

Photocatalytic reduction of chromium(VI) with titania powders in a flow system. Kinetics and catalyst activity

J. Giménez^{*}, M.A. Aguado, S. Cervera-March

Departamento de Ingeniería Química, Facultad de Química, Universidad de Barcelona, C / Martí i Franquès, 1, Planta 6, 08028 Barcelona, Spain

Received 14 June 1995; accepted 5 July 1995

Abstract

The photocatalytic reduction of chromium(VI) with titania powders has been studied using a continuous flow system. The kinetics and the influence of catalyst concentration and pH on the reaction rate have been analyzed. Kinetic results show a half-order reaction at pH lower than 4, and a first-order reaction for pH above 4. Deactivation of titania was found when reduction of chromium(VI) was carried out at pH higher than 4, due to the fouling of titania caused by chromium hydroxides. A model for catalyst deactivation has been developed. It describes the performance of the catalyst at the different experimental conditions tested. Furthermore, the results obtained in the kinetic studies are supported by data from electronic microscopy and adsorption techniques.

Keywords: Chromium; Kinetics; Photocatalysis; Pollution treatment; Semiconductors

1. Introduction

Heterogeneous photocatalytic processes have been used to catalyze redox reactions from synthesis to degradation [1–5]. Ultraviolet and/or visible light have sufficient energy to overcome the band gap of semiconductors and form electron–hole (e^-/h^+) pairs [1–5]. Some semiconductor materials such as CdS, α -Fe₂O₃, TiO₂, WO₃ and ZnO have been shown to be suitable photocatalysts [6–14]. Heterogeneous catalysis and photochemistry principles are used to explain these processes.

Photocatalytic reactions are being contemplated as an alternative in waste treatment [3,4,6,15–26]. Our study is focussed on chromium(VI), which is a highly toxic pollutant. It is present in the effluents of metallurgic, galvanoplastic, textile, tanning and paint industries [27,28]. The emissions of chromates are normally treated with reducing agents and the chromium(III) formed is precipitated as hydroxide. Chromates have already been reduced with suspensions of irradiated semiconductors in discontinuous devices at laboratory level [10,12,29].

Full characterization of the chemical reaction involves the determination of the kinetics and the study of the possible mechanisms. Gener-

^{*} Corresponding author.

ally, Langmuir type kinetics describe the photocatalytic degradation of organics [30,31]. An important aspect of the photocatalytic processes is the stability of the catalyst. Knowledge of these features is essential for industrial applications. In our case, a continuous flow device has been used that, unlike the batch devices, allows the steady state conditions to be reached. Thus, the variation of catalyst activity is not masked by the unsteady state conditions intrinsic to the batch reactors.

The aim of the present work is to study the kinetics of reduction of chromium(VI) to chromium(III) over titania, to analyze the activity of the catalyst, and to discuss the possible mechanisms.

2. Experimental

2.1. Device

A continuous system was used to effect the photocatalytic reduction of chromium(VI) over titania powder aqueous suspensions. This system has been largely described in previous papers [32,33]. The system is composed of a photoreactor, recirculation loops of gas and suspension, and a continuous feed of carrier gas and chromium solution. The same titania powders were used throughout an experiment.

The photoreactor is formed by two annular chambers around a UV mercury lamp (Philips HPK 125W). It was made of three concentric pyrex tubes joined with two metacrylate pieces as top and bottom. A thermostatic solution was passed through the internal chamber, which maintained the reaction temperature at 47°C. The photocatalyst suspension was placed in the external chamber, which was connected to the in–out gas and liquid recirculation tubes. It could be considered as a tank with perfect mixing flow due to the stirring action provided by the recirculation flows. The suspension volume in the reaction chamber was 200 ml, and the total suspension volume in the system was 340

ml. The photon flow rate entering the reactor ($\lambda < 400$ nm) was $1.7 \cdot 10^{-5}$ Einstein/s, equivalent to 8 W.

The reactant suspension was recirculated by a peristaltic pump (Multifix). A double-body syringe pump (Labotron T-50) was used to provide a continuous feed of chromium(VI) solution into the recirculation loop, and to remove the same amount of treated solution, through a membrane filter. Thus, the flow rate of liquid entering and leaving the system was the same, and the steady state could be reached. A septum located in the outlet permitted sampling of the treated effluent.

Air and/or argon were fed into the system to control the partial pressure of oxygen. The inner gas was bubbled into the reaction suspension. The main part of the outgoing gas was recycled into the reactor by a compressor. The rest was driven to a gas chromatograph (Hewlett Packard 5840A) for continuous analysis.

This experimental device allows control of the feed flow rate of liquid, the feed flow rate of gas, the recycling liquid flow rate, the recycling gas flow rate, the reaction volume and the reaction temperature.

2.2. Materials: photocatalyst and chemicals

Titania P25, supplied by Degussa, was used as photocatalyst. It has the following characteristics: it is non porous, it is composed of 80% anatase and 20% rutile (XRD analysis) and its specific surface area is $59 \text{ m}^2 \cdot \text{g}^{-1}$ (nitrogen physical adsorption using Accusorb 2100E from Micromeritics). The average crystal size is 27 nm (XRD analysis). Its average agglomerate size is 216 nm, evaluated using a TEM microscope H-800-MT from Hitachi, an H-8010 Scanning System and KEVEX-800 EDX Microanalysis, and a SEM microscope JSM 84011 from JEOL.

Potassium dichromate, sulfuric acid and sodium hydroxide were of analytical grade. Chromate concentration was determined by diphenylcarbazide colorimetric method [34].

