

# Photocatalytic Oxidation of Cadmium-EDTA with Titanium Dioxide

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Ethylenediaminetetraacetic acid (EDTA) forms stable complexes with toxic metals such as cadmium. Metal-EDTA chelates are chemically stable and occur in a number of waste situations. The viability of using photocatalytic oxidation with titanium dioxide to degrade Cd-EDTA was examined at concentrations from  $2 \times 10^{-5}$  to  $10^{-3}$  M at pH from 3 to 8. Initially a portion of the complex was adsorbed onto the  $\text{TiO}_2$  photocatalyst at low pH. However, independent of the degree of initial adsorption, Cd-EDTA was rapidly destroyed with little dependence on pH. Concurrently, in most cases cadmium was liberated as  $\text{Cd}^{2+}$  with no affiliation with organic reaction products; its fate depended on suspension pH. At low pH,  $\text{Cd}_{\text{aq}}^{2+}$  was released into solution. Also, organic carbon was released into solution as oxidation of adsorbed EDTA occurred. At higher pH the Cd was adsorbed onto the  $\text{TiO}_2$  at adsorption equilibrium levels. Major products detected include formaldehyde, formic acid, and acetic acid. Nitrate and glyoxylic, malonic, and oxalic acids were detected, but concentrations were low. The incomplete carbon balance and the lack of nitrate production suggest the production of organic amines from the degradation of Cd-EDTA. Release of the Cd as  $\text{Cd}^{2+}$  occurs after mineralization of only about half of the organic carbon.

## Introduction

Ethylenediaminetetraacetic acid (EDTA), a strong chelating agent, is used in applications such as metal plating, water softening, photography, textile and paper manufacture, and industrial cleaning. Chelating agents such as EDTA complicate the treatment of industrial effluents and other contaminated waters by reducing the efficiency of metal removal by precipitation, ion exchange, and other processes. Additionally, the migration behavior of metals and radionuclides in subsurface and aqueous environments is significantly altered by chelation. EDTA does not biodegrade rapidly and concerns from its effects are magnified by its persistence (1).

U.S. Department of Energy (DOE) wastes containing mixtures of radionuclides, heavy metals, and chelating agents have led to subsurface contamination through disposal to the ground surface, ponds, cribs, and landfills (2). Cadmium was a contributor to the metal burden present in groundwaters and was one of the most frequently reported metals found in soils and sediments. EDTA was representative of a class of chelating agents found at four production facilities

and concentrations of EDTA in groundwaters up to 31.4 mM have been found at the DOE Hanford site (3). Complexation of metals with chelating agents can lead to mobile aqueous complexes in soil and groundwater (4).

Advanced oxidation treatment processes have shown promise in the destruction of recalcitrant pollutants. One of these processes, photocatalytic oxidation (PCO), employs an illuminated semiconductor (usually titanium dioxide) activated with light to initiate the formation of oxidizing radical species, either hydroxyl radicals or direct electron transfer at the semiconductor surface (holes,  $h^+$ ). Limited work describes the titania-mediated PCO of EDTA. Furlong et al. (5) evaluated the PCO of EDTA and several amine derivatives. The extent of oxidation of each species was found to depend primarily upon how strongly it adsorbed onto the  $\text{TiO}_2$  surface. At pH 3–5, experimental PCO rates were slower for uncharged species and fastest for the divalent anions, including EDTA. The rates decreased with the number of acetate groups attached to each nitrogen atom; adsorption onto  $\text{TiO}_2$  increased with increasing deprotonation of the acetic acid groups. Low et al. (6) investigated the production of nitrate and ammonium ions from the photocatalysis of EDTA and other nitrogen-containing compounds. For EDTA, the ratio of ammonium to nitrate produced was 0.89, a value between aliphatic primary amines (1.89–6.38) and tertiary amines in an aromatic ring (0.08–0.69). Results suggested that the organic nitrogen was initially reduced to ammonia and that nitrate was produced from the oxidation of ammonium ions.

Recently, the PCO of several metal-EDTA complexes by  $\text{TiO}_2$  was investigated by Madden et al. (7). The reactivity at pH 4 was  $\text{Cu(II)} > \text{Pb(II)} > \text{Ni(II)} \approx \text{Cd(II)} \approx \text{Zn(II)} > \text{Cr(III)}$ .  $\text{Ni(II)-EDTA}$  and EDTA PCO rates decreased with increasing pH. Addition of  $\text{H}_2\text{O}_2$  or  $\text{Cu(II)}$  to  $\text{Ni(II)-EDTA}$  increased the degradation rate, the latter by exchange to form  $\text{Cu(II)-EDTA}$ .

The objective of this study is to examine the viability of treating aqueous Cd-EDTA via  $\text{TiO}_2$  semiconductor photocatalytic oxidation. Unlike biodegradation studies, PCO investigations have demonstrated success in degrading aqueous EDTA. Mineralization of the EDTA portion of the metal-EDTA complex is desired but may not be required in the treatment scheme. Key is destruction to the point of the separation of the metal and organic complexing agent. Once released, aqueous cadmium can be removed via traditional treatment methods or, employing the PCO system, can be adsorbed to the  $\text{TiO}_2$  surface at elevated pH values. Therefore, titania-mediated PCO offers a dual advantage of first degrading the chelate and then adsorbing the uncomplexed metal from solution. The adsorbed metal can then be stripped from the  $\text{TiO}_2$  surface and the  $\text{TiO}_2$  reused. Since adsorption of Cd(II), EDTA, and the complex all are strongly dependent on pH, particular emphasis will be given to maintaining a constant pH for the PCO of Cd-EDTA. Other areas of inquiry include observing the effect of different equimolar concentrations of Cd-EDTA; noting the consequences of varying the suspension pH; and examining the role that adsorption of the complex onto the  $\text{TiO}_2$  surface plays in determining the Cd-EDTA degradation rate. Reaction products of Cd-EDTA PCO and the fate of cadmium in the reaction system are also investigated.

## Materials and Methods

Deionized water (18M $\Omega$ ) used in all experiments was purified through a Hydro Service Model LPRO-20 ion exchange/reverse osmosis system. All chemicals employed were at least

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of reagent grade. Certified buffer solutions of pH 4, 7, and 10 were used to calibrate an Orion Model 520A pH meter and probe before every experiment.

Glass and plasticware used in experimentation were acid washed in 1 N HCl for 24 h before use. Labware used for metals solutions were rinsed thoroughly with deionized water after acid washing and placed in a drying oven. Glassware used with organic compounds were thoroughly rinsed in deionized water, rinsed with acetone, placed in a 400 °C-furnace for 3 h, and then allowed to cool.

**Batch Tests of Cadmium and Cadmium-EDTA Adsorption onto TiO<sub>2</sub>.** Aqueous Cd(II) or equimolar Cd(II)-EDTA solutions were prepared at the desired concentrations in a 1-L volumetric flask. Cd(II) ( $10^{-7}$ – $10^{-4}$  M) (from Cd(NO<sub>3</sub>)<sub>2</sub>, Fisher Sci.) and  $2 \times 10^{-5}$  to  $10^{-4}$  M Cd-EDTA (from Cd(ClO<sub>4</sub>)<sub>2</sub>, Aldrich; and disodium EDTA, EM Science, equimolar to Cd(II)) solutions were made with an ionic strength of  $5 \times 10^{-3}$  M NaNO<sub>3</sub> (J. T. Baker, in Cd(II) batch experiments) or NaClO<sub>4</sub> (VWR or Fisher, in Cd-EDTA batch experiments). The solution was then transferred to a 1-L Nalgene bottle and purged with N<sub>2</sub> for 30 min to minimize effects due to CO<sub>2</sub> and O<sub>2</sub>. Temperatures were ambient (22–25 °C). Several 100 mL samples were prepared with 2 g/L TiO<sub>2</sub> (Degussa P25). One control without TiO<sub>2</sub> was also employed. The sample pH was adjusted using HClO<sub>4</sub> (Fisher) or NaOH (Baker) to between 3 and 10. The bottles were wrapped in aluminum foil to prevent photodegradation, placed on a reciprocating shaker, and allowed to equilibrate overnight. The next day the bottles were removed from the shaker, and the pH was recorded. Thirty milliliters of the slurry was filtered through a 0.2 mm Supor-200 membrane filter (Gelman), in which the first few milliliters of the filtrate was discarded as a rinse.

