Diuron Degradation in Irradiated, Heterogeneous Iron/Oxalate Systems: The Rate-Determining Step

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The purpose of this study was to examine the various factors that control the kinetics of diuron degradation in irradiated, aerated suspensions containing goethite (α -FeOOH) and oxalate, in the following denoted as heterogeneous photo-Fenton systems. In these systems, attack by hydroxyl radicals (HO•) was the only pathway of diuron degradation. Studies were conducted in systems containing initially 80 or 200 mg L^{-1} goethite (corresponding to 0.9 or 2.25 mM) total iron) and 20, 50, 75, 100, 200, and 400 μ M oxalate at $3 \le pH \le 6$. Both oxalate concentration and pH greatly affected the rate of light-induced diuron transformation. In the presence of initial 200 μ M oxalate, the rate of diuron degradation was maximal at pH 4, coinciding with the maximal extent of oxalate adsorption on the surface of goethite. At pH 4, the rate of light-induced diuron degradation increased with increasing oxalate concentration, reaching a plateau at initial 200 µM oxalate, i.e., at the oxalate solution concentration at which the extent of oxalate adsorption on the surface of goethite reached a maximum. These experimental results suggest that the rate of Fe(II)(aq) formation through photochemical reductive dissolution of goethite, with oxalate acting as electron donor, determines the kinetics of diuron degradation in these heterogeneous photo-Fenton systems.

Introduction

One of the unresolved environmental problems consists of the pollution of soils and aquatic systems by chemicals used in agriculture. One of the widely used herbicides is diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] since it acts on a large variety of parasitic plants through inhibition of photosynthesis (1) (for the diuron structure, see Figure 1). Because its herbicidal activity is required during seed germination, diuron has to persist for 3-6 months; therefore, its degradation through chemical (hydrolysis) or biological processes is very slow. As a result, diuron is found in surface waters and groundwaters (1). On soil surfaces and in surface waters, light-induced degradation may be an alternative pathway to hydrolysis or microbial degradation. In laboratory studies, it has been shown that diuron degradation occurs efficiently by reaction with hydroxyl radicals (HO[•]) (2).



FIGURE 1. Structures of diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and the main degradation product found in this study, 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea.

In most surface waters, the major sources of HO[•] are photochemical reactions of the water constituents NO₃⁻ and colored dissolved organic matter (3, 4). On soil surfaces and in iron-rich surface waters, photolysis of iron(III) complexes with natural organic ligands (e.g., humic acids) acting as electron donors and subsequent thermal reactions including the Fenton reaction (oxidation of Fe(II) by H_2O_2) is likely to be a significant additional or even the main source of HO. (5, 6). In these heterogeneous environmental systems, a large fraction of iron is present as particulate or colloidal iron(III) (hydr)oxide (e.g., ref 7). Relative rates of HO[•] production and consumption have been determined in irradiated suspensions containing a well-defined iron(III) hydroxide phase and humic acid as an electron donor (6). [We define photolysis of Fe(III) complexes and subsequent thermal reactions including the Fenton reaction as "photo-Fenton systems".]

Oxidative transformation of atrazine through HO[•] attack has been studied in detail in homogeneous photo-Fenton systems containing oxalate as an electron donor (8). These authors have shown that both oxalate concentration and pH greatly affected the rate of atrazine degradation. For heterogeneous photo-Fenton systems, the question of whether surface or solution reactions are the rate-determining step requires resolution. This study investigates the effects of pH and oxalate concentration on the kinetics of light-induced diuron degradation in the presence of goethite. We have chosen these heterogeneous photo-Fenton systems as model systems for soil surfaces.

Hydroxyl Radical Formation in Heterogeneous Photo-Fenton Systems. Figure 2 shows the various surface and solution reactions, the intermediates and products formed in heterogeneous photo-Fenton systems in which iron(III) oxalate surface and solution complexes are photolyzed. Dissolved iron(II) [Fe(II)(aq)], the superoxide/hydroperoxyl radicals $(O_2^{\bullet-}/HO_2^{\bullet})$, and hydrogen peroxide (H_2O_2) are key intermediates. In systems containing initially a solid iron-(III) (hydr)oxide phase such as goethite (α -FeOOH), Fe(II)-(aq) formation proceeds initially via photolysis of iron(III) oxalate surface complexes (9, 10) (reaction sequence I in Figure 2). Thereby, the first essential step consists of the specific adsorption of oxalic acid on the surface of the iron-(III) (hydr)oxide. Adsorption of oxalic acid on the surface of a metal (hydr)oxide can be described with the surface complex formation model (11-13). According to this model, the pH dependence of adsorption of weak acids and anions can be predicted with the aid of a surface ligand exchange model incorporating the acid-base equilibria of both the anion and the (hydr)oxide.