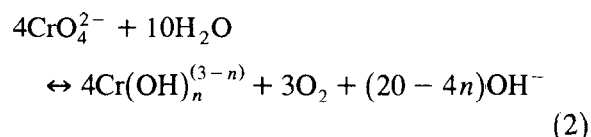
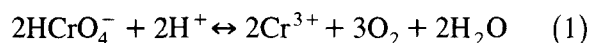
2.3. Experimental procedure

Chromate solutions were prepared in MQ-water, adjusting the pH with sulfuric acid or sodium hydroxide, and stored as pollutant solutions to be treated. The suspensions of titania in chromate solutions were prepared, adjusting the pH by adding sulfuric acid or sodium hydroxide, and sonicating for 5 minutes. The reactor and the recirculation system were filled with the chromate–titania suspension and they were purged with argon/oxygen to establish the desired oxygen partial pressure. At that moment, the lamp and the feed pump were turned on and the experiment started. Samples of treated solution were removed and stored for analysis. By varying the feed flow rate, feed pH and chromium(VI) concentration in the solution, it was possible to achieve different stationary values.

3. Results

3.1. Preliminary studies

The reduction of chromate solution by irradiating titania powders produced chromium(III) and oxygen. Equations involving different chromium species are postulated depending on the solution pH,



where n varies from 0 to 5. Chromate and hydrogen chromate are the predominant forms of chromium(VI) under the experimental conditions.

The adsorption of chromium(VI) on titania

Table 1
Experimental conditions and results

Exp.	pH _i	pH _f	c _c (g/l)	q (ml/h)	c _i · 10 ⁴ (M)	c _o · 10 ⁴ (M)	c _f · 10 ⁴ (M)
1	5.4	5.8	0.50	60	6.9	6.9	4.7
2	4.0	5.1	0.50	60	6.4	6.4	4.6
3	3.2	3.3	0.50	60	6.9	6.9	4.9
4	2.2	2.3	0.50	60	6.8	6.8	3.2
5	1.0	1.0	0.50	60	6.8	6.8	0.3
6	4.4	5.7	0.50	150	6.8	6.8	6.0
7	1.5	1.4	0.51	150	7.1	7.1	1.6
8	5.1	5.6	0.08	60	6.6	6.6	5.6
9	4.9	5.9	0.25	60	6.7	6.7	4.9
10	5.3	6.2	0.50	60	6.9	6.7	4.9
11	4.0	6.3	0.88	60	6.7	6.7	3.7
12	5.0	7.4	2.00	60	6.9	6.9	3.3
13	5.1	8.2	3.71	60	6.7	6.7	2.0
14	5.0	8.0	8.51	60	6.6	6.6	1.4
15	1.3	1.2	0.09	135	15.6	9.5	9.2
16	1.4	1.5	0.51	135	15.5	7.4	5.8
17	1.3	1.3	0.98	135	15.6	8.9	3.4
18	1.3	1.3	2.21	135	15.6	3.4	2.3
19	1.3	1.3	7.05	135	15.6	2.1	1.6
20	5.0	7.1	0.50	15	6.5	6.5	3.8
21	5.0	6.4	0.50	30	6.5	6.5	4.8
22	5.0	5.7	0.51	105	6.7	6.7	4.9
23	5.1	5.8	0.49	195	6.9	6.9	5.0

$T_R = 41.2^\circ\text{C}$, $V_R = 0.21$, $q_{RL} = 9.6$ ml/s, $q_{RG} = 40$ ml/s, $q_G = 0.8$ ml/s. The c_s values of the experiments at pH > 4.5 reported here are the lowest values attained along the experiments. The other variables were kept constant in all the experiments.

was corroborated. The adsorption isotherms, at pH 1 and 20°C, for two catalyst concentrations are shown in Fig. 1. The adsorption of chromates on titania is lower than that one found in the literature for mercury(II), platinum(IV), silver(I) or palladium(II) [35–38]. The adsorption isotherms were fitted to the square root of the chromium(VI) bulk concentration. The adsorption constants obtained were 0.015 ± 0.002 and 0.035 ± 0.003 , for 0.5 and 1 g titania per liter, respectively. Adsorption of chromate was not detected at pH above 5.

The point of zero charge of pure titania was 6.4, but it changed to 4.5 when the chromium(VI) concentration was $7 \cdot 10^{-4}$ M. Both values have been established by potentiometric measurements [39]. No reduction of chromate over titania was observed either without irradiation or without titania. A good reproducibility of experiments was observed. Oxygen did not influence the photoreduction of chromate. Liquid–gas mass transfer limitations were not detected [32,40]. The temperature had a low influence on the reaction rate [32].

3.2. Kinetics and pH effect

The operation conditions and the experimental results are summarized in Table 1.

The photocatalytic reduction of chromium(VI) was strongly dependent on pH. The highest reaction rate was obtained at the

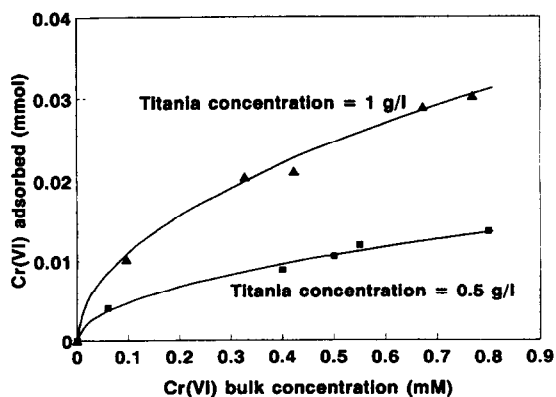


Fig. 1. Adsorption of chromates over titania at pH 1.3.

