Evaluation of the Treatment of Metal-EDTA Complexes Using TiO$_2$ Photocatalysis

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INTRODUCTION

Organic complexing agents are used in a variety of industrial applications that involve dissolved metals in aqueous systems. These chemicals are generally added to increase the metal ion solubility at a wide range of solution conditions. Metal plating industries often incorporate organic acids, such as tartaric acid, oxalic acid, and ethylene diamine tetraacetic acid (EDTA) into electroless plating baths so that the metals will chemically reduce onto the parts in a controlled manner (1). The processes that involve the decontamination of nuclear power reactors also incorporate these agents into the cleaning solutions to enhance the removal of radioactive metals from the contaminated surfaces (2). Recent studies in the environmental literature have also used solutions of organic complexing agents for the removal of toxic metals from contaminated soils. However, a result of this complexation of the metal ions is their increased chemical inertness, and the subsequent inability of many common treatment technologies to remove these metals from the waste water streams. Reference 3 studies the inhibitory effects of complexing agents on sulfide precipitation processes for metals removal (3). These effects are especially pronounced for the metal complexes of EDTA, which are stable over broad pH ranges for many metals. EDTA is a multi-dentate complexing agent which forms 1:1 complexes with almost all metals, and poses a particular problem for many metals-removal treatment processes. Specialized treatment processes can be employed for metal-EDTA complexes, but are generally only applicable to certain complexes in certain situations. Breaking the complex at very low pH's followed by cation-exchange is one method for removing the metal, but will not work for metals such as Cr(III), Fe(III), and Co(III) which have very high stability constants with EDTA. The EDTA can be displaced in some metal-complexes by adding thiocarbamate, which is then easier to treat. Electrolytic recovery can effectively treat strongly complexed metals, but suffers from mass transfer limitations when treating dilute solutions (4). However, no single current technology seems able to treat the metal complexes of EDTA. Studies employing other advanced oxidation technologies for treatment of metal-EDTA complexes have been performed, and include ozonation (5) and hydrogen peroxide accompanied by ultraviolet (UV) illumination (6).

The treatment of contaminated air and water using TiO$_2$ photocatalysis has been demonstrated in numerous studies involving many different contaminants and reactor configurations. Figure 1 below is a simplified schematic of the chemistry that occurs at the surface of illuminated TiO$_2$. Because it is a semiconductor, TiO$_2$ produces electron (e-) -hole (h+) pairs when it is illuminated with UV radiation at wavelengths of 390 nm or less. The holes at the TiO$_2$ valence band, having a potential of +2.7 V vs normal hydrogen electrode (NHE) at pH=7, can migrate to the catalyst surface and either 1) oxidize an adsorbed species directly by direct hole oxidation, 2) oxidize water or hydroxide to produce hydroxyl radicals, which then proceed to oxidize other species. or 3) oxidize other species in solution, such as Pb^{2+} (7,8). The electrons also formed can migrate to the surface to take part in reduction reactions. Having a potential of -0.5 V NHE at pH=7, the electrons an reduce species in solutions. These species include oxygen, which can form superoxide or perhydroxyl radicals, or certain aqueous metals that can be reduced to their metallic form onto the catalyst (9). Several studies have shown that the rates of the electron reduction reaction and the hole oxidation reaction are intrinsically interrelated (9,10). A desired oxidation reaction must facilitate a simultaneous reduction reaction and vice versa in order to achieve practical

