

TiO₂ catalysed reduction of Cr(VI) in aqueous solutions under ultraviolet illumination

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The photoassisted reduction of Cr(VI) to Cr(III) in aqueous suspensions of TiO₂ under ultraviolet (UV) illumination has been studied by determining the amount of Cr(VI) photoreduced at different irradiation times, the mass of catalyst in suspension, the Cr(VI) initial concentration and the pH. Samples of wastes from metal-surface treatment industries have been used to test this photocatalytic procedure for Cr(VI) elimination in a real case. It has been observed that the presence in these samples of certain species such as Fe(III) and Cr(III) at low concentrations can increase significantly the yield of Cr(VI) photoreduction. It is assumed that these cations act by maintaining the pH during the photoreduction process, preventing the alkalization by hydrolysis of the solution.

1. Introduction

The photochemical degradation of pollutants using semiconducting powders as catalysts is a subject of current interest [1]. This photocatalytic method is based on the reactive properties of the electron-hole pairs generated in the semiconductor particles under illumination by light of energy greater than the semiconductor bandgap. These charge carriers can reach the particle surface and react with species in solution with suitable redox potentials [2, 3]. This method has been successfully applied to the degradation of organic pollutants such as phenols, halogenated hydrocarbons, ionic and non-ionic surfactants, organophosphorus compounds, and so on [4–8]. However, less attention has been paid to the photocatalytic elimination of inorganic contaminants. Chromium(VI) is a very toxic pollutant which is present in a great variety of industrial wastes. The conventional methods of Cr(VI) elimination from the aqueous phase are based on the reduction to Cr(III) by reaction with a strong reducing agent at acid pH, followed by Cr(III) hydroxide formation in alkaline medium precipitation by adding an appropriate electrolyte to the solution. However, among other problems, this method is not suitable for the elimination of dilute Cr(VI) solutions.

In this work the photocatalytic elimination of Cr(VI) from aqueous dilute solution using TiO₂ as catalyst under different experimental conditions was studied. Furthermore, the yield of the elimination of Cr(VI) from real samples at different initial pH is also reported, and the effects of some species present in these samples are analysed.

2. Experimental details

All chemicals were of at least reagent grade and were used as received. The titanium dioxide (Degussa P-25)

was predominantly anatase as shown by X-ray diffraction (80% anatase and 20% rutile). The BET surface area of the TiO₂ determined from nitrogen adsorption at -196°C (Accusorb 2100 E Mercuritics) was $59.1\text{ m}^2\text{ g}^{-1}$. The average particle size, determined by transmission electron microscopy, was 27 nm.

Experiments were performed in an open thermostated cylindrical Pyrex cell of volume about 40 ml. The reaction mixture inside the cell was maintained in suspension by magnetic stirring. As a light source, a 125 W high-pressure mercury vapour lamp (Philips HPK) was used. The infrared (IR) fraction of the beam was removed by the water in the double wall of the photoreactor. The intensity of the incident light measured employing a uranyl oxalate actinometer was $2.3 \times 10^{-5}\text{ E in s min}^{-1}$. The oxygen concentration in solution was measured by a Clark-type oxygen electrode (Orion 9708). The concentration of Cr(VI) in solution was determined spectrophotometrically (Philips PU 8620 spectrophotometer) using diphenylcarbazide reagent.

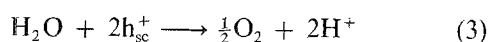
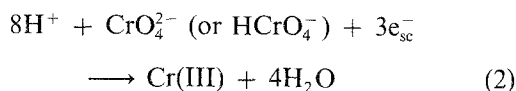
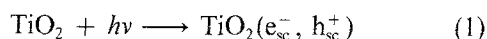
3. Results and discussion

Ultraviolet illumination of Cr(VI) solutions containing TiO₂ in suspension causes the reduction of Cr(VI) to Cr(III). For example, the irradiation for 30 min of 0.5 mM solutions of Cr(VI) in the presence of 4 g l^{-1} TiO₂ at pH 5.8 leads to a 66.7% elimination of the initial Cr(VI) and a pH increase of 1.3 units. This occurs because, under UV illumination, electron-hole pairs are created inside the semiconductor particles. After migration in the particle surface, the photogenerated electrons reduce Cr(VI) to Cr(III) and the holes oxidize water. At neutral pH the following processes takes place at the semiconductor-electrolyte

