2. Photosensitized Degradation of Azo Dyes on Fe, Ti, and Al Oxides. Mechanism of Charge Transfer during the **Degradation**

J. Bandara,[†] J. A. Mielczarski,[‡] and J. Kiwi^{*,†}

Institute of Physical Chemistry II, Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland, and Laboratoire LEM/UMR 7569 CNRS, INPL-ENSG, BP 40, 54501 Vandoeuvre-les-Nancy Cedex, France

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Azo dyes disappear in photocatalyzed processes mediated by either hematite or geothite and TiO₂ (anatase and rutile) under visible light irradiation. The details of the charge injection from the excited state from Orange II into the catalyst are reported by laser-pulsed spectroscopy. The electron injection from the Orange II to α -Fe₂O₃ occurs within the duration of the laser pulse ($<10^{-8}$ s) and is followed by two processes: charge recombination with a rate of 1.1×10^7 s⁻¹, followed by a slower process with a rate of 2.1×10^5 s⁻¹ between the dye and the HO[•] radical at the iron oxide surface. At pH 3 the electrostatic attraction between $FeOH_2^+$ and HOR^- leads to the formation of a strong complex between Orange II and α -Fe₂O₃ necessary for an efficient charge-transfer process. This interaction is seen to be much weaker at neutral pH values. The complex [Orange II…a-Fe2O3] was identified at acid pH. At a concentration of Orange II of about 2.3 mM, monolayer coverage of this dye on α -Fe₂O₃ was observed. Photocorrosion of α -Fe₂O₃ with mononolayer dye coverage is much higher than that with multilayer dye coverage under visible light irradiation. The photogenerated intermediates generated on the oxide surface by the adsorbed azo dye during irradiation were identified by FTIR and in solution by HPLC. Experimental observations with COD and BOD techniques confirmed the improved biodegradability of the intermediates generated in the presence of α -Fe₂O₃.

Introduction

Most of the azo dyes used in textile industries are resistant to bacterial degradation, and therefore common wastewater treatment cannot be employed to abate this class of compounds. Other methods used in the abatement of recalcitrant dyes include precipitation,¹ adsorption,² wet oxidation,³ and photocatalytic degradation.⁴ During heterogeneous photocatalytic degradation of colorant, the light could be absorbed by either the colorant or the oxide surface or both. If TiO_2 is used as photocatalyst, the photogenerated holes lead to the generation of OH radicals in solution and the conduction band electrons react with the oxygen⁵ adsorbed on the oxide dispersed in solution. But titania and other stable semiconductors possess a wide band gap, absorbing mainly light in the UV region. Visible light photosensitization of oxide surfaces by dyes adsorbed on these oxide surfaces has been reported.^{6,7} Kamat et al.^{8,9} have recently reported that charge injection from the azo dye takes place from the singlet state of some

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azo dyes into the conduction band of the semiconductor particle. To achieve an efficient charge injection process, the sensitizer potential has to be higher than the conduction band energy of the semiconductor. The photosensitized oxidation of various colorants such as methylene blue,¹⁰ rose bengal,¹¹ and many others has been reported on TiO₂.¹²⁻¹³

The motivation for this study is that there is no systematic study available using iron oxides to photosensitize the degradation of dyes. $^{14-16} \alpha$ -Fe₂O₃ has a flat band potential of 0.32 V versus NHE (pH 0) and a band gap of 2.2–2.3 eV. α -Fe₂O₃ exhibits poor photocatalytic activity^{17,18} under direct band excitation due to the short diffusion length of the photogenerated electron-hole pairs. Photocorrosion in the presence of inorganic acids in oxygenated solutions¹⁹ takes place under irradiation. The aim of this study is to investigate the iron-oxides mediated degradation under light of common textile dyes such as Orange II (Or II), Orange I (Or I), and Orange G (Or G). In Part 1 of this study,²⁰ we reported on the factors

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governing the adsorption of these azo dyes on iron oxides, and titania and alumina surfaces. Part 2 reports hereby the photosensitized degradation of azo dyes (Orange II, Orange I, and Orange G) on α -Fe₂O₃, α -FeOOH, TiO₂, and Al₂O₃ under visible light with regard to (a) the active crystalline phase of each semiconductor during the observed photodegradation, (b) the adsorption step importance during the dye abatement, and (c) the extent and kinetics of the azo dye degradation for each oxide surface. The dyes used during this study are well suited to harvest visible light (sunlight) as an economical light source.

Experimental Section

A. Materials. Orange II, Orange I, and Orange G, acids and bases, and FeCl₃ were Fluka p.a. and were used as received. Triple-distilled–deionized water was used during all experiments. α -Fe₂O₃ (150–160 m²/g) was prepared according to ref 20 or was a BASF product with a surface area of 150 m²/g. The anatase used was from British Tioxide with 55 m²/g, and the rutile was from the same supplier with 50 m²/g. The alumina used was γ -Al₂O₃ (170 m²/g ex-Engelhard).