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rates. This is due to the fact that buildup of electrons or holes within the TiO_2 particle will drive their recombination, and severely limit the numbers able to migrate to the surface. Because complexing agents involve the bonding of a metal to the organic ligand, both the oxidant (metal, if reducible) and the reductant (organic ligand) should be available to complete both reactions at the catalyst surface.
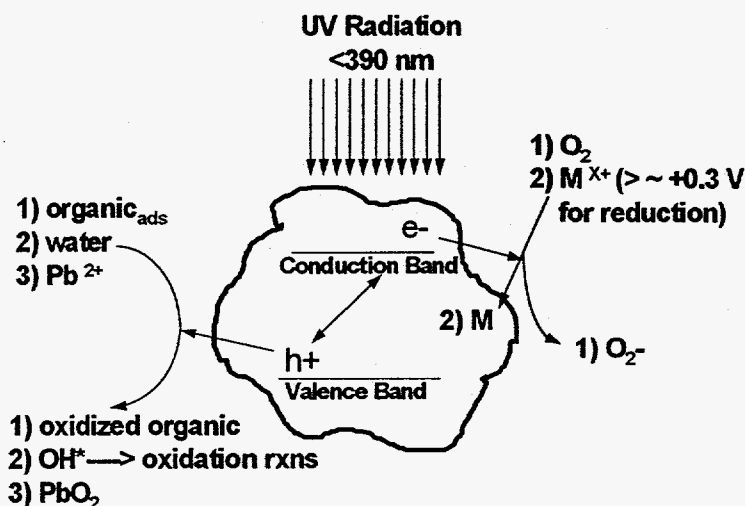
UV Radiation
<390 nm

1) organic$_{ads}$
2) water
3) Pb^{2+}

1) O$_2$
2) M^{X+} (> ~ +0.3 V for reduction)

e-
Conduction Band

2) M

h+
Valence Band

1) O$_2^-$

1) oxidized organic
2) OH* ---> oxidation rxns
3) PbO$_2$

Figure 1 - Schematic of the reactions at the surface of illuminated TiO_2

As alluded to above, only certain metals can be reduced even when a subsequent oxidation reaction is facilitated. This was shown to be related to the standard reduction potential for each metal (9,11). Metals with more positive reduction potentials (> +0.8 V NHE) such as Ag(I), Hg(II), and Pt(IV) can be reduced onto TiO_2 under aerobic conditions. Metals with less positive reduction potentials (< +0.3 V NHE) such as Ni, Cd, and Co are very difficult or impossible to reduce even under anaerobic conditions (9). Metals with intermediate reduction potentials, such as Cu(II) (+0.34 V NHE) can be reduced under certain anaerobic conditions but will tend to re-oxidize if then exposed to O_2 (12). Exceptions exist to many of the above statements, which often relate to the nature of the simultaneous oxidation reaction.

This study demonstrates the applicability of TiO_2 photocatalysis for the treatment of certain metal-EDTA complexes and EDTA alone. Some of the conditions for the oxidation of the EDTA alone in solution were investigated. The metal-EDTA complexes were studied with the focus on the metals removal. The metals chosen for this study were Pb, Cu, Ni, and Cd. These metal complexes should exhibit some ranges of treatability, as the reaction of these free metals with illuminated TiO_2 have been shown to be different in past studies. Ni and Cd are metals that are difficult or impossible to reduce by photocatalysis (redox potentials -0.25 and -.40 V NHE, respectively), Cu(II) is reducible by photocatalysis under certain conditions, and Pb has been shown to be oxidized by photocatalysis. In addition, all of these metals are toxic and regulated, and all form EDTA complexes over the pH ranges investigated in this study.

EXPERIMENTAL

All of the photocatalysis experiments were carried out in an annular recirculating photoreactor provided by the National Renewable Energy Laboratory (NREL) as depicted in Figure 2 below. Conditions that were common to every reaction conducted are as follows:

- 1300 ml solution volume
- 0.8 mM solution of the metal complexed with an equimolar amount of EDTA (these concentrations correspond to around 50 to 150 mg/l metal solutions)
- 0.1 wt% Degussa P-25 TiO_2 added to the solution, or 0.1 wt% of Au-Pt on Aldrich TiO_2 provided by NREL when specified

- 45 min period of no illumination prior to he reaction to allow for any complex adsorption onto the TiO$_2$
- Experiments conducted either open to air, purged with air, or purged with N$_2$; the mixing with the ambient gas took place in the mixing vessel where good entrainment of the gas in the liquid could be observed
- pH was controlled throughout the experiments in the mixing vessel using HNO$_3$ or NaOH
- 10 ml samples were taken from the mixing vessel at specified times and were filtered through Gelman 0.2 micron Teflon syringe filters prior to analysis