Photolysis of the Fe(III) surface complex is followed by dissociation of the oxalate radical, $C_2O_4^{\bullet-}$, from the surface and detachment of the reduced surface iron center from the crystal lattice and transfer into solution. The oxalate radical reacts with molecular oxygen yielding $O_2^{\bullet-}$, where $O_2^{\bullet-}$ is in equilibrium with HO_2^{\bullet} (p $K_a = 4.8$; *14*). The product of $HO_2^{\bullet/}$

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FIGURE 2. Light-induced iron cycling, and surface (- -) and solution (-) reactions in heterogeneous photo-Fenton systems.

 O_2 \leftarrow dismutation is H_2O_2 , by the following reactions (reactions II in Figure 2):

$$2\mathrm{HO}_{2}^{\bullet}/\mathrm{O}_{2}^{\bullet-} \xrightarrow{\mathrm{H}^{+}/2\mathrm{H}^{+}} \mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{O}_{2} \tag{1}$$

$$\operatorname{Fe(II)}(\operatorname{aq}) + \operatorname{HO}_{2}^{\bullet} / \operatorname{O}_{2}^{\bullet-} \xrightarrow{\mathrm{H}^{+}/2\mathrm{H}^{+}} \operatorname{Fe(III)}(\operatorname{aq}) + \operatorname{H}_{2}\operatorname{O}_{2} \quad (2)$$

Hydrogen peroxide formed from $HO_2^{\bullet}/O_2^{\bullet-}$ is another significant oxidant of Fe(II)(aq) by the Fenton reaction yielding HO[•] (reaction III in Figure 2):

$$Fe(II)(aq) + H_2O_2 \rightarrow Fe(III)(aq) + HO' + OH^-$$
 (3)

The rate constants of Fe(II)(aq) oxidation by $HO_2^{\bullet/O_2^{\bullet-}}$ and by H_2O_2 depend critically on the Fe(II)(aq) speciation (15– 17). In the presence of excess oxalate, Fe(III)(aq) is present as dissolved iron(III) oxalate complexes that undergo photolysis (18) (reactions IV in Figure 2) leading ultimately to OH[•] production (reactions II and III in Figure 2).

Experimental Section

Materials. All reagents were reagent grade. pH measurements were carried out with a combined glass electrode (Metrohm) standardized with appropriate buffer solutions (Merck). Diuron (technical grade) was obtained from Rhone-Poulenc. Oxalate (K₂C₂O₄, pro analysis, Merck) was used as purchased. All solutions were prepared in Nanopure water (Q-H₂O, grade Barnstead). The diuron degradation product, 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea (for the structure of this product, see Figure 1) was synthesized according to a procedure described by Crosby and Tang (19). Goethite was synthesized according to the procedure described by Atkinson and co-workers (20). Infrared spectra and X-ray diffraction patterns were identical with a pure goethite standard. The specific surface area as determined by Brunauer-Emmett-Teller (BET) measurements was 89 m² g⁻¹. Stock suspensions of goethite (1 g L⁻¹) were prepared every 2 weeks.

