A study on the removal of toxic metal-EDTA complex using solar light/TiO₂ system

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Abstract A circular reactor was placed outdoors to investigate the possibility of using natural sunlight in TiO₂ photocatalysis system for the removal of toxic metals (Cd, Cr, Cu, Hg, Ni, Zn) and EDTA complex. The results show that the system containing both solar light and TiO₂ more effectively removed metal-EDTA complex than either solar light or TiO₂ system alone. The removal of each metal was more than 90% in the presence of TiO₂/solar light, and EDTA (TOC basis) was reduced more than 80% in 120 min. Photocatalytic removal efficiency of heavy metal-EDTA increased with increasing TiO₂ dosage. However, over 1.5g/L of TiO₂ dosage, the efficiency reached a plateau.

Keywords Metal-EDTA complex, oxidation, photocatalytic, reduction, solar light, TiO₂

Introduction
The presence of organic chelates like EDTA (ethylenediaminetetraacetic acid), along with toxic metals in groundwater, soils, and sediments is of significant environmental concern because of metal-organic complex formation and resulting increased mobility of toxic species to adjacent groundwater and soil system (Thomas et al., 1997). Many common treatment technologies are unable to sufficiently remove these metals from wastewater streams since the treatment of waters containing this metal complex generally requires destruction of the complex. Chemical precipitation for metals removal, such as hydroxide and sulfide precipitation are also inhibited when the metals exist as metal-organic complexes (Bhattacharyya et al., 1984). For these reasons, it is important to find a new technology that is able to treat metal-EDTA complexes.

TiO₂-assisted photocatalysis, extensively studied for the oxidation of aqueous organic contaminants, has been recently developed for metal-organic complex degradation (Muhammad et al., 1997). Irradiation of TiO₂ creates holes and electrons in the valence and conduction bands, respectively (Eq. (1)). The resulting holes can react with surface bound hydroxyl groups to generate hydroxyl radicals (∑OH), and can oxidize EDTA (Eq. (2)), and toxic metal can be reduced by TiO₂(e⁻) (Eq. (4)) (Hisanaga et al., 1990).

\[
\text{TiO}_2 + h\nu \text{(UV or solar light)} \rightarrow \text{TiO}_2 (h^+ + e^-) \quad (1)
\]

\[
\text{TiO}_2 (h^+) + \text{OH}^-_{\text{sur}} \rightarrow \Sigma \text{OH} \quad (2)
\]

\[
\Sigma \text{OH} + \text{EDTA} \rightarrow \text{Oxidized Product} \quad (3)
\]

\[
\text{TiO}_2 (e^-) + \text{Metal}^{x+} \rightarrow \text{TiO}_2 + \text{Metal} \quad (4)
\]

TiO₂ photocatalysis has also dual advantages of first degrading the chelates and then adsorbing the uncomplexed metal from solution. The adsorbed metal can then be stripped from the TiO₂ surface.
The use of solar energy has been stimulated in recent years as a result of the potential use of concentrated solar photons for photochemical processes (Glatzmaier, 1991). However, the progress has been very slow, and there is no known solar photochemical process that has proven to be both practical and economic (Bolton, 1995).

The objectives of our study are (i) to examine the efficiency of treating toxic metal-EDTA complex using TiO$_2$ photocatalysis, and (ii) to assess feasibility and practicality of solar light application instead of UV for treating these metal complex wastes.

Materials and methods

Materials

The following reagents were used: EDTA ($C_{10}H_{14}N_2Na_2O_8\Sigma H_2O$, Junsei Chemical Co., Ltd), $K_2Cr_2O_7$, $HgSO_4$, $Cd(NO_3)_2\cdot4H_2O$, $CuSO_4\cdot5H_2O$, $Ni(NO_3)_2\cdot6H_2O$, $ZnSO_4$ (Shinyo Pure Chemicals Co., Ltd). The titanium dioxide (TiO$_2$) used was Degussa p-25, which is mostly anatase and has a BET (Brunauer-Emmett-Teller) surface area of 50 m$^2$/g and an average particle diameter of 30 nm. All the experiments used a 7 L solution illuminated with natural solar light from 10:00 a.m. to 4:30 p.m. Reactions were initiated at 0.1 wt% loading of Degussa P-25 TiO$_2$, a solute concentration of 0.4 mM and at pH 4.

Solar photocatalytic reactor system

First, we designed and constructed the 1.2 m$^2$ UV concentrating radiation systems (CPCs) (Figure 1) for photocatalytic processes. This concentrator module is 1.5 m (long) × 0.8 m (wide) with UV-transparent tubular receivers. The acceptance angle for the CPC is 52° either side of normal incidence. The polished aluminium is used as the reflective material because it is highly reflective in the UV range (300–380 nm) and quartz tube is used for tube receiver because it has excellent UV stability and transmissivity. The 8 modules are connected in series and the water flow directly from one to another and finally to the reservoir tank. A rotary pump (Cole-Parmer Instrument Co.) was continuously recirculating the suspension a batch vessel and the solar reactor by silicon pipes. At regular time intervals, aliquots were withdrawn through the three-way valve. Solar light intensity was measured using a Radiometer (VLX-3W Radiometer 9811-50, Cole Parmer Instrument Co.) at 365 nm at the same inclination angle as the plate. All the experiments, unless specified, were performed under the circumstance of random weather conditions (e.g. depending on the hours of day, atmospheric turbulence and other variation) between 10 a.m. and 4:30 p.m. at the Seoul National University campus located in Seoul, Korea (38° north latitude).