The pump flow rate ensures turbulent flow in the annular reactor, and thus efficient introduction of the solution and catalyst into the illuminated region (which is around 1 mm into the solution from the inner annulus). The inner annulus was kept free of TiO$_2$ powder deposits by the use of an in-line scrubber that would clear the surface every 10 min. Prior to the installation of the scrubber, it was noticed that the different complexes resulted in different degrees of TiO$_2$ deposition onto the surface. Although this TiO$_2$ could be considered to be illuminated, the illumination and mass transfer characteristics of a thin-film are different than that of a slurry, and different degrees of deposition could interfere with the ability to distinguish other kinetic phenomena. The inner tube was examined at the end of each run to ensure that only negligible film buildup had occurred, and 10 min scrubbing intervals were found to be adequate.
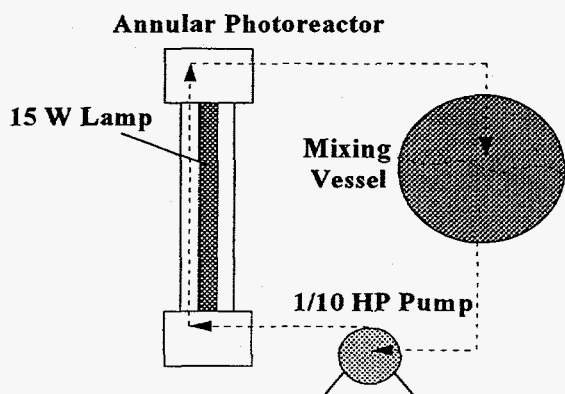

Figure 2 - Schematic of the NREL annular photoreactor

A crude schematic of the analytical strategy for this study is outlined in Figure 3. The schematic shows the metal (M)-EDTA complex being broken down by successive reactions at the surface of the TiO$_2$ particle. Ion chromatography, using a Dionex ISP 2000 Ion Chromatograph, was used to measure the concentration of the metal-EDTA complex. At some point in the oxidation, the EDTA is broken down to a subordinate product that allows removal of the metal by photodeposition (for Pb^{2+} and Cu^{2+}). Atomic absorption was therefore used to measure the concentration of the metal ion in solution, which would be the initial quantity added less the amount that was removed by photodeposition. The oxidation of the EDTA products will continue until full mineralization to inorganic carbon compounds is attained. Total Organic Carbon (TOC) analysis, using a Shimadzu TOC 5000 Analyzer, was used to measure the total quantity of organic species in solution.
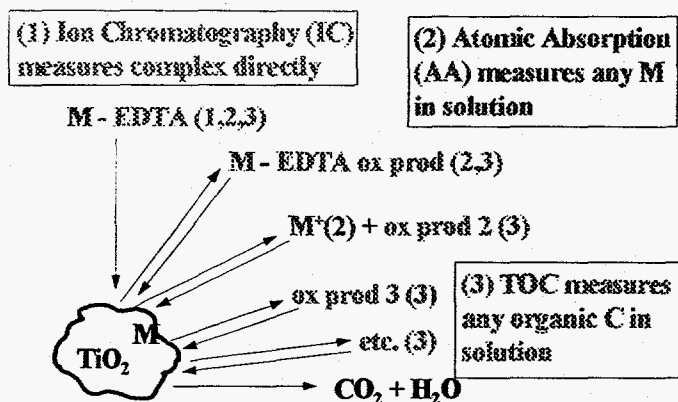
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┌─────────────────────────────┐   ┌──────────────────────┐
│ (1) Ion Chromatography (IC) │   │ (2) Atomic Absorption│
│ measures complex directly   │   │ (AA) measures any M  │
└─────────────────────────────┘   │ in solution          │
                                   └──────────────────────┘
         M - EDTA (1,2,3)

              M - EDTA ox prod (2,3)

                M⁺(2) + ox prod 2 (3)

                 ox prod 3 (3)      ┌──────────────────┐
                                    │ (3) TOC measures │
                      etc. (3)      │ any organic C in │
        TiO₂  M                     │ solution         │
                                    └──────────────────┘
                   CO₂ + H₂O
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Figure 3 - Schematic of the analytical strategy