B. Colloid Preparation. The preparation of the colloids for fast kinetic spectroscopy is described below. The α-Fe₂O₃ colloid was prepared in the following way:²² FeCl₃·3H₂O was ground into a fine powder, and the stock solution was prepared containing Fe³⁺ (50 mM). Next, 300 mL of this solution was added dropwise into 1200 mL of boiling water. The solution was subsequently refluxed at 100 °C followed by dialysis with a Spectra/POR dialysis membrane (molecular weight cutoff 14 000) at 100 °C to remove Cl⁻ ions until pH 3.5 was attained. The water in the dialysis bath was replenished every 2–3 h during this last operation. Colloidal particles were obtained with a particle size of 3–25 nm. Colloidal TiO₂ was prepared in the following way:²² TiCl₄ (Fluka) was slowly added to water at 0 °C. The solution was subsequently dialyzed until pH ~ 3.5 within a 3 day period.

C. Analysis of the Irradiated Solutions. The detection of the dissolved iron in solution was carried out by atomic absorption spectroscopy (Philips 800-2AAS). The sensitivity of this instrument is ~ 1 ppm. Spectrophotometric analyses of the solutions were carried out by way of a Hewlett-Packard 8452 diode array spectrophotometer. The total organic carbon (TOC) was monitored via a Shimadzu 500 instrument equipped with an ASI automatic sample injector. Detection of CO2 was carried out via a Carlo Erba gas chromatograph provided with a thermal conductivity detector and a Poropak Q column. Helium was used as a carrier gas for the determination of CO₂. Intermediate products of dye degradation were identified with a Varian HPLC provided with a 9065 Diode. A Phenomenex C-18 inverse-phase column was used, and the dye signals were detected at 229 and 254 nm. The gradient solution was regulated with a buffer consisting of ammonium acetate and methanol. Analysis of oxalic acid was carried out by means of an H-801 interaction column in an isocratic mode by way of ion liquid chromatography (Dionex DX-100 Ion Chromatograph). Cyclic voltammetry was employed to detect the oxidation potential of the substances under study. The electrochemical analyzer Autolab PGSTAT-20 was used in conjunction with a three-way electrode system. Glassy carbon, Ag/AgCl, and C were used as working electrode, reference electrode, and counter electrode, respectively. NaClO₄ (0.1 M) was used as electrolyte. The pH was adjusted either with NaOH or HClO₄.

The determination of the chemical oxygen demand (COD) was carried out in 2 mL solutions added to dichromate reagent. The mixture was digested at 150 °C for 2 h. The color developed during the oxidation was measured against a water blank in a calibrated Hach DR/890 colorimeter. The change of color due to the dichromate was followed at $\lambda = 430$ nm. Biological oxygen

 Table 1. First-Order Rate Constants for Orange II

 Disappearance

| concentration of Or II | rate constant (min ⁻¹) on α -Fe ₂ O ₃ | rate constant (min ⁻¹) on α -FeOOH |
|---------------------------|--|---|
| 0.15 | $2.0	imes10^{-2}$ | $0.34	imes 10^{-2}$ |
| 0.30 | $1.8	imes 10^{-2}$ | $0.39	imes10^{-2}$ |
| 0.60 | $1.5	imes 10^{-2}$ | $0.09	imes10^{-2}$ |
| 1.20 | $0.4	imes10^{-2}$ | $0.05	imes10^{-2}$ |

demand (BOD_5) was carried out to confirm the increase in biodegradability of pretreated solutions in a WTW 2000 Oxytop unit. $^{23}\,$

D. Laser Pulsed Photolysis Experiments. Laser photolysis was carried out by using the second harmonic ($\lambda = 347$ nm) of a JK-2000 Ruby laser operated in the Q-switched mode. The pulse width was about 15 ns, and the energy per pulse was ~10 mJ. The laser pulse energy was monitored with a photodiode. The mean average diameter of the laser light beam was 0.5 cm. The signals from the detector were recorded on a Tektronix TDS 640A digitizing oscilloscope. A 300 nm cutoff filter was used between the diode and the sample to avoid interference from the sample emission at wavelengths below 300 nm. Xe light was used for the detection of the intermediates, and in each case the appropriate Schott SKF band-pass filter was selected. The filter band-pass widths were $\Delta \lambda = 20$ nm and were centered at the λ of interest. All experiments were performed in 1 cm quartz cells.

E. Photoreactor and Irradiation Procedures. Photolysis was carried out inside the cavity of a Hanau Suntest solar simulator with a radiant flux of 90 mW/cm² and provided with air cooling regulated at ~30 °C. The lamp has a wavelength (λ) distribution with about 7% of the emitted photons between 290 and 400 nm. The profile of the photons emitted between 400 and 800 nm followed the solar spectrum. The irradiation vessels used were 60 mL cylindrical Pyrex flasks (cutoff $\lambda \approx 290$ nm), each containing 40 mL of reagent solution. A known amount of oxide was added, and the pH was adjusted using HCl or NaOH. The radiant flux in milliwatts per square centimeter was measured with a power meter of LSI Corp, Yellow Springs, CO.

