ALTERNATIVE METHODS OF PHENOL WASTEWATER CONTROL

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Summary

Methods for removal of phenol from large volume flow effluents by biological and chemical oxidation and adsorption are described. pH and temperature control and nutrient addition are necessary in biological systems, which may utilise trickling filters, aerated lagoons or activated sludge treatment. Adsorption by activated carbon produces the lowest level of phenol in the final effluent of all methods examined, but is the most expensive. Oxidation by chlorine is effective but needs careful control; chlorine dioxide may be an alternative. Hydrogen peroxide, potassium permanganate and ozone as oxidising agents have been examined. For very large effluent flows ozonation appears the least costly, use of hydrogen peroxide and potassium permanganate being competitive with ozone for smaller flows.

Introduction

Phenol is a poisonous crystalline compound commonly called carbolic acid. A monohydroxy derivate of benzene, it is prevalent in coking operations, refineries, steel mills, foundries and plastic manufacturing, with effluent loadings up to 200 mg/l.

The USEPA 1977 standard for phenols for the primary metals industry is given as a maximum average of daily values for a period of 30 consecutive days of 2 parts per billion by weight, and a 1983 limit of only one-tenth this amount. Incidentally, the 1983 phenol limit for this industry is only one-fifth the detectable limit — a value too small to measure in the laboratory by today's analytical methods.

Because chlorine used in drinking water combines with the phenols to form large molecular hydrocarbons, they are slowly degradable, and because of their persistence in the environment are water pollutants. When phenol in a concentration of several $\mu g/l$ combines with chlorine, it imparts an objectional medicinal taste to drinking water. For this reason, the U.S. Public Health Service limit on phenol is set at one ppb for drinking water supplies. Phenol

levels in concentrations greater than 50 ppb are toxic to some forms of aquatic life. The ingestion of one gram of phenol can be fatal in humans [1].

To investigate the feasibility of meeting the National Pollution Discharge Elimination System phenol levels, the Environmental Sciences Division of Envirex Inc. was engaged to study a number of industry sources with flows ranging from 5000 m^3/day to 11,000 m^3/day. The phenol concentrations from the sources ranged from 110 to 123 ppb.

In researching the literature, little information was found on removing phenols to levels below 0.5 mg/l (500 ppb). Tests conducted on refinery wastes with initial phenol concentrations of 275 mg/l (275,000 ppb) using reverse osmosis were not able to achieve a treated effluent of less than 59 mg/l. Solvent extraction's methods are extremely expensive for removal of phenols on flows of any magnitude. Deep well injection is questionable because of possible contamination of ground water supplies. Therefore, this evaluation was important to evaluate whether the 1977 and 1983 NPDES levels being considered could be met.

Because of the large volume of flow to be treated, such methods of phenol removal by solvent stripping using methylhexylketone, oil stripping and caustic treatment to absorb phenol were immediately discounted because of prohibitive costs. Biological oxidation was also eliminated as a practical treatment means because of large land space requirements and the nutrient deficient waste which would not sustain biological activity. However, biological treatment might be considered for smaller flows, with nutrients such as phosphorus and nitrogen added to obtain the necessary biological environment.

In addition to biological oxidation the commonly accepted means of phenol treatment are ozonation, O_3, chemical oxidation by potassium permanganate, $KMnO_4$; hydrogen peroxide, H_2O_2 and chlorine, Cl_2, along with carbon adsorption.

Phenol can be treated biologically using a number of process flow schemes. The phenol serves as an energy source as well as a source of carbon for synthesis of cell mass. End products in the aerobic reaction are carbon dioxide, water and biological cells. The organisms which can oxidize phenol are abundant in nature and can be found in natural waters and in the soil. These organisms will develop in the wastewater provided that the necessary nutrients for growth are present and provided that environmental conditions are favorable.

In biologically treating wastewaters, it is necessary to insure that wastewater pH and nutrient (nitrogen and phosphorus) concentrations be adjusted. The bacteria oxidizing phenol will grow between pH values of 6 to 9.5. The nutrients, nitrogen and phosphorus, may be required to provide a BOD_5 to nitrogen to phosphorus ratio of about 100:5:1. Lesser amounts of these nutrients may be found in practice after experimenting with the system. Temperature affects the rate of all biochemical reactions. Normally, the optimal temperature range for biochemical stabilization depends upon the species of bacteria predominant in the system. Ross and Sheppard [2] reported that at

10°C phenol is scarcely attacked but that rapid decomposition occurred at 38°C. Normally temperatures between 18—35°C are desirable for biological treatment processes.