Because of the large experimental matrix that is possible with these experiments (type of metal-EDTA complex, pH range, oxygen content, use of enhanced catalyst), it was not considered practical at this stage to try to address all these issues in detail. Rather, extreme conditions for the different metal-EDTA complexes were used that would hopefully best reflect general trends, and indicate most significant process variables involved. In keeping then with the goals of the study outlined in the Introduction, the specific sets of experiments that were performed to address these objectives are as follows:

- Effects of solution pH on the oxidation of EDTA alone using P-25 in open-to air experiments
- Effects of employing the NREL metallized catalyst in the EDTA oxidation
- Effects of pH and the presence/absence of oxygen in the treatability of Pb-EDTA
- Effects of the presence/absence of oxygen in the treatability of Cu-EDTA
- Treatability of the Cd- and Ni-EDTA complexes (metals do not photodeposit), including hydroxide precipitation following photocatalysis as a measure of the degree to which the metal is then treatable

RESULTS & DISCUSSION

Conditions for the Treatment of EDTA

Figure 4 below illustrates the treatability of EDTA alone by photocatalysis as a function of the solution pH. The degradation rate is enhanced at lower pHs, as is reflected by both the IC data for the EDTA compound and solution TOC. The effect, however, is more pronounced from pH=8 to pH=6 than from pH=6 to pH=4. The two data points at t=0 are the samples taken before and after the 45 min adsorption period., and show about equal extents of adsorption of EDTA from the IC data. At optimum conditions, it is seen that the EDTA is totally oxidized in the 60 min period. The slight yet detectable reduction in the TOC suggests that some extent of full mineralization is taking place. Explanations for the pH behavior are not straightforward with only this data as many pH dependent effects are occurring within the system, including the pH dependence of EDTA adsorption onto other hydrous oxides (reported elsewhere, 13), the pH dependence of the e- and h+ potentials (9,12), and the pH dependence of radical formations (9). But this data provided the general baseline condition of pH=4 which was used for most of the other experiments performed, with the assumption then that oxidation of other metal-organic complexes will correlate with EDTA oxidation. As will be discussed later, this assumption will not always hold true.
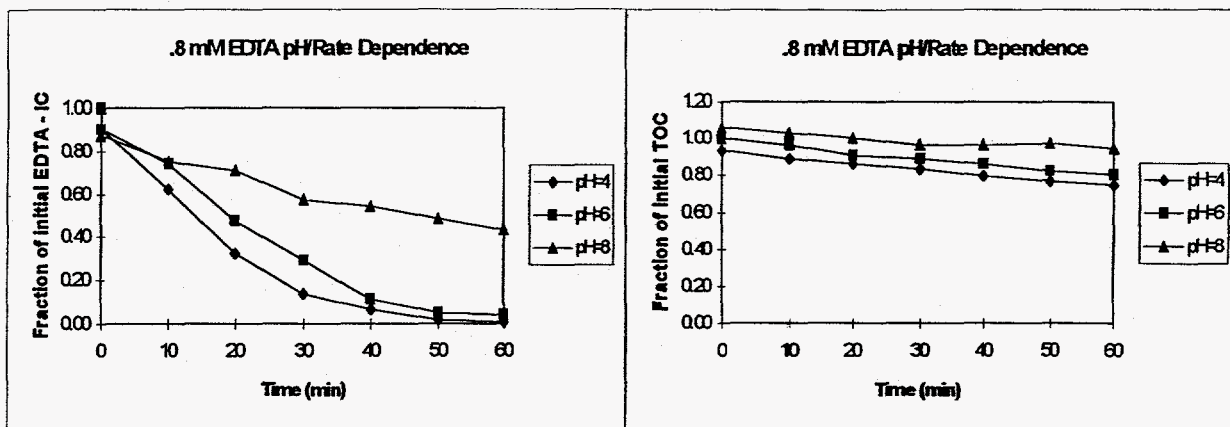
Figure 4 - EDTA degradation enhanced at lower pH

