

CONF-9603117--4

SAN 096-0454C

Evaluation of the Treatment of Metal-EDTA Complexes Using TiO_2 Photocatalysis

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FEB 2 / 1996

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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 can 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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