# Photocatalyzed Degradation of Metal-EDTA Complexes in $TiO_2$ Aqueous Suspensions and Simultaneous Metal Removal

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Cu(II)-, Fe(III)-, and Zn(II)-EDTA complexes are degraded rapidly in aerated aqueous suspensions of $TiO_2$ with a high-pressure mercury lamp (irradiation wavelength > ca.290 nm), accompanying a full removal of the metals. Total organic carbons (TOCs) in their solutions decrease with the irradiation time, however, TOCs remained after 5 h irradiation. Although Co(II)- and Ni(II)-EDTA complexes are degraded, the removal of their metals is slow. Mn(II)-EDTA complex is degraded incompletely even after 5 h irradiation.

A precipitation method is widely used for removal of hazardous heavy metals in wastewater. However, the method is not suitable when the water-soluble metal complexes with chelating agents such as ethylenediaminetetraacetic acid (EDTA) are contained because these complexes are hardly precipitated even under alkaline conditions.

Recently, photocatalytic reaction with $TiO_2$ has been studied for the destruction of water contaminants.[1-3] Although a variety of pollutants,[4] including EDTA,[5-7] can be degraded by the use of this reaction, the photocatalytic reaction of metal-EDTA complexes has not so far been reported.

Accordingly, we studied the photocatalyzed degradation of the metal-EDTA complexes in $TiO_2$ aqueous suspensions, and found that these complexes could be degraded readily, accompanying a simultaneous removal of the metals from the solution. In this letter, we report the degradation behavior of six metal-EDTA complexes.

Each of the metal-EDTA complex solutions was prepared by dissolving commercially available Mn(II)-EDTA, Fe(III)-EDTA, Co(II)-EDTA, Ni(II)-EDTA, Cu(II)-EDTA, or Zn(II)-EDTA (Dojindo Lab.) with distilled-deionized water. The $TiO_2$ used was P-25 (Nippon Aerosil Co.); BET surface area is 50±15 $m^2\ g^{-1}$ and a primary particle diameter is in the range of 15-40 nm.

The photocatalyzed degradation experiments were carried out as follows. To 20 $cm^3$ of an aqueous solution containing each of 6 μmol of the metal-EDTA complexes (pH 5-6) in a Pyrex test tube, 10 mg of $TiO_2$ was added. Air was bubbled through the solution at the rate of about 160 $cm^3\ min^{-1}$ in order to keep $TiO_2$ in suspended state. The suspension was then irradiated with a 400 W high-pressure mercury lamp (Riko Co.) through a Pyrex water jacket (irradiation wavelength > ca.290 nm) in a water bath thermostated at 30 °C. The quantity of the light entering the suspension, as measured by potassium tris(oxalato)ferrate(III) actinometry and corrected for fraction of light absorbed in the range of 290-410 nm, was found to be $3.04\times10^{15}$ photons $cm^{-3}\ s^{-1}$. A given amount of the suspension was withdrawn at timed intervals and $TiO_2$ was removed by centrifugation followed by filtration through a syringe equipped with a disposable filter (pore size, 0.2 μm). The amounts of the metal-EDTA complex, total metal, and total organic carbon (TOC) in the solution were measured by Dionex 2000i ion chromatograph equipped with Tohso IC-Anion-PW anion column (eluent: 1.0 mmol $dm^{-3}$ $Na_2CO_3$ - 0.375 mmol $dm^{-3}$ $NaHCO_3$), Hitachi 170-50 flame atomic absorption spectrophotometer, and Shimadzu TOC-500 TOC analyzer, respectively.

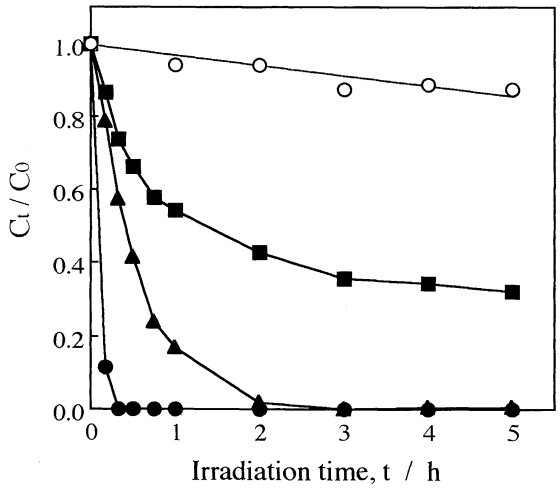


**Figure 1.** Variation of the amount of Cu(II)-EDTA, Cu, and TOC in the solution as a function of irradiation time.
Cu(II)-EDTA, 6 μmol; sample volume, 20 $cm^3$; $TiO_2$, 10 mg (Cu(II)-EDTA (●), Cu (▲), and TOC (■)) and without $TiO_2$ (Cu(II)-EDTA (○)); air flow rate, 160 $cm^3\ min^{-1}$; temperature, 30 °C.