Sample aliquots were measured for Cd(II) concentration using atomic absorption spectrophotometry (AAS). Equimolar  $10^{-4}$  M Cd(II)-EDTA sample filtrates were also subjected to TOC analysis as a measure of aqueous EDTA. The TOC recovery for EDTA in control experiments was greater than 99%. Equimolar  $2 \times 10^{-5}$  M sample aliquots were analyzed for aqueous Cd<sup>2+</sup> via specific ion electrode and Cd-EDTA<sup>2-</sup> using ion chromatography, in addition to Cd(II) (via AAS) and TOC. At each pH, the adsorbed Cd(II) and TOC levels were calculated by the difference between the control Cd(II) and TOC concentrations and those of the filtered samples.

**Photocatalytic Oxidation of Cadmium-EDTA.** All photocatalytic experimentation was completed in a recirculating batch reactor system (8, 9). The system included a 500-mL glass pot flask with three sampling ports, modified with two tubing connections to allow flow in and out. This flask was connected via Viton tubing and pump to a 46-cm long, 1.9-cm diameter Pyrex glass tube. The tube was fixed parallel to a Spectroline Model XX-15A 365 nm UV lamp with a 30 W output (Spectronics Corporation). Using ferrioxalate actinometry, a photon output of  $4 \times 10^{-4}$  Einsteins/min was estimated. Flow from the glass tube returned to the pot flask. The lamps and glass components were wrapped in aluminum foil to contain the light emitted from the lamps and prevent interferences from outside light.

To prepare the experiments, 545 mL of deionized water plus 15 mL of a concentrated NaClO<sub>4</sub> stock solution was added to the reactor, along with 2 g/L P25 TiO<sub>2</sub>. Oxygen was continuously supplied to the suspension throughout the preparation and experiment. The UV light was then turned on, and the suspension circulated for 1 h at a flowrate of 75 mL/min to oxidize any residual organic contamination in the suspension or reactor.

Following this cleaning period, the UV light was switched off, and 140 mL of a concentrated Cd-EDTA solution was added to the suspension to obtain an equimolar concentration of  $2 \times 10^{-5}$ ,  $10^{-4}$ , or  $10^{-3}$  M Cd(II)-EDTA, at  $5 \times 10^{-3}$  M NaClO<sub>4</sub>, in a total liquid volume of 700 mL. The hydraulic

retention time for the illuminated tube was 1.7 min and that in the mixing reactor was 6.7 min. A pH probe was placed inside one of the sampling ports, and acid or base was added to the reactor to adjust the suspension to the desired pH value. Conditions inside the flask were allowed to equilibrate for at least 20 min after pH adjustment. Finally, the UV light was turned on to initiate the PCO experiment.

Two experiments were run at each pH value at  $2 \times 10^{-5}$  and  $10^{-4}$  M Cd(II)-EDTA. The first experiment ran for 60 min and had sampling at the start of the experiment and at seven times throughout the experimental run. Each 20-mL sample was filtered through a 0.2 µm membrane filter (Gelman Sciences) into a precleaned glass container; the first few milliliters of filtered sample was wasted. Samples were immediately capped, labeled, and placed in a refrigerator until analysis.

The second experiment ran for 180 min with four samples being collected and processed as above. The UV light was switched off after 180 min, and a 40-mL unfiltered sample was collected into a clean flask. The pH in the reactor was raised to 8.0 with NaOH to adsorb free cadmium and desorb any adsorbed organic acids. A few drops of HClO<sub>4</sub> were added to the flask to lower the suspension pH to 2.5 in order to desorb any adsorbed cadmium and possibly to adsorb organic acids. After mixing for 10 min, samples from both were filtered and stored.

Forty milliliter samples were collected during  $10^{-3}$  M Cd(II)-EDTA experimentation. These samples were filtered, immediately capped, labeled, and placed in a refrigerator. Four PCO experiments were completed at pH 4 and 7 to collect reaction data up to 420 min.

All samples were analyzed for aqueous Cd(II), Cd<sup>2+</sup>, Cd-EDTA<sup>2-</sup>, and TOC. Additionally, the  $10^{-3}$  M solutions were tested for nitrate, formaldehyde, and malonic, maleic, glyoxylic, acetic, and formic acids as EDTA degradation products.

**Sample Preparation, Analyses, and Instrumentation.** Samples for Cd(II) analysis were measured using the flame and furnace components of a Perkin-Elmer Model 5100ZL atomic absorption spectrophotometer. Calibration curves for AAS analysis of cadmium were obtained using 1000 ppm aqueous cadmium standard (VWR). The detection limit for the flame portion was  $2.5 \times 10^{-7}$  M where correlation coefficients of nearly unity were obtained through  $1.8 \times 10^{-5}$  M. The detection limit for the furnace was  $10^{-8}$  M, and calibration remained linear through  $2 \times 10^{-7}$  M. An Orion cadmium ion activity electrode, model 94-98A, calibrated with Cd(ClO<sub>4</sub>)<sub>2</sub>, was used to quantify the aqueous Cd<sup>2+</sup> concentration. The detection limit of the electrode was  $10^{-7}$  M, and its response remained linear through  $10^{-2}$  M Cd<sup>2+</sup>.

Aqueous total organic carbon (TOC) was measured on a Shimadzu TOC-5000 analyzer. The detection limit of the TOC analyzer was 0.4 ppm. A Dionex DX-100 integrated ion chromatograph (IC) system equipped with an IonPac AS5 anion exchange column and guard was used to determine aqueous Cd-EDTA<sup>2-</sup>, nitrate, and malonic, maleic, and oxalic acid concentrations (standards all from Aldrich; malonic and maleic as disodium salts). The AS5 eluent was 1.7 mM sodium carbonate/2.8 mM sodium bicarbonate (both J. T. Baker), employed at a flow rate of 1.76 mL/min. An IonPac AS10 anion exchange column and guard with a 3.5 mM potassium tetraborate (Sigma) eluent was used to analyze acetic and formic acids at a flowrate of 0.76 mL/min. The quantifiable concentration ranges were  $10^{-6}$ – $10^{-3}$  M, and elution times were distinct enough that separation was easily obtained for all compounds.

A Shimadzu UV160U UV-visible recording spectrophotometer was used for the analysis of glyoxylic acid (standard from Aldrich) and formaldehyde (standard from J. T. Baker). Glyoxylic acid was detected at an absorbance of 520 nm

TABLE 1. Complexation Reactions in the Cd-EDTA System ( $I = 0 \text{ M}$ )

no.	equilibrium reactions	$\log K$ , 25 °C
1	$\text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CdOH}^+ + \text{H}^+$	$-10.1^a$
2	$\text{Cd}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_2^0 + 2\text{H}^+$	$-20.3^a$
3	$\text{Cd}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_3^- + 3\text{H}^+$	$-33.3^b$
4	$\text{Cd}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_{2(s,\beta)} + 2\text{H}^+$	$-13.65^a$
5	$\text{HEDTA}^{3-} \rightleftharpoons \text{H}^+ + \text{EDTA}^{4-}$	$-11.014^a$
6	$\text{H}_2\text{EDTA}^{2-} \rightleftharpoons \text{H}^+ + \text{HEDTA}^{3-}$	$-6.320^a$
7	$\text{H}_3\text{EDTA}^- \rightleftharpoons \text{H}^+ + \text{H}_2\text{EDTA}^{2-}$	$-2.25^c$
8	$\text{H}_4\text{EDTA}^0 \rightleftharpoons \text{H}^+ + \text{H}_3\text{EDTA}^-$	$-1.78^c$
9	$\text{Cd}^{2+} + \text{EDTA}^{4-} \rightleftharpoons \text{Cd-EDTA}^{2-}$	$14.7^c (I = 0.1 \text{ M})$
10	$\text{Cd-EDTA}^{2-} + \text{H}^+ \rightleftharpoons \text{Cd-HEDTA}^-$	$2.5^c (I = 0.1 \text{ M})$

<sup>a</sup> Reference 13. <sup>b</sup> Reference 12. <sup>c</sup> Reference 14.