Critical to successful phenol oxidation is the control of shock loads to the biological process. Numerous studies have shown that phenol concentrations in excess of 500 mg/l can result in a marked decrease in efficiency. Adaptation of the biological process to phenol will attenuate the effects of shock loads, but very high concentrations over extended periods of time will almost always be detrimental to the process.

The best way to solve this problem and to ensure process stability is to design completely mixed suspended growth systems using activated sludge or aerated lagoons with relatively long hydraulic detention times. With feeds of 200 to 300 mg/l, the phenol concentrations in the treated waste will be 0.2 to 0.5 mg/l (200 to 500 ppb), and the required aeration time will be approximately 24 hours. Fixed film systems such as trickling filters are less likely to effectively absorb shock loads unless designed in series.

Since the bio-oxidation systems for phenol are generally aerobic, oxygen is supplied by diffused or mechanical aeration. Approximately 2.5 kg of oxygen are required per kg of phenol at 30°C. This figure may vary substantially, depending upon nutrient source employed and other wastewater characteristics. Although activated sludge systems offer better control of the process and smaller area requirements, they do represent a higher capital investment and more sophisticated operation than the low solids aerated lagoon. In either case, the major operational cost will be in supplying oxygen, and the selection of oxygen transferring equipment should be analyzed carefully.

Horne and Hurst [3] reported successful bio-oxidation of phenols from coke plant wastes in an activated sludge system. Concentrations of from 100 to 800 mg/l phenol were reduced to 1 mg/l in the process loaded at food to mass values as high as 0.16 kg phenol per kg of biological solids. Phosphorus additions were required in a ratio of about 30 parts of phenol to 1 part of phosphorus.

Biological treatment of phenolic wastewaters in a trickling filter activated sludge series process was successfully undertaken by Ross and Sheppard [2]. Phenol concentrations of up to 280 mg/l were treated at an efficiency of 99.9%.

Wurm [4] reported on numerous alternatives to phenol removal from wastewaters. Activated sludge treatment of phenol containing wastewaters produced effluent phenol concentrations of less than 1 mg/l. Hydraulic retention times of 1.5 to greater than 2.5 hours with mixed liquor suspended solids of 2000—3000 mg/l were employed.

Dow Chemical Company [5] developed the following expression for estimating the total operating costs, including capital depreciation, for such facilities:

$$O = Q/812 \, (35000) + 0.2(Q/812)^{0.6} \, (444,000)$$

Where: O = Annual operating cost ($/year) and

Q = Daily Phenol Loading (LB Ph—OH/day)

Because of the operating problems associated with biological treatment processes, and the questionable ability of these processes to produce effluent phenol concentrations of less than 500 ppb on a consistent basis, this method of treatment would be not normally considered if phenol removal is the primary concern.

Phenol adsorption on granular activated carbon

Many solids have the ability to attract to their surface soluble materials such as phenol from solution. This phenomenon is called adsorption, by giving a solid a very porous structure, a very large surface per unit volume results. Certain porous solids are, therefore, excellent absorbents.

Activated carbon is one of these materials having a high adsorption capacity for phenols in wastewater. This material can be contracted with the phenol bearing wastewater either as a fine powder or as granules having a particle size usually in the range of from 0.4 mm diameter to 2.4 mm diameter. The use of granular carbon has been found convenient in the process of phenol removal from wastewater. Vessels can be filled with the carbon and the wastewater then can be passed through these carbon beds either using a fixed bed with upflow-down-flow configuration or by means of an upflow moving bed carbon column, thereby assuring good contact between the wastewater and the solid carbon. As the liquid passes through the bed, the phenol decreases and the carbon becomes loaded with the removed contaminants.