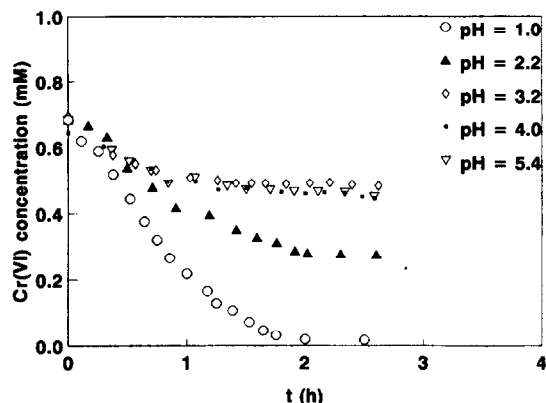


Fig. 2. Influence of pH on the reduction of chromium(VI) over titania.

lowest pH. Fig. 2 presents the variation of the chromium(VI) concentration versus time for experiments carried out at different pH (experiments 1–5 in Table 1).

As the reduction of chromates proceeded, an increase of pH was expected due to the generation of OH^- (Eqs. (1–2)). When the proton concentration was very low or very high compared with the OH^- production, the pH was not expected to vary substantially during the experiment. Considering that the chromate concentration in the reactor was never higher than 10^{-3} M, only in the experiments carried out between pH 3 and 10 did the pH vary significantly until steady state value was achieved. This pH value depended on the pH and flow rate of the feed. In general, the pH attained a constant value (± 0.1) after 30 min. The final value of pH will depend on the conversion achieved in the reaction.

Two different kinetic behaviour patterns were observed, depending on the solution pH:

(a) in the experiments carried out at pH lower than 4, the nominal concentration of chromium(VI) in the system evolved to steady state values and, consequently, stationary reaction rates were measured. As shown in Fig. 3, the variation of chromium(VI) concentration during the experiment (experiment 7 in Table 1) is represented by squares. For that pH the concentration decreased over the initial transient

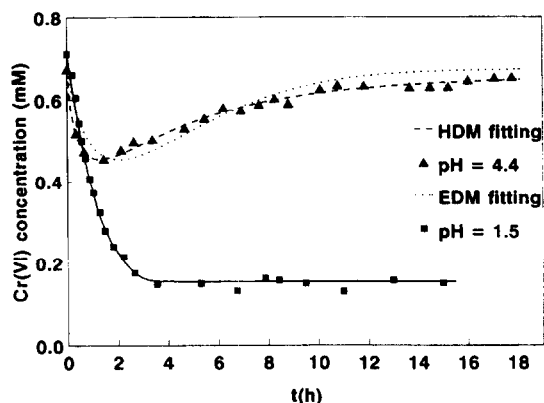


Fig. 3. Study of titania deactivation in the photoreduction of chromates in a flow system.

period (3 hours), and then reached a plateau and remained constant (the steady state was maintained for 11 hours). The stationary results obtained at different feed concentrations were fitted to a half-order kinetics for a catalyst concentration of 0.5 g/l (squares in Fig. 4) [32]. These kinetics was also proposed by other authors [13,40]. The half-order kinetics were also tested in the non-steady state part of the experiments by solving the mass balance for the system (solid line in Fig. 3). The same kinetics were also found in all the experiments at pH lower than 4 (see Table 2). Deactivation of the catalyst was not observed in these experiments, even after 15 hours.

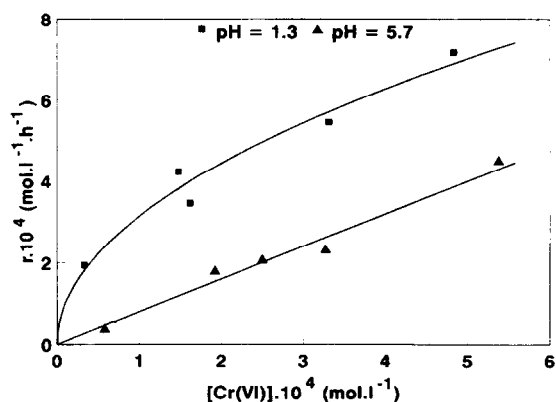


Fig. 4. Kinetics of the reduction of chromium(VI) at two different pH values.

Table 2

Variation of the half-order kinetic constant with various pH values

Exp.	pH _s	Kinetic constant (M ^{1/2} ·h ⁻¹)
3	3.3	0.0127
4	2.3	0.0290
5	1.0	0.0316

(b) When experiments were performed at pH higher than 4 the activity of the catalyst varied over time and the steady state was not reached. Triangles in Fig. 3 depict the evolution of the concentration of chromium(VI) in the system outlet over time (experiment 6, Table 1). At first, the concentration decreased to a minimum, but afterwards it rose to equal the inlet concentration. A hypothesis to explain this fact is that the deactivation of the catalyst was produced by the deposition of chromium(III) on the titania surface, because not all the stoichiometric chromium(III) was found in the outgoing flow after the reaction. Furthermore, outgoing samples were analyzed and the presence of Cr³⁺ in solution was not detected.

In addition to this preliminary evidence of catalyst deactivation, physical adsorption and electron microscopy techniques were used to confirm this hypothesis. The catalyst used in the experiments was again characterized to examine the effects of the photoreduction of chromium(VI).

No decrease of specific surface area was observed for catalysts used at pH < 4. In contrast, the surface area of titania used in experiments at pH above 4 was lower than that of blank titania and depended on the amount of chromate reduced. For example, the specific surface area of titania fell from 59 to 32 m²/g in experiment 6. This suggests that (at pH > 4) a substance (for instance, chromium hydroxide) could be deposited on titania and decrease its specific surface area and, therefore, reduce the number of active sites.

Electronic microscopy (SEM and TEM) also showed a surface modification for TiO₂. No

Table 3
Cr/Ti ratio in titania catalysts used at different experimental conditions

Exp.	pH _f	c _c (g/l)	Cr/Ti SEM	Cr/Ti TEM
6	5.7	0.50	0.05	0.11
7	1.4	0.51	0.00	–
9	5.9	0.25	0.07	0.20
13	7.0	3.71	0.02	0.06

differences were observed in the catalyst used at pH lower than 4 when compared to blank TiO₂, but some surface deposits were found at pH higher than 4.

