



TiO₂-photocatalytic transformation of Cr(VI) in the presence of EDTA: Comparison of different commercial photocatalysts and studies by Time Resolved Microwave Conductivity

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ABSTRACT

The photocatalytic efficiency for Cr(VI) transformation in the presence of etilendiaminetetraacetic acid (EDTA) at pH 2 over various commercial TiO₂ samples (Evonik P25, Cristal Global PC50, PC100 and PC500, Hombikat UV100, Fluka and Kemira S230) was evaluated. The decay was adjusted to a pseudo-first order kinetics in all cases and the photocatalytic activity of the samples was estimated from the kinetic constants. The order of the photocatalytic activity was PC500 \cong UV100 > P25 \cong PC100 > S230 \cong PC50 \gg Fluka and it strongly depends on the nature of the TiO₂ samples, especially on the specific surface area, except for S230 and for P25. The formation of the Cr(III)–EDTA complex in solution as a product of the Cr(VI) photocatalytic reduction was confirmed by visible spectrophotometry. Simultaneous kinetics of Cr(VI) reduction and of Cr(III)–EDTA formation has been determined for the first time and the results indicate that evolution of both species are related. TRMC measurements were applied for the first time to a reductive heterogeneous photocatalytic reaction of a metal ion system, and the experimental results were adjusted to a power law decay, relating the data to those of the photocatalytic experiments.

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1. Introduction

The photocatalytic reduction of Cr(VI) in water has been widely reported in the literature [1–3], both as an environmentally friendly process for the treatment of this pollutant [4–16]¹ as well as a simple system to evaluate the photocatalytic activity of various semiconductors [11,12,14,17–29]. This photocatalytic system, where Cr(III) is the final stable product, is unique: Cr(VI) is the only metal species whose reductive TiO₂-photocatalytic removal is not influenced by the presence of oxygen, at least at acid pH, in contrast with most metals, explained by the fast capture of electrons caused by a very strong association between Cr(VI) and TiO₂ through a charge-transfer complex [9,30]. However, the influence of the physical properties of the photocatalyst samples used in the reaction is

still under discussion and, from the point of view of photocatalysts offered in the market, this aspect should be analyzed.

Time Resolved Microwave Conductivity (TRMC) is a powerful tool for analyzing charge carrier lifetimes in TiO₂ [31–34]. The technique can be used also to understand the effect of species adsorbed or deposited on the surface of a semiconductor [35–38].

In this paper, the photocatalytic activity of various commercial TiO₂ samples, i.e., Evonik P25, Cristal Global PC50, PC100 and PC500, Hombikat UV100, Fluka and Kemira S230 was evaluated, and the results were related to those of TRMC measurements for the most representative samples.

2. Experimental

2.1. Chemicals and materials

P25 (Evonik), Hombikat UV100 (Sachtleben Chemie), PC50, PC100 and PC500 (Cristal Global), reagent TiO₂ (Fluka, 99%) and Finn-Ti S230 (Kemira) were used as received.

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¹ Only references from the last ten years are given.

Potassium dichromate was Prolabo (99.9%), and disodium etilendiaminetetraacetic acid (Na_2EDTA , 99%) was Merck. Nitric acid (68%, Prolabo) was used for pH adjustment. All other reagents were of analytical grade and used as received. All solutions and suspensions were prepared with distilled water.

Filtration of suspensions was performed through 0.2 μm Interchim cellulose acetate filters, 25 mm diameter.

2.2. Preparation of suspensions and TRMC samples

To prepare the suspensions to be irradiated, the following procedure was used: 200 mL of water were added to 0.25 g of TiO_2 in a 250 mL volumetric flask; then, the corresponding amount of a 10 mM Cr(VI) solution was added to get a final 0.8 mM concentration, and pH was adjusted to 2 with 1 M HNO_3 ; in the corresponding experiments, solid Na_2EDTA to get a 2 mM final concentration was introduced before adjusting the pH. Water was added in all cases to complete 250 mL. The suspension was ultrasonicated for 2 min, and 200 mL were used in each photocatalytic experiment, keeping the remaining 50 mL in the dark for 30 min to ensure adsorption equilibrium before irradiation; after filtration, the amount of Cr(VI) adsorbed onto the photocatalyst in this 50 mL suspension was measured and discounted from the initial concentration to evaluate changes in concentration due only to irradiation.

For TRMC measurements, the pure samples were evaluated directly as powders. To measure Cr(VI)-modified TiO_2 photocatalysts, samples were suspended at 1 g L^{-1} in 0.8 mM Cr(VI) solutions at pH 2 (HNO_3) (with EDTA in the indicated cases), stirred in the dark for 60 min and centrifuged for 10 min at 10,000 rpm. The supernatant was eliminated, the samples were dried at 35 °C for 24 h, and then stored in the dark. Blanks with water at pH 2 adjusted with 1 M (HNO_3 -modified TiO_2) were also prepared.