Tests for EDTA oxidation were also performed using a metallized catalyst that was provided by the National Renewable Energy Laboratory. As mentioned before, the catalyst was comprised of 0.5 wt % of Au and Pt each deposited onto Aldrich TiO_2. The deposition of Au or Pt onto TiO2 had shown improvements in certain photocatalytic processes in separate studies (14), therefore the combination of both metals deposited was investigated. The use of this Au and Pt catalyst has produced mixed results with respect to photocatalytic oxidation of different organics. Significant degradation rates over P-25 were seen in the oxidation of dilute aqueous solutions of ethylene glycol (15). Figure 5 below compares the degradation of the EDTA at pH=4 using both the P-25 and the NREL catalyst. The NREL catalyst shows inferior degradation of the EDTA both in the final EDTA concentration and the final TOC.
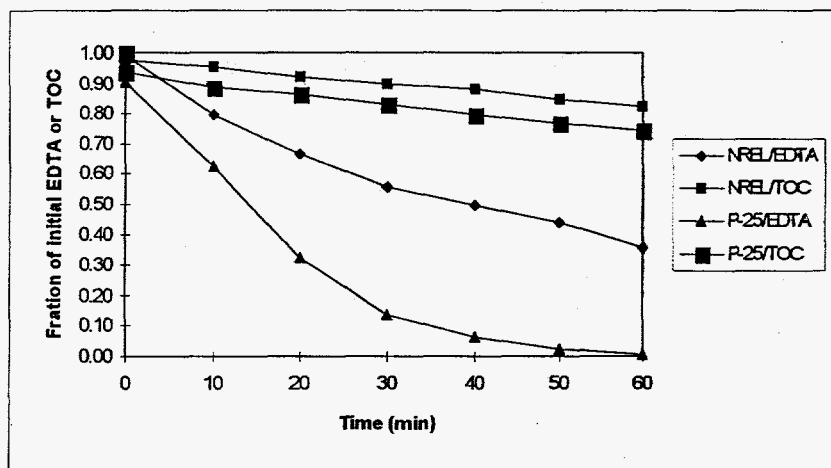
Figure 5 - NREL catalyst inferior to P-25 for EDTA oxidation

The results of other experiments evaluating the NREL catalyst vs. P-25 for treatability of certain metal-EDTA compounds should be discussed here. Reactions under identical condition using both these catalysts for treating Ni-EDTA, PbEDTA, and Cu-EDTA were performed in an illuminated batch reactor system. The results indicated that treatment of the Ni-EDTA compound was slightly enhanced using the NREL catalyst vs P-25 as more Ni was freed from complexation as indicated by pH precipitation on treated samples. Treatment of Pb-EDTA with either catalyst with respect to both complex oxidation and Pb oxide deposition showed very similar results. However, treatment of the Cu-EDTA complex using the NREL catalyst was detrimental vs. the use of P-25 with

respect to both the complex oxidation and Cu reduction (16). Thus metal-EDTA complexes are sufficiently different in their reactive natures to require individual evaluations for various treatment measures that are employed. This conclusion is supported in other studies (5).

Conditions for the Treatment of Pb-EDTA

Several experiments were performed to elucidate the behavior of the Pb-EDTA system with respect to pH and the presence/absence of oxygen. When the experiment is conducted at pH=4 in air, steady oxidation of the Pb-EDTA complex is observed with the complex being completely degraded, but only minimal deposition of the Pb is observed. When the experiment is conducted at pH=4 purging with nitrogen, slow degradation of the complex is observed with a corresponding slower deposition of Pb onto the catalyst. When the pH was raised to 6 with the other variables held constant, however, Pb deposition occurs steadily with essentially none left in solution at the end of 50 min. The results of this best case are shown in Figure 6 below. The degradation of the Pb-EDTA complex and the TOC reduction for both experiments is comparable, as was the case for EDTA alone evaluated at pH=4 and pH=6. In both cases, the Pb-EDTA degradation was zero-order until only < 0.1 mM of complex remained. Also, all experiments where Pb deposition was observed showed that the Pb-EDTA complex must be degraded first. That suggests both that the EDTA complex with Pb must first be degraded in order to allow Pb deposition, and that the expected weaker chelating agents that are EDTA oxidation products (5, 17) are sufficiently weak to allow the Pb to deposit.