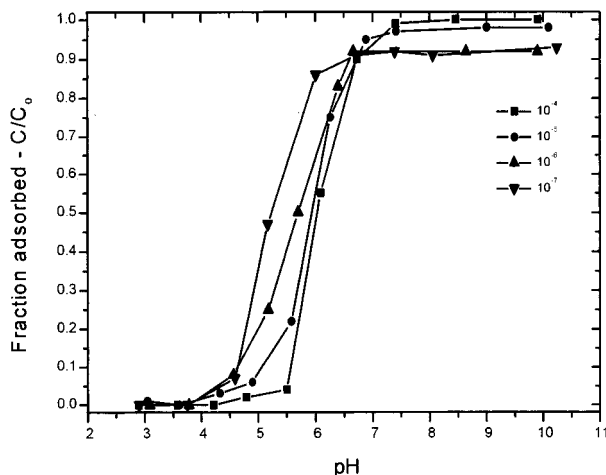


FIGURE 1. pH dependent adsorption of Cd(II) onto 2 g/L  $\text{TiO}_2$  ( $I = 5 \times 10^{-3} \text{ M NaNO}_3$ ).

following exactly the procedure of Kramer et al. (10). Phenylhydrazine hydrochloride (99%) (Aldrich) was added to the sample, and the mixture was placed in a 100 °C oven for 5 min. Upon cooling to room temperature, HCl and 99% potassium ferricyanide were added to the sample, the sample stood for 2 min and was then analyzed. The detection limit for glyoxylic acid was  $4 \times 10^{-7} \text{ M}$ , and absorbance remained linear through  $3 \times 10^{-6} \text{ M}$ . Formaldehyde was analyzed at 415 nm with a Nash reagent (11). Ammonium acetate (Fisher) and acetylacetone (Sigma) were added to the sample, and it was placed in a 60 °C oven for 30 min. The detection limit for formaldehyde was  $10^{-5} \text{ M}$ , and absorbance remained linear through  $8 \times 10^{-4} \text{ M}$ .

Aqueous speciation calculations were completed using the equilibria of Table 1 with activity corrections from the Davies equation (12).

## Discussion of Results

**Adsorption of Cadmium and Cadmium-EDTA onto  $\text{TiO}_2$ .** Cadmium Adsorption onto  $\text{TiO}_2$ . Adsorption of cadmium onto  $\text{TiO}_2$  as a function of pH at four different concentrations is shown in Figure 1. The cadmium/ $\text{TiO}_2$  system exhibits a typical metal-like adsorption pattern described by increased metal adsorption at higher pH values. Numerous researchers have suggested that covalent and electrostatic interactions between the metal and the oxide surface produce the adsorption over a narrow pH range. The adsorption edge shifts to higher pH values as the total Cd(II) concentration is increased. Higher Cd(II) concentrations produce competition for adsorption sites and exhaust the more active binding sites; subsequent surface complexation occurs with weaker sites, shifting the adsorption edge.

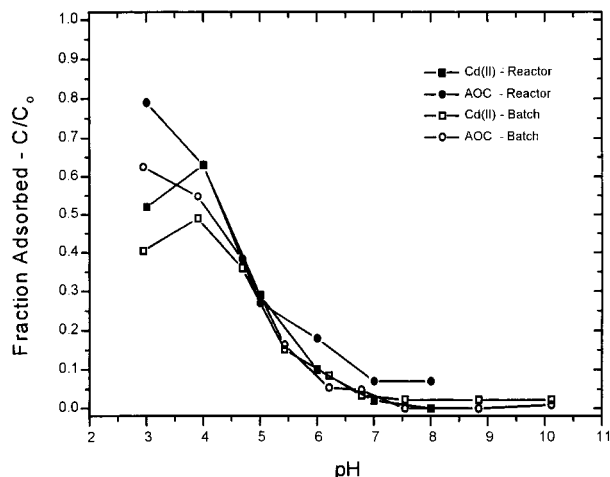


FIGURE 2. Reactor and batch adsorption comparisons of  $10^{-4} \text{ M}$  equimolar Cd(II) and EDTA onto 2 g/L  $\text{TiO}_2$  ( $I = 5 \times 10^{-3} \text{ M NaClO}_4$ ; flow rate = 75 mL/min).

TABLE 2. Cd-EDTA Linear Adsorption Constant,  $K_{\text{ads}}$ , at Various pH and Total Cd-EDTA Concentrations

pH	$K_{\text{ads}}$	
	$2 \times 10^{-5} \text{ M Cd-EDTA}$	$10^{-4} \text{ M Cd-EDTA}$
3		4.12
4		2.38
5	6.20	0.42
6	0.61	0.12
7	0.17	0.02
8		0.02

**Cadmium-EDTA Adsorption onto  $\text{TiO}_2$ .** Shown in Figure 2 are the equimolar adsorption of Cd(II) and EDTA (as TOC) onto  $\text{TiO}_2$  at  $10^{-4} \text{ M}$  for both batch experiments and the flow reactor, demonstrating ligand-like adsorption trends. The flow reactor results are after 20 min in the stirred PCO system. The adsorption of both species are similar between the two systems. Two adsorption domains exist, diverging at pH 4 to 4.5. Above these pH values, adsorbed Cd(II) and EDTA are identical. Below these values, the EDTA adsorbed is greater more significant at lower pH. The 1:1 correspondence of Cd(II) and EDTA adsorption indicates that cadmium and EDTA are complexed, and the pH relationship indicates that the EDTA is bridging cadmium to the  $\text{TiO}_2$  surface (15–17). The increasing difference between EDTA and Cd(II) adsorption at very low pH results from dissociation of the Cd-EDTA complex. Vohra and Davis (18) similarly found that in the adsorption of Pb(II)-EDTA onto  $\text{TiO}_2$ , Pb(II)-EDTA dissociates and the adsorption of Pb(II) decreases below pH 3.

To estimate concentrations of adsorbed Cd-EDTA throughout the PCO experiments, a simple linear isotherm relationship is assumed. Values of this adsorption constant,  $K_{\text{ads}}$ , were determined based on the initial adsorbed and initial aqueous Cd-EDTA concentrations in the PCO reactor:

$$K_{\text{ads}} = \frac{[\text{Cd-EDTA}_{\text{ads}}^{2-}]}{[\text{Cd-EDTA}_{\text{aq}}^{2-}]} \quad (1)$$

Adsorption constants were calculated for pH values of 3–8 at  $10^{-4} \text{ M}$  and 5–7 at  $2 \times 10^{-5} \text{ M}$  (Table 2). Values of  $K_{\text{ads}}$  are greater at low pH.  $K_{\text{ads}}$  is systematically larger for  $2 \times 10^{-5} \text{ M}$  than for  $10^{-4} \text{ M}$  Cd(II)-EDTA due to the stronger adsorption of the complex at reduced concentrations.