X-ray microanalysis revealed the presence of chromium in samples of titania used in experiments carried out at pH > 4. With these analysis, it was possible to calculate the ratio of peak areas of Cr/Ti on the catalyst samples. These data are summarized in Table 3. The mapping of chromium over used titania showed that chromium was adsorbed equally on all the surface of titania.

Under these evidences, it is considered that photoreduced chromium(III) remains on the titania surface and produces deactivation. In this case, the reaction rate has to be calculated by the initial rate method. In Fig. 4 (see triangles), the reaction rate is represented in front of the chromium concentration at pH 5.7. First-order kinetics was found in these experiments. The fact that the deactivation has not been reported in the literature for the photoreduction of chromium(VI) is probably due to the use of batch reactors, in which the steady state is not reached, different variables are changing with time, and the deactivation of the catalyst may be masked [10,29]. However, the deactivation of titania by chlorine in the photocatalytic treatment of organochlorated compounds has been observed [23,41].

The experimental curves of the chromate concentration in the outgoing flow versus time at pH > 4 have been fitted to a kinetic model that includes deactivation. Hyperbolic and exponential functions have been considered as math-

ematical descriptions of the deactivation. These models have been used to describe the deactivation of catalyst by fouling or coking processes [42]. These models are based on the assumption that the kinetic constant varies as the reaction proceeds, according to a function such as:

$$k = k_0 \cdot f(x) \quad (3)$$

where k is the kinetic constant (h^{-1}), k_0 is the kinetic constant for the blank catalyst (h^{-1}), and $f(x)$ is an adimensional deactivation function. Here, the deactivation was assumed to be caused by the chromium hydroxide $\text{Cr}(\text{OH})_n^{(3-n)}$ (reaction product), which remained deposited on the titania surface. Consequently, in each deactivation model proposed there is a function of the ratio of amount of Cr^{III} produced and the amount of titania. Two models have been proposed:

$$\text{Exponential model: } f(c_p) = \exp(-\alpha \cdot c_p) \quad (4)$$

$$\text{Hyperbolic model: } f(c_p) = (1 + \alpha \cdot c_p)^{-1} \quad (5)$$

where α is the deactivation coefficient, and c_p is the ratio between the amount of Cr^{III} produced and the amount of catalyst used (g Cr/g TiO₂).

Considering a reaction rate of first order with respect to chromium(VI) concentration in the reactor and the deactivation models (Eqs. (4) and (5)), the following kinetic expressions are obtained:

$$r = k_0 \cdot \exp(-\alpha \cdot c_p) \cdot c \quad (6)$$

$$r = k_0 \cdot (1 + \alpha \cdot c_p)^{-1} \cdot c \quad (7)$$

where c is the concentration of Cr^{VI} in the reactor.

The available experimental data are in good agreement with the evolution of Cr^{VI} concentration predicted by these models. The evolution for each model can be obtained by solving the mass balance of Cr^{VI} and Cr^{III} (product) in non-steady state conditions. Considering that the reaction rate is very low compared with the recirculation flow rate, the liquid phase can be

considered as a perfect mixing flow, and the mass balances will be the following:

$$\text{Cr}^{\text{VI}}: V_T \cdot (dc/dt) = q \cdot c_1 - q \cdot c - V_R \cdot r \quad (8)$$

$$\text{Cr}^{\text{III}}: c_c \cdot V_T \cdot (dc_p/dt) = V_R \cdot r \quad (9)$$

where V_T is the total volume of the system (l), c is the concentration of Cr^{VI} in the reactor (considered the same as at the system outlet), c_c is the catalyst concentration (g/l), r is the reaction rate ($\text{mg} \cdot \text{l}^{-1} \cdot \text{h}^{-1}$), t is the reaction time, q is the feed flow rate (ml/h), c_1 is the concentration of Cr^{VI} in the feed, and V_R is the reaction volume (l).

Combining kinetic (Eqs. (6) and (7)) and mass balance expressions (Eqs. (8) and (9)), a differential equation for each kinetic model is obtained. A first integrated form of these differential equations is:

$$V_T \cdot (dc/dt) = q \cdot c_1 - q \cdot c - \frac{V_R \cdot k_0 \cdot c}{1 + \frac{\alpha \cdot V_R \cdot k_0}{V_T \cdot c_c} \cdot \int_0^t c \cdot dt} \quad (10)$$

$$V_T \cdot (dc/dt) = q \cdot c_1 - q \cdot c - \frac{V_R \cdot k_0 \cdot c}{\left(1 + \frac{2 \cdot \alpha \cdot V_R \cdot k_0}{V_T \cdot c_c} \cdot \int_0^t c \cdot dt\right)^{1/2}} \quad (11)$$

The analytical integration of these equations is not possible. The difference finite method was used to integrate them. k_0 and α values were optimized to achieve a minimum square difference between the calculated chromium(VI) concentrations and the experimental values. The best fittings were obtained for the hyperbolic deactivation (Eq. (7)). In Fig. 3, the deactivation hyperbolic (HDM) and exponential (EDM) models are depicted for experiment 6 (Table 1).

For the same kinetics, a decrease in kinetic constant is obtained when pH increases, and α varies around 65.