F. FTIR Experiments. Adsorbed species on the catalyst surface were analyzed by the diffuse reflectance infrared fourier transform (DRIFT) technique using a Bruker IFS 55 instrument. The oxide samples were analyzed diluted in KBr at a 1:5 ratio. The oxide samples were equilibrated with the different dye solutions, filtered, and dried at room temperature to remove the adsorbed water.

Results and Discussions

A. Kinetics of Azo Dye Degradation on α-Fe₂O₃ and α-FeOOH. Comparison of the Observed Degradation Kinetics with TiO₂ and Al₂O₃. The disappearances of Orange II in the presence α -Fe₂O₃ and α-FeOOH under light for different initial dye concentrations were carried out, and the results are shown in Figure 1a and b for α -Fe₂O₃ and α -FeOOH. The actual concentration of Orange II is defined as the sum of the amount of dye remaining in the solution and the amount adsorbed on the oxide surface. The dye remaining on the surface was desorbed from the iron oxide by increasing the solution pH value up to pH \sim 12. Figure 1 shows that degradation rates of Orange II on both α -Fe₂O₃ and α -FeOOH decrease with increasing dye concentration. Table 1 gives the initial rate constants of Orange II decomposition on both iron oxides. The disappearance of Orange II in Figure 1 follows an approximate pseudo-first-order decay kinetics. The calculated first-order rate constants are given in Table 1.

From the above results, the catalytic activity of α -FeOOH for the decomposition of Orange II is seen to be rather inefficient compared to that of α -Fe₂O₃.

Figure 2 indicates that the disappearance of Orange II on both iron oxides does not follow Langmuir-Hinshel-

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Figure 1. Orange II disappearance as a function of dye concentration in the presence of hematite under Suntest solar-simulated irradiation (80 mW cm²). Hematite 1.5 g/L, pH 3.1. (b) Orange II disappearance as a function of dye concentration in the presence of geothite under Suntest solar-simulated irradiation (80 mW cm²). Geothite 1.5 g/L, pH 3.



Figure 2. Initial rate of the disappearance of Orange II versus the concencentration of Orange II: (a) hematite; (b) geothite. The inset shows the reciprocal of the initial rate versus the reciprocal value of the initial concentration of Orange II.

wood kinetics, since in this case the initial rate for α -Fe₂O₃ should increase until a concentration $\sim 6.5 \times 10^{-4}$ M and then attain a plateau. The attempt to plot a linearized Langmuir–Hinshelwood (L–H) equation with the data plotted in Figure 2 is shown in the inset to this figure. r_0

is the initial reaction rate and C_0 the initial concentration of Orange II.

$$\frac{1}{r_0} = \frac{1}{k} + \frac{1}{kK} \frac{1}{C_0} \tag{1}$$

A plot of r_0^{-1} versus C_0^{-1} (eq 1) should give a straight line with a slope K^{-1} (*K* is the adsorption constant) and an intercept k_r^{-1} (*k* is the rate constant of Orange II disappearance). In Figure 2, increasing the dye concentration to values above 6.5×10^{-4} M led to a decrease in the rate of Orange II disappearance due to (a) higher Orange II concentration beyond the value of 6.5×10^{-4} M (Figure 2) with multilayer dye coverage of α -Fe₂O₃ (Figure 3-1 in Part 1 of this study²⁰) seeming to preclude light absorption by the iron oxide and (b) self-quenching of Orange II* (D*) as the dye concentration is increased.²⁴ The disappearance of Orange II on the α -Fe₂O₃ surface under light irradiation seems therefore to involve charge transfer eq 2 with concomitant quenching of the excited state.

Orange II/
$$\alpha$$
-Fe₂O₃ $\xrightarrow{h\nu}$ [Orange II*/ α -Fe₂O₃] \rightarrow
Orange II*+ α -Fe₂O₃⁻ (2)

If the light is absorbed directly by α -Fe₂O₃, the disappearance of Orange II relates to the formation of surface complexes' charge separation processes induced by light. An increase in the initial rate in Figure 2 was observed as the concentration of Orange II was increased in solution, and this is result suggested by eq 3 below.

$$[\text{Orange II/Fe}_2\text{O}_3] \xrightarrow{h\nu} \\ [\text{Orange II/Fe}_2\text{O}_3 (h^+, e^-)] \xrightarrow{h\nu, \text{O}_2} \\ [\text{Orange II}^{\bullet+}/\text{Fe}_2\text{O}_3(e^-_{cb})]/\text{O}_2^-_{ads} (3)$$