**Photocatalytic Oxidation of Cadmium-EDTA.** Without  $\text{TiO}_2$ , the photolysis of  $10^{-4} \text{ M}$  equimolar Cd-EDTA at pH 5



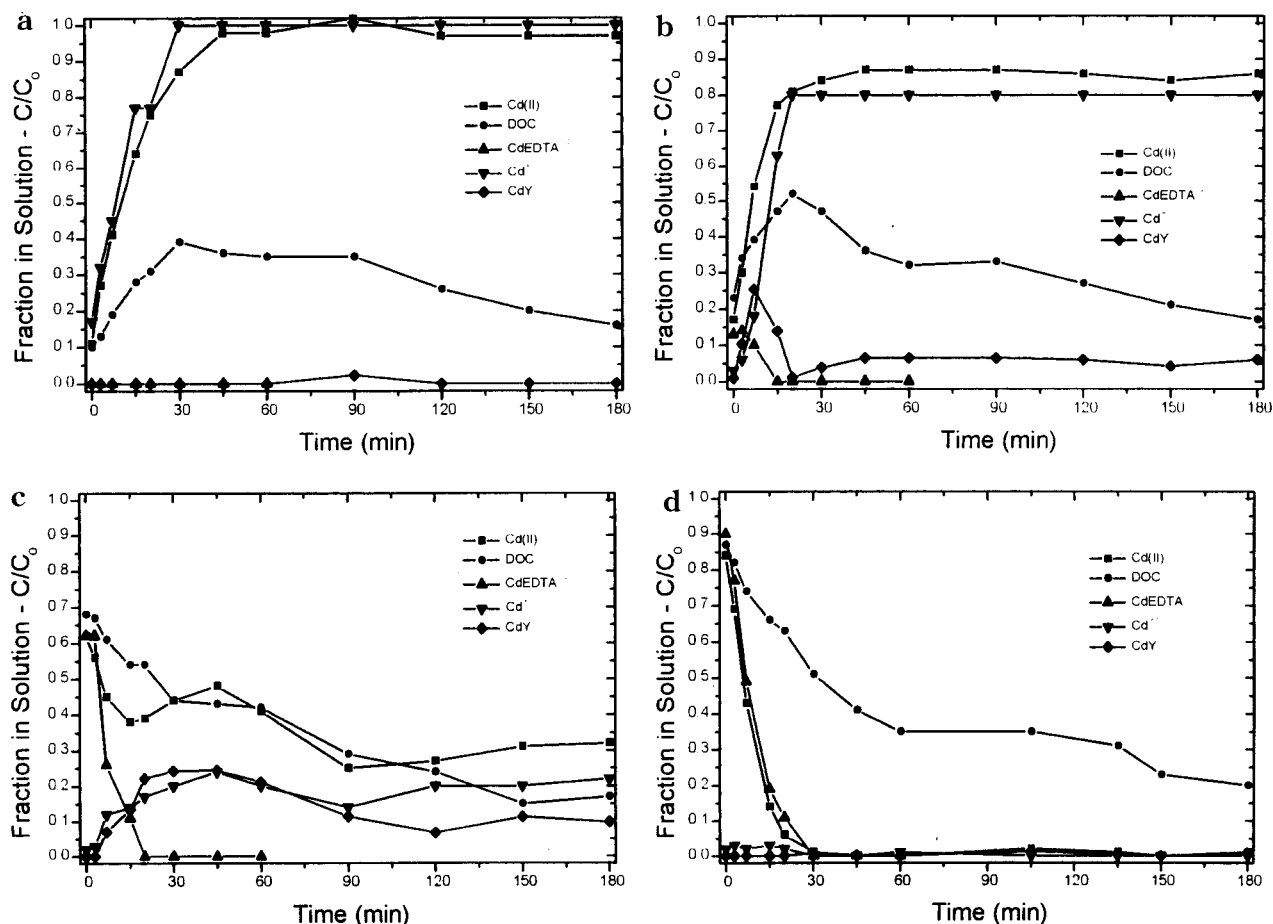


FIGURE 3. Distribution of aqueous species from PCO of Cd-EDTA ( $2 \times 10^{-5}$  M Cd-EDTA; 2 g/L  $\text{TiO}_2$ ;  $I = 5 \times 10^{-3}$  M  $\text{NaClO}_4$ ; flow rate = 75 mL/min; Cd-Y species calculated from mass balance): (a) pH 4, (b) pH 5, (c) pH 6, and (d) pH 7.

produced levels of Cd(II) and DOC that were essentially unchanged, indicating that neither cadmium, EDTA, nor Cd-EDTA $^{2-}$  are photoreactive under the UV light alone. The presence of the catalyst,  $\text{TiO}_2$ , is required to photooxidize the Cd-EDTA species.

Figure 3a–d shows results from the PCO of  $2 \times 10^{-5}$  M equimolar Cd-EDTA at pH 4 to 7. Similarly, PCO results from  $10^{-4}$  M Cd-EDTA at pH 3–8 are shown in Figure 4a–f. The initial distributions of species vary widely due to varying degrees of Cd-EDTA adsorption at different pH. The partial dissociation of Cd-EDTA at low pH introduces additional species, i.e., aqueous  $\text{Cd}^{2+}$  and uncomplexed EDTA species that can compete with the oxidation of the complex.

For PCO analysis, total cadmium ( $\text{Cd(II)}_T$ ) and total organic carbon ( $\text{TOC}_0$ ) mass balances are divided into the following aqueous and adsorbed quantities

$$\text{Cd(II)}_T = \text{Cd(II)}_{\text{aq}} + \text{Cd(II)}_{\text{ads}} \quad (2a)$$

$$\text{TOC}_0 = \text{DOC} + \text{AOC} + \text{inorganic carbon} \quad (2b)$$

where  $\text{Cd(II)}_T$  and  $\text{TOC}_0$  were measured from a premixed Cd-EDTA blank solution (no  $\text{TiO}_2$ ). Adsorbed cadmium ( $\text{Cd(II)}_{\text{ads}}$ ) concentrations were calculated by the difference between  $\text{Cd(II)}_T$  and  $\text{Cd(II)}_{\text{aq}}$  that was measured at each sampling period. Adsorbed organic carbon (AOC) could only be determined at the start of PCO by the difference between  $\text{TOC}_0$  and the initial dissolved organic carbon (DOC) concentration.

Specific measurements of Cd-EDTA $^{2-}_{\text{aq}}$  and  $\text{Cd}_{\text{aq}}^{2+}$  allowed the  $\text{Cd(II)}_T$  and  $\text{TOC}_0$  levels to be further subdivided into the following aqueous and adsorbed cadmium- and carbon-containing species:

$$\text{Cd(II)}_{\text{aq}} = \text{Cd-EDTA}^{2-}_{\text{aq}} + \text{Cd}_{\text{aq}}^{2+} + \text{Cd-Y}_{\text{aq}} \quad (3)$$

$$\text{DOC} = \text{Cd-EDTA}^{2-}_{\text{aq}} + \text{Cd-Y}_{\text{aq}} + \text{solution organic products} \quad (4)$$

$$\text{Cd(II)}_{\text{ads}} = \text{Cd-EDTA}^{2-}_{\text{ads}} + \text{Cd}_{\text{ads}}^{2+} + \text{Cd-Y}_{\text{ads}} \quad (5)$$

$$\text{AOC} = \text{Cd-EDTA}^{2-}_{\text{ads}} + \text{Cd-Y}_{\text{ads}} + \text{adsorbed organic products} \quad (6)$$

Aqueous cadmium hydrolysis species, i.e.,  $\text{CdOH}^+$ , are negligible between pH 3 and 8. Cd-Y represents an unspecified cadmium-ligand species produced from the oxidation of Cd-EDTA. Cd-Y $_{\text{aq}}$  was calculated from the Cd mass balance of eq 3.

Figures 3 and 4 show that independent of the solution pH and the initial concentration, Cd-EDTA $^{2-}_{\text{aq}}$  was undetectable by at least 30 min. Also, three different pH regimes are observed for the release characteristics of  $\text{Cd(II)}_{\text{aq}}$ , which arise from the adsorption behaviors of Cd-EDTA and  $\text{Cd}^{2+}$  at low, intermediate, and higher pH. The reaction patterns for DOC are also dependent upon the degree of initial complex adsorption. Except at pH 3,  $\text{Cd}^{2+}$  is negligible at the start of PCO because of the formation of the complex, and its appearance characteristics depend on the suspension pH.