Measurement of Dissolved Iron and Hydrogen Peroxide. The concentration of Fe(II) was measured colorimetrically using the ferrozine method (*21*) with a modified procedure. A total of 2 mL of the sample, after filtration through a 0.2- μ m cellulose nitrate filter (Sartorius), was added to 100 μ L of H₂SO₄ (3.6 M) in a 1-cm quartz cell. After the solution was mixed, 200 μ L of ferrozine solution (5 mM) and 100 μ L of ammonium acetate buffer (pH 4.5) were added. The absorbance was measured at the maximal absorption of the iron(II)–ferrozine complex ($\lambda_{max} = 562 \text{ nm}, \epsilon_{562} = 27\ 000 \text{ M}^{-1} \text{ cm}^{-1}$, as determined by a calibration curve). At the Fe(II)(aq) and oxalate concentrations used in the experiments, oxalate was not found to interfere with the Fe(II)(aq) measurements. For the measurement of the concentration of total dissolved iron, the procedure was the same as for the Fe(II)(aq) measurement except that 100 μ L of a reducing agent (104 g of OHNH₃Cl and 200 mL of 32% HCl in 500 mL of bidistilled water) was used instead of H₂SO₄ in the first step. Also, the sample/reducing agent mixture was left to stand for several minutes before addition of the ferrozine and buffer to allow complete reduction of Fe(III)(aq) to take place.

Hydrogen peroxide was analyzed using the DPD method developed by Bader and co-workers (*22*), modified to minimize interference by Fe(II)(aq) and Fe(III)(aq). Bipyridine was added to complex Fe(II)(aq); EDTA was added to complex Fe(III)(aq). The modified procedure consisted in the following steps: 0.4 mL of phosphate buffer solution (pH 6, 0.5 M phosphate) and 0.1 mL of bipyridine solution (0.01 M) were premixed in a 1-cm quartz cell; 2 mL of the sample, 0.02 mL of EDTA solution (0.01 M NaEDTA), and 0.03 mL of DPD (*N*,*N*-diethyl-*p*-phenylenediamine) reagent (1% in 0.1 M H₂-SO₄) were then added, followed by 0.03 mL of POD (horseradish peroxidase) reagent (about 0.8 g mL⁻¹). The absorbance at 551 nm was measured within 45 s.

HPLC Analysis of Diuron and Diuron Degradation Products. Separation of diuron and its metabolites was performed with reversed-phase HPLC, using a C₁₈ Spherisorb column (5 μ m) from PhaseSep (Waters), 250 × 4 mm, and isocratic elution: methanol 70%–water 30%. Absorbance was measured continuously in the range of 190–500 nm. Diuron peaks were normally quantified at 250 nm.

Adsorption Experiments. The adsorption isotherm of oxalate was established at pH 4 in the dark by equilibrating aliquots of 50 mL containing 200 mg L⁻¹ goethite and various oxalate concentrations in Erlenmeyer flasks at constant temperature (25 \pm 2 °C) for 30 min. NaClO₄ was used as an inert electrolyte (I = 0.005 M). The suspensions were stirred during the equilibration time. The suspensions were then filtered through a 0.2- μ m cellulose nitrate filter (Sartorius), and the concentration of oxalate was determined in the filtrates using capillary electrophoresis with a glass capillary of 75 μ m i.d. and 60 cm length, as described by Bürgisser and Stone (23). The electrolyte consisted of 25 mM phosphate buffer (pH 7) and 0.5 mM tetradecyltrimethylammonium bromide. Samples were injected in the hydrostatic mode for 30 s. A constant run voltage of 25 kV was applied. Oxalate was detected at 198 nm. The response was linear between 20 µM and 1 mM oxalate. The concentration of adsorbed oxalate was then calculated as the difference between the total oxalate concentration and the equilibrium oxalate solution concentration.

The pH dependence of oxalate adsorption was established in suspensions containing 200 mg L⁻¹ goethite and 1 mM oxalate. The procedure was the same as used for the oxalate adsorption isotherm, except that oxalate was analyzed in the filtrates by measuring the β -counts of ¹⁴C-labeled oxalate.

Irradiation Experiments. All irradiation experiments were carried out in a 350-mL Pyrex reactor, equipped with a water jacket at constant temperature (25 ± 1 °C). The suspensions were irradiated with a XENON-short arc lamp (XBO, Osram, maximum power 1000 W) with PTI (Photon Technology International) 02-A5000 arc lamp housing and PTI LPS 1000 power supply. The xenon lamp in combination with Pyrex lenses for UV cutoff at approximately 300 nm was used for sunlight simulation. Irradiation of suspensions was performed at 500 W lamp power, corresponding to approximately 1.25 kW m⁻² (50 cm² irradiated area), which is about the