The Pb removal at higher pH's can be explained as the formation of the oxide, which then deposits on the catalyst.. The oxide formation has been proposed in former studies to liberate protons as follows (7):

$$Pb^{2+} + 2H_2O + 2\,hole+ \text{----------} > PbO_2 + 4\,H^+$$
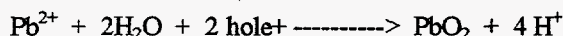
Thus at a higher pH, this reaction would be expected to proceed farther to the right. However, other studies have explained Pb removal in photocatalytic experiments by different mechanisms, such as adsorption (18) or possibly Pb reduction. Also, Pb precipitation as the hydroxide is possible at higher pHs, although at pH=6 all Pb should still be in solution at the 0.8 mM concentration (19). Due to the fact that oxygen is present in these experiments, and that dense particles were observed on the catalyst using high-resolution transmission electron microscopy, the reduction and adsorption mechanisms for Pb removal from solution were respectively deemed to be unlikely with respect to the oxide formation. A complication to this explanation is the fact that metallized catalysts were required in two different studies to achieve practical rates of Pb oxide deposition (7,8).
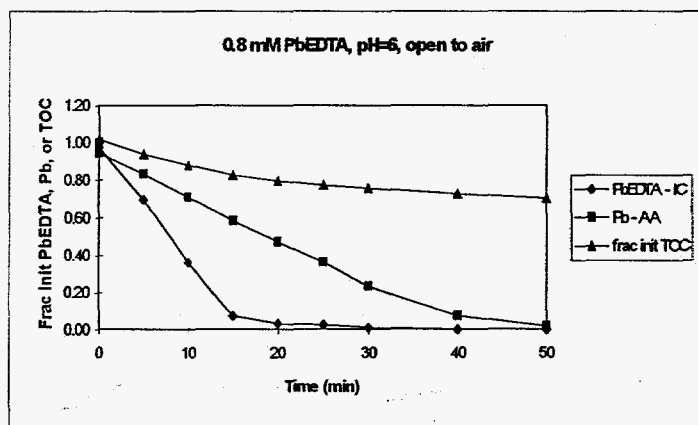

Figure 6 – Favorable Conditions for the Treatment of Pb-EDTA

Conditions for the Treatment of Cu-EDTA

For the Cu-EDTA system, the presence/absence of oxygen was identified as a major process variable that affecting both the treatment of the complex and the removal from the solution by reduction. Figure 7 below illustrates the effects of the absence/presence of oxygen at experiments conducted at pH=4. In the nitrogen purged case (on the left) it is seen that the removal of the Cu^{2+} from solution follows the degradation of the complex. This also suggests that some complex removal must take place prior to the reduction of Cu as well. It further suggests that the reduction of freed Cu is facilitating the oxidation of the CuEDTA complex and complex oxidation products. This is also supported by the fact that the TOC reduction progresses at a noticeably slower rate after all of the Cu has been reduced, indicating that further oxidation of the complex oxidation products is hindered by the lack of an electron acceptor. This behavior is consistent with another study that investigated the effects of the organic hole scavenger on the reducibility of Cu by photocatalysis in anaerobic environments (12). In contrast, the graph on the right of Figure 7 shows the treatment of the CuEDTA complex in the presence of oxygen in an air purge. The oxygen is a much more efficient electron acceptor, as is indicated by the very fast removal of the CuEDTA complex and no reduction of the Cu throughout the experiment. This experiment also shows that the TOC reduction in this experiment is greater than any other aerobic experiment performed involving EDTA alone or other metal-EDTA complexes. A possible explanation includes the generation of less refractory or more adsorbing oxidation products in the degradation of the CuEDTA complex.
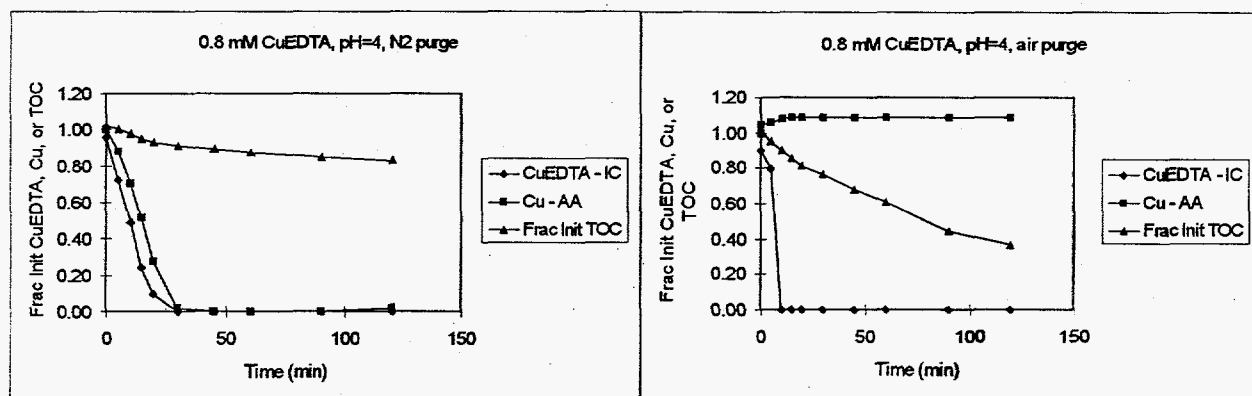