Besides reacting with chemisorbed O_2 , the h^+ can react with $OH^{-}/H_{2}O$ adsorbed on the oxide surfaces to generate OH or HOO radicals, as will be discussed below in the text (eq 6). The disappearance of Orange II was also observed to be dependent on the irradiation wavelength (λ) used. Even at $\lambda > 500$ nm the Orange II disappearance was observed beyond the range of optical absorption of the quantized colloid α -Fe₂O₃ particles, ^{13,14} lending support to the sensitization mechanism suggested in eq 2. The activities of α -Fe₂O₃ and α -FeOOH were also tested for Orange I and Orange G. The latter dye has other functional groups than those of Orange II (see Part 1 of this study²⁰). Two bulky sulfonic groups in the naphthalene ring make the adsorption of Orange G on α -Fe₂O₃ more difficult. Disappearance of Orange G was observed to be slower on α -Fe₂O₃ than in the case of Orange II and Orange I. This was due to the poorer adsorption of Orange G on α -Fe₂O₃ compared to Orange II.

B. Comparison of the Degradation of Orange II on α-Fe₂O₃, TiO₂, and Al₂O₃. The disappearance of Orange II was also carried out on TiO₂(anatase) and γ -Al₂O₃. Figure 3 shows the disappearance of Orange II on α-Fe₂O₃, TiO₂ (trace b), and Al₂O₃ (trace c) under Suntest light irradiation in a solution with an initial pH of 3.0. Al₂O₃ is shown to be practically inactive for the degradation of azo dyes, since the small decrease observed for Orange II with Al₂O₃ is attributed to the photobleaching of Orange II due to the presence of the O₂(air) in the

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Figure 3. Disappearance of Orange II as a function of time on solutions containing (a) α -Fe₂O₃, (b) TiO₂, and (c) γ -Al₂O₃ under Suntest irradiation using 1.5 g/L of each oxide at pH 3.

Table 2. Rate Constants for or II Disappearance versus Initial Dye Concentration on TiO_2

| initial Or II concn (mM) | rate constant (min ⁻¹) |
|--------------------------|------------------------------------|
| 0.15 | $1.2	imes 10^{-2}$ |
| 0.30 | $0.7	imes10^{-2}$ |
| 0.60 | $0.6	imes10^{-2}$ |
| 1.20 | $0.2	imes10^{-2}$ |

solution. Table 2 shows the initial rate constants of Orange II decomposition on TiO_2 as a function of the initial dye concentration.

The failure of Al_2O_3 (trace 3) shows the importance of the semiconducting properties of the support during photoinduced abatement of this dye. Also a higher surface density of Orange II was found on α -Fe₂O₃ than on TiO₂, which may justify the trend reported in Figure 3.^{20,25}

C. Laser Spectroscopy of Transient Intermediates. Laser flash photolysis was carried out to sort out the details of the charge injection process on the three colloidal oxides reported in Figure 4. This figure shows the spectral contributions of Orange II and Orange II onTiO₂, α -Fe₂O₃, and γ -Al₂O₃ oxide species. Spectra a, b, and c show a higher absorption than spectrum d of Orange II alone due to the significant contribution of the colloid to the total absorbance.

Transient absorption spectra induced by the 347 nm laser pulse of α -Fe₂O₃/Orange II and TiO₂/Orange II are shown in Figure 5 in traces a and b. Figure 5c shows the spectrum of Orange II in air-saturated solution. The bleaching of the ground state with a maximum at $\lambda \sim 480$ nm and with absorption at $\lambda > 500$ nm and < 380 nm is seen in trace c. The bleaching at $\lambda \sim 480$ nm reflects the depletion of ground-state molecules by the excited states with a larger adsorption coefficient. The absorption bands at around 550 nm and below 360 nm have been assigned to the Orange II⁺⁺ cation radical by Kamat et al.⁹ It has recently been reported that intersystem crossing between the singlet and the triplet in Orange II is almost negligible.²⁶ Therefore, it can be assumed that the singlet state of Orange II is involved in the charge-transfer

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Figure 4. UV–vis spectra of adsorbed Orange II on colloidal (a) TiO₂, (b) α -Fe₂O₃, (c) γ -Al₂O₃, and (d) Orange II in solution at pH 3. For other details see text. Initial concentration of Orange II 0.6 mM, pH 3.5, equilibration time 24 h.



Figure 5. Transient absorption spectra of (a) Orange II adsorbed on hematite, (b) Orange II adsorbed on TiO₂, and (c) free Orange II. For other details see text.

process. Figure 5b shows that Orange II adsorbed on colloidal TiO₂(e⁻_{cb}) still presents the characteristic bleaching of this dye at $\lambda = 480$ nm. The broad absorption > 500 nm is attributed to the transient Orange II+ radical cation9 in conjunction with the $TiO_2(e^-_{cb})$ species created during the dye–oxide redox reaction. The TiO_2 colloid at $\lambda < 385$ nm does not show any optical absorption or transient signals. Optical absorption after the laser pulse due to colloidal α -Fe₂O₃ alone was not observed in the nanosecond time scale, since the absorption occurs within the time of the pulse duration. Figure 5a shows the transient spectra of Orange II-adsorbed α -Fe₂O₃ with a broad absorption in the 360-630 nm region. Above 10^{-5} s the characteristic bleaching of the Orange II was observed, indicating efficient charge transfer. The absorption in the 530-600 nm range by Orange II/α -Fe₂O₃ can be attributed to the conduction band electrons and the one-electron oxidation products of Orange II (see reaction 2). The light-induced electron transfer leads to the oxidation product Orange⁺⁺ and conduction band electrons. Redox events will be further explored below (Figure 6).