FIGURE 3. Concentration versus time courses of diuron (\diamond), Fe(II)(aq) (\bullet), Fe(III)(aq) (\bigcirc), and H₂O₂ (\checkmark) in an irradiated, aerated suspension containing initially 80 mg L⁻¹ goethite, 200 μ M oxalate, and 10 μ M diuron at pH 4. The figure shows also the effect of excess 2-propanol on diuron degradation (\blacklozenge).

sunlight intensity at mid-latitude summer noon, as estimated by ferrioxalate actinometry (8). The test volume was 250 mL in all irradiation experiments, and the optical depth was 3.8 cm. The suspensions were stirred before and throughout the experiments and left open to the ambient air. NaClO₄ was used as an inert electrolyte (I=0.005 M). The pH was adjusted by addition of HClO₄ or NaOH and kept constant by automatic titration of HClO₄ during the experiments if necessary. Diuron from an aqueous solution was added after an equilibration time of the goethite/oxalate suspension of at least 45 min, followed by another 10 min of equilibration before starting irradiation. The initial diuron concentration was 10 μ M in all irradiation experiments. The dark control experiments were performed as described for the irradiation experiments, except that the suspensions were kept in the dark.

Results and Discussion

Pathways of Light-Induced Diuron Degradation in These Heterogeneous Photo-Fenton Systems. Irradiation (with λ > 300 nm) of an aerated suspension containing initially 80 mg L⁻¹ goethite (corresponding to 0.9 mM total iron), 200 μ M oxalate, and 10 μ M diuron at pH 4.0 resulted in rapid disappearance of diuron, accompanied by the formation of dissolved iron [both Fe(II)(aq) and Fe(III)(aq)] and H₂O₂ (Figure 3). The Fe(II)(aq) concentration reached a maximum after about 10 min of irradiation, followed by its decrease due to Fe(II)(aq) reoxidation, while Fe(III)(aq) and H_2O_2 accumulated in the systems on the time scale of the experiment. In the presence of excess 2-propanol (0.28 M), no degradation of diuron was observed at otherwise the same conditions (Figure 3), whereas the kinetics of formation of dissolved iron was not affected (data not shown). 2-Propanol is known to react efficiently with HO' with a second-order rate constant, $k = 3 \times 10^9 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$ (24). This provides evidence that attack by HO' is the only pathway of diuron degradation in these heterogeneous photo-Fenton systems.

In a deaerated, irradiated suspension containing initially 80 mg L^{-1} goethite, 200 μ M oxalate, and 10 μ M diuron at pH 4.0, the rate of diuron degradation was smaller by a factor of 6 than in the aerated suspension under otherwise the same conditions (data not shown). A much smaller rate of diuron disappearance is expected in deaerated suspensions since molecular oxygen is needed to produce HO₂·/O₂·- by reaction of O₂ with C₂O₄·- (reaction II in Figure 2). The fact that the rate of diuron disappearance did not drop to zero in irradiated, deaerated suspensions is most likely due to oxygen

contamination. In the absence of oxalate, no diuron degradation was observed after 10 h of irradiation (data not shown) indicating that the presence of oxalate is a prerequisite for HO[•] formation through reactions I-III (see Figure 2). Adsorption of diuron on the surface of goethite was negligible in the pH range used in this study. Hence, diuron degradation does not occur on the surface of goethite, e.g., through surface ligand-to-metal charge-transfer reactions, but in solution by reaction with HO. Irradiation of an aqueous solution of diuron (100 μ M) at λ > 300 nm in the absence of oxalate and goethite did not result in diuron degradation within the time scale typical for our experiments in this study. This is not surprising since light absorption by diuron is insignificant above 300 nm. In the absence of light, neither diuron was degraded nor dissolved iron was formed during 24 h in a broad pH range (3 < pH < 7) and at various oxalate concentrations (data not shown).

Degradation Products of Diuron in these Heterogeneous Photo-Fenton Systems. We have determined only one diuron degradation product by HPLC analysis with UV/VIS detection. This product was identified as 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea (for the structure, see Figure 1) by comparison with an authentic sample. It represented 40–50% of the initial diuron concentration after 15 min of irradiation of a goethite–oxalate–diuron suspension under the experimental conditions shown in Figure 3. This product did not adsorb on the surface of goethite under our experimental conditions, i.e., no loss was observed in a suspension containing 80 mg L⁻¹ goethite, 200 μ M oxalate, and 10 μ M 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea at pH 4, even after 24 h of stirring in the dark.

