Journal of Photochemistry and Photobiology A: Chemistry 147 (2002) 71–76

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Simultaneous photocatalytic Cr(VI) reduction and dye oxidation in a TiO_2 slurry reactor

S.G. Schrank, H.J. José, R.F.P.M. Moreira*

Department of Chemical and Food Engineering, Federal University of Santa Catarina, Campus Universitário, Trindade, 88040-670 Florianópolis, SC, Brazil

Received 1 November 2001; accepted 6 November 2001

Abstract

The semiconductor photocatalytic reduction is a relatively new technique for the removal of dissolved metal ions, such as Cr(VI) and organic compounds in wastewater. Many studies concern only the catalytic activity of TiO_2 with single substrates. However, for practical applications it is necessary to evaluate the photocatalytic simultaneous reduction and oxidation reactions. In this paper, we report the results of a study on the simultaneous Cr(VI) reduction and the Luranzol S Kong dye (from the tannery industry) oxidation by photocatalysis. The experiments were performed in a UV reactor system with a lamp of 150 W, using TiO_2 as a catalyst. We evaluated the effect of pH and concentration of pollutants on the kinetics of the reactions. Isolated tests showed that both Cr(VI) and Luranzol S Kong are degraded in acidic pH, according to the Langmuir–Hinshelwood kinetic model. In neutral pH, the Cr(VI) is not reduced, but this might be explained by the fact that Cr(VI) is not adsorbed on TiO_2 surface. The dye is almost completely degraded by both acidic and neutral pH. Under UV irradiation, photo-induced Cr(VI) reduction is observed in both Cr(VI)–TiO_2 and dye–Cr(VI)–TiO_2, and dye oxidation is observed in both dye–TiO_2 and dye–Cr(VI)–TiO_2. The concentration of Cr(VI) and dye, and the pH are the main parameters influencing both reactions. In the simultaneous reduction–oxidation process, the reduction of Cr(VI) proceeds quicker than it does in the single process, showing synergism between the oxidation and reduction reactions.

Keywords: Photocatalysis; Dye; Cr(VI); Photooxidation; Photoreduction

1. Introduction

Metal ions have infinite lifetimes, and build up their concentrations in food chains to toxic levels. As a result, in today's highly industrialized society, we are living in an environment with a multitude of potentially harmful toxic metal ions [1].

The presence of heavy metals in aquatic bodies has been known to cause pollution problems. The major source of heavy metals is the improper discharge of various industrial wastewater [2]. Precipitation, activated carbon adsorption, ion exchange, and membrane separation are common methods currently adopted for the disposal or recovery of metal ions in wastewater. All these methods have their own advantages and disadvantages. The source of the wastewater and the concentration level of the contaminants are the two main factors that influence the efficiencies of the above methods [1–3].

Chromium occurs in two common oxidation states in nature, Cr(III) and Cr(VI). Hexavalent chromium is toxic and carcinogenic. On the other hand, Cr(III) is readily precipitated or sorbed on a variety of inorganic and organic substrates at neutral or alkaline pH. The environmental importance of this process derives from the variety of sources which generate Cr(VI) in effluent streams: chrome plating, electronic, metallurgical, timber and leather tanning industries [3–8].

These effluents must be treated and the Cr(VI) concentration reduced because its presence affects the nitrification process of aquatic environments and produces a substantial increase of the organic matter present in them. The maximum concentration of Cr(VI) allowed varies from country to country. This limit is usually established at about 0.05 ppm [9].

Advanced oxidation processes (AOP) have demonstrated their usefulness in the purification of drinking water and cleaning of industrial wastewater, achieving a total or partial mineralization of organic pollutants [10].

This photocatalytic method is based on the reactive properties of electron–hole pairs generated in the semiconductor particles under illumination by light of energy greater than the semiconductor bandgap [11,12].

---

* Corresponding author

E-mail address: regina@enq.ufsc.br (R.F.P.M. Moreira).

1010-6030/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(01)00626-8

Many studies on photocatalytic decontamination concern only the single component systems. There exist few studies that have been carried out concerning decontamination of the complex systems which are the actual situations of the environmental pollution.