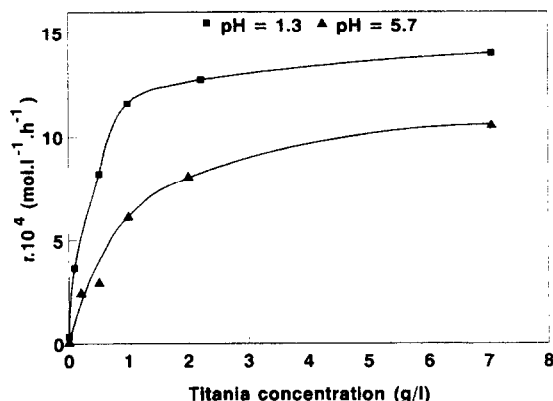


Fig. 5. Variation of the reaction rate of chromium(VI) reduction over titania at two pH values vs. catalyst concentration, for chromium concentration of $7 \cdot 10^{-4}$ M.

3.3. Influence of the catalyst concentration

In Fig. 5, the reaction rates of photoreduction of chromate at pH 1.3 and 5.7 have been plotted versus the catalyst concentration for a Cr^{VI} concentration of $3.4 \cdot 10^{-4}$ M. In the case of pH 1.3, the stationary reaction rate was represented, and in the case of pH 5.7, the initial reaction rate was plotted. In both cases, the reaction rate increases with the catalyst concentration. However, for catalyst concentrations higher than $1 \text{ g} \cdot \text{l}^{-1}$, no significant differences in the reaction rate were observed. That is, for this experimental device, a plateau is reached around a titania concentration of $1 \text{ g} \cdot \text{l}^{-1}$.

For a pH higher than 4, the kinetic parameters were calculated. The value of α is around $80 \text{ g TiO}_2/\text{g Cr}$. The variation of k_0 vs. the catalyst concentration follows the same form as the reaction rate. In addition, the results of the microanalysis of the titania used at the different catalyst concentrations are shown in Table 3. As the catalysts concentration decreases, the ratio Cr/Ti increases in samples irradiated for the same time.

4. Discussion

In the photoreduction of chromate, different chemical species could be found in the reaction

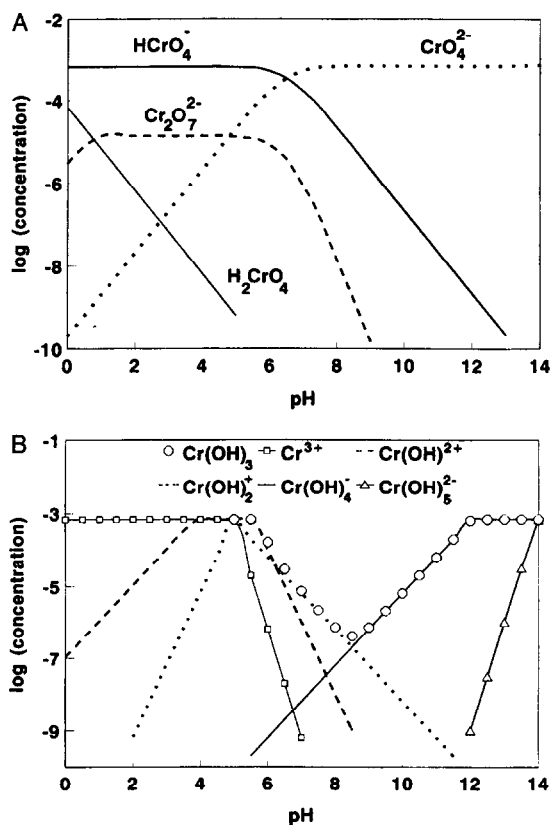


Fig. 6. Predominance diagrams in aqueous solution: (A) Cr^{VI} species and (B) Cr^{III} species, for chromium concentration of $7 \cdot 10^{-4}$ M.

medium. The predominance diagrams for chromate and Cr^{III} (Fig. 6A and 6B), evaluated from equilibrium constant data [43], show the variation of the species concentration with pH. The predominant species of Cr^{VI} are HCrO₄⁻ or CrO₄²⁻ (Fig. 6A). Chromium(III) concentrations of $3 \cdot 10^{-3}$ M are insoluble at pH between 5.5 and 12 for chromium(VI) concentrations of $6.7 \cdot 10^{-3}$ M (Fig. 6B). Species as Cr(OH)_{*n*}^(3-*n*) have been postulated to be present at pH > 4, and Cr³⁺ at pH < 4. In summary, the following species were supposed to be in the solution: chromate species (HCrO₄⁻, CrO₄²⁻), chromium(III) species (Cr³⁺, Cr(OH)²⁺, Cr(OH)₂⁺, Cr(OH)₃, Cr(OH)₄⁻, Cr(OH)₅²⁻), H₂O, H⁺, OH⁻, H₂O₂ (as intermediate species in the water oxidation) and O₂.

The chemistry of the bulk affects the chemistry of the photocatalyst surface. The point of zero charge for the titania used is at pH 6.4. However, the presence of charged compounds in solution modifies the point of zero charge to 4.5. Therefore, at pH lower than 4.5, the catalyst surface has a positive charge due to the excess of protons adsorbed, and the chromium(VI) anions can reach it more easily than at pH higher than 4.5, where the catalyst surface has a negative charge. In those systems, TiO₂ acts as a buffer due to the H⁺ or OH⁻ adsorbed depending on the bulk pH.

Adsorption isotherms of chemicals on semiconductors calculated in the dark are not quantitatively applicable under illuminated conditions, due to a process of dehydration of the titania surface and a change in the water structure of the double layer near to the titania surface [44–46]. The charge scavengers are chemisorbed on the photocatalyst surface or located in the double layer, as demonstrated by FTIR-CIR measurements for salicylic and formic acid [44,47]. However, if the scavenger is a charged species with opposite charge to that of titania surface, it will be located preferentially in the double layer.

