



Preservation of the photocatalytic activity of TiO₂ by EDTA in the reductive transformation of Cr(VI). Studies by Time Resolved Microwave Conductivity



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ABSTRACT

P25 TiO₂ was found to be deactivated after Cr(VI) (0.8 mM) photocatalytic experiments at pH 2 in the absence of EDTA, but this deactivation was not found in the presence of the organic compound (2 mM), which preserves the activity of the photocatalyst. The results were confirmed by TRMC measurements. The preservation of the activity by the presence of EDTA can be a general behavior of reducing oligocarboxylic acids present together with Cr(VI) in the photocatalytic system, where Cr(III) soluble complexes can be formed and Cr(III) deposition onto the TiO₂ surface is prevented. The treatment of a set of diluted Cr(VI) solutions (0.8 mM) in successive experiments with the reused photocatalyst was more efficient for Cr(VI) removal in the presence of EDTA (2 mM, 700 s total irradiation time) than the use of a more concentrated sample (Cr(VI), EDTA) with the same photocatalyst submitted to a longer irradiation (900 s), indicating a good strategy for application. A change in the kinetics from a pseudo-first order at the lowest concentration to an almost zero order at the highest concentration takes place and is analyzed.

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1. Introduction

The photocatalytic reduction of Cr(VI) in water has been widely reported in the literature either for Cr(VI) treatment or as a simple model system to evaluate the photocatalytic activity of semiconductors [1–25].¹ This photocatalytic system, where Cr(III) is the final stable product, is unique: Cr(VI) reduction is synergistically enhanced by the presence of some organic compounds and is the only metal species whose reductive TiO₂-photocatalytic removal under UV or visible light is not influenced by the presence of oxygen, at least at acid pH. Noticeably, Cr(VI) removal using other photocatalysts (from which graphitic carbon nitride modified with formate is one example, at least under visible irradiation [26]) is actually inhibited by O₂ [2].

However, a progressive deactivation undergone by TiO₂ during the Cr(VI) photocatalytic reduction under certain experimental conditions takes place [3,27–29] and should be thoroughly investigated and interpreted. Previous studies proposed that the observed deactivation is due to the partial adsorption or photodeposition of Cr(III) on the surface of TiO₂ particles, which might retard the reaction [3]. In fact, it has been proven that Cr(III)-doped TiO₂ photocatalysts are less active than pure TiO₂, and this behavior has been associated to the capture of e_{CB}⁻ at the Cr(III) centers [30,31]. In a recent paper [25], the simultaneous kinetics of Cr(VI) reduction and of Cr(III)–EDTA formation have been determined for the first time, and the results indicated that evolution of both species were related. The formation of the Cr(III)–EDTA complex in solution as a product of the Cr(VI) photocatalytic reduction was confirmed by visible spectrophotometry in the same work.

In the present work, the analysis of Cr(VI) photocatalytic reaction on TiO₂ Evonik P25 in the absence and in the presence of EDTA is revisited and related with Time Resolved Microwave Conductivity (TRMC) results. The effect of successive experiments on the photocatalytic activity is described, in order to find the better strategy for the possible reuse of the photocatalyst in applications.

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¹ References from the last ten years are mostly given.

2. Experimental

2.1. Chemicals and materials

TiO₂ P25 (Evonik) was used as received. Potassium dichromate was Prolabo (99.9%), and disodium ethylenediaminetetraacetic acid (Na₂EDTA, 99%) was Merck. Nitric acid (68%, Prolabo) was used for pH adjustments. Solutions and suspensions were prepared with distilled water. 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 TiO₂ in a 250 mL volumetric flask; then, the corresponding amount of a 100 mM Cr(VI) solution was added to get a final 0.8 or 3.2 mM concentration, and pH was adjusted to 2 with 1 M HNO₃; in the corresponding experiments, solid Na₂EDTA to get a 2 or 8 mM final concentration was introduced before adjusting the pH. Water was added in all cases to complete 250 mL. The suspensions were ultrasonicated for 2 min, and 200 mL were transferred to the photocatalytic reactor and recirculated for 30 min to ensure that the system reached the adsorption equilibrium; the remaining 50 mL were stirred in the dark for 30 min to ensure also 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 value to evaluate changes in concentration due only to irradiation.

For TRMC measurements, the pure samples were analyzed directly as powders. In the case of Cr(VI)-modified TiO₂ samples, P25 was suspended at 1 g L⁻¹ in 0.8 mM Cr(VI) solutions at pH 2 (HNO₃) (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 (HNO₃-modified TiO₂ samples) were also prepared.

2.3. Photocatalytic runs

The reactor used in the photocatalytic experiments has been previously described [25]. Briefly, it consisted of a Pyrex recirculating batch annular photoreactor with an 8 W Philips fluorescent black light lamp, fed by a 15 W ballast ($\lambda_{\text{max}} = 365 \text{ nm}$). The TiO₂ suspension (200 mL) was poured in a glass reservoir and continuously recirculated at 600 mL min⁻¹ to the photoreactor by means of a Heidolph PD5006 peristaltic pump. The system was freely open to the air. The whole setup was thermostatted at 25 °C. The total incident photon flux, $q_{n,p}^0/V$, determined by potassium ferrioxalate actinometry, was 95 μeinstein s⁻¹ L⁻¹, determined under the same conditions of flow rate and volume as in the runs. In the successive experiments with the same TiO₂ sample, after complete Cr(VI) removal, the corresponding amount of Cr(VI) solution to get a 0.8 mM concentration was added to the 200 mL reaction volume together with a new addition of solid EDTA to get a 2 mM concentration (when necessary); finally, pH was adjusted again to 2 with HNO₃. 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 [32]. The concentration of Cr(III)-EDTA in solution was measured at 540 nm ($\epsilon = 14 \text{ m}^2 \text{ mol}^{-1}$ [33]), where neither free Cr(III) [34–36] nor Cr(VI) species [27,37,38] interfere. Other possible complexes of Cr(III) with EDTA photocatalytic degradation byproducts were supposed not to interfere, as established in a previous work [25]. 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. The values of the parameters of the equations used to adjust the temporal evolution of Cr(VI) and Cr(III)-EDTA were obtained by fitting using the software Origin 7.5.