The formation of the N-formyl derivative involves an abstraction of a hydrogen atom from the methyl group through HO• attack. The alkyl radical (R•) reacts with oxygen to form a peroxyl radical (RO•), which leads to an alcoxyl radical (RO•) via formation and subsequent decomposition of the unstable intermediate ROOOOR (*25*). The classical β -scission of RO• yields the N-formyl derivative (*26*).

It is worth noting that in a previous study on light-induced diuron degradation in homogeneous systems, where HO[•] was formed through photolysis of dissolved iron(III) hydroxo complexes [mainly Fe(OH)²⁺] (2), the N-formyl derivative was also the major diuron degradation product. However, at least five additional products were identified that corresponded to attack of HO[•] at the methyl groups or at the aromatic ring. We did not find these additional products in this study. This discrepancy between this and the previous study (2) could be due to fast degradation of these additional products by HO[•] and/or to their adsorption on the goethite surface, preventing them from being detected by HPLC.

Kinetics of Light-Induced Diuron Degradation in these Heterogeneous Photo-Fenton Systems. As Figure 3 shows, the rate of diuron degradation was constant after an induction period. An induction period has also been observed in the degradation of atrazine by HO[•] in homogeneous photo-Fenton systems (8). This phenomenon occurs because Fe(II)(aq) and H_2O_2 have first to produce HO[•] that degrade a considered pollutant. However, in the study by Balmer and Sulzberger (8), atrazine degradation obeyed first-order kinetics after the induction period, whereas in this study, a constant rate of diuron degradation was observed after an induction period (see Figure 3). To rationalize a constant rate of diuron degradation, sources and sinks of HO[•] have to be considered.

In these systems, HO[•] is formed through the Fenton reaction with a formation rate (r_f) :

$$r_{\rm f} = k_{\rm F}[{\rm H}_2{\rm O}_2][{\rm Fe(II)(aq)}] \tag{4}$$

where $k_{\rm F}$ is the second-order rate constant of the Fenton reaction. Possible sinks of HO[•] are as follows: (i) reaction



FIGURE 4. pH dependence of diuron degradation in irradiated, aerated suspensions containing initially 200 mg L⁻¹ goethite, 200 μ M oxalate, and 10 μ M diuron. The inset shows the rate of diuron degradation, i.e., the slope of the linear parts of the diuron concentration versus time curves, as a function of pH.

with diuron, (ii) reaction with diuron degradation products, and (iii) reaction with oxalate. Although the initial oxalate concentration was 20 times higher than that of diuron in the experimental system shown in Figure 3, oxalate is nevertheless unlikely to be an important sink of HO[•] as compared to diuron and its degradation products. This is to be expected in view of the relatively low second-order rate constants of oxalate reaction with HO[•] which are $7.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for $C_2O_4^{2-}$ and $4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for $HC_2O_4^{--}$ (16). However, reactions of diuron degradation products with HO[•] are likely to be diffusion-controlled. The rate of HO[•] consumption can then be expressed as

$$r_{\rm c} = k_{\rm HO^{\bullet},D}[\rm HO^{\bullet}][D] + \sum k_{\rm HO^{\bullet},DP_{\rm i}}[\rm HO^{\bullet}][DP_{\rm i}] \qquad (5)$$

where the second term in eq 5 is the rate of HO[•] consumption through reaction with diuron degradation products, DP.

The rate of diuron degradation through reaction with HO[•] is

$$-\left(\frac{[\mathbf{D}]}{\mathrm{d}t}\right) = k_{\mathrm{HO},\mathrm{D}}[\mathrm{HO}^{\bullet}][\mathbf{D}]$$
(6)