As mentioned in the results, the pH has a great influence on the reaction rate of reduction of chromium(VI). A decrease in the pH has two combined effects. On the one hand, the Nernst redox potential for chromate reduction increases. On the other hand, the positive charge of titania particles increases. This fact could increase the adsorption of chromate by electrostatic attraction. Furthermore, the desorption of the product formed (chromium(III) species) could be favoured by electrostatic repulsion. At pH > 4.5, the catalyst surface is negatively charged. Under these conditions the adsorption of anions, such as chromate, is more difficult which is due to the electrostatic repulsion. Otherwise, in these conditions the product formed (insoluble chromium hydroxide) could be adsorbed more easily on the titania surface, decreasing the active surface of the catalyst. As found in experiment 6, the effective kinetic

Table 4
Variation of k_0 and α with variable pH values, for pH values higher than 4

Exp.	pH _i	pH _f	k_0 (h ⁻¹)	α (g TiO ₂ / g Cr)
6	4.4	5.7	2.09	61
20	5.0	7.1	0.61	66
21	5.0	6.4	0.63	46
22	5.0	5.7	1.70	87
23	5.1	5.8	3.25	69

constant decreased from 2.09 to 0 after 15 hours of experiment (Table 4). Then at the final part of the experiment, no reduction of chromate happened. At this moment, all the titania was inactive. Considering that the atomic radius of chromium(III) and hydroxyl anions are 0.63 and 1.45 Å, respectively [48], and evaluating the amount of the chromium hydroxide formed, it is possible to calculate that chromium hydroxide was supported in several layers on the titania, and after an average of 5 layers, it deactivates the titania. The adsorption of chromium(III) is favoured by the strong interaction with titanium(IV) due to the similar size and charge of those atoms (ionic radius is 0.69 and 0.68 Å, respectively [48]) [49–51]. Chromium(III) does not absorb light in the UV spectrum (Fig. 7). Then the chromium(III) adsorbed on titania does not influence the amount of light reaching the catalyst (Fig. 7), and its only effect is to block the e⁻/h⁺ transfer in the process.

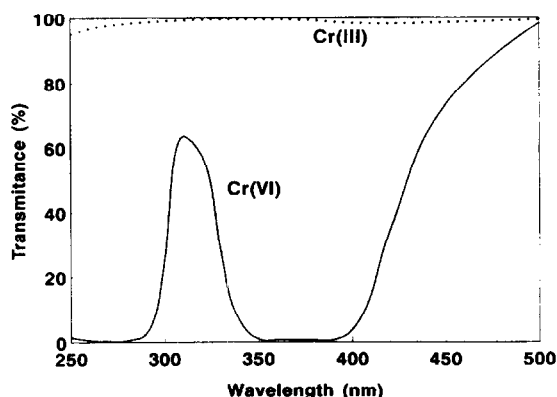


Fig. 7. Light absorption spectra for chromate solution and chromium(III) solution (chromium concentration of $7 \cdot 10^{-4}$ M).

From the results, it was found that oxygen, which could be photoadsorbed on titania [55,56], does not influence the photocatalytic reduction of chromium(VI). This behaviour represents a difference with respect to that observed in the photocatalytic treatment of other metals such as mercury [35,56]. It is true that oxygen competes with metals for the e⁻ trapping on the catalyst surface. However, the reduced form of oxygen can react with chromate species and be reoxidized to oxygen [57], and chromates become Cr³⁺ species. Thus, oxygen only plays the role of an intermediate in the electron transfer, but not of a competitor as it does in the case of other metals like mercury [35].

Several explanations for the kinetic order will be discussed. Heterogeneous kinetics models (Langmuir–Hinshelwood–Hougen–Watson, LHHW) have been applied to photocatalytic processes [24,52–54,62]. These models applied to chromium(VI) reduction did not explain at first the apparent half-order for the nominal concentration of chromium(VI). Additional considerations had to be made [63,64].

Chromates absorb light in the 300–400 nm range (see Fig. 7). Then the amount of light reaching the photocatalyst depends on the amount of chromate in solution. The absorption of light by the solution increases with the chromium concentration, and the expected reaction rate decreases, since less radiation reaches the catalyst. The amount of light absorbed also depends on the catalyst concentration. It may be supposed that those factors can be responsible of this half-order. However, it is reported that the same reaction on titania membranes irradiated from the back leads to a half-order kinetics, and in that case no preliminary absorption of light by chromates is present [40].

Half-order can also be explained by dissociative adsorption, as in the case of methanol on Pt/TiO₂ [61]. The reaction rate varies with the square root of methanol concentration, and this behaviour is explained by the dissociation of alcohol on the basic sites of titania [65]. In the case of inorganic compounds, ions are formed

in solution and the adsorption isotherm has a specific expression. Compared with the adsorption of uncharged molecules, the adsorption of small ions is strong and determined by electric interactions. The ion adsorption is influenced by other ions next to them [66]. Various types of ion adsorption can be distinguished: (a) ions chemically bound to the surface and contributing to the surface charge, (b) ions not chemically bound to the surface but contributing to the surface excess. The shapes of the adsorption isotherms are strongly dependent on the part of the double layer where the ion is located (surface, Stern layer or diffuse layer). Generally, the adsorption isotherm process in the diffuse layer depends on the square-root of the ion concentration in the bulk. Assuming this theory, when the concentration of chromium(VI) is very low, its concentration in the catalyst interphase is proportional to the square root of the bulk concentration. If the reaction takes place in the diffuse layer, the rate will be proportional to the concentration in the diffuse layer and, consequently, to the square root of the bulk concentration. This is the case when the charge of the particle is positive, and the amount of chromate in the interphase is larger than in the bulk. Then, the reaction rate will be controlled by the reaction between the chromium(VI) species in the double layer and one of the reaction intermediates, for instance, hydrogen peroxide or $\text{OH}\cdot$ radical [46,58–61]. Thus, these facts could explain the half-order kinetics observed at low pH.

