# DISCHARGE COMPLIANCE AT WOOD TREATING PLANTS

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## INTRODUCTION

Wood treating plants have waste waters that often use several different unit processes of waste treatment to prepare the water for discharge from the plant. These waste water treatment practices often include oil removal via dissolved air flotation assisted by coagulating/flocculating chemicals. Further treatment can consist of additional solids removal followed by biological treatment for removal of dissolved organic materials. These dissolved organics are measured by methods such as the BOD, COD and TOC tests. Chemical oxidation can be used to remove the peaks from fluctuating concentrations of phenolics and, thereby, reduce the toxicity of the treated stream to the biological unit processes. Chemical oxidants can be used to remove/destroy essentially all of the phenolic material where the biological process is unavailable. In addition, post treatment or polishing of effluents following biological treatment can reduce refractory materials that have passed through biological treatment unchanged. Oxidative polishing steps are often required to meet the effluent limitations placed on phenol and substituted phenols.

## BASIC PROCESSES

### I. Oil And Liquid/Solids Separation

Waste water treatment practice often incorporates a process of water clarification where process oils and insoluble material are separated from the water flow. Often water clarification is accomplished via dissolved air flotation (DAF) because of the presence of process oils. Low molecular weight, high charge density cationic polymers may be used to facilitate coagulation. This initial coagulant addition is often followed by the addition of a small amount of high molecular weight anionic polymer to prepare a better floc for removal in dissolved air flotation units.

Jar testing of various polymeric materials can quickly determine an economic chemical program to assist the physical clarification process. The benefits of such a program consist of improved recovery of oils for return to the process and a waste water conditioned for further treatment for suspended solid removal.

## II. Removal Of Phenolic Materials

Biological treatment processes such as the activated sludge process are often used for phenol oxidation where the space is available. In addition to the physical space necessary for biological unit processes which include aeration, clarification, and sludge dewatering, the expertise must be available to manage these processes to achieve the desired reduction in phenolic and biological oxygen demand (BOD) concentrations. Once the capital dollars have been spent and the biological unit processes have been installed, properly managed biological processes can run very cost effectively.

Biological waste water treatment is subject to upset when the bacteria under aeration receive waters that shock their metabolic systems. These shocks can be caused by wide fluctuations in concentrations of various organic materials, changes in pH and/or temperature, and the introduction of toxic materials. Phenols in high concentration are toxic, but can be biologically oxidized as long as the concentration is low and steady. Fluctuating concentrations of phenols represent a toxic shock to the microorganisms and can wipe out the activated sludge process.

Equalization basins are used to minimize any fluctuations in waste water properties prior to the biological aeration process where space is available. Where space is lacking, chemical oxidation of the phenolics with hydrogen peroxide or chlorine dioxide may be used to even out the higher concentrations. In this way oxidation chemistry is used to prepare or detoxify the waste. Then a high percentage of the required waste oxidation is carried out by the microorganisms.

The next unit process following biological oxidation is a clarification step needed to achieve liquid/solids separation. Here, microorganisms and other solids are removed from the water, usually by sedimentation/clarification. The underflow from a clarifier containing these solids is wasted from the system. A percentage of this flow is recycled to the head of the aeration system to provide needed solids concentration in aeration. The wasted solids can be further dewatered via centrifugation or filtration. Dewatering will increase the concentration from generally less than 5% to a concentration of approximately 15-20%. The treated overflow waters from the clarification process should be ready for discharge to the environment depending upon specific regulations.

Where discharge requirements call for additional phenolic concentration reductions, the waste water may be further polished with oxidants to meet these more stringent discharge requirements. The oxidant of choice at this juncture is generally chlorine dioxide, which is capable of reducing phenolics to levels below 0.02 ppm.

## Implementation of Oxidation Processes

The Fenton System which utilizes hydrogen peroxide and an iron catalyst to oxidize phenol at a pH of approximately 4.0 is most often used when phenol concentrations exceed 50 ppm. Since this reaction is exothermic, consideration should be given to heat dissipation when concentrations of phenol exceed 2000 ppm. In addition, technical assistance should be obtained to advise on all aspects of hydrogen peroxide handling. All tanks, lines, valves, pumps and fittings must be made of compatible materials in order to satisfy handling this very strong oxidant. In the presence of incompatible materials, including organic contamination, 1 liter of 50% hydrogen peroxide can quickly decompose to 100 liters of oxygen and steam. With expansion potential of this magnitude, special considerations must be given to materials of construction, tank passivation, venting and preventing the trapping of hydrogen peroxide between two valves.

The Fenton reaction often requires precise pH adjustment. Once the proper pH is achieved, the iron catalyst is mixed into the system in conjunction with hydrogen peroxide addition. Optimal results will be achieved only when both the catalyst and oxidant are intimately mixed in the system. Intimate mixing can be easily achieved in pipe systems by injecting the chemicals into the center of the flow using chemical injection quills constructed from compatible materials.

In pond situations, high volume pumps may be required to move a sufficient volume to achieve adequate mixing of the pond waters.

At phenol concentrations of 50 ppm or less, chlorine dioxide usually becomes the oxidant of choice on an economic basis. See TABLE I for the stoichiometric ratios of both chlorine dioxide and hydrogen peroxide required to oxidize a given quantity of phenolics. Since neither oxidant is specific for phenolics, actual bench testing should be done on specific waste waters to determine the amount of oxidant required for budgeting purposes.

Due to its physical properties, chlorine dioxide cannot be shipped as a compressed gas and, therefore, is manufactured on site from precursor chemicals. See TABLE I for methods of chlorine dioxide generation and maximum theoretical yield.

The maximum theoretical yield for the various chemical methods of generation of chlorine dioxide from chlorite are given in TABLE I. From these methods, chlorine dioxide as a dissolved gas in water is manufactured on site at concentrations of approximately 2000 ppm or less. The generator stream is piped directly to the point of application which makes the chlorine dioxide application very safe and convenient to handle.

## TABLE I

## MAXIMUM THEORETICAL YIELD

<u>100% Yield</u>

A. Gaseous Chlorine Generation

$$\underline{\underline{2NaClO_2}} + Cl_2 \rightarrow \underline{\underline{2ClO_2}} + 2NaCl$$

B. Acidified Hypochlorite Generation

$$\underline{\underline{2NaClO_2}} + NaOCl + 2HCl \rightarrow \underline{\underline{2ClO_2}} + 3NaCl + H_2O$$

<u>80% Yield</u>

A. Hydrochloric Acid Generation

$$\underline{\underline{5NaClO_2}} + 4HCl \rightarrow \underline{\underline{4ClO_2}} + 5NaCl + 2H_2O$$

<u>50% Yield</u>

A. Sulfuric Acid Generation

$$\underline{\underline{4NaClO_2}} + 2H_2SO_4 \rightarrow \underline{\underline{2ClO_2}} + 2Na_2SO_4 + HCl + HClO_3 + H_2O$$

## TABLE II

## CONDITIONS REQUIRED FOR PHENOLIC OXIDATION

Dosage Ratios By Weight

| pH | $ClO_2$:0OH | $H_2O_2$:0OH | Fe(II):0OH |
|---|---|---|---|
| 4-10 | 1.5 | -- | -- |
| 3-5 | -- | 2.0 | 0.15 |

Figure I

Schematic Of Unit Processes