Table 1. Percentage of Cr(VI) photoreduced at different irradiation times at neutral and acid pH. Initial Cr(VI) concentration 0.5 mM; mass of TiO₂ 4 g l⁻¹; temperature 25° C

Time (min)	Cr(VI) (%)	
	pH 7.00	pH 5.76
15	35.0	48.0
20	56.1	66.7
30	73.0	87.3
45	94.0	100
60	100	-

interface [9]:



All of the experiments were performed in an open photoreactor in the presence of oxygen in solution at a mean concentration of 0.3 mM. In this case oxygen can also be reduced by the photogenerated holes to give H₂O₂, which remains adsorbed on the TiO₂ surface [10–12]:



Consequently, oxygen competes with Cr(VI) for the photogenerated TiO₂ electrons, decreasing the yield of the Cr(VI) photoreduction. If nitrogen is passed through the suspension to eliminate the oxygen, the amount of Cr(VI) photoreduced increases notably. So, by bubbling nitrogen for 30 min before illumination, all of the Cr(VI) initially in solution is photoreduced under the same experimental conditions.

The amount of Cr(VI) photoreduced depends on the irradiation time and on the mass of semiconductor in suspension. Some relevant results obtained from experiments carried out with neutral and acid suspensions are summarized in Tables 1 and 2. As can be seen, the yield of Cr(VI) photoreduction increases with increasing both the irradiation time and the mass of TiO₂ in suspension. Furthermore, the percentage of Cr(VI) photoreduced are significantly greater at

Table 2. Percentage of Cr(VI) photoreduced in the presence of different amounts of TiO₂ in neutral and acid suspensions. Initial Cr(VI) concentration 0.5 mM; irradiation time 20 min; temperature 25° C

Mass TiO ₂ (g l ⁻¹)	Cr(VI) (%)	
	pH 7.00	pH 5.76
4	56.1	66.7
8	87.6	99.2
12	100	100

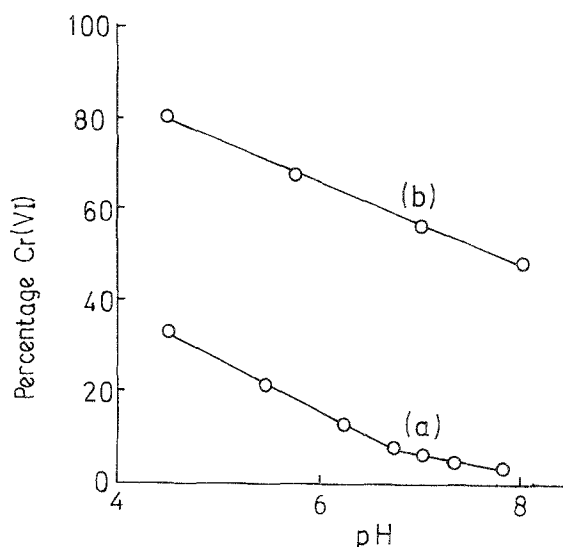


Fig. 1. Percentages of Cr(VI) adsorbed on TiO₂ particles in the dark (curve a) and reduced under UV illumination (curve b) at different initial pH. See text for experimental conditions.

acid than at neutral pH. On the other hand, we find that the amount of Cr(VI) photoreduction decreases slightly with decreasing initial Cr(VI) concentration; thus, for 0.5, 0.4 and 0.25 mM initial concentrations in the presence of 4 g l⁻¹ TiO₂ at pH 5.76, the amounts of Cr(VI) photoreduced after 20 min of illumination were 0.33, 0.31 and 0.24 mM, respectively, which correspond to yields of 66.7, 77.8 and 96.5%. This behaviour can be ascribed to the absorption of a fraction of the incident UV light by the Cr(VI) solution. In fact, a linear dependence between the absorbance of 360 nm light (main emission line of the mercury lamp) and the Cr(VI) concentration up to 1 mM has been observed.