When the pH increases, the charge of the catalyst particles becomes negative. Thus, the chromium(VI) species have the same charge as the catalyst particles. Consequently, the concentration of chromium(VI) anions in the double layer decreases and becomes smaller than in the bulk. As a consequence, the reaction rate decreases. Under these conditions, the adsorption isotherm becomes linear and the kinetics order changes, giving an explanation for the order one kinetics observed at pH higher than 4.

The shape of the curves representing the

influence of the catalyst concentration on the reaction rate has been discussed in detail elsewhere for this type of annular photoreactor with particles in suspension [24,67,68]. Light absorption and scattering phenomena were invoked to explain that performance. The concentration of about $1 \text{ g}\cdot\text{l}^{-1}$, where a plateau for the rate is reached, is dependent on the reactor geometry, light source, catalyst nature and sacrificial substrates (Fig. 5).

5. Conclusions

Titania is able to catalyze the reduction of Cr^{VI} to Cr^{III} in the presence of UV-light. Good yields are obtained at pH lower than 2, and the activity of the catalyst remains constant. Under these conditions, the kinetic order is 1/2 with respect to the Cr^{VI} concentration. This apparent kinetic order can be explained considering the ion adsorption isotherms of chromate ions over charged surfaces.

At pH higher than 4, the kinetics changes to order one and a deactivation of the catalyst appears as the reaction proceeds. Experimental evidences support the hypothesis that this deactivation is due to the $\text{Cr}(\text{OH})_n^{(3-n)}$ produced in the reaction, which remains deposited on the titania surface. First-order kinetics combined with a hyperbolic model for the catalyst deactivation can describe the process.

Acknowledgements

The authors are grateful to the 'Comisión Interministerial de Ciencia y Tecnología (CICYT)' (projects MAT89-0682-C03-03 and AMB92-1021-C02-01) and to 'Plataforma Solar de Almería-IER-CIEMAT' (project 65/90) for funds received to carry out this work. The authors are also grateful to the Electron Microscopy Service of the University of Barcelona for the valuable collaboration in the characterization of the semiconductor photocatalyst.

