GRANULAR IRON OXIDE AS A CATALYST IN CHEMICAL OXIDATION OF ORGANIC CONTAMINANTS

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ABSTRACT

Oxidation of organic contaminants, such as chlorobenzene and n-chlorobutane, by hydrogen peroxide (H$_2$O$_2$) and ozone (O$_3$) in water has improved significantly in the presence of granular iron oxide mineral, goethite. It is believed that the hydroxyl radical produced by the catalytic decomposition of H$_2$O$_2$ or O$_3$ over the goethite surface was responsible for oxidation of the surface-bound organic compounds. The oxidation rate of the organics was directly proportional to the dosage of the catalyst and the dosage of the oxidant, H$_2$O$_2$ or O$_3$. The apparent rate of the oxidation reactions was determined by the intrinsic reaction rates on the catalyst surface rather than the mass-transfer rates of the oxidant and the organic compound. The catalytic process was also effective in removing the total organic carbon (TOC) of the solutions indicating that it is capable of achieving complete mineralization.

INTRODUCTION

Chemical oxidation is a viable process for destruction of various organic contaminants in aqueous medium. Ozone (O$_3$) and hydrogen peroxide (H$_2$O$_2$) are two of the major oxidants that have been used successfully for this purpose at ambient temperature and pressure. Ozone is an effective oxidant but is selective in its reactions, for example preferring compounds with unsaturated bonds to compounds such as chlorinated aliphatics. Therefore, the rate constant of reactions of molecular ozone may range from about 10$^8$ to less than 10$^{-2}$ M$^{-1}$s$^{-1}$. Hydrogen peroxide alone is a poor oxidant for the majority of the organic contaminants except for a few, such as certain phenols. However, hydrogen peroxide and ozone applied simultaneously (H$_2$O$_2$/O$_3$), hydrogen peroxide or ozone exposed to ultraviolet light (H$_2$O$_2$/UV, O$_3$/UV), or hydrogen peroxide in the presence of iron salts
(H₂O₂/Fe) have been effective in oxidizing a variety of organic substances in waters and wastewaters. The primary oxidant in these catalytic systems is believed to be hydroxyl radical (OH·) which is generated by decomposition and reactions of hydrogen peroxide and ozone. The hydroxyl radical is a highly reactive and a non-selective oxidant for organic contaminants in water.

The mixture of hydrogen peroxide with iron salts, which is usually referred to as "Fentons Reagent" when a ferrous salt is used, is effective only in acidic pH range of about 2–4 (Sedlak and Andren, 1991; Bowers, et al., 1989; Walling, 1975). This pH limitation usually makes the application of this process difficult. In the presence of dissolved iron, ozone is known to decompose faster, although this might not result in any improved oxidation of organics. Whether ozone or hydrogen peroxide is used with ferrous or ferric salts, colloidal precipitates of ferric hydroxides form in the reaction mixtures, and the separation of these particles requires the use of additional processes, such as coagulation, sedimentation and filtration.

According to some recent studies hydrogen peroxide can oxidize organic pollutants in the presence of alumina-supported iron oxides (Dore, 1990; Tyre, et al., 1991). Ozone was also found effective in the presence of the same catalyst for oxidation of phenol (Al-Hayek, et al., 1989) and treatment of industrial wastewater (Munter, et al., 1985; Basila and Broersma 1977; Turk, 1977). The catalyst in these studies was Fe₂O₃/Al₂O₃, and the iron content was less than 5 percent of the total mass of the catalyst. Bull and McManamon (1990) reported oxidation of sulfur compounds, e.g., sulfide by hydrogen peroxide and an iron catalyst. This catalyst was prepared by adsorption of ferrous ion on a zeolite support. Kitajima et al. (1978) and Onu et al. (1977) demonstrated the formation of superoxide ion during the decomposition of hydrogen peroxide on supported metals and metal oxides. In addition, Gurol and Ravikumar (1994) demonstrated that pentachloro phenol and trichloro ethylene adsorbed on sand particles can be oxidized by hydrogen peroxide even without additional iron salt. They suggested that hydroxyl radical, which might be generated by the interaction of hydrogen peroxide with the natural iron content of the sand (800 mg iron/kg of sand), was responsible of the oxidation. Furthermore, a mixture of colloidal iron oxide (goethite) and hydrogen peroxide was used under acidic conditions to effectively treat pentachloro phenol-contaminated sand (Watts et al., 1993). All these observations indicate that solids which contain iron, e.g., iron oxide minerals and sand, might be capable of of creating Fenton-like reactions on their surface in the presence of hydrogen peroxide or ozone.

Based on these observations, the present study was undertaken to investigate the feasibility of using O₃ and H₂O₂ in the presence of granular size pure iron oxide for removal of organic pollutants from waters. The separation of granular particles in full scale applications should be easier than the colloidal particles. Furthermore, these granules can be used in packed-bed column operations.

**APPROACH**

The catalyst used in this study was granular goethite (α-FeOOH), which is a common mineral with a very low solubility in water (Ksp=10⁻³⁹, Stumm and Morgan, 1981). The granules purchased from Aldrich Chemical Company had a diameter of 0.3–0.6 mm and a density of 3.85 g/cm³.

The experiments with H₂O₂ were conducted in a completely-mixed slurry reactor operated in batch mode (Figure 1). The model organic compound used for the H₂O₂ study