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Figure 6. (a) Transient absortion after the laser pulse at $\lambda = 347$ nm of Orange II adsorbed on colloidal hematite at pH 3.0. For other details see text. (b) Transient absortion after the laser pulse of Orange II adsorbed on colloidal TiO₂ at pH 3.0. For other details see text.

The transient decay of Orange II adsorbed on α -Fe₂O₃ and TiO₂ colloids at $\lambda = 550$ nm is shown in Figure 6a and b, respectively. The fast charge injection from Orange II to the colloid after the laser pulse was found in Figure 6a. Fast decay is observed suggesting an efficient charge-transfer process between the dye and the colloidal particle. The fast kinetic process is shown in Figure 6a and b, where MO is the oxide colloid

Orange II/MO
$$\rightarrow$$
 Orange II^{•+}/MO e_{ch}^- (4)

At later stages of the reaction ($t > 10^{-5}$ s in Figure 6a), bleaching of Orange II was observed. The electron injection from several dyes to semiconductor colloids has been reported in the range 10^{-8} s.^{25–27} Analysis of Figure 6a revealed a bimodal decay with a fast and a slow component with rates of 1.1×10^7 and 2.1×10^5 s⁻¹, respectively. This suggests two different decay paths. The fast decay is due to charge recombination by back electron transfer from either the conduction band or an MO surface state²⁴ to Or II⁺⁺ obeying first-order kinetics. This reaction would proceed with a rate of 1.1×10^7 s⁻¹.

$$MO e_{ch}^{-}/Orange II^{+\bullet} \rightarrow Orange II-MO$$
 (5)

The recombination reaction 5 describes is a process that proceeds at a much lower rate than the rate for the charge injection mentioned above. The slower component decay (Figure 6a and b) suggests that the photogenerated Or*+ decays also by an alternative channel with a rate of 2.1 \times 10⁵ s⁻¹ through reaction with the HO* radical at the semiconductor/water 24,25 interface





Scheme 2. Reactions for Orange II on Semiconductor Oxides

Normal Income and a second and the second

| dye sensitization | direct band gap excitation |
|--|--|
| dye + h \longrightarrow dye 'dye + MO \longrightarrow dye MO(e') + O ₂ \longrightarrow O ₂ + MO dye ⁺⁰ \longrightarrow products dye ⁺⁰ + O ₂ \longrightarrow products | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ |
| | $(Or II^{\circ}, Or II^{+\circ}) + (O_2^{\circ}, HO^{\circ}) \longrightarrow products$ |

These HO[•] radical attack on the adsorbed Orange II may then proceed

$$HO^{\bullet} + Or II \longrightarrow HO^{\bullet} - Or II \qquad \qquad HO^{\bullet} + Or II^{+\bullet}$$
decay products (7)

The decay kinetics of Orange II* on TiO₂ is presented in Figure 6b. The decay comprised two components. The fast and slow components' decay proceeded with rates 8.8 \times 10⁷ and 2.5 \times 10⁷ s⁻¹, respectively (Figure 6b). Similar behavior has been reported for tetramethyl–phenylene-diamine (TMPD) on TiO₂^{25,26} and in related work by Fox.²⁷ For TiO₂ related systems the sensitization processes are summarized in Scheme 1. The processes are outlined in Scheme 2.

The azo dye molecules tested have more positive oxidation potential than the conduction band energy of Al_2O_3 . This precludes the electron transfer from Orange II* to the conduction band of Al_2O_3 , explaining the lack of Orange II decomposition on Al_2O_3 . The energy from the optical excitation provides the driving force for electron injection from the dye molecules into the conduction band of iron and titanium oxides. This driving force is calculated by eq 8

$$\Delta G^{\circ} = -nF[E_{\rm cb} - E^{\circ}(\mathrm{D}^+/\mathrm{D}^{\circ})]$$
(8)

where ΔG° is the standard free energy change for the reaction, *n* is the number of electrons transferred in the redox process, *F* is the Faraday constant, *E* is the energy level position of the oxide semiconductor, and D⁺/D^{\circ} is the redox potential of the dye. Both α -Fe₂O₃ and TiO₂ have more positive conduction bands than Orange II, Orange I, and Orange G excited levels. Therefore, the electron transfer is thermodynamically allowed. The calculated standard free energies (ΔG^*) at pH 3.0 are -1.31 and -0.983 eV for α -Fe₂O₃ and TiO₂, respectively. Table 3 gives the excited redox potentials of the dyes and the conduction band levels of the oxides, indicating the favorable charge transfer in the presence of TiO₂ and α -Fe₂O₃ but not in the case of γ -Al₂O₃.