**Kinetics of Cd-EDTA $^{2-}$  Degradation.** Figure 5 shows comparisons of Cd-EDTA degradation at various pH for  $10^{-4}$  M Cd-EDTA; similar trends were found at  $2 \times 10^{-5}$  M. The complex concentration is lowest at the lowest pH due to adsorption. Negligible adsorption occurs at pH 7 and 8. Even

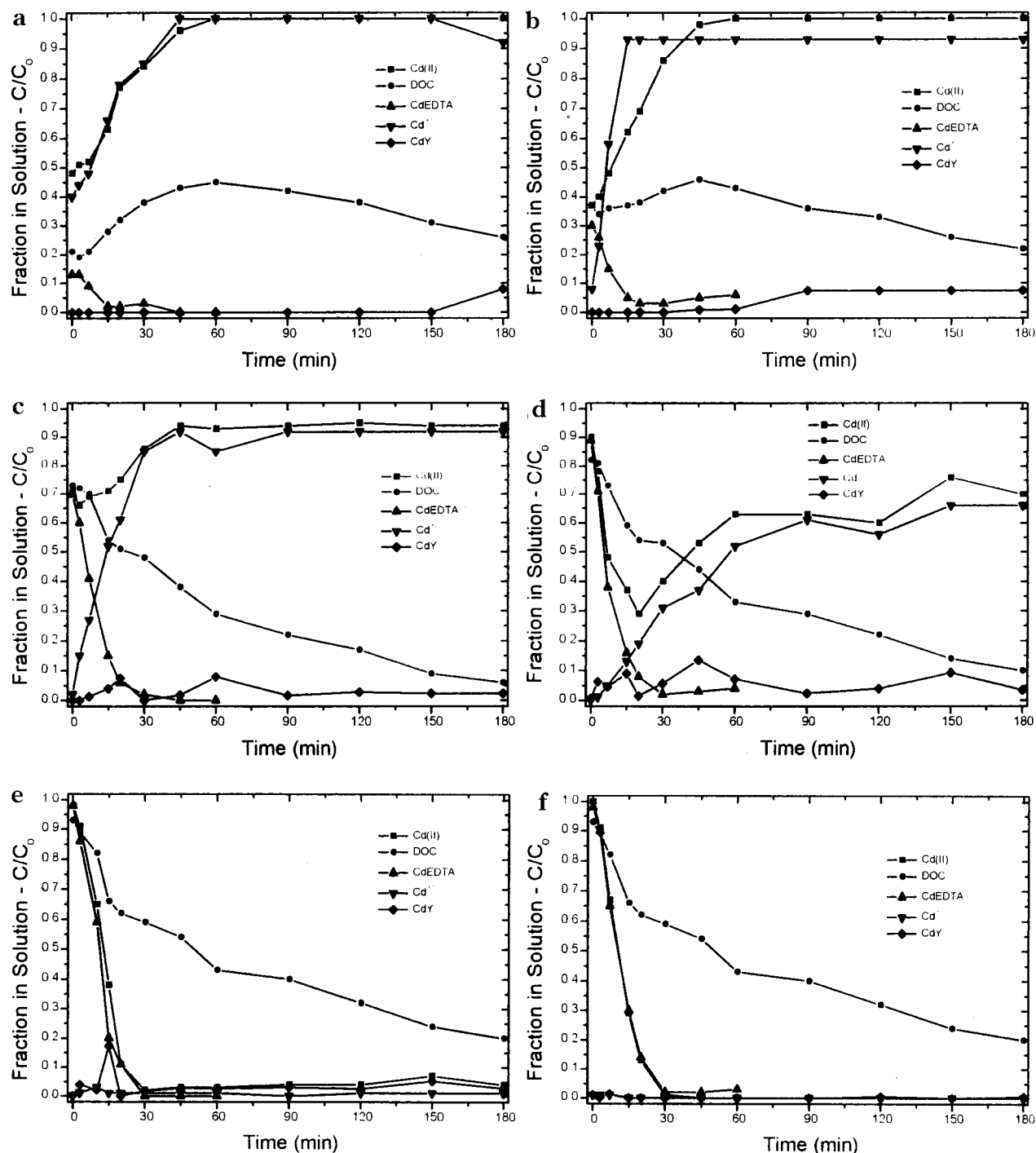


FIGURE 4. Distribution of aqueous species from PCO of Cd-EDTA ( $10^{-4}$  M Cd-EDTA; 2 g/L  $\text{TiO}_2$ ;  $I = 5 \times 10^{-3}$  M  $\text{NaClO}_4$ ; flow rate = 75 mL/min; Cd-Y species calculated from mass balance): (a) pH 3, (b) pH 4, (c) pH 5, (d) pH 6, (e) pH 7, and (f) pH 8.

though the distribution between surface and solution Cd-EDTA varies by nearly an order of magnitude, by 30 min this species becomes undetectable at all pH. Thus it seems that parallel adsorbed-phase and solution reactions are occurring in these systems and that the rates of the two pathways are not drastically different.

The Cd-EDTA $^{2-}_{\text{ads}}$  concentration was estimated using the isotherm expression (eq 1) and the constants of Table 2, thus allowing the computation of  $[\text{Cd-EDTA}^{2-}_{\text{T}}]$  by

$$\text{Cd-EDTA}^{2-}_{\text{T}} = \text{Cd-EDTA}^{2-}_{\text{aq}} + \text{Cd-EDTA}^{2-}_{\text{ads}} = \frac{\text{Cd-EDTA}^{2-}_{\text{aq}} (1 + K_{\text{ads}})}{(7)}$$

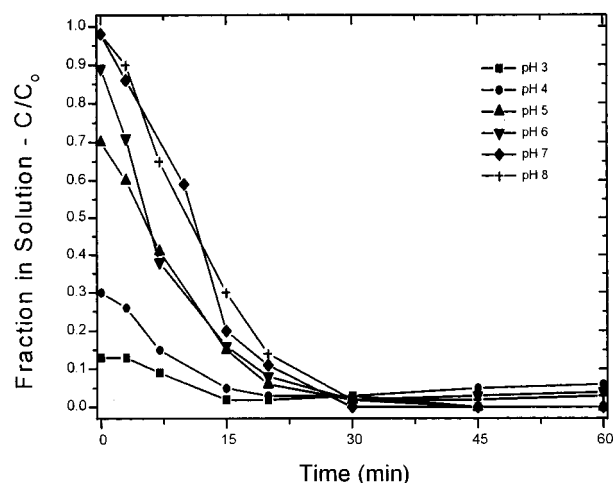
Accordingly, a total initial Cd-EDTA degradation rate,  $r_{\text{T}}$ , can be defined as the sum of the aqueous ( $r_{\text{aq}}$ ) and adsorbed ( $r_{\text{ads}}$ ) initial rates.

$$r_{\text{T}} = r_{\text{aq}} + r_{\text{ads}} \quad (8)$$

The linear portions of the aqueous, adsorbed, and total Cd-EDTA concentrations with respect to time were fitted with a best-fit line, encompassing approximately the first 20 min of data. These calculated rates are presented in Table 3. The adsorbed phase and solution rates are equal at about pH 5.8 at  $2 \times 10^{-5}$  M Cd-EDTA and at pH 4.5 for  $10^{-4}$  M. Below these pH values,  $r_{\text{ads}}$  dominates and, at higher pH,  $r_{\text{aq}}$  controls the

TABLE 3. Total, Adsorbed, and Aqueous Initial Reaction Rates for Cd-EDTA PCO

pH	initial PCO rate (mol·L <sup>-1</sup> ·min <sup>-1</sup> )					
	10 <sup>-4</sup> M Cd-EDTA			2 × 10 <sup>-5</sup> M Cd-EDTA		
	total	adsorbed	aqueous	total	adsorbed	aqueous
3	3.6 × 10 <sup>-6</sup>	2.9 × 10 <sup>-6</sup>	7.0 × 10 <sup>-7</sup>			
4	4.1 × 10 <sup>-6</sup>	2.8 × 10 <sup>-6</sup>	1.3 × 10 <sup>-6</sup>			
5	4.6 × 10 <sup>-6</sup>	1.4 × 10 <sup>-6</sup>	3.3 × 10 <sup>-6</sup>	1.9 × 10 <sup>-6</sup>	1.6 × 10 <sup>-6</sup>	2.6 × 10 <sup>-7</sup>
6	4.1 × 10 <sup>-6</sup>	4.6 × 10 <sup>-7</sup>	3.6 × 10 <sup>-6</sup>	9.8 × 10 <sup>-7</sup>	3.7 × 10 <sup>-7</sup>	6.1 × 10 <sup>-7</sup>
7	4.4 × 10 <sup>-6</sup>	7.4 × 10 <sup>-8</sup>	4.3 × 10 <sup>-6</sup>	8.1 × 10 <sup>-7</sup>	1.2 × 10 <sup>-7</sup>	6.9 × 10 <sup>-7</sup>
8	4.1 × 10 <sup>-6</sup>		4.1 × 10 <sup>-6</sup>			

FIGURE 5. Disappearance of aqueous Cd-EDTA<sup>2-</sup> from PCO at various pH (10<sup>-4</sup> M Cd-EDTA; 2 g/L TiO<sub>2</sub>; I = 5 × 10<sup>-3</sup> M NaClO<sub>4</sub>; flow rate = 75 mL/min).

oxidation of Cd-EDTA, following adsorption trends. Nevertheless, the consistent disappearance of Cd-EDTA by 30 min at all pH is reflected in the lack of variation in  $r_T$ . Assuming pH independence, an average total PCO rate can be calculated, equal to  $1.2 \times 10^{-6} \pm 5.6 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$  at  $2 \times 10^{-5} \text{ M}$  and  $4.1 \times 10^{-6} \pm 3.6 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$  at  $10^{-4} \text{ M}$ . The average total rate differs by a factor of only 3.4 with the 5-fold change in initial concentration, suggesting a reaction order less than one.