References

- [1] M. Grätzel, *Energy Resources through Photochemistry and Catalysis*, Academic Press, New York, 1983.
- [2] M. Schiavello, *Photoelectrochemistry, Photocatalysis and Photoreactor. Fundamentals and Developments*, Nato Asi Series, Series C: Mathematical and Physical Sciences, Vol. 146, Reidel, Dordrecht, 1985.
- [3] M. Schiavello, *Photocatalysis and Environment. Trends and Applications*, Nato Asi Series, Series C: Mathematical and Physical Sciences, Vol. 237, Kluwer Academic Publishers, Dordrecht, 1988.
- [4] N. Serpone, E. Borgarello and E. Pelizzetti, in M. Schiavello (Editor), *Photocatalysis and Environment. Trends and Applications*, NATO ASI Series, Series C: Mathematical and Physical Sciences, Vol. 237, Kluwer Academic Publishers, Dordrecht, 1988, pp. 527–565.
- [5] N. Serpone and E. Pelizzetti, *Photocatalysis. Fundamentals and Applications*, Wiley, New York, 1989.
- [6] M.A. Aguado and M.A. Anderson, *Solar Energy Mater. Solar Cells*, 28 (1993) 345.
- [7] M. Ashokkumar and P. Maruthamathu, *J. Photochem. Photobiol. A: Chem.*, 49 (1989) 249.
- [8] V. Augugliaro, L. Palmisano, A. Sclafani, C. Minero and E. Pelizzetti, *Toxicol. Environ. Chem.*, 16 (1988) 89.
- [9] L. Borrell, S. Cervera-March, J. Giménez, R. Simarro and J.M. Andújar, *Solar Energy Mater. Solar Cells*, 25 (1992) 25.
- [10] J. Doménech and J. Muñoz, *J. Chem. Res. (S)*, (1987) 106.
- [11] J. Kiwi, *J. Phys. Chem.*, 89(12) (1985) 2437.
- [12] H. Reiche, W.W. Dunn and A.J. Bard, *J. Phys. Chem.*, 83(17) (1979) 2248.
- [13] H. Yoneyama, Y. Yamashita and H. Tamura, *Nature*, 282(20/27) (1979) 817.
- [14] H. Yoneyama, Y. Ohkubo and H. Tamura, *Bull. Chem. Soc. Jpn.*, 54 (1981) 404.
- [15] M. Barbeni, E. Pramauro, E. Pelizzetti, E. Borgarello and N. Serpone, *Chemosphere*, 14 (1985) 195.
- [16] J.M. Herrman, M.N. Mozzanega and P. Pichat, *J. Photochem.*, 22 (1983) 333.
- [17] H. Hidaka, H. Kubota, M. Grätzel, N. Serpone and E. Pelizzetti, *Nouv. J. Chim.*, 9 (1985) 67.
- [18] C. Hsiao-Y., C.L. Lee and D.F. Ollis, *J. Catal.*, 83 (1983) 418.
- [19] R.W. Matthews, *Water Res.*, 20 (1986) 569.
- [20] R.W. Matthews, *J. Phys. Chem.*, 91 (1987) 3328.
- [21] D.F. Ollis, E. Pellizzetti and N. Serpone, in N. Serpone and E. Pellizzetti (Editors), *Photocatalysis. Fundamentals and Application*, Wiley, New York, 1989, p. 626.
- [22] A.L. Pruden and D.F. Ollis, *Environ. Sci. Technol.*, 17 (1983) 628.
- [23] A.L. Pruden and D.F. Ollis, *J. Catal.*, 82 (1983) 404.
- [24] J. Sabaté, S. Cervera-March, R. Simarro and J. Giménez, *Chem. Eng. Sci.*, 45(10) (1990) 3089.
- [25] J. Sabaté, S. Cervera-March, R. Simarro and J. Giménez, *Int. J. Hydrogen Energy*, 15(2) (1990) 115.
- [26] D.F. Ollis, *Environ. Sci. Technol.*, 19 (1985) 480.
- [27] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd edn., Vol. 6, John Wiley and Sons, New York, 1979.
- [28] N.L. Nemerow, in H. Blume (Editor), *Aguas residuales industriales. Teoría, Aplicaciones y Tratamiento*, Madrid, 1977.
- [29] J. Doménech and J. Muñoz, *Electrochim. Acta*, 32(9) (1987) 1383.
- [30] C.S. Turchi and D.F. Ollis, *J. Catal.*, 122 (1990) 178.
- [31] J. Cunningham and S. Srijaranai, *J. Photochem. Photobiol. A: Chem.*, 43 (1988) 329.
- [32] M.A. Aguado, J. Giménez and S. Cervera-March, *Chem. Eng. Commun.*, 104 (1991) 71.
- [33] M.A. Aguado, J. Giménez, R. Simarro and S. Cervera-March, *Solar Energy*, 49(1) (1992) 47.
- [34] Standard methods for the examination of water and wastewater, APHA-AWWA-WPCF, 14th edn., 1975.
- [35] M.A. Aguado, S. Cervera-March and J. Giménez, *Chem. Eng. Sci.*, 50 (1995) 1561.
- [36] J.M. Herrman, J. Disdier and P. Pichat, *J. Phys. Chem.*, 90 (1986) 6028.
- [37] J.M. Herrman, J. Disdier and P. Pichat, *J. Catal.*, 113 (1988) 72.
- [38] K.H. Stadler and H.P. Boehm, *Proc. 8th Int. Congr. Catalysis*, Vol. IV, Verlag Chemie, Weinheim, West Germany, 1984, p. 487.
- [39] P. Pichat, J.M. Herrman, J. Disdier, H. Courbon and M.N. Mozzanega, *Nouv. J. Chim.*, 5 (1981) 627.
- [40] J. Sabaté, M.A. Anderson, M.A. Aguado, J. Giménez, S. Cervera-March and Ch.G. Hill, Jr., *J. Mol. Catal.*, 71 (1992) 57.
- [41] D.F. Ollis, C.Y. Hsiao, L. Budiman and C.L. Lee, *J. Catal.*, 88 (1984) 89.
- [42] R. Hughes, *Deactivation of Catalysts*, Academic Press, New York, 1984.
- [43] O. Budevsky, *Foundations of Chemical Analysis*, Ellis Horwood Limited, Rochester, 1979.
- [44] M.A. Aguado, M.A. Anderson, M.I. Tejedor, Ch.G. Hill, Jr., *J. Photochem. Photobiol. A: Chem.*, in press.
- [45] D.N. Misra, *Nature (Phys. Sci.)*, 240 (1972) 14.
- [46] G. Munuera, V. Rives-Arnau and A. Saucedo, *J. Chem. Soc. Faraday Trans. 1*, 75 (1979) 736.
- [47] S. Tunesi and M.A. Anderson, *J. Phys. Chem.*, 95(8) (1991), 3399.
- [48] J.G. Stack and H. Wallace, *Chemistry Data*, S.I. Book Edition, John Murray, London, 1975.
- [49] R.G. Pearson, *J. Am. Chem. Soc.*, 85 (1963) 3533.
- [50] R.G. Pearson, *Science*, 151 (1966) 172.
- [51] R.G. Pearson, *J. Chem. Educ.*, 45 (1968) 581.
- [52] R.W. Matthews, *J. Phys. Chem.*, 92 (1988) 6853.
- [53] C.S. Turchi and D.F. Ollis, *J. Phys. Chem.*, 92 (1988) 6852.
- [54] D.T. Schwartz, M.S. Thesis, University of California, Davis, 1985.
- [55] A. Gonzalez-Elipe, G. Munuera and J. Soria, *J. Chem. Soc. Faraday Trans. 1*, 75 (1979) 748.
- [56] A. Lozano, J. García, X. Doménech and J. Casado, *J. Photochem. Photobiol. A: Chem.*, 69 (1992) 237.
- [57] A.H. Boonstra and A.H.A. Mutsaers, *J. Phys. Chem.*, 79 (1975) 1694.
- [58] G. Czapski and J. Israel, *J. Chem.*, 7 (1969) 375.
- [59] P. Meriaudeau and J.C. Vadrine, *J. Chem. Soc. Faraday 1*, 72 (1976) 472.

- [60] V.V. Nikisha, B.N. Shelimov and V.B. Kazanskii, *Kinet. Katal.*, 15 (1974) 676.
- [61] H.G. Völz, J. Kämpf and H.G. Fitzky, *Farbe Lack*, 78 (1972) 1037.
- [62] J. Torres and S. Cervera-March, *Chem. Eng. Sci.*, 47(15/16) (1992) 3857.
- [63] R.M. Noyes, *J. Am. Chem. Soc.*, 78 (1956) 5486.
- [64] J. Cunningham and S. Srijaranai, *J. Photochem. Photobiol. A: Chem.*, 58 (1991) 361.
- [65] I. Carrizoza, G. Munuera and S. Castañar, *J. Catal.*, 49 (1977) 265.
- [66] J. Lyklema, in G.D. Parffit and C.H. Rochester (Editors), *Adsorption from Solutions at the Solid/Liquid Interface*, Academic Press, New York, 1983.
- [67] J.C. Escudero, R. Simarro, S. Cervera-March and J. Giménez, *Chem. Eng. Sci.*, 44(3) (1989) 583.
- [68] S. Esplugas, S. Cervera-March and R. Simarro, *Chem. Eng. Commun.*, 51 (1987) 221.