where $k_{\text{HO},\text{D}}$ is the second-order rate constant of reaction of diuron with HO[•], which is 4.6×10^9 M⁻¹ s⁻¹ (27). A constant rate of diuron degradation, after an induction period (see Figure 3), suggests that the HO[•] concentration increases according to the decrease of [D], without reaching a steadystate within the time scale of the experiment shown in Figure 3. This is plausible considering that the HO[•] formation rate $(r_{\rm f})$ increases with irradiation time due to the increase of [Fe(II)(aq)]·[H₂O₂] (see Figure 3). The rate of HO[•] consumption $(r_{\rm c})$, on the other hand, is unlikely to increase with irradiation time. At the maximum, $r_{\rm c}$ would remain constant if all the diuron degradation products would react with HO' with the same second-order rate constant as diuron and if no mineralization would take place. A suitable tool to obtain more quantitative information on the mechanisms controlling the kinetics of light-induced diuron degradation in these heterogeneous photo-Fenton systems is mathematical kinetic modeling. This was, however, beyond the realm of this study and will be published later.

Effect of pH on Light-Induced Diuron Degradation. Figure 4 shows diuron degradation at various pH values in irradiated, aerated suspensions containing initially 200 mg L^{-1} goethite (corresponding to 2.25 mM total iron), 200 μ M



FIGURE 5. pH dependence of oxalate adsorption on the surface of goethite, established in suspensions containing 200 mg L⁻¹ goethite and 1 mM oxalate. As expected, the extent of adsorption of oxalic acid on the surface of goethite was maximal near the second p K_a value of oxalate, which is p $K_a = 3.8 \pm 0.2$ (28, 29).

oxalate, and $10 \,\mu$ M diuron. At all pH values, the rate of diuron degradation was constant after an induction period and was strongly pH-dependent. The inset in Figure 4 shows the rate of diuron degradation, i.e., slopes of the linear portion of the diuron concentration versus time curves, as a function of pH. The rate was maximal at pH 4 and decreased strongly above and slightly below this pH value. The shape of the rate versus pH curve shown in the inset in Figure 4 strongly resembles the pH dependence of the extent of oxalate adsorption on the surface of goethite in suspensions containing 200 mg L⁻¹ goethite and no diuron (Figure 5). This supports the contention that the pH dependence of oxalate adsorption determines to a large extent the pH dependence of diuron degradation in these heterogeneous photo-Fenton systems.

However, the pH dependence of solution reactions also has to be considered: The quantum yield of photolysis of dissolved ferric iron complexes depends on the Fe(III)(aq) speciation, and the rate constant of the Fenton reaction depends on the Fe(II)(aq) speciation. According to speciation calculations (not shown), Fe(III)(aq) is present as Fe^{III}(C₂O₄)₂and $\text{Fe}^{\text{III}}(C_2O_4)_3^{3-}$ for 200 μ M oxalate concentration over the whole pH range shown in Figure 4. Both of these iron(III) oxalate complexes are efficiently photolyzed (30). Regarding Fe(II)(aq), $[Fe^{II}(C_2O_4)]$ increases with increasing pH according to speciation calculations (not shown). Fe^{II}(C₂O₄) is oxidized by H₂O₂ at a rate constant of $k_{\rm F} = 3.1 \times 10^4 \,{\rm M}^{-1} \,{\rm s}^{-1}$ (16), whereas $k_{\rm F}$ involving Fe²⁺ is orders of magnitude smaller: $k_{\rm F}$ = 53-76 M^{-1} s⁻¹ (15-17). Therefore, the Fenton reaction, resulting in HO[•] generation, is faster at higher pH. On the basis of these arguments, the sharp drop in the rate of lightinduced diuron degradation above pH 4 (see inset in Figure 4) cannot solely be due to dissolved iron speciation. Rather, it reflects mainly the pH dependence of oxalate adsorption on the surface of goethite as well as the pH dependence of the efficiency of detachment of reduced surface iron species from the crystal lattice of goethite (29) (for the latter, see discussion below). The decrease of the rate of diuron degradation below pH 4 could reflect both the pH dependence of oxalate adsorption to the surface of goethite and the pH dependence of Fe(II)(aq) speciation and thus of the Fenton reaction rate.