Eventually the carbon nearest the feed point becomes loaded to capacity with phenol and must be replaced by fresh or reactivated carbon. The replacement carbon would not actually be added near the water feed point, but would be added to the system where the treated water exists. This counter-current method of contacting solid and liquid gives the most efficent utilization of carbon. It can be accomplished in a number of ways, the simplest being the use of multiple contactors or columns in series. In this arrangement, the first contactor of carbon is replaced when exhausted and the flow of water is changed to make that contactor the last in the series.

To make the cost of operation reasonable, exhausted carbon must be re-activated and reused. Thermal reactivation is presently the only practical method. Using a multiple-hearth furnace or rotary kiln, the exhausted carbon is heated to 925°C in a stream-air atmosphere. Low pressure, wet air oxidation at somewhat lower temperature may also be employed for carbon regeneration. These procedures burn off the adsorbed phenols and other organics, and restores the carbon to nearly virgin condition. A carbon loss of approximately 5—10% results. In phenol removal studies [6] done by Calgon, two adsorbers in series, each 8 ft (2.44 m) inside diameter and 35 ft (10.67 m) high containing 18,000 pounds (5486 kg) of granular carbon were used. Phenols in the feed

wastewater ranged from 16 to 183 mg/l. The total phenols in the first stage adsorber outlet ranged from 7 to 54 mg/l. The second stage outlet averaged less than 1 mg/l. The carbon loss after regeneration averaged 5.5%.

Bench scale pilot tests conducted at a large foundry by Envirex Inc. indicated that phenol contents of less than 1 ppb could be obtained. A carbon column packed with 1.22 m of granular activated carbon (Calgon Filtrasorb No. 400) was operated at a surface loading rate of 1.8 l/m². The wastewater was fed to the column at 24°C, pretreated with 1 mg/l of anionic polyelectrolyte (Betz Chemical Company No. 1120) for removal of suspended solids. One series of raw waste feed samples averaged 585 ppb of phenols, and the second series of samples averaged 123 ppb of phenols in the feed flow. A break through did not occur in the effluent. Phenol concentration in all effluent samples from the carbon column were nondetectable, indicating less than 1 ppb of phenol. The carbon exhaustion rate was 3,300 parts of carbon per part of phenol removed.

Of the treatment schemes tested, carbon adsorption was found to be the most expensive. This estimate included the carbon contact vessels, carbon regeneration systems and associated appurtenances, including protective buildings. The operational cost per year to treat a flow of 9 million m³ annually to reach phenol levels of less than 1 ppb, would be 15 c per m³ based on 1976 cost estimates.

Chlorination to remove phenols

Clarified phenol effluent samples were chlorinated at four levels; and chlorine contact maintained for twenty minutes prior to analysis for residual phenol and chlorine concentrations. The wastewater had a phenol concentration of 123 ppb after pretreatment to remove suspended solids. A summary of these tests is contained in Table 1. With chlorine treatment, a residual chlorine must be maintained, as well as controlling the pH between a range of 7.0 to 8.3 to prevent the formation of objection taste forming chlorophenols. A chlorine dosage of 12 mg/l is the minimum recommended; it re-

TABLE 1

Removals by chlorination

Chlorine dosage (mg/l)	Cl: phenol ratio	Residual chlorine (mg/l)	Phenol concentration (ppb)	
			Initial	Final
1.2	9.8:1	0.27	123	97
12.0	98:1	1.60	123	n.d.*
24.0	196:1	5.10	123	n.d.
36.0	392:1	7.50	123	3

* Non detectable.

moved all of the phenols and maintained a reasonable chlorine residual. At 36 mg/l chlorine dosage the final pH was 8.4, which is outside the pH limits for chlorophenol formation. The recommended chlorine dosage for removal of phenols would be at a ratio of approximately 100 chlorine to one of phenol.

To treat a waste flow of 25 m³/day would require a yearly expenditure of approximately $ 50,000 based on 1976 estimates. The initial cost of the chlorinator was not considered, as the major cost is in the use of the chlorine. An additional capital cost for the chlorine contact tanks would be approximately $ 70,000.

There are several shortcomings in using the chlorination method for phenol removal. First is the sophistication of correct chlorine dosage and the need for careful pH control. If the effluent is underchlorinated, dangerous and more toxic chlorophenols are generated. This may be the result of flow and initial phenol concentration fluctuations. Chlorine combining with other chemicals can also form toxic carcinogens in drinking water. Secondly is the handling problem associated with chlorine. There is a scarcity of chlorine on the present market. The cost of chlorine is expected to rise dramatically. Therefore, chlorination is not considered a favorable means of phenol removal.

