United States
Environmental Protection
Agency

Research and Development

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/S2-83-060 Oct. 1983

EPA

Project Summary

Wet Oxidation and Ozonation of Specific Organic Pollutants

C. Robert Baillod and Bonnie M. Faith

This study was undertaken to assess the applicability of wet oxidation and ozonation to the treatment of wastewater containing five specific pollutants typical of the 114 organic compounds included on the EPA priority pollutant list. The pollutants, phenol; 2-chlorophenol; 4-nitrophenol; 1,2-dimethylphthalate and 1,2-dichloroethane were selected for study on the basis of their occurrence, structure, water solubility, and volatility. The ability of the wet oxidation and ozonation processes to oxidize these pollutants in aqueous solution was studied using batch laboratory-scale experiments. In the case of wet oxidation, efforts were made to determine the influence of temperature, pH value, catalyst, and reaction time on the degree of pollutant destruction. In addition, an economic evaluation was made of a wet oxidation process designed to treat a refractory petrochemical waste stream. For ozonation, information was developed on the degree of pollutant destruction as influenced by ozone dosage and contact time. For both processes, the fate of pollutants were studied by measuring products of incomplete oxidation. The ozonation results showed that 1,2-dichloroethane was rapidly volatilized and the remaining four pollutants could be removed to less than detectable concentrations, in 5 to 10 minutes, at initial ozone usage rates of 3.9 to 5.9 moles of ozone per mole of compound removed. The wet oxidation results indicate that all five pollutants could be oxidized under the conditions of temperature (204° C to 260° C) and oxygen pressures studied. The removal rates for each substance depended on temperature, pH, and catalyst and were adequately described by semi-empirical, first-order kinetics. For both processes, a significant amount of organic carbon remained in solution after the specific pollutants had been removed. This carbon was slowly oxidized and consisted primarily of organic acids and aldehydes. A wet oxidation process was designed to treat a 37.8 l/min (10 gal/min) of a high COD (70,000 mg/l) petrochemical waste which was inhibitory to a biological treatment process. A detailed economic evaluation of this process indicated that an investor's interest rate of 20 percent could be attained at a treatment charge of $69 per 1000 gallons ($17.81 per cubic meter) or $0.16 per pound of COD removed ($.35 per Kg COD removed).

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Experimental Results

Semi-batch ozonation experiments showed that:

Phenol, 2-chlorophenol, 4-nitrophenol and 1,2-dimethylphthalate could be removed to less than detectable concentrations (in 5 to 10 minutes) through ozonation at initial ozone utilization ratios of 3.9 to 5.9 moles of ozone per mole of specific pollutant. However, the removal rates were limited by the rate of ozone mass transfer. During the initial stages of the ozonation experiments, reaction in the diffusive film enhanced the mass transfer rate.

A significant amount of total organic carbon remained in solution after the specific pollutants had been removed

and this carbon was slowly oxidized. Increasing the initial pH from 6 to 10: a) increased the specific pollutant removal rate for phenol and 4-nitrophenol, but decreased the rate for 2-chlorophenol, and b) decreased the total organic carbon removal rates for phenol and 2-chlorophenol.

Batch wet oxidation experiments showed that:

All five specific pollutants studied could be oxidized under the conditions of temperature and oxygen pressured studied. The removal rates depended on the substances and on temperature and were adequately described by semi-empirical first-order kinetics.

Alkaline pH levels markedly increased the rate of specific pollutant removal and only slightly increased the rate of total organic carbon removal. However, over the one-hour reaction period, alkaline pH levels gave markedly lower removals for total organic carbon and chemical oxygen demand.

Cupric ion acted as a catalyst and increased the rate and extent of removal of specific pollutants and total organic carbon.

A significant amount of total organic carbon remained in solution after the specific pollutants had been removed and this carbon was slowly oxidized. More than three-fourths of this carbon was accounted for by low molecular weight acids, acetaldehyde and acetone.

Bioassay tests using *Daphnia magna* indicated that wet oxidation achieved 90 to 99 percent detoxification for phenol, 2-chlorophenol and 4-nitrophenol.

Although acetic acid was a major end evident during ozonation. Conversely, oxalic acid was a relatively minor product during wet oxidation, but was very significant in ozonation.

C. Robert Baillod and Bonnie M. Faith are with Michigan Technological University, Houghton, MI 49931.
***Ronald J. Turner** is the EPA Project Officer (see below).*
The complete report, entitled "Wet Oxidation and Ozonation of Specific Organic Pollutants," (Order No. PB 83-254 060; Cost: $16.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

☆U.S GOVERNMENT PRINTING OFFICE 1983—659-017/7202