Total Cr content on TiO₂ either before or after irradiation was determined by Wavelength Dispersive X-ray Fluorescence (WDXRF) measurements, as described previously, using a Venus 200 MiniLab, Panalytical WDXRF equipment with a Sc anode X-ray tube (excitation conditions: 50 kV and 4 mA) [25]. The amount of Cr on TiO₂ before irradiation in the presence of EDTA was determined before the addition of the organic compound to avoid the thermal Cr(VI) reduction by EDTA during the drying process of the samples [33]. The amount of Cr on the TiO₂ samples was expressed as equivalent concentration (mmol of Cr/g of TiO₂), i.e. as the concentration of total Cr (mM) in a suspension containing 1 g L⁻¹ of TiO₂. The samples were initially prepared as described for the TRMC measurements (Section 2.2), mixing them at the end with cellulose (40% TiO₂-60% 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. TRMC measurements

Measurements were carried out in the Helmholtz Zentrum Berlin (Germany) with the experimental setup described previously [25,39]. 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 ±5 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. The values of I_D and k_D were obtained by fitting using the software Origin 7.5.

3. Results and discussion

3.1. Successive photocatalytic experiments of Cr(VI) removal with a same P25 sample in the absence of EDTA

Six successive experiments in the Cr(VI) photocatalytic system reusing the same P25 sample in the absence of EDTA were performed. For all experiments, the amount of Cr(VI) removed by adsorption on TiO₂ before irradiation represents ≈5% (≈0.04 mM) of the total initial Cr(VI) (0.8 mM). A progressive strong deactivation of the photocatalyst was evident for the decay of Cr(VI), as observed in Fig. 1. Throughout the successive experiments, a green color of increasing intensity was observed on the photocatalyst surface.

Table 1
Kinetic parameters extracted from the fitting of data from Fig. 1 with Eq. (2), and equivalent Cr concentration over TiO₂ before and after the successive experiments.

Experiment	$k_0 \times 10^3 \text{ (s}^{-1}\text{)}$	$k \times 10^3 \text{ (s}^{-1}\text{)}$	R^2	Cr on TiO ₂ (mmol g ⁻¹)
Before irradiation	–	–	–	0.05
1st	0.1 ± 0.009	1.28 ± 0.11	0.95	0.30
2nd	0.1 ± 0.005	0.62 ± 0.03	0.98	ND
3rd	0.1 ± 0.008	0.25 ± 0.02	0.98	ND
4th	0.1 ± 0.007	0.15 ± 0.01	0.99	1.04
5th	0.1 ± 0.017	0.06 ± 0.01	0.95	ND
6th	0.1 ± 0.014	0.05 ± 0.007	0.97	1.02

ND: not determined.

As said before, deactivation of TiO₂ in the Cr(VI) photocatalytic reduction in the absence of donors has been previously reported [3,28]. Kinetic models like half or first order, and Langmuir–Hinshelwood, among others, were applied in previous works to fit the experimental data [3,9,19,28,40–42]. However, the best fittings of our experimental points were obtained with a mixed zero and first order kinetics, according to Eq. (1):

$$\frac{d([\text{Cr(VI)}]/[\text{Cr(VI)}]_0)}{dt} = - \left(k_0 + k \times \frac{[\text{Cr(VI)}]}{[\text{Cr(VI)}]_0} \right) \quad (1)$$

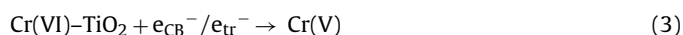
where k_0 and k are the zero order and the pseudo-first order constants, respectively. The profiles in Fig. 1 were then successfully fitted ($R^2 > 0.95$) by the integrated Eq. (2):

$$\frac{[\text{Cr(VI)}]}{[\text{Cr(VI)}]_0} = \frac{(k_0 + k)}{k} \times \exp^{-k \times t} - \frac{k_0}{k} \quad (2)$$

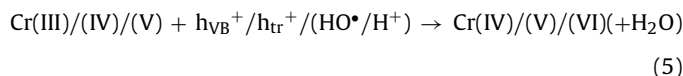
Cr(III) in solution could not be spectrophotometrically observed at the end of the experiment because, at pH 2 in the absence of complexing agents, Cr³⁺ is the only Cr(III) species in aqueous conditions, and its absorbance in the near UV–vis region is almost negligible (at $\lambda_{\text{max}} = 580 \text{ nm}$, $\epsilon = 1 \text{ m}^2 \text{ mol}^{-1}$ [36]). The concentration of Cr(III) in solution after each experiment was actually calculated from the difference between the total initial Cr(VI) concentration and Cr on TiO₂ after irradiation measured by WDXRF. Although other authors could measure Cr(III) by direct spectrophotometry after photocatalytic Cr(VI) reduction, the Cr(III) concentration under their conditions was much higher [22,43].

As reported, the photocatalytic Cr(VI) reduction in water under regular illumination proceeds through three successive one-electron reduction steps, ending in Cr(III) [1,2]. It has been indicated that a rapid formation of a charge-transfer complex between the hexavalent metal ion and TiO₂ takes place [14,44], followed by the

reaction of CB or trapped electrons with Cr(VI) to yield Cr(V), a highly feasible process given the reduction potential of the couple ($E^0_{\text{Cr(VI)/Cr(V)}} = +0.55 \text{ V}$ [45]²) and the redox levels of P25 CB electrons ($E^0 = -0.3 \text{ V}$ [46]). In the absence of an adequate electron donor, the limiting step is the anodic process, i.e. the very slow water oxidation [1,2]:



HO[•] recombines to give H₂O₂, which in turn ends in O₂ as the final stable product. However, h_{VB}^+ , h_{tr}^+ and HO[•] can react with the reduced Cr species, causing a decrease in the efficiency of the process due to a short-circuiting:



In Table 1 are shown the kinetic parameters of the curves extracted from Fig. 1, together with the equivalent Cr concentration for the different TiO₂ samples after irradiation. k_0 can be related to a Cr(VI) reduction mechanism independent of the Cr(VI) concentration; the values are the same after the successive experiments, indicating that this pathway is not affected by deactivation. Hongxiang et al. [47] described experiments of Cr(VI) adsorption on P25 ($[\text{Cr(VI)}]_0 = 0.05\text{--}0.8 \text{ mM}$, 1 g L^{-1} , pH 2.5 with HNO₃), finding that the amount of Cr(VI) adsorbed is almost constant, in the 0.02–0.03 mM range, similar to the values reported here ($\approx 0.04 \text{ mM}$). If it is assumed that Cr(VI) adsorption is not affected by the successive reuses, the concentration of the Cr(VI)–TiO₂ complex can be considered almost constant during all the irradiation period for the successive experiments. Therefore, the zero order contribution to the kinetics could be related to the light induced degradation of the complex [44]. Experiments to prove this hypothesis are underway.

