Phenol Destruction with Chlorine Dioxide

Chlorine dioxide (ClO_2) is effective as both a disinfectant and an oxidant in water and wastewater treatment. Its selective reactivity makes chlorine dioxide a powerful non-chlorinating oxidizing agent useful in many water treating applications for which chlorine and other oxidizing agents are unsuitable. Chlorine dioxide is very effective at oxidizing phenols and substituted phenols in industrial wastewaters. Its reaction with phenol is much faster and more complete at neutral and alkaline pHs than achieved by hydrogen peroxide or potassium permanganate.

Application Description

Surface water often contains phenols from industrial effluents. Undesirable phenolic wastes are produced by many industries including the chemical, plastics and resins, coke, steel and petroleum industries.

Phenol is one of the EPA's Priority Pollutants. Under Section 313 of the Emergency Planning and Community Right to Know Act of 1986 (EPCRA), releases of more than one pound of phenol into the air, water and land must be reported annually and entered into the Toxic Release Inventory (TRI). Phenol has a high oxygen demand and can readily deplete oxygen in the receiving water, with detrimental effects on those organisms that abstract dissolved oxygen for their metabolism. Phenol is persistent in the environment when released in large quantities, or if it is continuously released from a source.

The EPA developed The National Recommended Water Quality Critiera[1] to provide guidance to States and Tribes in adopting water quality standards under section 304(a) of the Clean Water Act (CWA). These criteria provide a basis for controlling discharges or release of pollutants. This document sets a maximum national recommended water quality criterion for human health (consumption of water and organism) level for phenol of 21 mg/L. In addition it recommends an organoleptic (taste and odor) effect criteria for phenol of 0.30 mg/L.

Treatment Alternatives

Phenols may be treated by chemical oxidation, bio-oxidation, or adsorption. Chemical oxidation has a low capital cost, but a high operating cost. Bio-oxidation has a high capital cost and a low operating cost. Adsorption has a high capital cost and a high operating cost. The appropriateness of any one of these methods will depend on a combination of factors, the most important of which are the phenol concentration, and any other chemical pollutants that may be present in the wastewater. Depending on these variables, a single or a combination of treatments will be used.

Wastewater with a phenol concentration of 500–2000 mg/L or greater is a good candidate for phenol recovery by solvent extraction and adsorption on granular activated carbon.

Wastewater with an intermediate or low phenol concentration is not a good candidate for solvent extraction, although if the capital investment could be justified, adsorption on activated carbon or biological removal is a choice. If the water is toxin free, biological treatment can reduce 200-300 mg/L phenol to 0.5-1.0 mg/L.

Wastewater with a phenol concentration of 5 mg/L or less is not a good candidate for biological treatment or adsorption. Removal must be accomplished with chemical oxidants, the most commonly used being chlorine dioxide, hydrogen peroxide and potassium permanganate.

Three scenarios where chemical oxidation is appropriate:

1. Batch Treatment: To treat a small batch of wastewater high in phenols, if it is cheaper than incineration or biological treatment.
2. Pre-treatment: As a pretreatment before biological treatment to remove toxins from a high-phenol waste.
3. Polishing: As a final polishing step after other treatment or for dilute phenol waste streams low in other organics.

Chlorine Dioxide

In contrast to the sluggish behavior of hydrogen peroxide, chlorine dioxide reacts very rapidly with phenols and substituted phenols. Chlorine dioxide cost-effectively destroys phenols in waste or drinking water without forming objectionable by-products. Treatment with chlorine dioxide can destroy chlorophenols. Phenol composition may affect reaction ratios, with substituted phenols increasing chlorine dioxide demand. Water pH influences reaction rate. The primary product of this reaction is benzoquinone, but oxidation can lead to a mix of benzoquinone and organic acids, or organic acids alone. The final products vary with pH and reactant ratios.

Below pH 10, a minimum of 1.5 mg/L of chlorine dioxide oxidizes 1 mg/L of phenol to benzoquinone. Above pH 10, an average of 3.3 mg/L of chlorine dioxide oxidizes 1 mg/L of phenol to a mixture thought to be low molecular weight, nonaromatic, carboxylic acids (such as oxalic and maleic acids) and suspended solids in the effluent, which could be detrimental in direct discharge applications. At pH 7, the phenol reaction is rapid and complete; all phenols are consumed.

Alternatives Oxidants

Hydrogen peroxide does not destroy phenols unless catalyzed by ferrous sulfate. Hydrogen peroxide-ferrous sulfate requires acidic pH's between 3 and 5 to be effective. Even at an ideal pH of 4 the reaction is very slow and results in high solids loading and increased disposal costs.

Potassium permanganate has been widely used for phenol oxidation. Potassium permanganate is a strong oxidant, which yields insoluble MnO2 as a byproduct. This may result in high solids loading and significant disposal costs.

Chlorine reacts with phenols to form highly toxic chlorophenols. These chlorophenols can also cause taste and odor problems in drinking water.

Advantages of Chlorine Dioxide

- ClO_2 reacts rapidly and has the lowest chemical cost when used for removal of phenol concentrations of less than 5 mg/L.
- ClO_2 does not require pH adjustment and does not increase solids loading.
- ClO_2 phenolic compounds completely without the formation of chlorinated byproducts when applied in the correct ratio.
- ClO_2 does not form chlorophenols.

Feed Requirements

For industrial applications, dosages will vary depending on the application. Dose rate may be determined by completing a chlorine dioxide demand study. Chlorine dioxide should be applied at a sufficient dose rate to completely consume phenol and avoid any secondary reactions leading to chlorinated by-products.

For once-through systems, or systems where treated water may enter a U.S. waterway, the concentration of residual chlorite ion should be monitored such that it does not exceed the requirements of the NPDES permit and is in compliance with local, state and federal regulations.

For more information on dosage requirements specific to your application, contact your Siemens Representative.

Method of Feed

Chlorine dioxide is a gas produced by activating sodium chlorite with an oxidizing agent or an acid source. Sodium chlorite is converted to chlorine dioxide through a chlorine dioxide generator and applied as a dilute solution. Chlorine dioxide solutions should be applied to the processing system at a point and in a manner which permits adequate mixing and uniform distribution. The feed point should be well below the water level to prevent volatilization of the chlorine dioxide. Avoid co-incident feeding of chlorine dioxide with lime or powdered activated carbon.

Chlorine Dioxide Analysis

Residual chlorine dioxide concentrations should be determined by substantiated methods, which are specific for chlorine dioxide. Chlorine dioxide solutions can be analyzed by iodometric and amperometric titrations, and spectrophotometri-cally, with the standard DPD (N,N-diethyl-*p*-phenylenediamine) method. These methods are described in detail in *Standard Methods for the Examination of Water and Wastewater*[2].

4500-ClO_2 B	Iodometric Method
4500-ClO_2 D	DPD-Glycine Method
4500-ClO_2 E	Amperometric Method II

References

1. National Recommended Water Quality Criteria –Correction, *EPA 822-Z-99-001,* April 1999.
2. *Standard Methods for the Examination of Water and Wastewater,* APHA, AWWA and WEF, Washington, D.C. (20th Ed., l998).

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