The photoreduction process takes place by electron transfer from illuminated TiO₂ to Cr(VI) anionic species probably adsorbed at the semiconductor surface. In fact, from dark experiments it has been observed that some Cr(VI) is adsorbed on the TiO₂ particles. In curve a of Fig. 1, the percentage of Cr(VI) adsorbed at different initial pH after 25 min of mM Cr(VI) solution in the presence of TiO₂ (4 g l⁻¹) at 25° C is shown. As can be seen, the amount of Cr(VI) adsorbed decreases linearly with increasing pH. However, a change of slope at approximately pH 6.7 occurs, which coincides with the point of zero charge (pzc) of the TiO₂ used in the experiments. The pzc was determined by measuring the differences in pH before and after the semiconductor was added to water at different initial pH. Consequently, it can be assumed that for pH lower than 6.7, the positive excess charge at the TiO₂ particles due to the specific adsorption of H⁺ ions favours the approach of anionic Cr(VI) species to the semiconductor surface, whereas for higher pH excess of adsorbed OH⁻ ions has the opposite effect, leading to low levels of adsorbed Cr(VI).

These results explain the observed decrease of the amount of Cr(IV) photoreduced with increasing initial pH (see curve b of Fig. 1). On the other hand, according to Reaction 2 the redox potential of the Cr(VI)/

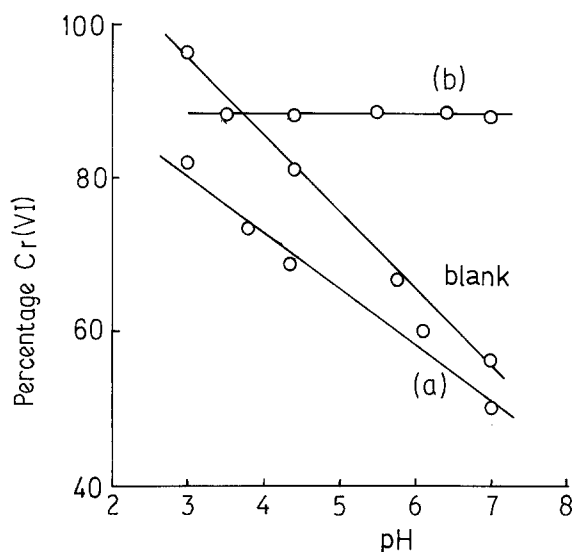


Fig. 2. Percentages of Cr(VI) photoreduced for samples A, B and blank at different initial pH. See text for experimental conditions.

Cr(III) couple shifts 157 mV per pH unit towards more anodic values, whereas the potential of the photogenerated electrons in the conduction band of TiO_2 shifts 59 mV per pH unit [13]. Another factor is the increase in the Cr(III)/Cr(VI) ratio with time, which shifts the potential negatively, thereby offsetting the pH effect. Thus, from a thermodynamic point of view, the photoreduction of Cr(VI) should take place more readily with high solution pH.

3.1. Experiments with real samples

Two samples (A and B) from wastes of the metal-surface treatment industry, kindly supplied by Tenneco SA and Henkel Iberica SA, respectively, were used to check the applicability of this photocatalytic method for Cr(VI) elimination in a real case. The chemical compositions of these two samples are shown in Table 3. Figure 2 shows the percentage of Cr(VI) photoreduced at different initial pH after 20 min of UV illumination of TiO_2 suspensions (4 g l^{-1}), which have been diluted approximately four times to make 0.5 mM solutions, and a blank sample that consists of a 0.5 mM Cr(VI) aqueous solution.