In the present paper, we studied the adsorption and photocatalytic reactions using Luranzol S Kong (a dye extensively used in tannery industries) and hexavalent chromium ($K_2Cr_2O_7$) in both single and mixed systems.

2. Experimental

2.1. Device

A bath reactor system (Heraeus 400 ml) was used to perform the photocatalytic reduction of Cr(VI) and oxidation of black dye over titania powder aqueous suspensions. The total suspension volume in the system was 300 ml. The reaction mixture inside the reactor was maintained in suspension by means of a magnetic stirrer. A 150 W medium pressure mercury lamp, surrounded by a quartz thimble, was used as a UV source and the reactor was equipped with a water-jacket to maintain constant temperature (28 °C).

2.2. Materials: photocatalyst and chemicals

Titania P25, supplied by Degussa (80% anatase and 20% rutile; specific area 59 m^2/g) was used as a photocatalyst.

Potassium dichromate, chloridric acid and sodium hydroxide were of analytical grade. The dichromate concentration was determined by the diphenylcarbazide colorimetric method [13]. The total chromium concentration was determined by atomic absorption spectrometry (AAS).

Luranzol S Kong dye was supplied by a tannery firm and was used as received. The dye concentration in aqueous solution was determined using a Hach Spectrophotometer at 610 nm.

2.3. Experimental procedure

The dichromate solutions and black dye solution were prepared in distilled water, adjusting the pH with chloridric acid or sodium hydroxide and monitoring by pHmeter Quimis Q 400A. The Cr(VI) solution and dye solution were added to the reactor along with a predetermined amount of TiO_2.

After the pre-warmed light source was turned on, aliquots of the reaction solution were withdrawn periodically. The aqueous samples were centrifuged (Centrifugal Presvac DCS—16 RV) and filtered using a 0.22 μm membrane filter to remove TiO_2 particles.

2.4. Adsorption tests

The adsorption tests were performed using solutions of Cr(VI) and dye at different pH, in single system or mixed system. The tests were performed in a shaker at 28 °C for 4 h. Five different masses of photocatalyst, in the range 0.5–6 g/l, were contacted with 200 ml of solution containing Cr(VI) or the black dye, and the pH was adjusted by adding HCl or NaOH.

After 4 h, the dye and Cr(VI) concentrations were measured. The amount of Cr(VI) adsorbed was determined by mass balance and the Cr(III) was measured from the difference between the quantities of total chromium and Cr(VI).

3. Results and discussion

3.1. Adsorption equilibrium of Cr(VI) and dye in single system

Previous tests showed that no observable reduction of Cr(VI) or oxidation of dye over TiO_2 was observed either without irradiation or without catalyst.

The adsorption isotherms of Cr(VI), at pH 2.5 and 28 °C, is shown in Fig. 1. No adsorption was observed at pH 7.0. This result agrees with Giménez et al. [12], who demonstrated that no adsorption was detected at pH above 5.0. This fact can be explained because the negative charge on the photocatalyst surface at pH 7.0 repels the dichromate ion.

The equilibrium isotherm for the adsorption of Cr(VI) at pH 2.5 is linear and the equilibrium constant is given in Table 1. The dye is also more adsorbed at pH 2.5 than at pH 7.0 as shown in Fig. 1. The equilibrium constant (Table 1) is higher than that for Cr(VI), indicating the high affinity of the dye with the TiO_2 surface.

3.2. Photocatalytic reactions

3.2.1. Reactions with single substrate: Cr(VI)

Photocatalytic reduction of Cr(VI) has been studied by several researchers using a semiconductor catalyst such as CdS, WO or TiO_2 [1,3,4,9,14]. The general results are that Cr(VI) can be easily reduced photocatalytically under UV irradiation [4].

The temporal concentration variation of Cr(VI) by UV/TiO_2 photocatalytic reduction for solution pH 2.5 is shown in Fig. 2. No photoreduction was detected at pH 7.0, probably because no adsorption normally occurs in this condition.