⁽²⁷⁾ Fox, M. A.; Dulay, M. T. J. Photochem. Photobiol., A: Chem. 1986, 91, 98.



Figure 7. Transient traces after the laser pulse at 347 nm of Orange II adsorbed on α -Fe₂O₃ at different pH values: (a) pH 3; (b) pH 4.0; (c) pH 5.0; (d) pH 6.0; (e) Orange II alone at pH 3.

 Table 3. Excited State Redox Potentials for Different Azo Dyes

| dye | D*/D+ (V vs NHE) excited state redox potential | oxide | <i>с</i> ь at pH 3.0 (NHE) |
|-------|--|--|-------------------------------|
| Or II | -1.44 | α -Fe ₂ O ₃ | +0.02 |
| Or I | -1.43 | TiO ₂ (anatase) | -0.44 |
| Or G | -1.40 | γ -Al ₂ O ₃ | <-3.00 |

 Table 4. Two-Component Decay of Orange II on Hematite as a Function of pH

| pH | k_1 (s ⁻¹) | k_2 (s ⁻¹) |
|---------------|--------------------------|--------------------------|
| 3.0 | $3.56 	imes 10^5$ | $4.13	imes10^6$ |
| 4.0 | $4.12	imes10^5$ | $4.12	imes10^6$ |
| 5.0 | $4.56	imes10^5$ | $4.03	imes10^6$ |
| 6.0 | $4.13	imes10^5$ | $4.02	imes10^6$ |
| Or II, pH 3.0 | $8.80 	imes 10^5$ | |
| | | |

D. Charge Transfer as a Function of pH and Dye Coverage of the Colloid. The effect of pH on Orange II disappearance was examined by laser spectroscopy. The bimodal decay of the transient after the laser pulse is shown in Figure 7. Laser flash photolyses at different pH values after the dye adsorption on α -Fe₂O₃ was carried out at pH 3.0. The adsorption at pH 3 allows us to have the same amount of dye at pH values > 3, since desorption up to pH > 6 does not proceed when the pH is stepwise increased beyond pH 3. This allows us to analyze the charge transfer and degradation at different pH values starting from the same initial material. The absorbance in Figure 7 is assumed to be proportional to the magnitude of the charge transfer, since the amplitude of the dye transient signal in acid solution is significantly higher for pH 3 than for pH 6. The strong complex formation between Orange II and α -Fe₂O₃ at acid pH is seen as the origin of an efficient charge-transfer process due to FeOH₂⁺ and HOR⁻ electrostatic attraction taking place in acid pH.²⁰

The rate constant for the two-component decay at different pH values of Orange II on α -Fe₂O₃ colloid is shown in Table 4. It is clearly seen that the k_1 and k_2 values do not vary as a function of pH even though the absorption



Or II concentration (mM)

Figure 8. Yield of Orange II⁺⁺ formation as a function of Orange II concentration in solution at pH 3 at $\lambda = 550$ nm. For other details see text.

increases at more acidic pH values.²⁰ This observation supports the earlier results²⁰ that Orange II adsorption does not proceed on α -Fe₂O₃ due to electrostatic forces alone, which become weaker with an increase in pH. The origin of the bonding is due to the formation of an iron sulfonate surface complex whose strength is independent of pH. The results presented in Table 4 also suggest that at different pH values the decay follows the same mechanism.

However, on TiO₂ colloids Orange II disappearance was observed at both acidic and basic pH values and the transient reflected well-known charge-transfer processes involving sensitization due to the dye.^{17,21,22,25}

Figure 8 shows the optical absorption after the laser pulse changes as a function of the Orange II amount adsorbed on the α -Fe₂O₃ colloid. The absorbance shown at $\lambda = 550$ nm represents the amplitude of the Or⁺⁺ transient signal after the laser pulse. This amplitude is taken as being directly proportional to the efficiency of the charge injection from Orange II to the $\alpha\mbox{-}Fe_2O_3$ colloid. The yield of Or*+ is seen to increase with surface coverage in Figure 8, attaining a maximum at about 2.3×10^{-2} M. The region below the maximum Orange II concentration in Figure 8 represents from submonolayer up to monolayer coverage. Beyond the maximum, the yield of Or^{•+} decreased due to the competition of the reaction, leading to the formation of Or^{+} (eq 3) by charge injection and the self-quenching process described already in eq 4 as multilayer formation becomes predominant in solution.