**Aqueous Cd(II) and Cd<sup>2+</sup> Trends.** At low pH (4 and 5), the Cd<sub>aq</sub><sup>2+</sup> and Cd(II)<sub>aq</sub> concentrations both increase as PCO proceeds (Figures 3a,b and 4b,c). Cd<sub>aq</sub><sup>2+</sup> increases from zero to equal to the Cd(II)<sub>aq</sub> concentration between 30 and 45 min, corresponding to the time that Cd-EDTA<sup>2-</sup><sub>aq</sub> falls to undetectable. After 45 min these values reach Cd(II)<sub>T</sub>, indicating complete conversion of all Cd-EDTA to Cd<sub>aq</sub><sup>2+</sup>. The only evidence of a complexed species, Cd-Y<sub>aq</sub>, is found at pH 5 in  $2 \times 10^{-5} \text{ M}$  (Figure 3b) where it increases to 25% of Cd(II)<sub>T</sub> at 7 min and becomes negligible at around 20 min.

At pH 6 (Figures 3c and 4d), Cd(II)<sub>aq</sub> no longer increases as Cd-EDTA<sup>2-</sup> is oxidized. Three distinct trends are exhibited. First, as PCO begins, Cd(II)<sub>aq</sub> decreases, coinciding with the Cd-EDTA<sup>2-</sup><sub>aq</sub> concentration. Thus, Cd produced from Cd-EDTA<sup>2-</sup><sub>aq</sub> degradation is in some form that is readily adsorbed onto the photocatalyst and not released into solution. After approximately 10 min, the Cd(II)<sub>aq</sub> decrease becomes less than that for Cd-EDTA<sup>2-</sup><sub>aq</sub>. Figure 3c shows significant difference between Cd(II)<sub>aq</sub> and (Cd-EDTA<sup>2-</sup><sub>aq</sub> + Cd<sub>aq</sub><sup>2+</sup>), suggesting significant formation of Cd-Y<sub>aq</sub>; this species is present but at lower relative levels at  $10^{-4} \text{ M}$  Cd-EDTA (Figure 4d). Last, Cd(II)<sub>aq</sub> increases significantly at  $10^{-4} \text{ M}$  and slightly at  $2 \times 10^{-5} \text{ M}$  as the previously adsorbed intermediate becomes oxidized. At this point, complexation is nullified as most of the Cd(II) is accounted for as Cd<sup>2+</sup>. At the end of the

experimental period some Cd(II) remains adsorbed, apparently as Cd<sup>2+</sup>.

Compounds such as iminodiacetic acid (IDA), glycine (GLY), ethylenediaminediacetic acid (EDDA), nitrilotriacetic acid (NTA), and ethylenediamine (EN) have been detected in the ozonation or PCO of EDTA (5, 19, 20). These compounds have stability constants with Cd<sup>2+</sup> ranging from  $10^{4.7}$  to  $10^{9.8}$  (21). One or more of these products can complex with Cd(II)<sub>aq</sub> at pH 6, and the complex may adsorb onto the TiO<sub>2</sub>. Cd-NTA (22) and other similar metal organic complexes (23, 24) are adsorbable onto hydrous oxides. As this secondary complex is destroyed via PCO, the cadmium is then released. At lower pH, these aminocarboxylic acids do not complex cadmium due to their partial protonation and weak degree of complexation, and cadmium is immediately released after the destruction of the EDTA.

At pH 7 and 8, the complex is initially 90–100% in solution as little adsorption occurs. PCO of Cd-EDTA<sup>2-</sup><sub>aq</sub> produces an equivalent Cd(II)<sub>aq</sub> disappearance rate, indicating the intermediate release and adsorption of Cd as the complex is destroyed. Any degradation products cannot compete with the strong adsorption of Cd(II)<sub>aq</sub> onto TiO<sub>2</sub>, and no evidence of Cd-Y<sub>aq</sub> exists. DOC decreases continually throughout the experiments, indicating no poisoning of the photocatalyst by Cd adsorption.

Free EDTA and Cd<sub>aq</sub><sup>2+</sup> exist initially at pH 3 in  $10^{-4} \text{ M}$  and pH 4 in  $2 \times 10^{-5} \text{ M}$ , different from the higher pH values (Figures 3a and 4a). However, similar to the other low pH experiments, cadmium is released as Cd<sub>aq</sub><sup>2+</sup> immediately as Cd-EDTA is oxidized. Cd<sub>aq</sub><sup>2+</sup> and Cd(II)<sub>aq</sub> are always equal and represent 100% of the input Cd by 30–45 min, which corresponds to the time where Cd-EDTA<sup>2-</sup><sub>aq</sub> becomes undetectable.

Under all conditions, PCO from 60 to 180 min produces Cd(II)<sub>aq</sub> concentrations that are essentially constant. At pH 3 to 5 Cd<sub>aq</sub><sup>2+</sup> is equal to Cd(II)<sub>aq</sub> and all cadmium is dissolved. At pH 6, again Cd<sub>aq</sub><sup>2+</sup> equals Cd(II)<sub>aq</sub>, but a significant portion of the cadmium is adsorbed. Essentially no cadmium remains in solution at pH 7 and 8 as it is completely adsorbed by the TiO<sub>2</sub>.

To investigate the Cd(II) adsorption further, Cd(II)<sub>aq</sub> concentrations were compiled from 60 to 180 min at each pH to obtain an average aqueous cadmium concentration and a corresponding amount adsorbed ( $\pm 1$  standard deviation). Values of the adsorbed amount were compared with Cd(II)<sub>ads</sub> from the overnight batch adsorption experiments as shown in Figure 6. (The  $2 \times 10^{-3} \text{ M}$  Cd(II) PCO measurements were compared with  $10^{-5} \text{ M}$  Cd(II) batch adsorption experiments.) Excellent agreement at all pH values indicates that the Cd-EDTA complex has been broken and that all Cd(II) exists as Cd<sup>2+</sup> after 60+ min of PCO.