In each test, total chromium $(\mathrm{Cr(III)} + \mathrm{Cr(VI)})$ was measured by AAS and it was observed that the total chromium

Table 1
Equilibrium constant for adsorption of Cr(VI) and dye at pH 2.5 and 7.0, in single and mixed system

	Equilibrium constant, K_a (l/g)	
	pH 2.5	pH 7.0
Cr(VI)	0.040 ± 0.013	Nil
Dye	1.951 ± 0.193	0.141 ± 0.035

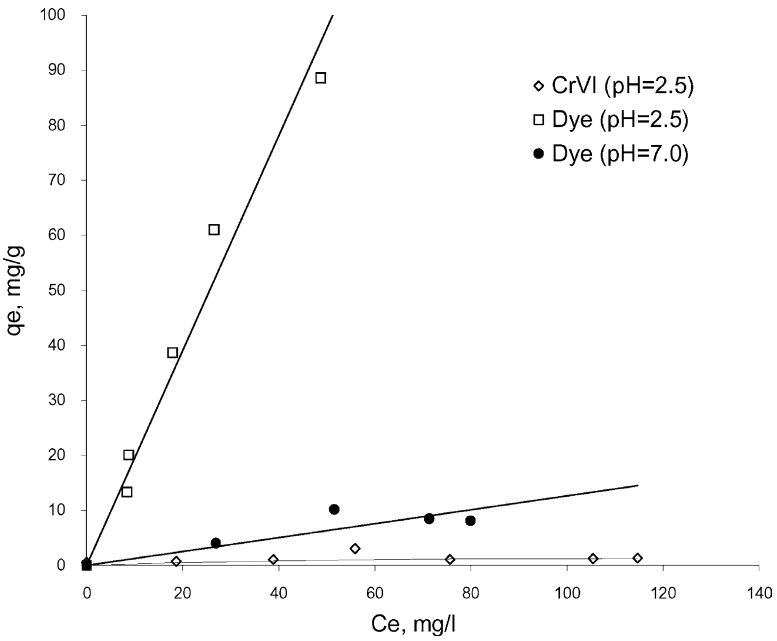

Fig. 1. Equilibrium isotherms of Cr(VI) and dye at pH 2.5 and 7.0.

content remained constant as the reaction proceed. This fact indicates that there is no precipitation of Cr(III) at pH 2.5 and no irreversible adsorption on the catalyst.

Kinetic studies showed that Cr(VI) reduction under UV irradiation is according to the Langmuir–Hinshelwood equation (1) [2,4]

$$-r = -\frac{dC}{dt} = \frac{k_r K_e C}{1 + K_e C} \quad (1)$$

where K_e is the apparent equilibrium of adsorption constant and k_r the apparent reaction rate constant. Cassano et al. [15] have demonstrated that this kinetics model is an simplified model because k_r incorporates the local volumetric rate of radiation energy absorption and K_e incorporates several kinetic rate constants. Using the initial rate method, the constants of Eq. (1) were evaluated (Table 2).

Table 2
Kinetics constant and apparent equilibrium constant for Cr(VI) photoreduction in single system using TiO_2-P25 Degussa at pH 2.5

pH	UV lamp (W)	k_r (mg/l min)	K_e (l/mg)	Reference
2.5	150	0.398	9.60×10^{-2}	This work
2.5	250	1.196	6.64×10^{-2}	Lin et al. [4]
3.0	15	0.072	5.97×10^{-2}	Ku and Jung [2]

It can be observed that there is no concordance between the equilibrium constants K_e determined in reactional