On the other hand, k is a measure of the photocatalytic activity of the samples after successive experiments. The decreasing values in Table 1 clearly indicate that an inhibition takes place through the reuse of the photocatalyst. k decreases also with the increase of the amount of Cr on the TiO₂ surface, as can be appreciated from the 1st up to the 4th exp., indicating a close relationship between the deactivation and this amount; the decrease in k continues between the 4th and the 6th exps. despite no change is observed in the amount of Cr on TiO₂, due probably to the low detection limit of the WDXRF technique to detect small changes. This relationship between the increase in surface Cr content (as Cr(III)), as can be inferred from the green color of the photocatalyst after the experiments seen by us and by others [48] and the deactivation of the TiO₂ has been proposed before [3,27–29,48].

² All standard reduction potentials vs. NHE.

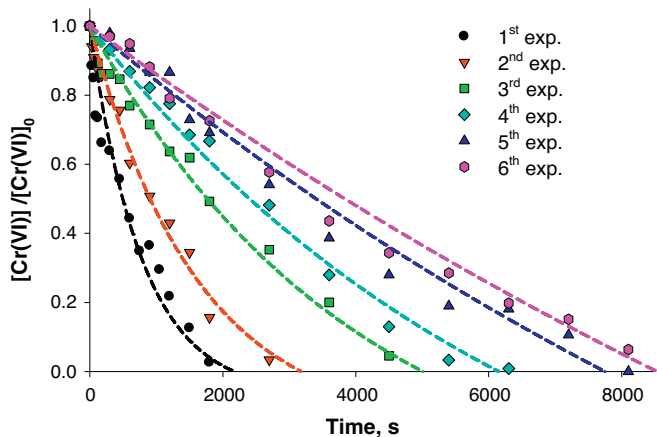


Fig. 1. Temporal evolution of the normalized Cr(VI) concentration ($[\text{Cr(VI)}]/[\text{Cr(VI)}]_0$) in the absence of EDTA in six successive experiments reusing the same P25 sample. Conditions: $[\text{Cr(VI)}]_0 = 0.8 \text{ mM}$, $[\text{TiO}_2] = 1 \text{ g L}^{-1}$, $V_{\text{suspension}} = 200 \text{ mL}$, pH 2 (HNO₃), $q_{\text{h},p}^0/V = 95 \mu\text{einstein s}^{-1} \text{ L}^{-1}$. Dashed lines represent the fitting of the data to Eq. (2).

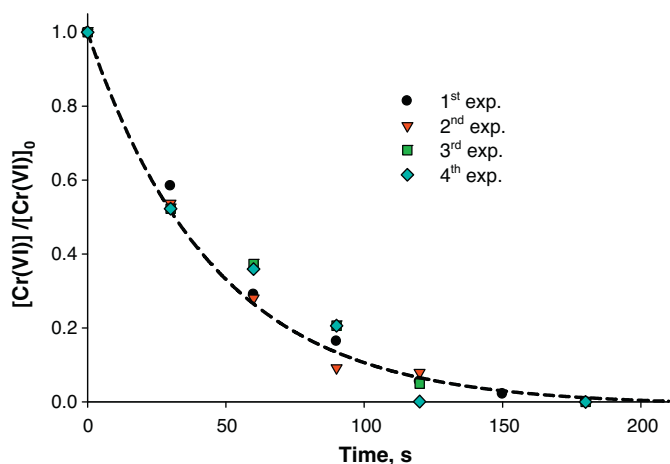
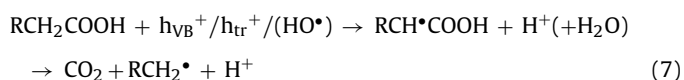
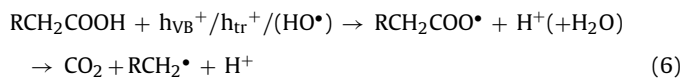


Fig. 2. Temporal evolution of the normalized Cr(VI) concentration ($[\text{Cr(VI)}]/[\text{Cr(VI)}]_0$) in the presence of EDTA in four successive experiments with the same P25 sample. Conditions: $[\text{Cr(VI)}]_0 = 0.8 \text{ mM}$, $[\text{EDTA}]_0 = 2 \text{ mM}$, $[\text{TiO}_2] = 1 \text{ g L}^{-1}$, $\text{pH } 2$ (HNO_3), $V_{\text{suspension}} = 200 \text{ mL}$, $q_{n,p}^0/V = 95 \mu\text{einstein s}^{-1} \text{ L}^{-1}$. The dashed line represents the fitting of the data to Eq. (9).

3.2. Successive photocatalytic experiments of Cr(VI) removal with a same P25 sample in the presence of EDTA

Fig. 2 shows the results of four successive experiments similar to those of Fig. 1 but in the presence of 2 mM EDTA. The amount of Cr(VI) removed by adsorption on TiO_2 and by dark thermal reaction with EDTA before irradiation represents $\approx 10\%$ of the total initial Cr(VI) (i.e. $\approx 0.8 \text{ mM}$) for the initial experiments; this value increases for the successive experiments (2nd to 4th) to around 15% of the initial Cr(VI). This could be due to a dark reaction between Cr(VI) and EDTA degradation products, process that has been not reported yet. The formation of Cr(III)–EDTA as the final photocatalytic product [49] was confirmed by the appearance of two peaks at 390 and 540 nm in the spectra of the filtered samples [25,37], reinforced by the violet color of the solution [37,50]; in contrast with the green deposit observed on the photocatalyst surface in the experiments in the absence of EDTA, here the surface turned to violet, which can be associated to the formation of Cr(III)–EDTA on the surface [33,37,50].