Finally, measurements of dissolved Cd(II) after 180 min and adjustment to pH 8 demonstrated that essentially all Cd(II)<sub>aq</sub> was removed from solution via adsorption onto the TiO<sub>2</sub>, again suggesting that cadmium is in the adsorbable Cd<sub>aq</sub><sup>2+</sup> form after PCO at all pH. Acid addition after PCO desorbed cadmium that became adsorbed during reaction

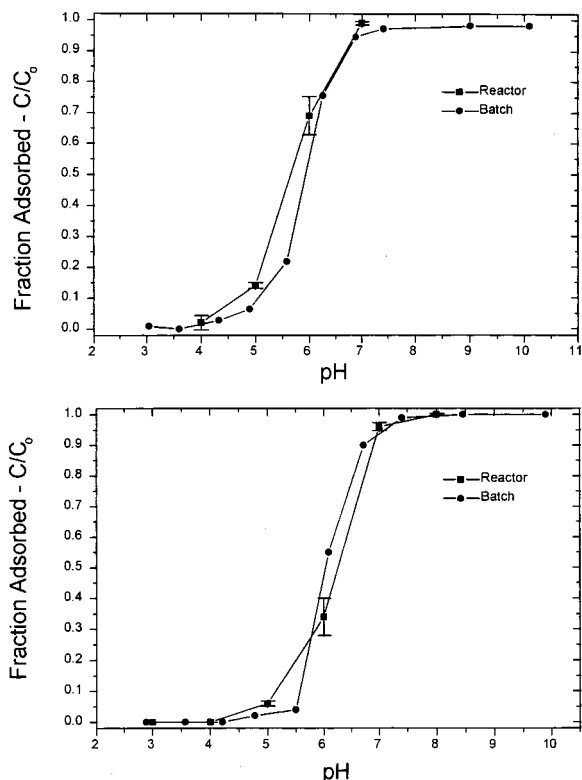


FIGURE 6. Comparison of adsorbed Cd(II) averaged from 60 to 180 min inside the PCO reactor to the Cd(II) batch adsorption of Figure 1 (2 g/L  $\text{TiO}_2$ ;  $I = 5 \times 10^{-3}$  M  $\text{NaClO}_4$ ; flow rate = 75 mL/min; error bars =  $\pm 1$  standard deviation): (a)  $2 \times 10^{-5}$  M Cd-EDTA PCO compared with  $10^{-5}$  M Cd(II) adsorption and (b)  $10^{-4}$  M.

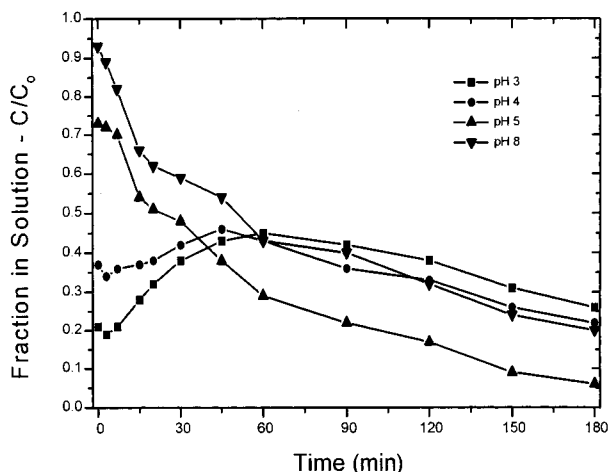


FIGURE 7. Disappearance of DOC from PCO at various pH ( $10^{-4}$  M Cd-EDTA; 2 g/L  $\text{TiO}_2$ ;  $I = 5 \times 10^{-3}$  M  $\text{NaClO}_4$ ; flow rate = 75 mL/min; pH 6 and 7 not shown for sake of clarity).

at higher pH. All cadmium was recovered at lower pH and nearly all is accounted for as  $\text{Cd}^{2+}$ .

**DOC Degradation.** For pH 4 and 5 at  $2 \times 10^{-5}$  M and pH 3 and 4 at  $10^{-4}$  M, the DOC actually increased during the first few minutes of reaction. It reached a maximum that corresponded with the disappearance of  $\text{Cd-EDTA}^{2-}_{\text{aq}}$ , indicating that the EDTA was oxidized to an intermediate species that, unlike the reactant, was not attracted to the  $\text{TiO}_2$  surface and was released into solution. As the oxidation proceeds, the decreases in DOC demonstrate mineralization. Figure 7 compares the DOC patterns from the PCO of  $10^{-4}$  M Cd-EDTA. At and above pH 5 (pH 6 in  $2 \times 10^{-5}$  M), increasing DOC is no longer seen. The DOC steadily decreased

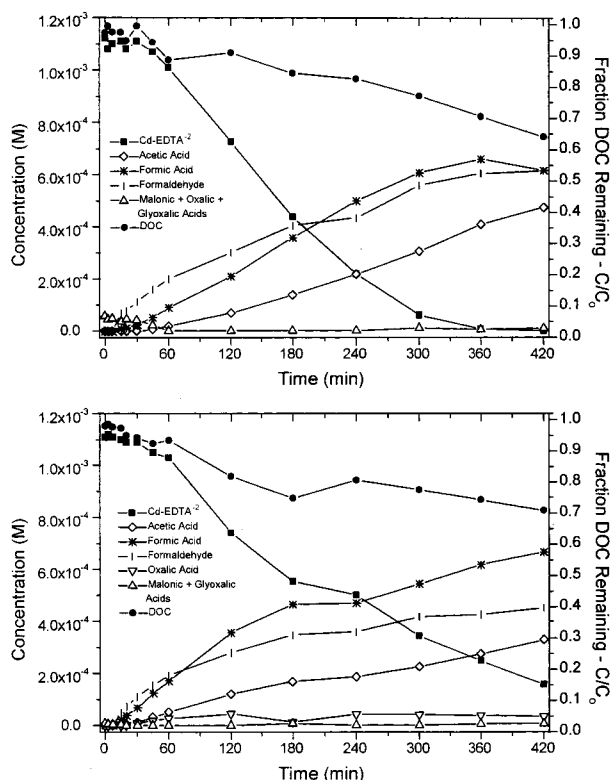


FIGURE 8. Distribution of aqueous species from PCO of  $10^{-3}$  M Cd-EDTA (2 g/L  $\text{TiO}_2$ ;  $I = 5 \times 10^{-3}$  M  $\text{NaClO}_4$ ; flow rate = 75 mL/min): (a) pH 4 and (b) pH 7.

as  $\text{Cd-EDTA}^{2-}_{\text{aq}}$  was being oxidized. Little Cd-EDTA was adsorbed at these higher pH values, and any desorption of organic intermediates was masked by the higher solution DOC content.

Independent of the initial surface/solution distribution of  $10^{-4}$  M Cd-EDTA and the solution pH, about 20–26% of  $\text{TOC}_0$  remains in solution after 180 min of PCO, except for pH 5 in which 6% remains. PCO at  $2 \times 10^{-5}$  M produces residual DOC of 15–20%. Thus, the overall mineralization rates are essentially equal, independent of the type, and degree of adsorption of intermediates produced. These results suggest that the total amount of oxidant produced by the PCO system is constant, which is also supported by the pH independence of the Cd-EDTA disappearance rate.

A dual surface hole-hydroxyl radical mechanism, proposed by Sun and Pignatello (25), serves to explain why the fastest oxidation rates occur at pH 5 at  $10^{-4}$  M Cd-EDTA. Through this mechanism, direct oxidation by valence band holes and indirect oxidation by surface hydroxyl radicals are responsible for the oxidation of Cd-EDTA and its oxidation products. Adsorption of Cd-EDTA and its reaction products is necessary for direct electron transfer to valence band holes. Electron transfer apparently stems from the ability of carboxylate groups of organic acids to coordinate directly with  $\text{Ti}^{4+}$  surface metal centers (25). Since reaction with holes on the  $\text{TiO}_2$  surface is direct while the formation of hydroxyl radicals and subsequent reaction with substrate involves a series of steps, the overall oxidation rate of adsorbed organics should be faster than that of the solution degraded species. Overlap of the two pathways occurs at pH 5 where both adsorbed and solution-phase oxidations are significant, producing the maximum rate.