Effect of Oxalate Concentration on Light-Induced Diuron Degradation. Figure 6a shows diuron degradation at various initial oxalate concentrations in irradiated, aerated suspensions containing initially 80 mg L⁻¹ goethite and 10 μ M diuron at pH 4. Again, at all oxalate concentrations, the



FIGURE 6. Effect of different initial oxalate concentrations on diuron degradation in irradiated, aerated suspensions containing initially 80 mg L⁻¹ goethite and 10 μ M diuron at pH 4. (a) Diuron concentration vs time courses. (b) Rate of diuron disappearance as a function of the initial oxalate concentration.

rate of diuron degradation was constant after an induction period and exhibited a strong dependence on oxalate concentration. Figure 6b shows the rate of diuron degradation, i.e., the slope of the linear portion of the diuron concentration versus time curves in Figure 6a, as a function of the initial oxalate concentration. At 200 μ M initial oxalate concentration, the rate of diuron degradation reaches a plateau. This behavior is typical for surface-controlled reactions. The initial oxalate concentration, at which the maximal rate is reached, coincides with maximal adsorption of oxalate on the surface of goethite (Figure 7). According to Figure 7, the surface concentration of oxalate (Γ_{ox}) can be described as a Langmuir function of the equilibrium oxalate solution concentration (*31*):

$$\Gamma_{\rm ox} = \Gamma_{\rm max} \frac{K^{\rm s}[{\rm HC}_2 {\rm O}_4^{-}]}{1 + K^{\rm s}[{\rm HC}_2 {\rm O}_4^{-}]} \tag{7}$$

where K^{s} is the conditional equilibrium constant of the adsorption equilibrium and Γ_{max} is the concentration of total surface sites to which oxalate can get adsorbed with $\Gamma_{max} = [\equiv Fe^{III}OH] + [\equiv Fe^{III}C_2O_4^{-1}]$. From a Langmuir fit through the adsorption data (see Figure 7), we calculated K^{s} to be $K^{s} = 2.6 \times 10^4 \text{ M}^{-1}$ at pH 4 and 25 °C.

Oxalate concentration affects the rate of both surface and solution reactions. Figure 8 shows the Fe(II)(aq) concentration versus time for various initial oxalate concentrations at pH 4. With increasing initial oxalate concentration, the initial rate of Fe(II)(aq) formation increased, because of increasing



FIGURE 7. Adsorption isotherm of oxalate adsorption on the surface of goethite, established in suspensions containing 200 mg L^{-1} goethite at pH 4 and 25 \pm 2 °C.



FIGURE 8. Concentration vs time courses of Fe(II)(aq) in irradiated, aerated suspensions containing initially 80 mg L⁻¹ goethite, 10 μ M diuron, and various oxalate concentrations at pH 4 (same experiments as shown in Figure 6).

oxalate surface concentrations and thus increasing rates of Fe(II)(aq) production through photochemical reductive dissolution of goethite (see eq 9). However, at high oxalate concentrations (400, 200, and 100 μ M initially), [Fe(II)(aq)] decreased after having reached a maximum (see Figure 8). This is the result of the effect of oxalate concentration on Fe(II)(aq) speciation and thus on the rate constant of the Fenton reaction. $Fe^{II}(C_2O_4)$, which is the predominant Fe(II)(aq) species at high oxalate concentrations, is much more rapidly oxidized by H₂O₂ than is Fe²⁺ (rate constants given above). Regarding the rate of diuron degradation as a function of the initial oxalate concentration (see Figure 6b), one would expect a significant difference with 200 and 400 μ M initial oxalate concentration if Fe(II)(aq) speciation and thus the Fenton reaction rate would control the kinetics of diuron degradation. The fact that this is not observed (see Figure 6b) indicates that surface reactions determine the kinetics of diuron degradation.

In Figure 9, the rate of diuron disappearance and the initial rate of Fe(II)(aq) formation are plotted as a function of the concentration of adsorbed oxalate (calculated from the results shown in Figures 6 and 8). The experimental data can be fitted with straight lines with a break at $6.5-7 \ \mu M$ adsorbed oxalate. A linear dependence of rates on surface concentrations is expected for surface controlled kinetics.