As expected, the Cr(VI) photocatalytic reduction in the presence of EDTA was much faster than the reaction without the donor, due to the combination of two important factors: (i) the presence of a hole scavenger more efficient than H_2O , which reduces the recombination rate, and (ii) the generation of strong reducing organic radicals from EDTA by oxidation by holes or HO^\bullet , capable of enhancing Cr(VI) reduction, and schematically expressed by Eqs. (6) and (7) [1,25]:



Interestingly, in contrast with the results in the absence of EDTA, no deactivation of the sample was observed after the successive reuses. The temporal profiles of the experiments with EDTA could

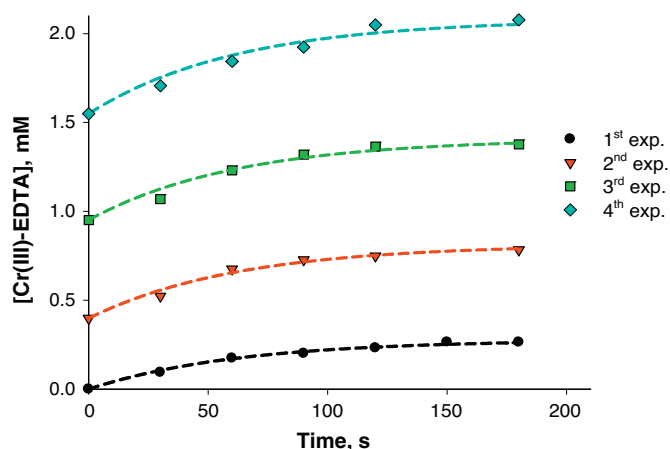


Fig. 3. Temporal evolution of Cr(III)–EDTA in four successive experiments with the same P25 sample. Conditions of Fig. 2. The dashed lines represent the fitting of the data to Eq. (10).

be fitted to a simplified expression of Eq. (2), responding to a pseudo-first order kinetics:

$$\frac{[\text{Cr(VI)}]}{[\text{Cr(VI)}]_0} = \exp^{-k_c \times t} \quad (8)$$

where k_c is the pseudo-first order constant. This type of kinetics has been widely reported for Cr(VI) photocatalytic reduction in the presence of donors [9,15,17,25]. The zero order contribution indicated in Eq. (2) was discarded from the kinetic analysis, as k_c is more than 200 times higher than k_0 ($\approx 1 \times 10^{-4} \text{ s}^{-1}$, Table 1), evaluated at $t=0$ as in Section 3.1. Thus, the zero order process cannot be appreciated under these conditions.

Fig. 3 shows the temporal evolution of Cr(III)–EDTA, which could be fitted to Eq. (10), corresponding to a pseudo-first order kinetics:

$$[\text{Cr(III)–EDTA}] = C_\infty \times (1 - \exp^{-k_f \times t}) + C_0 \quad (9)$$

where C_∞ is the amount of Cr(VI) transformed into Cr(III)–EDTA at the end of the reaction, C_0 the concentration of Cr(III)–EDTA before the experiment, and k_f is the pseudo-first order constant for the complex formation.

Table 2 shows the kinetic parameters of the curves extracted from Figs. 2 and 3, together with the Cr concentration on TiO_2 after irradiation.

As explained in our previous work [25], the difference between $[\text{Cr(VI)}]_0$ and C_∞ can be explained by the amount of Cr attached on TiO_2 and the existence of other Cr(III) species in solution that could not be detected by direct spectrophotometry. Throughout the successive experiments, C_∞ increases, probably due to an excess of EDTA that accumulates and increases the yield of Cr(III)–EDTA. If the lifetime of intermediate Cr species is short [51] and the yield of the different Cr(III) species is constant, then k_f should be similar to k_c , as observed by us with TiO_2 photocatalytic samples different to P25; for this photocatalyst, k_f was found somewhat smaller, and the difference was associated to the existence of the two crystalline phases, rutile and anatase, where different reactive sites can give different distribution of Cr(VI) reduction products [25]. C_0 , i.e. the initial Cr(III)–EDTA is higher in each experiment, and the difference of this value with the sum ($C_\infty + C_0$) of the previous experiment can be ascribed to Cr(VI) thermal reduction by EDTA [33], or its degradation products before the experiment.

The presence of EDTA protects the surface and prevents the progressive deactivation of TiO_2 for the photocatalytic Cr(VI) reduction. This observation comes from the simple comparison of the

Table 2
Kinetic parameters extracted from the fittings of the results of Figs. 2 and 3 to Eqs. (8) and (9), respectively, and values of Cr on TiO₂.

Exp.	$k_c \times 10^3 \text{ (s}^{-1}\text{)}$	R^2	$C_\infty \text{ (mM)}$	$k_f \times 10^3 \text{ (s}^{-1}\text{)}$	$C_0 \text{ (mM)}$	R^2	Cr on TiO ₂ (mmol g ⁻¹)
Before irradiation	–	–	–	–	–	–	0.07
1st	21.7 ± 0.5	0.99	0.28 ± 0.01	16 ± 0.3	0	0.99	0.11 ^a
2nd	21.7 ± 0.5	1	0.42 ± 0.01	16 ± 0.6	0.40 ± 0.01	0.98	ND
3rd	21.7 ± 1.0	0.98	0.46 ± 0.02	16 ± 0.7	0.95 ± 0.02	0.97	ND
4th	21.7 ± 1.0	0.98	0.53 ± 0.02	16 ± 0.7	1.54 ± 0.02	0.97	0.23 ^a

^a Concentrations measured at the end of the experiment.

amount of Cr on the surface. Although Tables 1 and 2 indicate that this amount is higher compared with the initial one before irradiation, in the systems with EDTA the amount is much lower, especially after the 4th exp. (four times lower in the presence EDTA, i.e. 1.03 vs. 0.23 mmol g⁻¹). This clearly indicates that the release of Cr(III) from the surface is the main effect that avoids the catalyst deactivation, and the decrease on the Cr(III) surface concentration has been observed previously [49]. It has to be mentioned that not all donors prevent the catalyst deactivation, as it has been reported for salicylic acid [27,52]. The difference between the salicylic acid and the EDTA system can be attributed to the fact that soluble Cr(III)–EDTA complexes can be formed, which are not retained on the photocatalyst surface, avoiding the catalyst deactivation.