Figure 7 - Cu-EDTA Treatment - Cu Reducible in Absence of Oxygen

Conditions for the Treatment of Ni-EDTA & Cd-EDTA

As stated earlier, Ni and Cd represent heavy metals where no reduction is expected to occur (9), and therefore no experiments were performed in the absence of oxygen. Only baseline experiments for both compounds were performed at pH=4 in air-purged setups. Because the oxidation products of these compounds are most likely weaker chelating agents where the metal is still bound to some extent, it was desired to investigate the quantity of metal that would be amenable to precipitation as the metal-hydroxide at higher pH's. The fraction of metal that could be precipitated would then correspond to the fraction of metal that was bound to subordinate chelating agents whose affinity for the metal is weaker than that of the hydroxide precipitate. This was performed by simply taking samples of the solution before and after photocatalytic treatment, raising the pH to the minimum solubility for the metal (ca 10.2 and 11.2 for Ni and Cd, respectively (19)), filtering the solution, and measuring the filtrate for the remaining metal concentration. The data for both systems is summarized below. The degradation behavior of both systems is very similar, with complex disappearing as a slow zero-order process. As expected, no removal of metal from the solution was observed. The degradation of the Cd-EDTA appears somewhat slower here, but the lower final TOC in the solution suggests that different kinetic pathways are occurring in the two systems. The table below shows the effectiveness of the hydroxide precipitation and filtration on the solutions before and after treatment by photocatalysis. It shows that both metal-complexes are oxidized to

an extent to allow partial metal removal by hydroxide precipitation. It also shows that significantly more Cd was available for removal, which is consistent with the lower final TOC data This is also consistent with the fact that Cd has a lower stability constant with EDTA than Ni (log K = 16.5 and 18.6 for Cd and Ni, respectively (20)), which may indicate lower stability constants with the subordinate chelating oxidation products.
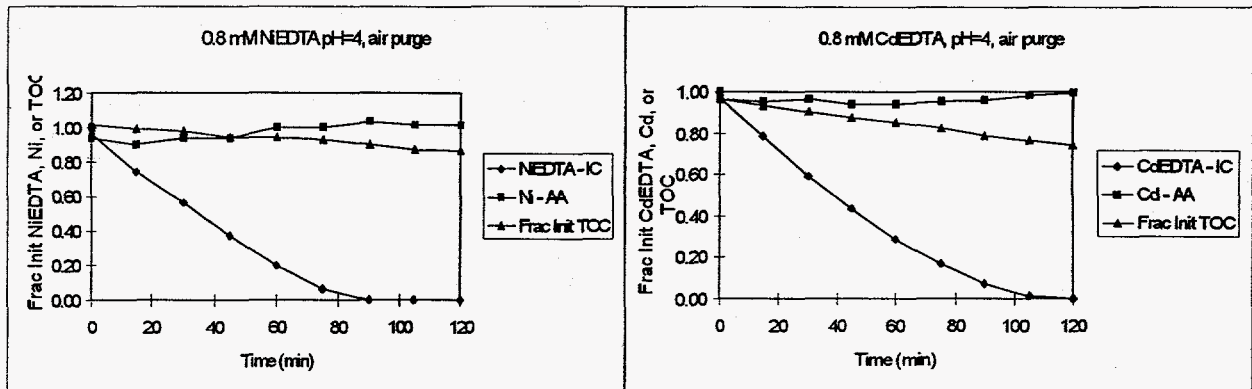
High pH Precip. / Filtration	NiEDTA	CdEDTA
Amt Removed Before TiO_2 Treatment	0 %	3 %
Amt Removed After TiO_2 Treatment	24 %	61 %