Little change in DOC occurred from final adjustments of pH to 2.5 and 8 at  $10^{-4}$  M. The negligible stripping at pH 8 indicated that very little organic carbon was adsorbed onto the  $\text{TiO}_2$  after 180 min of PCO. Thus, organic carbon is being



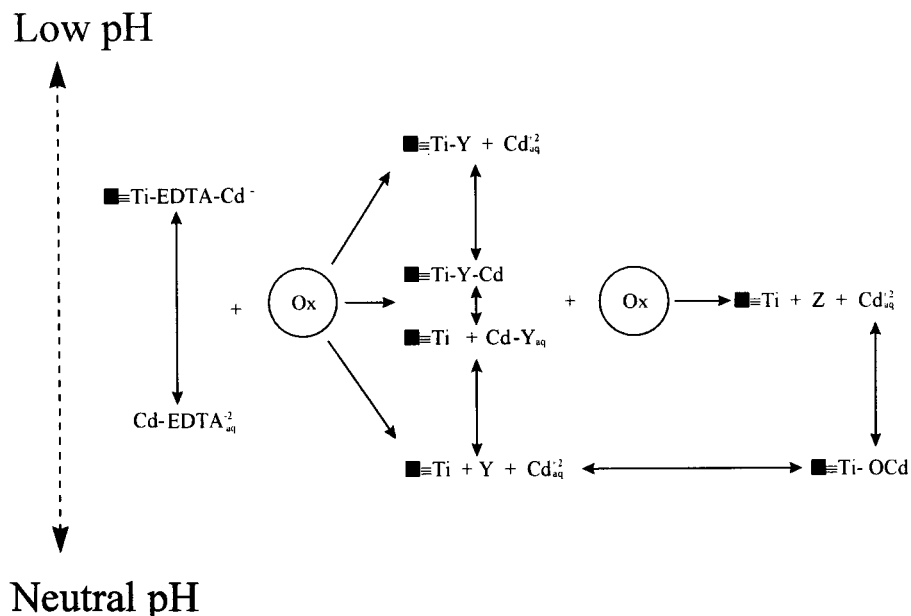


FIGURE 9. General mechanisms involved in the PCO of Cd-EDTA and the fate of cadmium.

oxidized, and DOC measured at longer times represents the TOC in the system; organic carbon is not accumulating on the TiO<sub>2</sub> surface. Even adjustment to pH 2.5 produced no adsorption of the residual DOC.

**Determination of Reaction Intermediates.** Figure 8a, b shows the PCO of 10<sup>-3</sup> M Cd-EDTA at pH 4 and 7, respectively, over a 7-hr reaction time. Initially, the complex is primarily all in solution at both pH values. At pH 4 some adsorption is expected, but it is masked by the high solution concentration. These data indicate that the PCO of Cd-EDTA is faster at pH 4 than at pH 7. After 360 min, Cd-EDTA<sup>2-</sup> (aq) is <10<sup>-6</sup> M at pH 4. At pH 7, Cd-EDTA<sup>2-</sup> (aq) was reduced to 14% of its initial concentration after 420 min. At the end of the experiments, DOC was 64% and 71% of TOC<sub>0</sub> at pH 4 and 7, respectively.

Intermediate species from the PCO were documented during these runs. Samples were analyzed for acetic, formic, malonic, maleic, glyoxylic, and oxalic acids, and formaldehyde. Malonic (concentrations found: 5 × 10<sup>-6</sup> to 3 × 10<sup>-5</sup> M), oxalic (10<sup>-6</sup> to 4 × 10<sup>-5</sup> M), and glyoxylic (5 × 10<sup>-7</sup> to 10<sup>-6</sup> M) acids were grouped together in Figure 8a,b because their concentrations were small compared with the other plotted species. Maleic acid was not found at detectable levels.

Formaldehyde, acetic acid, and formic acid were produced at significant levels, and their concentrations increased steadily throughout the experiments. On a concentration basis formic acid was greater than formaldehyde at pH 7; concentrations of these species were similar at pH 4. Acetic acid was produced at lower levels at both pH values but was greater than the formic acid level on a carbon basis. Formic acid and oxalic acid were produced in greater quantities at pH 7 than at 4 even though more Cd-EDTA was reacted at pH 4. Greater acetic acid and formaldehyde production occurred at pH 4. At the end of the reaction time, all quantified intermediate species comprised 36% of the aqueous carbon (DOC) at pH 4. At pH 7, 47% of the carbon could be accounted for, however, 19% of the carbon comes from the residual Cd-EDTA<sup>2-</sup> (aq).

Organic amines likely account for the incomplete carbon mass balance from Cd-EDTA PCO. Support for organic nitrogen compounds as constituting the remainder of the carbon mass balance stems from several facts. First, the PCO of Cd-EDTA at both pH 4 and 7 displayed a consistently low conversion to nitrate (5–8% of the nitrogen molar balance—not shown in Figure 8a,b). Second, no more than two carbons

make up the intermediate species detected in appreciable quantities. The production of species with three or more carbons from the cleavage of Cd-EDTA must include nitrogen from the ethylenediamine backbone. Third, uncharged species such as acetaldehyde from the PCO of EDTA (5) may escape detection by the IC methodology employed. Last, other researchers have detected amines from the ozonation of EDTA, which may demonstrate products similar to the PCO of Cd-EDTA. Morooka et al. (19) and Gilbert and Hoffman-Glewe (20) have detected several amine species from the ozonation of EDTA, including NTA, IDA, and glycine.

The pK<sub>a</sub> values for maleic, malonic, acetic, formic, oxalic, lactic, glyoxylic, and pyruvic acids range from 6.33 to 2.55 (21, 26). Increase of the suspension pH from 4 to 7 and concurrent dissociation should make these acids more susceptible to hydroxyl radical attack. The data of Figure 8a,b support this discussion. At pH 4, partial adsorption of the Cd-EDTA complex apparently facilitates its complete removal and the lower DOC concentration at the end of the PCO through surface hole and hydroxyl radical attack. At pH 7, adsorption of the complex is not favored, and thus, removal occurs predominantly through solution-phase hydroxyl radical attack. Adsorption of reaction intermediates is also not favored, and their oxidation should also occur in solution.

**General Mechanisms Involved in the PCO of Cd-EDTA.** Based on the previous discussions, Figure 9 summarizes the general mechanisms involved in the PCO of Cd-EDTA and the fate of cadmium during the reaction. Initially, Cd-EDTA equilibrates with the TiO<sub>2</sub> surface. At low pH values, a large portion of the complex is adsorbed; at high pH, the complex exists mostly in solution. Once PCO is initiated, the oxidant, Ox, either a valence band hole or a hydroxyl radical depending on whether the degradation occurs on the TiO<sub>2</sub> surface or in solution, reacts with the complex. At low pH, as Cd-EDTA is oxidized, cadmium is immediately released into solution as Cd<sub>aq</sub><sup>2+</sup>. An intermediate organic species, Y, results from the oxidation of the complex at the surface/solution interface. Y is expected to be NTA, IDA, or similar species. At pH 6, the degradation produced Cd–Y, both adsorbed and in solution. Further oxidation destroys the Cd–Y complex, and Y is oxidized to intermediate species Z, which do not adsorb and do not complex strongly with Cd(II). Z compounds include acetic acid, formic acid, and formaldehyde. Cadmium is liberated as Cd<sub>aq</sub><sup>2+</sup>, and a metal-like adsorption equilibrium is established between the metal and the oxide surface. At



high pH, Cd-EDTA<sup>2-</sup><sub>aq</sub> is oxidized to Y<sub>aq</sub> and Cd<sub>aq</sub><sup>2+</sup>, upon which the free cadmium is immediately adsorbed. Subsequently, Y is further oxidized in solution to Z. These simple compounds are mineralized with continued PCO.

Overall experimental results indicate that using TiO<sub>2</sub> semiconductor photocatalysis to oxidize the Cd-EDTA complex is a viable treatment alternative for removing both cadmium and EDTA from solution. Total observed initial removal rates of Cd-EDTA were essentially independent of pH. At low pH (pH 3–5), Cd<sub>aq</sub><sup>2+</sup> was released into solution immediately as aqueous and adsorbed Cd-EDTA were oxidized. Desorption of oxidized AOC, resulting in an increase in DOC, occurred when a large portion (>50%) of the complex was initially adsorbed. At intermediate pH (pH 6), cadmium was complexed by (most probably) aminocarboxylic species resulting from the PCO of Cd-EDTA. Further PCO of these metal–ligand compounds released cadmium. The free cadmium then adsorbed at the solution/surface interface at levels predicted for adsorption equilibria. At pH 7–8, once aqueous Cd-EDTA was oxidized, cadmium became adsorbed, matching that expected for free cadmium, and DOC steadily decreased. Conversion of Cd-EDTA to Cd<sup>2+</sup> occurred with only about 50% mineralization of the organic carbon. Continued PCO mineralized the remaining DOC without affecting the fate of the cadmium.

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