E. Dissolution of Iron Oxide as a Function of Dye Concentration in Solution. If the Orange II–MO complex leads to a ligand-to-metal charge transfer (LMCT), then it is possible to suggest reaction 9 to describe the α -Fe₂O₃ photocorrosion in solution of Orange II.

$$> \mathrm{Fe^{III}Or} \xrightarrow{k_{a}(\mathrm{L}), k_{r}} > \mathrm{Fe^{II}Or}^{\bullet +} \xrightarrow{k_{p}} > \mathrm{Fe^{II}} + \mathrm{product}$$
(9)

where $k_a(L)$ is the specific rate of light absorption, k_r is that of the back reaction, and k_p is the rate constant of product formation. Up to monolayer coverage of α -Fe₂O₃ the corrosion of the oxide leads to Fe²⁺ ion release from the iron oxide surface to the solution. With multilayer coverage of Orange II no dissolution of Fe²⁺ was observed. An important step is the rate constant of product formation. Up to monolayer coverage of α -Fe₂O₃ the corrosion of the oxide leads to Fe²⁺ ion release from the iron oxide surface to the solution. With multilayer coverage of Orange II no dissolution of Fe²⁺ was observed. An important step is the detachment of Fe²⁺ from the oxide surface and the regeneration of > Fe^{III} by a suitable oxidant such as O₂

$$> \mathrm{Fe}^{2+} \underbrace{\overset{\mathrm{H}^{+}, k_{\mathrm{det}}}{\longleftarrow}} > \mathrm{Fe}^{\mathrm{II}} \underbrace{\overset{\mathrm{O}_{2}, k_{\mathrm{ox}}}{\longrightarrow}} > \mathrm{Fe}^{\mathrm{III}} + \mathrm{O_{2}}^{\bullet^{-}}$$
(10)

where k_{ox} is the reoxidation rate constant of the surface and k_{det} is the rate constant of Fe ion detachment of the oxide surface. Applying steady-state assumptions for the charge-transfer step and for the \equiv Fe^{II} concentration, the rate of iron dissolution on the surface is shown in eq 11.

rate =
$$k_{a}(\lambda)$$
[=Fe^{III}Or] $\frac{k_{p}}{k_{p} + k_{f}} \cdot \frac{k_{ox}}{k_{det} + k_{ox}}$ (11)

Taking a concentration of 2.7×10^{-4} M for the O_2 in solution, the first-order rate constant for the surface Fe^{2+} reaction⁶ with O_2 is $6.0 \times 10^{-9} \, s^{-1.6}$ The rate constant for the detachment of Fe^{2+} from the hematite surface⁶ was observed to be $5.04 \times 10^{-5} \, s^{-1}$ at the low Orange II coverage of $\sim 0.5 \times 10^{-3}$ M (see Part 1, 20 Figure 3). The photodissolution and reoxidation processes competing on the α -Fe₂O₃ surface could be accounted for by eq 12 for low dye coverage and for high dye coverage by eq 13. In the latter case further dissolution of Fe²⁺ is precluded in solution

$$Fe^{3+}$$
(lattice/surface) + $e^{-}_{cb} \rightarrow$
 Fe^{2+} (lattice/surface) (12)

$$Fe^{2+}$$
(lattice/surface) + Or II \rightarrow
 Fe^{3+} (lattice/surface) + Or^{•-} (13)

At low surface coverage for each electron transferred from Orange II to α -Fe₂O₃ one Fe²⁺ should be detached into the solution if the reaction is fast. This was not observed, suggesting that the Fe²⁺ detachment is hindered by O₂-induced reoxidation (section A, reaction 3). At high surface coverage, the Orange II* does not transfer charge to the α -Fe₂O₃, since excited-state quenching of the dye by a neighboring dye molecule is faster than the charge transfer to the iron oxide.

F. Intermediate Analyses by HPLC and FTIR. Solution intermediates produced during the photocatalyzed degradation were identified by HPLC. The intermediates retained on the catalyst surface were investigated by FTIR. For a set irradiation time, the pH was increased for each sample to desorb the intermediates to be used for HPLC analyses.



During the initial stages of Orange II photocatalyzed disappearance on α -Fe₂O₃ (~30 min, Figures 1–3), the following intermediates were identified by HPLC: (A) sulfobenzoic acid, (B) 1,2-naphthol, (C) 1,2-naphthaquinone, and (D) sulforanilic acid. For a set irradiation time, the pH was increased for each sample to desorb the intermediates to be used. Compounds A, B, and C were major intermediates with a small amount of D as a minor species. Compound D is highly unstable and has been reported to decompose to A.^{17,24} Minor chromatographic species were not identified. The amounts of the unidentified minor species were observed to grow at the expense of B and C decreasing with time between 30 and 240 min. Identification of the decomposition products during photocatalyzed degradation of Orange II on TiO_2 was carried out separately. The decomposition products were similar to those found in the case of α -Fe₂O₃. For α -FeOOH a lower concentration of intermediate products was found due to the lower catalytic activity of α -FeOOH observed during Orange II decomposition.