3.3. Experiments with different Cr(VI) initial concentrations in the presence of EDTA

A separate experiment was performed with a 4-fold higher Cr(VI) concentration ([Cr(VI)]₀ = 3.2 mM, [EDTA]₀ = 8 mM, i.e. keeping the same Cr(VI)/EDTA molar ratio; results are shown in Fig. 4. In the same plot, the experiments from Figs. 2 and 3 are included, indicating the total irradiation time used in the four successive experiments. The discontinuity in the Cr(III)–EDTA concentration between the final time of one experiment and the initial time of the following in the experiments with 0.8 mM Cr(VI) is related to the thermal reaction between Cr(VI) and EDTA [33] or its degradation products.

The experimental data obtained at the highest concentration could not be fitted to Eq. (8); instead, Eq. (10) was used:

$$[\text{Cr(VI)}] = A_1 \times \exp^{-k_c t} - k'_0 \times t + C_1 \quad (10)$$

where k_c and k'_0 are the pseudo-first order and zero order constants, respectively, A_1 represents the amount of Cr(VI) reduced through

Table 3
Kinetic parameters extracted from the fittings of the results of Fig. 3 to Eqs. (10) and (11).

Kinetic parameter	Value	Equation
$k_c \text{ (s}^{-1}\text{)}$	$21.7 \pm 0.7 \times 10^{-3}$	(10)
$A_1 \text{ (mM)}$	0.60 ± 0.1	(10)
$k'_0 \times 10^3 \text{ (mM s}^{-1}\text{)}$	$3.1 \pm 0.1 \times 10^{-3}$	(10)
R^2	0.99	(10)
$k_f \times 10^3 \text{ (s}^{-1}\text{)}$	$16 \pm 1.7 \times 10^{-3}$	(11)
$k_{f0} \times 10^3 \text{ (mM s}^{-1}\text{)}$	$1.7 \pm 0.1 \times 10^{-3}$	(11)
$C_\infty \text{ (mM)}$	0.2 ± 0.03	(11)
$C_0 \text{ (mM)}$	0	(11)
R^2	0.99	(11)

the pseudo-first order process and ($A_1 + C_1$) the Cr(VI) concentration in solution at $t=0$ (≈ 3.2 mM). The temporal evolution of Cr(III)–EDTA was fitted to Eq. (13):

$$[\text{Cr(III)-EDTA}] = C_\infty \times (1 - \exp^{-k_f t}) + k_{f0} \times t + C_0 \quad (11)$$

where C_∞ , k_f and C_0 have the same meaning as in Eq. (10), and k_{f0} is the zero order constant for the complex formation. The initial Cr(III)–EDTA concentration was negligible. Table 3 shows the kinetic parameters of the curves extracted from Fig. 4, fitted with Eqs. (12) and (13).

Comparing the values of Tables 2 and 3, it can be observed that k_c and k_f are the same for both studied initial Cr(VI) concentrations (0.8 and 3.2 mM), indicating that initially the kinetic regime is the same at both concentrations; however, for the highest concentration, the pseudo-first order regime only takes place in the first 150 s (see Fig. 4), and then stops, while both Cr(VI) removal and Cr(III)–EDTA formation continue through a zero order process. Thus, at the highest concentration, a change in the kinetic regime takes place; we found no simple explanation for this phenomena, but an arrest in the first order process due to a precipitation of

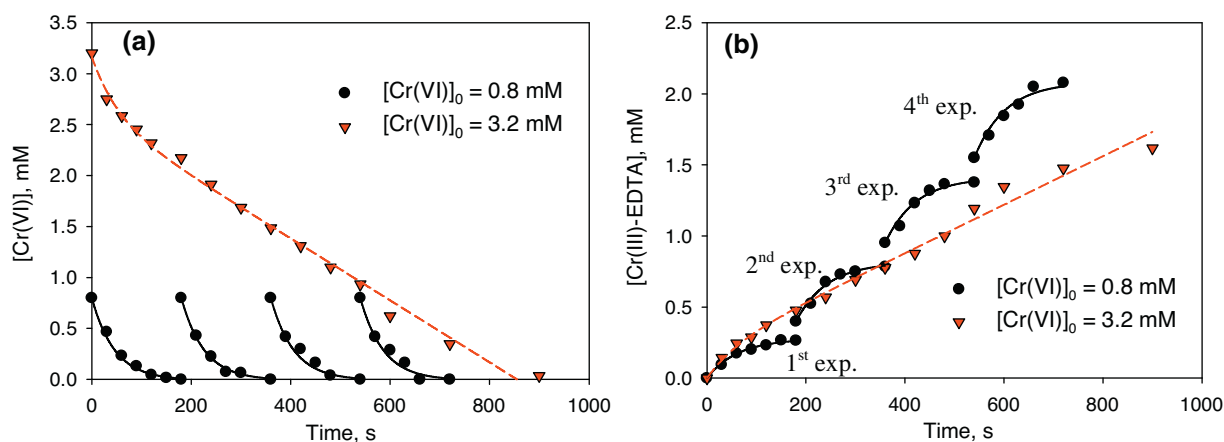


Fig. 4. Comparison for the photocatalytic reduction of the same amount of Cr(VI) between 4 successive experiments and a single experiment with initial concentrations of Cr(VI) and EDTA 4 times higher and the same P25 sample. Conditions: for [Cr(VI)]₀ = 0.8 mM (black circles), same of Fig. 2; for [Cr(VI)]₀ = 3.2 mM (red triangles): same of Fig. 2 except [Cr(VI)]₀ = 3.2 mM, [EDTA]₀ = 8 mM. (a) [Cr(VI)] evolution; black solid line: fitting to Eq. (8); red dotted line: fitting to Eq. (10). (b) [Cr(III)–EDTA] evolution; black solid line: fitting to Eq. (9); red dashed line: fitting to Eq. (11). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