As can be seen, for sample B the yield of Cr(VI) photoreduction obtained were greater than those reported when the blank sample was used, except at

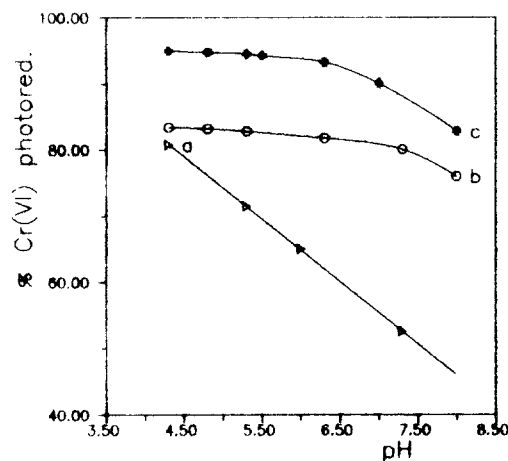


Fig. 3. Percentages of Cr(VI) photoreduced after 20 min of irradiation at different pH from initial 0.5 mM Cr(VI) initial solutions containing 4 g l^{-1} TiO_2 in suspension in the absence (curve a) and in the presence of 0.1 mM Cr(III) (curve b) and 0.1 mM Fe(III) (curve c).

high acid medium, having a constant value of around 90%. On the contrary, the percentages of Cr(VI) photoreduced for sample A were lower than those for the blank sample although a less marked pH dependence was observed.

A key parameter in the Cr(VI) photoreduction is the pH change during the process. For blank samples the shift toward more alkaline medium depends on the initial pH. So, for neutral solutions the pH change was 1.5, whereas for initial pH 3 the corresponding pH change was about 2.5 units. However, when sample B was used the pH during Cr(VI) photoreduction hardly varied over the whole range of initial pH studied.

In fact, it can be assumed that the Fe(III) and Cr(III) ions present in sample B maintain, by hydrolysis, the pH of the solution during photoreduction. This is made clear by observing the effect of adding small amounts of Fe(III) and Cr(III) to a Cr(VI) solution on the photoreduction process. Figure 3 shows the percentages of Cr(VI) photoreduced at different pH from an initial 0.5 mM Cr(VI) solution with 4 g l^{-1} TiO_2 during 20 min of illumination in the absence (curve a) and in the presence of 0.1 mM of Cr(III) (curve b) and 0.1 mM of Fe(III) (curve c). It can be seen that in the interval of precipitation of $\text{Cr}(\text{OH})_3$ (pH between 5.4 and 7.4), the yield of Cr(VI) photoreduction remains constant with respect to the initial pH, whereas outside this pH range the percentage of Cr(VI) photoreduced decreases with increasing pH, but at a lower rate than in the absence of Cr(III), due to the formation of hydroxycomplexes in solution [14]. A similar behaviour is produced in the presence of Fe(III); in this case the interval of precipitation ranges from 3.4 to 5.8 and, consequently, the yield of Cr(VI) photoreduction remains constant with respect to the initial pH in these acid media. Furthermore, the higher yields obtained for the photoreduction in the presence of Fe(III) than those reported in the presence of Cr(III) is a consequence of the greater solubility product of the Fe(III) hydroxide and greater stability of the corresponding hydroxy complexes [14]. Thus,

Table 3. Chemical composition of samples A and B

Ion	A (mM)	B (mM)
Cr(VI)	1.95	2.05
Cr(II)	—	0.71
Fe(III)	—	0.029
NO_3^-	—	3.43
SO_4^{2-}	0.75	—
Cl^-	4.82	—
PO_4^{3-}	0.01	—
CO_3^{2-}	—	0.029

the combined effect of both Cr(III) and Fe(III) is responsible for the high yields and for the constant value of the percentage of Cr(VI) photoreduced in the interval of pH from 3.5 to 7 observed when sample B was used (see Fig. 2, curve c).

The other ionic components in samples A and B have little influence on Cr(VI) photoreduction. As was shown in [15], the presence of NO₃⁻, SO₄²⁻ and Cl⁻, at least up to 10 mM, does not significantly affect the yield of the process. On the other hand, CO₃²⁻ and PO₄³⁻ ions, which act as buffer agents, tend to maintain the pH during the photoprocess increasing, slightly the efficiency of Cr(VI) photoreduction [15].

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