Regarding Fe(II)(aq) formation, the slopes in Figure 9 correspond to the rate coefficient (k_p) of Fe(II)(aq) formation



FIGURE 9. Initial rates of Fe(II)(aq) formation and rate of diuron disappearance, after the induction period, as a function of the surface concentration of oxalate in irradiated, aerated suspensions containing initially 80 mg L⁻¹ goethite and 10 μ M diuron at pH 4 (same experiments as shown in Figures 6 and 8).

through photoreductive dissolution of goethite, with oxalate acting as electron donor:

$$\frac{\mathrm{d}[\mathrm{Fe(II)}(\mathrm{aq})]}{\mathrm{d}t} = k_{\mathrm{p}}[\equiv \mathrm{Fe^{III}C_2O_4}^-]$$
(8)

where \equiv Fe^{III}C₂O₄⁻ stands for an iron(III) oxalate surface complex undergoing photolysis upon absorption of light. The rate coefficient k_p is the product of the specific rate of light absorption by an iron(III) oxalate surface complex (k_a), the quantum yield of primary photoproduct formation (Φ), and the efficiency of detachment of reduced surface iron from the crystal lattice (η_{det}) (32):

$$\frac{\mathrm{d}[\mathrm{Fe(II)}(\mathrm{aq})]}{\mathrm{d}t} = k_{\mathrm{a}} [\equiv \mathrm{Fe}^{\mathrm{III}} \mathrm{C}_{2} \mathrm{O}_{4}^{-}] \Phi \eta_{\mathrm{det}}$$
(9)

The change in k_p at a threshold value of the oxalate surface concentration could be due to a transition from a bidentate, binuclear iron(III) oxalate surface complex at small surface coverage to a monodentate, binuclear iron(III) oxalate surface complex at high surface coverage. This hypothesis needs to be experimentally verified with the help of methods such as attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) that allow elucidation of the structure of surface complexes (33). The efficiency of detachment of reduced surface iron from the crystal lattice of goethite (η_{det}) is expected to depend critically on the structure of a surface complex. For thermal, ligand-catalyzed dissolution of minerals, it has been demonstrated that surface metal centers in a bidentate, mononuclear surface complex are more readily detached from the crystal lattice of a metal (hydr)oxide as compared to surface metal centers in a bidentate, binuclear surface complex. The reason is that, in the latter case, two surface metal centers have to be transferred simultaneously into solution (31). The intriguing observation that the rate of diuron disappearance increases linearly with increasing oxalate surface concentration with a break at 6.5–7 μ M adsorbed oxalate indicates that Fe(II)(aq) production through photochemical reductive dissolution of goethite is the ratedetermining step of diuron degradation in these heterogeneous systems.

Environmental Significance. This study shows that a pollutant which does not absorb light at environmentally relevant wavelengths is efficiently degraded in irradiated aqueous systems containing goethite and oxalate at pH values that are relevant for soil systems. Iron(III) (hydr)oxides and

carboxylic acids such as oxalic acid are common constituents of soil surfaces (*34*). This study suggests that a surface reaction is the rate-determining step in diuron degradation in these heterogeneous photo-Fenton systems. Both pH and oxalate concentration are critical factors in controlling the concentration and the type of iron(III) oxalate surface complexes formed and, thereby, the rate of Fe(II)(aq) production through photoreductive dissolution of the iron(III) (hydr)oxide phase. This study extends significantly our knowledge of the environmental factors, i.e., pH and electron donor concentration, that control the kinetics of indirect photochemical transformation of pollutants in heterogeneous environmental systems. It helps bridge the gap between homogeneous laboratory systems and soil surfaces.

Regarding soil surfaces, the question arises whether lightinduced degradation of a pollutant occurs also with mineral phases that are not in suspension but merely covered by water layers. Using in situ ATR-FTIR, Kesselman-Truttmann and Hug (35) found an enhanced light-induced degradation of a fluorescent whitening agent (4,4'-bis(2-sulfostyryl)biphenyl, DSBP) on rutile and anatase surfaces that were covered by only a few water layers. These authors attributed this surface-catalytic effect to DSBP attack by HO' in addition to its photolysis. With iron(III) (hydr)oxide phases, the only efficient pathway of HO[•] formation is photolysis of Fe(III) complexes and subsequent thermal reactions including the Fenton reaction, as shown in this study with goethite suspensions. The question remains to be answered whether the pathway of HO[•] production as shown in Figure 2 is also effective on iron(III) (hydr)oxide phases that are covered by only a few water layers. A suitable tool to assess this question is in situ ATR-FTIR.

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