron transfer reducing steps ending in Cr(III), the stable final product. These assumptions were validated by EPR experiments in which Cr(V) species were detected. Our research group also reached to very important conclusions concerning the role of dissolved O<sub>2</sub> in the Cr(VI) RHP, which was the object of controversy for many years. However, research of our team and some other investigations showed no particular effect of O<sub>2</sub>, confirmed by studies with platinized TiO<sub>2</sub> and by spectroscopic evidences of the formation of a charge-transfer complex between Cr(VI) and TiO<sub>2</sub>, showing the

existence of a strong interaction of the metal ion with the semiconductor surface. The behavior of Cr(VI) contrasts strongly with that of other metal ions such as Hg(II), whose reduction is greatly inhibited by O<sub>2</sub>. In this sense, Cr(VI) RHP is a unique system and the fact that its photocatalytic reduction can be made in air represents an important technological advantage.

RHP of Cr(VI) has been reported to take place also under visible irradiation, in the presence of dyes such as alizarin red or hydroxoaluminiumtricarboxymonoamide phthalocyanine chelated to TiO<sub>2</sub>. The mechanism is different, involving excitation of the dye to a singlet state from which it can inject electrons to the TiO<sub>2</sub> conduction band, leaving behind a radical cation that replaces holes or HO<sup>•</sup> as usual oxidant entities. However, the reducing power of the system remains intact, making possible Cr(VI) reduction. Cr(V) formation was confirmed by EPR measurements. The inhibition 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.