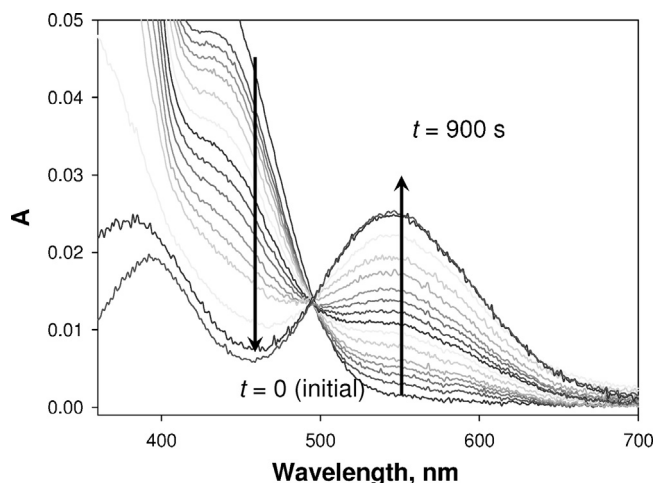


Fig. 5. Spectra of the samples at different reaction times for the experiment starting with $[\text{Cr(VI)}]_0 = 3.2 \text{ mM}$ and 8 mM EDTA. Conditions of Fig. 4. Black arrows indicate the increase in the irradiation time for the different samples.

EDTA in its acidic form (where the compound is most in a neutral or protonated form [53]) cannot be ruled out, given its low solubility (0.5 g L^{-1} [54,55]) at low pH values; as EDTA is degraded, the precipitate is redissolved, but its dissolution rate might be the kinetic control.

The yield of Cr(III)–EDTA formed through the pseudo-first order process is 33%, calculated as C_∞/A_1 , and close to the value of 35% that can be obtained for the 1st exp. with $[\text{Cr(VI)}]_0 = 0.8 \text{ mM}$ ($C_\infty/[\text{Cr(VI)}]_0$). For the zero order process, this yield is 56%, calculated as the ratio between k_{f0} and k'_0 ; this difference clearly indicates that a change in the mechanism is taking place, as the kinetic regime changes under this condition.

Fig. 5 shows the spectra of the samples at different reaction times for the experiment in conditions of Fig. 4. Similar spectra were obtained for the successive experiments at the lowest concentration (Figs. 2 and 3); however, at 3.2 mM Cr(VI), the change in Cr(VI) concentration is more marked and spectroscopic changes are easier to be observed. An isosbestic point at $\lambda = 494 \text{ nm}$ can be observed, meaning that there are only two absorbing species in the system, i.e. Cr(VI) (initial spectra) and Cr(III)–EDTA (final spectra).

3.4. TRMC measurements of the TiO_2 samples

3.4.1. Fundamentals of TRMC

Basic concepts of TRMC have been reported elsewhere [39,56–60]. Briefly, the technique is based on the measurement of the change of the microwave power reflected by a solid sample, $\Delta P(t)$, induced by laser-pulsed illumination. The relative difference $\Delta P(t)/P$ can be correlated to the difference of conductivity $\Delta\sigma(t)$, according to [39]:

$$\frac{\Delta P(t)}{P} = A\Delta\sigma(t) = Ae \sum_i \Delta n_i(t) \mu_i \quad (12)$$

where A is a sensitivity factor, e is the electron charge, $\Delta n_i(t)$ is the number of excess charge carriers i at time t , and μ_i is their mobility. In the specific case of TiO_2 , Δn_i is reduced to electrons in the CB because their mobility is much larger than that of the holes [39,56]. The determination and explanation of the main parameters was explained previously [25]: the maximum of the signal (I_{max}) indicates the number of the excess charge carriers created by the laser pulse, while the decay ($I(t)$) is related to the decrease of the excess electrons by recombination or trapping. The $I_{40 \text{ ns}}/I_{\text{max}}$ ratio reflects fast processes, mainly recombination [61], while the decay observed at longer times (after 200 ns) is related to slow processes,

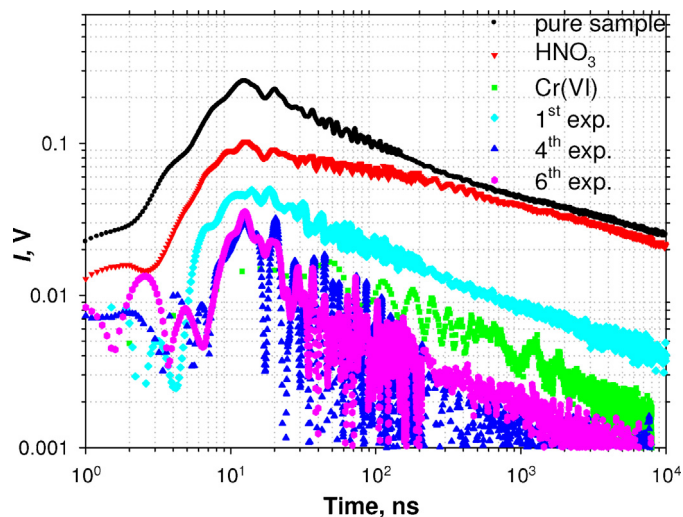


Fig. 6. TRMC measurements for successive experiments with the same P25 sample. Pure sample: unmodified P25. HNO_3 : P25 previously suspended at 1 g L^{-1} in HNO_3 at pH 2. Cr(VI): P25 previously suspended at 1 g L^{-1} in 0.8 mM Cr(VI) at pH 2 (HNO_3). 1st, 4th and 6th expts.: P25 after the respective photocatalytic experiment in conditions of Fig. 1.

i.e. interfacial charge transfer reactions and decay of excess electrons controlled by the relaxation time of trapped holes [46]. In our previous paper [25], the decay of the TRMC signal of TiO_2 samples was successfully fitted to a power decay:

$$I = I_D \times t^{-k_D} \quad (13)$$

where I_D is the intensity of the signal due to charge carriers recombining after 200 ns, and k_D is an adimensional parameter related to the lifetime [39,61].