Figure 9 shows the FTIR results of Orange II disappearance on iron and titanium oxides. On α -Fe₂O₃, anatase, and rutile oxide surfaces similar IR peaks were observed, suggesting a common reaction mechanism. The disappearance of A, B, and C was followed with time on the metal oxides employed. With multilayer surface coverage by Orange II, no change was observed in the FTIR spectra with time. Variation of the peaks in Figure 9 was only observed with submonolayer and monolayer coverage of the azo dye. The bands of 1452, 1552, 1572, 1599, and 1623 cm⁻¹ were assigned to C=C stretching vibrations.³⁰ The CH-bands were observed at 832 and 832 cm⁻¹. The weak peaks at 1405 and 1318 cm⁻¹ are assigned to O-H bending vibrations and deformation while the band at 1256 $\rm cm^{-1}$ is assigned to the C–O–H stretching vibration. The weak peak at 1452 cm⁻¹ on the shoulder of the O-H bending band is due to the N=N bond. For α -Fe₂O₃ and TiO₂ the peaks reported in Figure 9a and b were seen to decrease under light irradiation with concomitant formation and growth of the peaks due to the degradation intermediates.

G. COD and BOD₅ Analysis of Treated Solutions. Chemical oxygen demand (COD) and biological oxygen demand (BOD) experiments were carried out after the phototreatment in order to confirm the biodegradabilty and oxidability of the intermediates formed. Table 5 reports on the COD and BOD₅ values obtained for Orange II degradation on α -Fe₂O₃ and TiO₂. After the photochemical treatment under Suntest lamp irradiation, COD values decrease, suggesting that the long-lived intermediates produced are more easily oxidizable than the unpretreated Orange II. This was confirmed by the BOD₅ value observed for the photochemically treated solutions. It is interesting to note that the COD value in the case of α -Fe₂O₃ is lower than the value found for TiO₂. This indicates a better catalytic effect of the iron oxide relative to TiO₂ as mediator during Orange II degradation to more readily biodegradable intermediates in solution.

Conclusion

The results obtained during azo dye photocatalytic decomposition on iron oxides were compared with those for other oxides such as TiO_2 and Al_2O_3 . Azo dyes disappeared from solution when α -Fe₂O₃ and TiO_2 were used as mediators in photocatalytic-induced reactions. α -FeOOH or Al_2O_3 (wide band gap Al_2O_3) does not show this effect. Dye abatement occurs via charge or electron transfer from an excited dye molecule to the iron oxide or TiO_2 . The process is highly dependent on the solution pH and the dye concentration on the surface of the mediator. The higher degradation rate seen at acid pH is due to the efficient electron-transfer process due to strong surface complex bond formation. This effect is less marked in neutral/basic pH solutions. The strong surface complex formation seems to favor efficient charge transfer. On TiO₂

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Figure 9. (a) FTIR spectra of adsorbed Orange II on α -Fe₂O₃ with irradiation time: (a) time zero; (b) 4 h; (c) 24 h. (b) FTIR spectra of adsorbed Orange II on α -FeOOH with irradiation time: (a) time zero; (b) 4 h; (c) 24 h. (c) FTIR spectra of adsorbed Orange II on TiO₂ anatase with irradiation time: (a) time zero; (b) 4 h; (c) 24 h. (d) FTIR spectra of adsorbed Orange II on TiO₂ rutile with irradiation time: (a) time zero; (b) 4 h; (c) 24 h. (d) FTIR spectra of adsorbed Orange II on TiO₂ rutile with irradiation time: (a) time zero; (b) 4 h; (c) 24 h. (d) FTIR spectra of adsorbed Orange II on TiO₂ rutile with irradiation time: (a) time zero; (b) 4 h; (c) 24 h.

 Table 5. Pretreatment of Orange II Solutions on Hematite and Titania^a

| | COD | BOD_5 |
|---|-----|---------|
| untreated Or II ($6.0 	imes 10^{-4}$ M) | 200 | 15 |
| lpha-Fe ₂ O ₃ /Or II (6.0 $	imes$ 10 ⁻⁴ M) | 110 | 95 |
| pretreated for 4 h under light | | |
| $TiO_2/Or II (6.0 \times 10^{-4} M)$ | 132 | 105 |
| pretreated for 4 h under light | | |

^a Suntest simulator used (90 mW/cm²).

azo dye degradation occurs by dye sensitization and direct band-gap excitation. It was found to be less affected by the solution pH than the case for α -Fe₂O₃, owing to the formation of a weaker surface complex on TiO₂. α -Fe₂O₃ and TiO₂ led to the formation of highly biodegradable intermediates in solution, which allows for subsequent coupling of the expensive pretreatment with low-cost biological degradation. This is an interesting option from

the applied point of view. During this study the azo dye abatement was seen to proceed by (a) LMCT processes involving ligands adsorbed on the mediator oxide, (b) photooxidation of adsorbed species by the holes of the valence band of the semiconductor employed, and (c) oxidation of the adsorbed azo dye by the HO[•] radical resulting from the scavenging of the electrons adsorbed on O_2 or holes by the catalyst surface HO[•] groups.

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