2.3. Photocatalytic runs

Irradiation runs were performed in a Pyrex recirculating batch annular photoreactor, 160 mm length, 40 mm outer diameter and 30 mm inner diameter. Inside the inner tube, an 8 W Philips fluorescent black light lamp was placed, fed by a 15 W ballast. This lamp emits predominantly at 365 nm. A TiO_2 suspension (200 mL) was poured in a glass reservoir and continuously recirculated (600 mL min^{-1}) to the photoreactor by means of a peristaltic pump. The irradiated volume in the photoreactor was 110 mL. The system was freely open to the air because, as reported, molecular oxygen does not interfere with the Cr(VI) photocatalytic reduction over TiO_2 under acidic conditions [1,2]. The whole setup was thermostatted at 298 K. The total incident photon flux, $q_{n,p}^0/V$, determined by potassium ferrioxalate actinometry, was 95 $\mu\text{einstein s}^{-1} \text{L}^{-1}$, using the same conditions of flow rate and volume as in the experiments.

The experiments were performed at least by duplicate and the standard deviation among replicates was never higher than 10%.

2.4. Analytical determinations

For the spectrophotometric determinations, samples (1 mL) were taken from the reservoir, filtered and brought to 10 mL with water. Cr(VI) was determined by measuring the absorbance at 352 nm [39]. The more sensible but more complicated diphenylcarbazide method was found not necessary for these Cr(VI) concentrations [8]. The concentration of Cr(III)-EDTA in solution was measured at 540 nm as previously reported, using $\varepsilon = 14 \text{ m}^2 \text{ mol}^{-1}$ [40]. Neither free Cr(III) [40,41] nor Cr(VI) species [4,30,42] interferes at this wavelength. However, Cr(III) can form complexes with ethylenediamine- $\text{N,N}'$ -triacetic acid (ED3A) [42], ethylenediaminediacetic acid (EDDA) [43]

ethylenediaminemonoacetic acid (EDMA) [44] and iminodiacetic acid (IDA) [45], having UV-vis spectra similar to that of Cr(III)-EDTA, with maximum ε values also at 540 nm and in the same order of magnitude (6–13 $\text{m}^2 \text{ mol}^{-1}$). These compounds have been found as products of EDTA photocatalytic degradation, although reported to be formed in very low amounts [46,47]. Therefore, it will be assumed that the measured absorbance corresponds only to the Cr(III)-EDTA complex, affected by some minor error without influence on our conclusions. A double-beam Varian UV-vis recording spectrophotometer, model Cary UV 300, was used for the spectrophotometric measurements, and calibration curves were obtained in all cases.

Total Cr content on TiO_2 either before or after irradiation was determined by Wavelength Dispersive X-Ray Fluorescence (WDXRF) measurements, using a Venus 200 MiniLab, Panalytical WDXRF equipment with a Sc anode X-Ray tube. The excitation conditions were 50 kV and 4 mA. As thermal Cr(VI) reduction by EDTA can take place during the drying process of the samples [40], the amount of Cr on TiO_2 before irradiation was determined before the addition of the organic compound. The amount of Cr in the TiO_2 samples was expressed as equivalent concentration (mmol of Cr/g of TiO_2), i.e., as the concentration of total Cr (mM) in a suspension containing 1 g L^{-1} of TiO_2 . The samples were initially prepared as described for the TRMC measurements, mixing them at the end with cellulose (40% TiO_2 –60% cellulose) and compressing the mixture in order to obtain a pellet. The calibration curves were prepared similarly by mixing pure P25 with the corresponding amount of Cr(VI) in water.

2.5. BET area measurements

Measurements were carried out by N_2 adsorption at 77 K (molecular surface area 0.162 nm^2) on a Micromeritics ASAP 2020 equipment. Before analysis, the samples were heated under vacuum at 373 K for 8 h.

2.6. TRMC measurements

Measurements were carried out in the Helmholtz Zentrum Berlin (Germany) with the experimental setup described previously [31]. The incident microwaves were generated by a Gunn diode of the K_a band (28–38 GHz) and the experiments were performed at 31.4 GHz. Pulsed light source was a Nd:YAG laser providing an IR radiation at $\lambda = 1064 \text{ nm}$. Full-width at half-maximum (FWHM) of one pulse was 10 ns; repetition frequency of the pulses was 10 Hz. UV light (355 nm) was obtained by tripling the IR radiation. The light energy density received by the sample was 1.3 mJ cm^{-2} . In order to have a more accurate value of the signal at the maximum (I_{max}) and at 40 ns after the maximum ($I_{40\text{ns}}$), the values reported for both parameters were averaged within $\pm 5 \text{ ns}$ of the corresponding time. The uncertainty of the measurements was of 0.005 V for times shorter than 100 ns (i.e. when the signal is maximum), and of 0.001 V for longer times.

3. Results and discussion

3.1. Photocatalytic experiments of Cr(VI) decay with different TiO_2 samples

In Table 1, some physical properties of the TiO_2 samples used in this work are indicated, with BET area values measured in our laboratories and compared with reported values taken from the literature [4,12,17,37,48–52].

In Fig. 1, results of the photocatalytic decay of Cr(VI) (0.8 mM) in the presence of EDTA (2 mM) at pH 2 using different TiO_2 samples (1 g L^{-1}) are shown. These conditions were chosen according to results obtained in previous works to warrant a low Cr(VI) filter

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