Adsorbed or deposited species on the photocatalyst surface can absorb photons, and these processes can hinder the creation of charge carriers by acting as a shield or UV filter for TiO_2 , being detrimental for the photocatalytic activity; in terms of TRMC results, decrease of I_{max} and I_D can be observed in these cases but lifetimes of charge carriers are barely affected. The adsorbed species can behave also as impurities or defects, enhancing recombination and decreasing all TRMC parameters, being also in consequence detrimental for the activity. Finally, interfacial charge transfer processes can occur between the charge carriers and the adsorbed species, and the result is an enhancement of the photoactivity [58,61]. TRMC parameters related to long times are generally changed by these charge transfer processes [61].

3.4.2. Results of TRMC measurements

Fig. 6 depicts the results of TRMC measurements of the P25 samples filtered after selected experiments of Fig. 1. The TRMC results of the pure sample, and the pure sample after contact with a HNO_3 solution (pH 2) and after contact with the Cr(VI) solution before irradiation are also shown. The sample after contact with HNO_3 served as a blank to circumvent a possible influence of nitrate on the

Table 4
Decay parameters of the TRMC signal corresponding to Fig. 6.

Sample/condition	I_{max} (V)	$I_{40 \text{ ns}}/I_{\text{max}}$	I_D (V)	k_D
Pure sample	0.226	0.538	0.133	0.259
HNO_3	0.096	0.774	0.105	0.252
"Initial"	0.015	0.676	0.017	0.478
1st exp.	0.046	0.538	0.036	0.344
4th exp.	0.021	0.202	0.006	0.388
6th exp.	0.025	0.221	0.012	0.453

TRMC measurements. In Table 4 are shown the TRMC parameters extracted from Fig. 6.

As shown in Fig. 6 and Table 4, the presence of the surface modifying agents, HNO₃ and Cr(VI) adsorbed on the TiO₂ surface (no irradiation) modified the TRMC parameters of the pure sample, causing a decrease of I_{\max} and I_D , i.e., the parameters related to the amount of charge carriers. The effect of nitrate adsorbed on the TRMC signal of TiO₂ was explained previously [25,46] and will be not described here; in general, this species has a small influence on the signal when compared with the modification by Cr(VI) or Cr(III) [25], as seen in Table 4.

Although the effect of Cr(VI) as a modifier of the surface is to modify TRMC values by different processes, it has been stated that the main effect responsible for the decrease of I_{\max} and for effects at long times is probably the fast electron transfer of electrons to adsorbed Cr(VI) (Eq. (3)) [39,46,58] after excitation by the laser pulse.

Samples measured after the Cr(VI) photocatalytic reaction (1st exp., Table 4) show a decrease on I_{\max} and I_D compared with the blank, i.e. the HNO₃-modified sample. However, these effects are less important than in the Cr(VI)-modified (“initial”) sample because, after the photocatalytic reaction, Cr is mainly on the surface as Cr(III). It is not expected that Cr(III) can be an e_{CB}⁻ acceptor, as the reduction of Cr(III) to Cr(II) over TiO₂ is not possible ($E^0_{\text{Cr(III)/Cr(II)}} = -0.424 \text{ V}$ [45] vs. $E^0 = -0.3 \text{ V}$ for P25 CB electrons [46]). In contrast, Cr(III) has been reported to act as a recombination center, thus decreasing the lifetime of charge carriers [30,31,56]. A decrease on the lifetime of charge carriers (lower $I_{40\text{ns}}/I_{\max}$ and higher k_D) compared with the pure or the HNO₃-modified samples can be noticed.

In effect, according to Table 1, the amount of Cr attached to the surface is higher than before irradiation (0.30 and 0.05 mmol g⁻¹, respectively). A similar effect is observed when the samples coming from the 1st and the 4th exps. are compared, although, as can be seen in Fig. 5, the decrease of the signal is too sharp to allow a strict TRMC analysis. In the sample from the 4th exp., the higher amount of Cr on the surface (1.04 mmol g⁻¹) provokes a very important change on the lifetime of fast and slow charge carriers. After the 6th exp., very small changes are observed in the TRMC parameters, in agreement with the fact that the amount of Cr over TiO₂ did not change either (Table 1). As said, a small decrease in k is observed (Table 1), indicating that the photocatalyst deactivation still continues, but it cannot be appreciated in the TRMC parameters. The higher k_D values observed after the successive experiments, indicative of shorter lifetimes of long-lived charge carriers and high recombination, also confirm the observed deactivation. The decreased photocatalytic activity and the progressive deactivation that takes place (Fig. 1) parallel the TRMC results. It can be anticipated that if Cr(III) could be easily removed from the surface, then this decrease in the photocatalytic activity should not be observed.

Results of TRMC measurements for the system with EDTA can be observed in Fig. 7. The initial P25 sample, in previous contact with a solution containing Cr(VI) and EDTA, without irradiation, is included, together with the results of a sample in contact with HNO₃ at pH 2 with EDTA and without Cr(VI), as a test for the effect of the donor on the TRMC signal. The analysis of data of Fig. 7 is presented in Table 5, together with the amount of Cr found on the TiO₂ surface after the reaction.