Figure 8 - Photocatalytic Treatment of Ni-EDTA and Cd-EDTA Similar, and Enhances Subsequent Metals Removal by Hydroxide Preciptation Followed by Filtration

Preliminary Economic Comparison Between Photocatalysis and Ozone Treatment of EDTA

The data generated in this study will be used to make a crude economic comparison between photocatalysis and ozone treatments for EDTA degradation. This is possible because of research conducted where the treatability of EDTA using ozone was evaluated (5). This study also evaluated the effects of different metal ions present and pH on the degradation of EDTA, as well as identifying the major by-products throughout the course of the reaction This comparison is not intended to be complete in an engineering economic sense; rather it will serve as a basis for discussion for the decision for employing one technology over the other. Because of the ambiguity surrounding the final system configurations for each, no capital costs will be estimated; only relevant operating costs will be compared.

The characteristics of the two studies that are relevant to the operating economic analysis will be given for each:

Photocatalysis

- 1.2 L of 0.8 mM EDTA solution treated
- 0.1 wt % TiO2 added as a slurry to the solution
- illuminated with a 15 W blacklight
- 60 min required for complete EDTA degradation at pH=4

Ozone Treatment

- 1.0 L of 1.0 mM EDTA solution treated
- 10 mg ozone/min-L addition rate

- 40 min required for complete EDTA degradation at pH=7

Relevant cost assumptions:
- scaled ozone degradation time to 0.8 mM linearly due to approximate zero order kinetics (0.8 * 40min = 32 min)
- 1000 L of solution to treat; direct scale-up of cost to treat study volume to 1000 L
- catalyst cost - $1.50 for 1000 L (based on analysis in (21)) for photocatalysis
-- $ 0.1/ kWh
- 20 Wh / g ozone for ozone treatment (22)
- no power consumption included for pumps or other flow equipment for either case; it is assumed that these will be similar in both situations as good mass transfer characteristics for both systems should be maintained
- no equipment replacement, such as the lamps for photocatalysis or ozonator parts, are included

Based on the above assumptions, the basic operating costs are as follows:

Photocatalysis : $1.50 catalyst + $1.25 lamp power = $ 2.75 per 1000 L treated
Ozone Treatment : $0.64 ozone generation costs

Given only the degradation of a dilute EDTA solution then, it seems that ozone treatment would be clearly favorable over photocatalysis. Of course, in situations where simultaneous metals removal is desired (Cu-EDTA and Pb-EDTA as shown above) photocatalysis offers a clear advantage in being able to facilitate the complex degradation and photodeposition simultaneously under the prescribed conditions. As shown above, however, this is only possible when the metal is able to photodeposit by some mechanism. And, as also discussed above, because each complex may behave differently under different treatments, the treatability of EDTA alone cannot be extended to say that photocatalysis will necessarily be inferior to ozone treatment in all cases of interest.

CONCLUSIONS

This study has demonstrated the feasibility of TiO_2 photocatalysis to treat EDTA and several metal-EDTA complexes that can be found in industrial wastewaters. For the EDTA complexes of metals capable of photodeposition, such as Cu and Pb, certain reaction conditions were shown to facilitate the simultaneous complex degradation and photodeposition of these metals onto the catalyst. With metals that do not easily photodeposit, such as Ni and Cd, it is shown that the complex degradation is still facilitated, and can enhance other metals removal processes after photocatalytic treatment. Because the treatment of these metal-EDTA complexes typically requires special measures, there may exist situations where TiO_2 photocatalysis could actually be the preferred method of treatment. However, its use should be compared economically to other more established advanced oxidation technologies. This necessity is demonstrated in the economic comparison to ozone treatment for EDTA degradation alone, where ozone treatment appears to be the clear choice in this application.

ACKNOWLEDGEMENTS

DISCLAIMER

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