Analysis

The aliquots were first centrifuged to separate the solid. Then, the supernatant was analyzed for each metal (Cd, Cu, Hg, Ni, Zn) amount using inductively-coupled-plasma
(ICP) (Perkin-Elmer optima 3000DV, Cole-Parmer Instrument Co.). When necessary, the samples for metals analysis were stabilized in 2% HNO₃ (Fisher, Optima Grade) or 2% HCl (Fisher, Ultrex Grade). The Cr(VI) was analyzed colorimetrically using dipenylcarbazid by Standard Methods (APHA, 1992). TOC was measured for indirect EDTA analysis using a Shimazu TOC-5000 analyzer.

Results and discussion
Control experiment
The control experiments were conducted under the conditions of pH 4 in order to examine the adsorption on TiO₂ powder without solar light, as well as the removal of heavy metal-EDTA by solar light in the absence of TiO₂. It was found that the dark condition reaction (TiO₂ only) and TiO₂-free reactor (solar photolysis only) gave nearly no removal of metals and EDTA.

Removal of metals-EDTA using solar light
To investigate the possibility of using sunlight for the removal of metal-EDTA complex, the reactor was placed outdoors as mentioned earlier. The weather conditions are shown in Table 1 and Figure 2.

A 0.4 mM of each metal, 0.4 mM of EDTA, TiO₂ amounts of 1 g/L, and the flow rate of 5 L/min were used. The results were shown in Figure 3 and 4. It was found that the removal of each heavy metal was more than 90%, and EDTA (TOC basis) was more than 80% in about 120 min in the presence of solar light and TiO₂, and the removal were almost the same in both clear and cloudy days. However, the removal efficiency under the rainy sky condition is around 10–15% in heavy metal removal except Hg (about 35%) and less than 20% in EDTA (TOC basis) reduction. The fact is that the destruction of the heavy metal-EDTA cannot be achieved well under a rainy sky condition. This means that, under a rainy sky, the

Table 1  Comparison of weather condition from 10:00(a.m.) to 4:30(p.m.)

<table>
<thead>
<tr>
<th>Date</th>
<th>10/05/1999</th>
<th>10/06/1999</th>
<th>10/08/1999</th>
<th>10/10/1999</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light intensity (mW/cm²)</td>
<td>Max: 1.24</td>
<td>Max: 1.10</td>
<td>Max: 0.76</td>
<td>Max: 0.11</td>
</tr>
<tr>
<td></td>
<td>min: 0.46</td>
<td>Min: 0.34</td>
<td>Min: 0.32</td>
<td>Min: 0.001</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>Max: 34.60</td>
<td>Max: 32.44</td>
<td>Max: 30.80</td>
<td>Max: 19.00</td>
</tr>
<tr>
<td></td>
<td>Min: 23.80</td>
<td>Min: 23.80</td>
<td>Min: 22.70</td>
<td>Min: 12.00</td>
</tr>
<tr>
<td>Weather status</td>
<td>Clear</td>
<td>Clear</td>
<td>Cloudy</td>
<td>Rainy</td>
</tr>
</tbody>
</table>

Figure 2  Light intensity variation of experiment dates
photocatalytic reduction and oxidation are very slow and cannot use electrons and holes as fast as they are generated. Similar results were obtained in reduction of Cr(VI) to Cr(III) with EDTA as a hole scavenger (Prairie et al., 1993).

The effect of changing amount of TiO₂
The effect of TiO₂ concentration on the removal of each metal-EDTA complex was investigated under the clear sky condition.

The results are shown at Figures 5 and 6. Changing TiO₂ concentration from 0.5 g/L to 1.0 g/L dramatically increased the reduction of each metal and TOC removal. This indicates that, as the amount of TiO₂ increases, the TiO₂ surface area exposed will increase, resulting in increase in the reaction rate. However, further increase of TiO₂ to more than 1.5 g/L did not improve metal and TOC removal. It seems that particle-particle interactions may produce deleterious effects such as light shielding and agglomeration at higher TiO₂ concentration (Huang et al., 1996; Prairie et al., 1993). For any additional amount this limit will only increase the thickness of the layer of TiO₂ and not the surface area.

Conclusions
We demonstrated the application of photocatalytic oxidation and reduction processes of toxic metal-EDTA complex using solar light-illuminated TiO₂. It has been found that natural sunlight can be a powerful driving force for the TiO₂/solar light reaction. Despite

![Figure 3](image1.png)

Figure 3: Removal efficiency of each metal by TiO₂ with solar light according to experimental date (0.4 mM metal, 0.4 mM EDTA, TiO₂ = 1 g/L, pH = 4, flow rate = 5 L/min, open to air)

![Figure 4](image2.png)

Figure 4: Removal efficiency of EDTA by TiO₂ with solar light according to experiment date (0.4 mM metal, 0.4 mM EDTA, TiO₂ = 1 g/L, pH = 4, flow rate = 5 L/min, open to air)
the good removal efficiency of the reactor, further developments to achieve better destruction yields are still necessary.

References