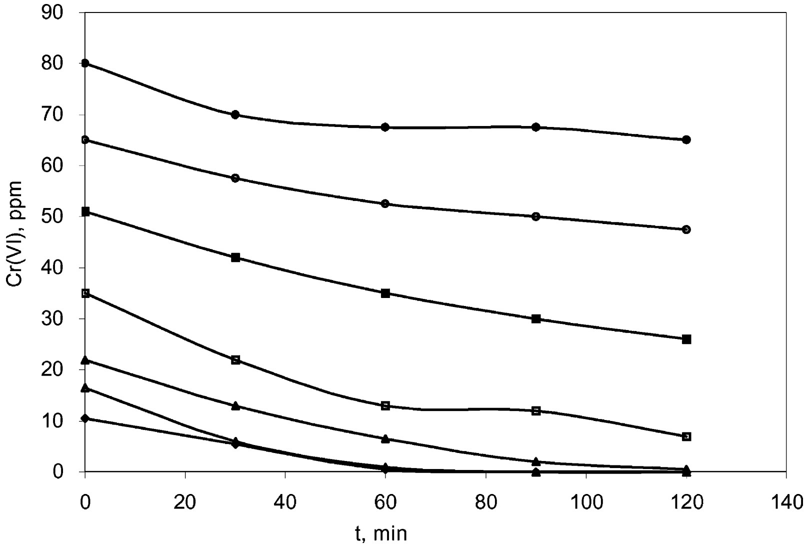

Fig. 2. Photocatalytic reduction of Cr(VI) on TiO_2 with different Cr(VI) initial concentrations under UV irradiation at pH 2.5, $[TiO_2] = 1$ g/l.

system (Table 2) and that determined in the adsorption system (Table 1). However, these values are in the same order of magnitude indicating that the reaction occurs mainly on the surface of the solid.

The k_r value is dependent on the geometry of the reactor and UV light source [15,16]. We should note that the k_r value found by Lin et al. [4], using a more powerful UV lamp, is higher than that found in this work. The same conclusion may be reached by comparing results found by Ku and Jung [2].

The mechanism of photocatalytic Cr(VI) reduction is not very clear, but is fairly well described by the capture of photo-excited conduction band electrons followed by reduction, according to Eqs. (2) and (3), depending on the pH [3,4].

In acidic medium

$$Cr_2O_7{}^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad (2)$$

For alkaline solutions

$$Cr_2O_7{}^{2-} + 14H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^- \qquad (3)$$

In the absence of reducing agents, H_2O accepts the valence band holes, and the following photocatalytic redox cycle takes place (Eq. (4)).

$$2H_2O + 2h^+ \rightarrow H_2O_2 + 2H^+ \qquad (4)$$

3.2.2. Reactions with single substrate: dye

Luranzol S Kong dye is extensively used in the tannery industry. For practical applications, the photocatalytic reactions among organic compounds in the presence of Cr(VI) should be studied.

Table 3
Langmuir–Hinshelwood parameters for oxidation of Luranzol S Kong dye in single system

pH	k_r (mg/l min)	K_e (l/mg)
2.5	26.25	1.04×10^{-3}
7.0	2.05	15.6×10^{-3}

The photooxidation of Luranzol S Kong, in the absence of Cr(VI), was studied at pH 2.5 and 7.0 (Fig. 3). We may observe that, for concentrations of dye lower than 25 ppm, at both pH 2.5 and 7.0, the degradation of dye follows a pseudo-first order kinetic.

At pH 2.5, the kinetics of degradation is pseudo-first order. However, at pH 7.0, a Langmuir–Hinshelwood mechanism could be fitted to the experimental data. The kinetic constants are summarized in Table 3.

It is worth noting that the adsorption constant for both pH 2.5 and 7.0, obtained from the dark adsorption isotherm (Table 1), is significantly different from that determined from the Langmuir–Hinshelwood equation (Table 3) in the photocatalytic process. Similar results have been reported by other researchers [17–20]. The photoadsorption and the fast photoreaction of substrate on the TiO_2 surface make the observed K_e under irradiation conditions different from that in the dark. Chen et al. [21] have demonstrated that the K_e from the Langmuir–Hinshelwood equation is an apparent constant that also incorporates other kinetic constants.

The mechanism of dye degradation under UV/TiO_2 has been described, involving the steps shown in Eqs. (5)–(12) [16]. $TiO_2(h^+)$ and $TiO_2(e^-)$ represent the electron-deficient and electron-rich parts in the structure of TiO_2, and S