The effect of HNO₃ and Cr(VI) as surface modifiers has been explained above for the system without EDTA. The presence of EDTA adsorbed on the TiO₂ (absence of Cr(VI)) barely changes the fast TRMC parameters (I_{\max} and $I_{40\text{ns}}/I_{\max}$) in comparison with the sample with HNO₃. This can be attributed to a low adsorption of neutral or protonated EDTA on the TiO₂ surface at pH 2. The changes in the slow TRMC parameters (lower I_D and k_D) with respect to the

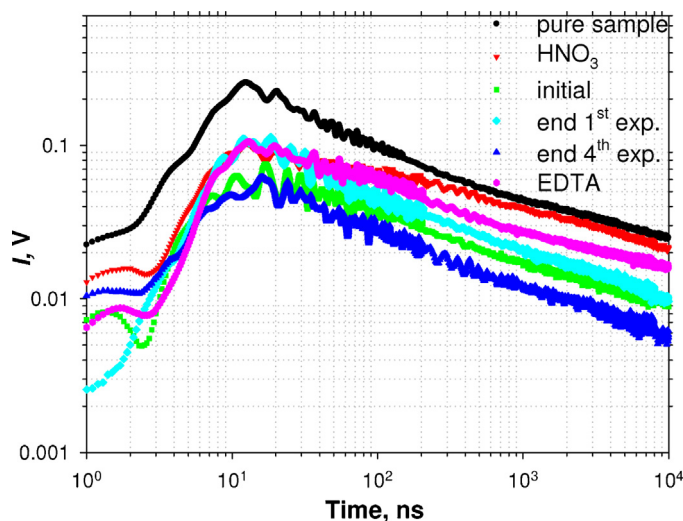


Fig. 7. TRMC measurements for successive experiments on a same P25 sample. Pure sample: unmodified TiO₂. HNO₃: P25 previously suspended at 1 g L⁻¹ in HNO₃ at pH 2. Initial: P25 previously suspended at 1 g L⁻¹ in 0.8 mM Cr(VI) and 2 mM EDTA in HNO₃ at pH 2 before irradiation. End 1st and 4th exps.: P25 after the respective experiment of irradiation in conditions of Fig. 2. EDTA: P25 previously suspended at 1 g L⁻¹ in 2 mM EDTA in HNO₃ at pH 2.

sample modified with HNO₃ are not very important and may be due to experimental error. In the case of the sample modified with Cr(VI)-EDTA before irradiation (“initial”), as expected, a decrease on I_{\max} and I_D compared with the pure or HNO₃-modified sample is observed, with a low or nil effect on the lifetime.

After the 1st exp. in the presence of EDTA, equivalent Cr on TiO₂ increases almost 50% over the initial value. Reduction of Cr(VI) to Cr(III) causes a less decrease of I_{\max} compared with the “initial” sample; a clear decrease of the lifetimes of fast and slow charge carriers caused by Cr(III) acting as recombination center is observed. Comparison of TRMC results between the samples from the 1st and 4th exps. indicates a decrease in I_{\max} and I_D after four reuses, with no change in the value of k_D ; $I_{40\text{ns}}/I_{\max}$ seems to increase, but this effect could be more linked to the decrease on I_{\max} than to an increase in $I_{40\text{ns}}$. The results can be related to the amount of Cr on the surface, which is twice after the 4th exp. (0.23 vs. 0.11 mmol g⁻¹, Table 2). Although Cr(III) has a low absorption in the range of emission of the laser [36,43], this absorption can be slightly higher in the presence of EDTA and on the TiO₂ surface; thus, a minor contribution as a UV light filter cannot be ruled out, causing the same effect.

Comparing now samples in the absence and presence of EDTA, results related to the Cr-modified sample before irradiation (“Cr(VI)” in Fig. 6 and Table 4 and “initial” in Fig. 7 and Table 5), it is possible to see that the amount of charge carriers are higher in the sample with EDTA; this increase can be very well explained by the occurrence of the thermal reduction of Cr(VI) by EDTA [33] when the sample is dried before the TRMC measurement, which increases the amount of Cr(III) on the surface (0.05 vs. 0.07 mmol g⁻¹, in the

Table 5
Decay parameters of the TRMC signal corresponding to Fig. 7.

Sample/condition	I_{\max} (V)	$I_{40\text{ns}}/I_{\max}$	I_D (V)	k_D
Pure P25	0.226	0.538	0.133	0.259
HNO ₃	0.096	0.774	0.105	0.252
EDTA	0.096	0.712	0.076	0.240
“Initial” ^a	0.059	0.776	0.053	0.262
1st exp.	0.102	0.558	0.077	0.307
4th exp.	0.054	0.655	0.045	0.312

^a Prepared in the presence of EDTA.

absence and in presence the of EDTA, Tables 1 and 2, respectively). This reduction is, of course, not complete, and residual Cr(VI) can be responsible for the smaller I_{\max} and I_D when comparing the “initial” sample with the sample after the 1st exp. with EDTA, despite Cr on TiO₂ is higher for this last sample.

The presence of Cr(III) on the surface in the initial sample with EDTA is also evidenced and confirmed by the change of color of the sample, which turned from yellow to violet [33,50]; this change of color did not occur in the absence of EDTA. Comparing now the results after the 1st exp., equivalent Cr on TiO₂ is much smaller with EDTA than in its absence (0.11 and 0.30 mmol g⁻¹, respectively); for this reason, if both experiments are compared with the blank (i.e., the HNO₃-modified sample), this amount of Cr barely changes I_{\max} in the system with EDTA.

4. Conclusions

Successive experiments for the photocatalytic reduction of Cr(VI) in the absence of a sacrificial donor showed a progressive decrease on the photocatalytic activity of P25. However, the presence of EDTA protects the photocatalyst and prevents its progressive deactivation. This effect of EDTA could be extended as a general behavior of other reducing oligocarboxylic acids, able to form soluble complexes with Cr(III). This makes very advantageous and promising the application of photocatalytic systems for Cr(VI) removal from effluents where both type of pollutants, metal ions and organic acids, are present and can be simultaneously removed.

The beneficial effect of EDTA in the photocatalytic reduction of Cr(VI) was also confirmed by TRMC experiments. It was observed that as EDTA inhibited the deposition of Cr(III) through the successive experiments, the necessary long lifetime of charge-carriers created on TiO₂ by illumination was maintained, in close relationship with the photocatalytic activity.

It was also observed that the treatment of a set of diluted Cr(VI) samples with the reused photocatalyst is more efficient than the use of a concentrated sample with the same photocatalyst under a longer irradiation.

Two final comments follow. (1) The results of this work regard only experiments with the pattern photocatalyst P25 and may be not valid for other photocatalysts. (2) Despite EDTA clearly enhances the photocatalytic treatment of Cr(VI), the application of this process to a real wastewater containing Cr(VI) and EDTA should include a further treatment step for the removal of the formed Cr(III)-EDTA, as this complex can be oxidized under environmental conditions back to the toxic Cr(VI) [62].

Acknowledgments

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