Figure 1 shows the result of the photocatalyzed degradation of Cu(II)-EDTA complex. Cu(II)-EDTA complex is degraded very slowly without $TiO_2$ under irradiation. The addition of $TiO_2$ remarkably accelerated the degradation of Cu(II)-EDTA complex; that is, Cu(II)-EDTA complex decomposed completely after the irradiation for only 20 min. However, TOC remained even in the suspension irradiated for 5 h. On the other hand, the amount of copper in the solution decreased with an increase of the irradiation time and was scarcely detected after 2 h. The color of the $TiO_2$ particles changed gradually from white to gray with the irradiation time and the suspension became transparent after 1 h by the settlement of $TiO_2$ particles as shown in Table 1. Bard *et al.*[8,9] reported that copper is deposited on $TiO_2$ surface by the UV-irradiation of $CuSO_4$ containing aqueous suspension of $TiO_2$. In this experiment, the decrease in the amount of copper in the solution and the settlement of $TiO_2$ particles may also be due to the photodeposition of copper on the surface of $TiO_2$ during the photocatalyzed degradation. In general, the separation of the fine $TiO_2$ particles from the suspension is very

**Table 1.** Concentration changes of Metal-EDTA complexes, total metals, and TOCs and transmittance of the supernatant solution after irradiation for 1 h

| Sample | $(C_1/C_0)$[a] | | | Transmittance[b] |
|---|---|---|---|---|
| | Complex | Total Metal[c] | TOC | % |
| Cu(II)-EDTA | N.D. | 0.17 | 0.55 | 59 |
| Cu(II)-EDTA[d] | 0.94 | — [e] | — [e] | |
| Fe(III)-EDTA | — [e] | < 0.01 | 0.36 | 37 |
| Fe(III)-EDTA[d] | — [e] | 0.43 | 0.79 | |
| Zn(II)-EDTA | 0.06 | 0.30 | 0.38 | 73 |
| Co(II)-EDTA | 0.24 | 0.94 | 0.99 | 17 |
| Ni(II)-EDTA | 0.24 | 0.85 | 0.82 | 39 |
| Mn(II)-EDTA | 0.67 | 0.81 | 0.95 | 46 |
| No Metal-EDTA[f] | | | | < 1 |

[a]Ratio of the concentrations at t=1 (h) versus t=0 (h). [b]Transmittance of the supernatant solution stood for 1 h after irradiation versus the filtrate ($\lambda$=550 nm). The filtrates show no absorption at 550 nm, except for that of Co(II)-EDTA. [c]Total concentration of metal remained in the solution. [d]$TiO_2$ was not added. [e]Not measured. [f]Only $TiO_2$ was added in distilled-deionized water.

difficult, however, the recovery of $TiO_2$ particles was easy because of their spontaneous settlement in this experiment.

The photocatalyzed degradation of Fe(III)-EDTA, Zn(II)-EDTA, Co(II)-EDTA, Ni(II)-EDTA, and Mn(II)-EDTA complexes was also investigated. Table 1 summarizes the concentration ratios ($C_1/C_0$) of the metal-EDTA complexes, total metals, and TOCs in the solutions after irradiation for 1 h. For Fe(III)-EDTA complex $C_1/C_0$ was not measured, however, it is certain that Fe(III)-EDTA complex is degraded readily by the photocatalytic reaction because the amounts of iron and TOC in the solution decreased rapidly. Zn(II)-EDTA complex is also degraded completely after the irradiation for at least 1 h. The amounts of zinc and TOC in the solution also decreased rapidly. Although Co(II)-EDTA and Ni(II)-EDTA complexes are degraded almost completely after irradiation for 2 h, the decrease in the concentrations of the metal and the TOC was slower than those in the cases of Cu(II)-EDTA, Fe(III)-EDTA, and Zn(II)-EDTA complexes. The photocatalyzed degradation of Mn(II)-EDTA complex was slowest among the metal-EDTA complexes investigated; more than 40% of the complex remained in the solution even after 5 h irradiation. Similar to the experiment for Cu(II)-EDTA complex, $TiO_2$ particles were settled appreciably after 1 h irradiation of Fe(III)-, Zn(II)-, Co(II)-, Ni(II)-, and Mn(II)-EDTA complexes, as shown in Table 1.

From these results, it is found that several metal-EDTA complexes can be degraded rapidly by the photocatalytic reaction with $TiO_2$, accompanying the simultaneous removal of the metals from the solutions. The photocatalyzed degradation method is simple and does not need special equipments except for light source. In addition, the recovery of $TiO_2$ particles from the suspension is easy. Therefore, this method may be applicable for wastewater treatment containing various metal-EDTA complexes. Furthermore, we suggest that previous addition of metal salts to $TiO_2$ aqueous suspensions containing water contaminants may enable $TiO_2$ particles to separate.

## References

1 Y.Kikuchi, K.Hashimoto, and A.Fujishima, *Kagaku Kogyo*, **1995**, 937.
2 M.Murabayashi, *Kagaku Kogyo*, **1995**, 943.
3 D.F.Ollis, E.Pelizzetti, and N.Serpone, "Photocatalysis," ed by N.Serpone and E.Pelizzetti, John Wiley & Sons, New York(1989), pp.603-637.
4 M.R.Hoffmann, S.T.Martin, W.Choi, and D.W.Bahnemann, *Chem. Rev.*, **95**, 69(1995).
5 G.K.-C.Low, S.R.McEroy, and R.W.Matthews, *Environ. Sci. Technol.*, **25**, 460(1991).
6 F.Sabin, T.Türk, and A.Vogler, *J. Photochem. Photobiol. A: Chem.*, **63**, 99(1992).
7 M.R.Prairie, L.R.Evans, B.M.Stange, and S.L.Martinez, *Environ. Sci. Technol.*, **27**, 1776(1993).
8 H.Reiche, W.W.Dunn, and A.J.Bard, *J. Phys. Chem.*, **83**, 2248(1979).
9 M.D.Ward and A.J.Bard, *J. Phys. Chem.*, **86**, 3599(1982).