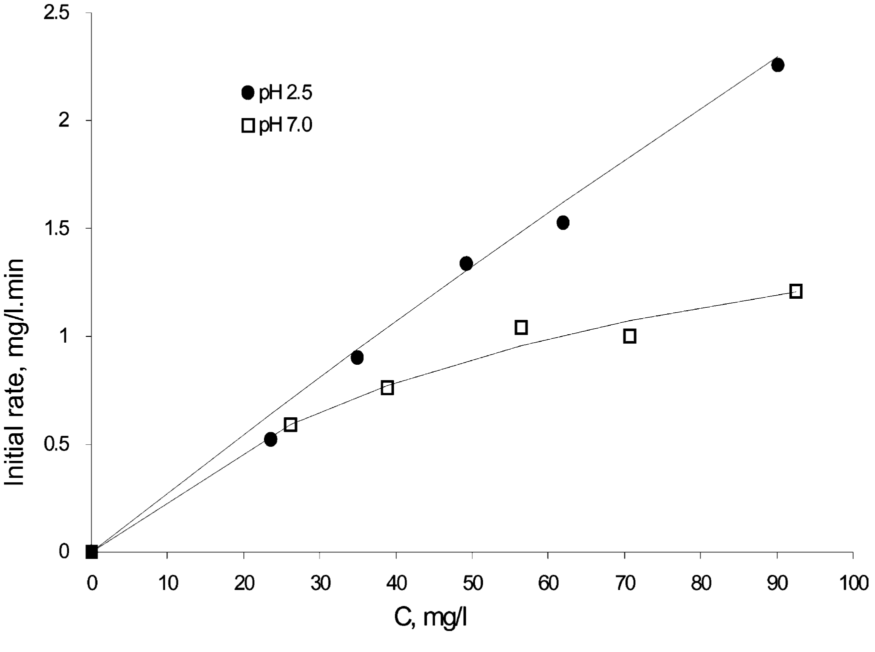

Fig. 3. Initial rate photooxidation of dye at different initial concentrations: (●) pH 2.5; (□) pH = 7.0; $[TiO_2] = 1$ g/l.

represents the Luranzol S kong dye.

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^-/h^+) \quad (5)$$

$$TiO_2(h^+) + H_2O \rightarrow TiO_2{}^+OH^\bullet + H^+ \quad (6)$$

$$TiO_2(h^+) + S \rightarrow TiO_2 + S^{+\bullet} \quad (7)$$

$$TiO_2(h^+) + OH^- \rightarrow TiO_2 + OH^\bullet \quad (8)$$

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2{}^- \quad (9)$$

$$OH^- + O_2 \rightarrow OH^\bullet + O_2{}^- \quad (10)$$

$$OH^\bullet + O_2{}^- \rightarrow OH^- + O_2 \quad (11)$$

$$OH^\bullet + S \rightarrow \text{products} \quad (12)$$

In this mechanism, the dye is degraded both in the bulk solution, through reaction with hydroxyl free radical, and on the surface of the solid, reacting with the photogenerated hole.

3.2.3. *Reactions with Cr(VI) and black dye mixture*

Several papers show photocatalytic reactions with pure Cr(VI) but a few demonstrate reactions of Cr(VI) in mixtures with organic compounds. Many organic compounds have been reported added to aqueous solution to serve as hole scavengers and inhibit the recombination of electrons and holes [2]. However, the information on the effect of these organic compounds on the photocatalytic reduction of metal ion is scarce.

Theoretically, the photocatalytic reduction of Cr(VI) should be more efficient in the Cr(VI)–dye system than in the single system because of the promoter effect by photocatalytic degradation of the dye. In such metal ion–organic compound coexisting systems, the dye receives holes from the valence band directly or indirectly and is oxidized [5].

Fig. 4 shows the effect of the presence of dye on the Cr(VI) reduction in acid medium. The first feature that can be pointed out is that the photoreduction of Cr(VI) in the mixed system is significantly faster than the single one. This fact could be explained because the oxidation of dye consumes photo-excited holes promptly and efficiently, which attenuates electron–hole recombination and promotes photocatalytic Cr(VI) reduction on TiO_2.

The evaluation of the kinetics parameters was performed using the Langmuir–Hinshelwood model as represented in Fig. 5. The calculated parameters are $k_r = 1.019 \pm 0.406$ mg/l min and $K_e = 0.0174 \pm 0.0129$ l/mg, which are significantly different from the parameters in Table 2 for the single system of Cr(VI).

On the other hand, the presence of Cr(VI) also increases the photoxidation of dye in the acidic medium (Fig. 6). This fact could be ascribed to fast reaction in the hole photogenerated in the presence of Cr(VI) (Eq. (7)), whose photoreduction is also favored in the presence of organic compounds as reported above. This aspect is important due to the high affinity of the dye to the TiO_2 surface, as found through adsorption tests.

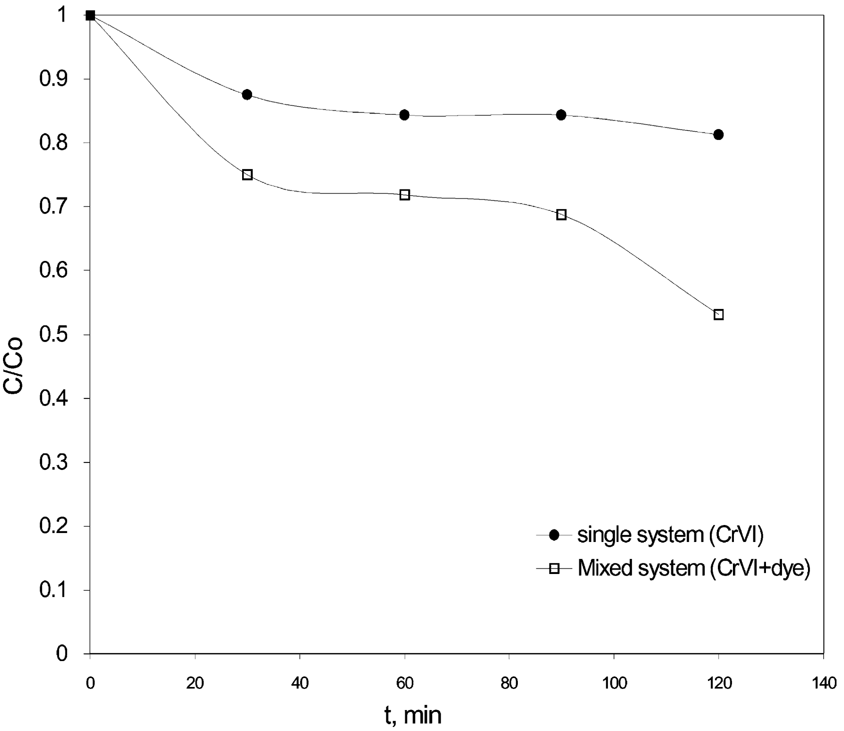

Fig. 4. Kinetics of Cr(VI) reduction in single system and in mixed system (100 ppm dye) at pH 2.5, [TiO_2 = 1 g/l].

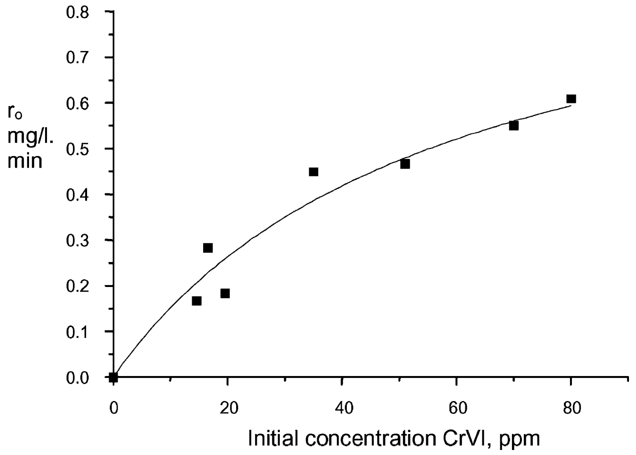

Fig. 5. Initial rate of Cr(VI) reduction in the presence of 100 ppm of dye at pH 2.5.

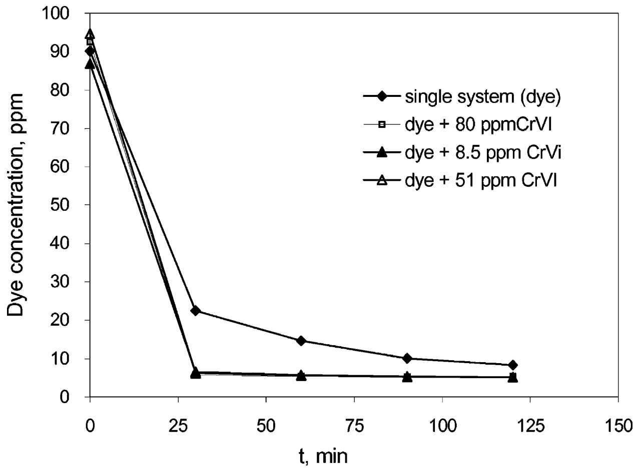

Fig. 6. Kinetics of dye oxidation in single system and in the presence of several Cr(VI) concentrations at pH 2.5, [$TiO_2 = 1$ g/l].

4. Conclusions

The adsorption of Cr(VI) and Luranzol S Kong is highly dependent on pH and increases in acidic pH. The Cr(VI) and Luranzol S Kong photoreactions can be described by the Langmuir–Hinshelwood equation and are faster in acidic conditions than in neutral pH.

In the mixed system, the reduction of Cr(VI) is faster than in the single system because the oxidation of dye consumes photo-excited holes promptly and efficiently, attenuating electron–hole recombination and promoting photocatalytic Cr(VI) reduction on TiO_2. The oxidation of dye is also faster in the mixed system than in the single system.

Acknowledgements

Authors thank PROJETO COURO (CNPq/IEL/FIESC) for supporting part of this work.

References

[1] D. Chen, A. Ray, Chem. Eng. Sci. 56 (2001) 1561.
[2] Y. Ku, I.-L. Jung, Water Res. 35 (2001) 135.
[3] L.B. Khalil, W.E. Mourad, M.W. Rophael, Appl. Catal. B: Environ. 17 (1998) 267.
[4] W.-Y. Lin, C. Wei, K. Rajeshwar, J. Electrochem. Soc. 140 (1993) 2477.
[5] H. Fu, G. Lu, S. Li, J. Photochem. Photobiol. A 114 (1998) 81.
[6] J. Muñoz, X. Domènech, J. Appl. Electrochem. 20 (1990) 518.
[7] M. Litter, Appl. Catal. B: Environ. 23 (1999) 89.
[8] J.A. Navío, G. Colón, M. Trillas, J. Peral, X. Domènech, J.J. Testa, J. Padrón, D. Rodríguez, M.I. Litter, Appl. Catal. B: Environ. 16 (1998) 187.
[9] M.A. Aguado, J. Giménez, S. Cervera-March, Chem. Eng. Commun. 104 (1991) 71.
[10] B. Serrano, H. Lasa, Chem. Eng. Sci. 54 (1999) 3063.
[11] G. Cólon, M.C. Hidalgo, J.A. Navío, J. Photochem. Photobiol. 138 (2001) 79.
[12] J. Giménez, M.A. Aguado, S. Cervera-March, J. Mol. Catal. A 105 (1996) 67.
[13] APHA, AWWA, WEF, Standard Methods for Examination of Water and Wastewater, 19th Edition, Publication Office, American Public Health Association, Washington, 1995.
[14] C.R. Chenthamarakshan, K. Rajeshwar, E. Wolfrum, Langmuir 16 (2000) 2715.
[15] A.E. Cassano, O.M. Alfano, M.I. Cabrera, J. Catal. 172 (1997) 370.
[16] M.R. Hoffman, S.T. Martin, W. Choi, D. Bahnemann, Chem. Rev. 95 (1995) 69.
[17] J. Zhao, H. Oota, H. Hidaka, E. Pelizetti, N. Serpone, J. Photochem. Photobiol. 69 (1992) 251.
[18] A. Mills, S. Morris, J. Photochem. Photobiol. 71 (1993) 75.
[19] T. Sauer, H. José, R.F.P.M. Moreira, in: Proceedings of the Third Enpromer, 2001, p. 1243.
[20] F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizetti, N. Serpone, Appl. Catal. B: Environ. 15 (1998) 147.
[21] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, Water Res. 33 (1999) 1173.