Chlorine dioxide

The possible consideration of chlorine dioxide (ClO_2) is a possible alternative to using chlorine gas. Some acceptance of chlorine dioxide as an oxidant for phenol removal has arisen largely from the fact that offensive chlorophenols could be formed when the phenol-bearing waters are treated with chlorine. However, the chemical behavior and oxidation characteristics of chlorine dioxide in treating wastewaters are not well understood and constitute a subject of some controversy. Like ozone, the instability of gaseous chlorine dioxide necessitates on site generation. The generation is accomplished by means of the reaction between chlorine and sodium chlorite in an acid solution.

Chemical oxidation for phenol removal

Both hydrogen peroxide and potassium permanganate, are oxidising agents that can be used to remove phenol. With an initial phenol concentration of 500 mg/l at a temperature of 49°C and an initial pH of 5.5 with a 30 minute retention time, and using a 4 to 1 hydrogen peroxide to phenol ratio with a 0.01% solution of ferrous sulfate, it is possible to achieve a phenol reduction to 3 ppb. Figure 1 shows hydrogen peroxide to phenol removal ratios. Because hydrogen peroxide has to be treated with a ferrous salt catalyst at a pH of 1.5, known as Fenton's reaction, and then the pH raised to 11 to remove phenol, the associated costs involved would make potassium permanganate a more desirable choice.
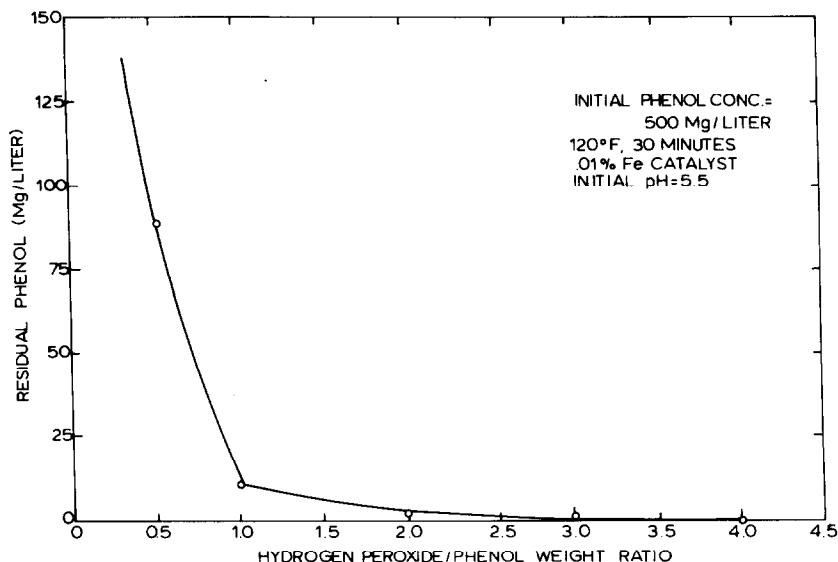
Fig. 1. Removal by hydrogen peroxide.

Potassium permanganate is a powerful oxidizing chemical used to destroy phenolic compounds. It is fed in dry form, and is not corrosive. Potassium permanganate keeps indefinitely when stored in a cool, dry and dark environment. Although it presents no health hazard in its handling, there is some fire hazard which can be controlled with the addition of water. During the reaction, an insoluble compound of manganese dioxide (MnO_2) is formed. This inert product is not considered a pollutant, and exhibits certain sorptive properties which often render it beneficial to the coagulation and sedimentation of low turbidity waters. However, this also presents the operational disadvantage of separating the insoluble hydrous manganese dioxide sludge. This usually presents little problem in subsequent sedimentation of filtration processes. When utilized in removing phenol in a holding tank, the phenol is oxidized rapidly at a pH of 8.5 to 9.5. A retention time of from one to three hours is sufficient to insure complete oxidation of the phenol. The initial reaction takes place almost immediately, and almost 90% of the phenol is oxidized in the first ten minutes.

It is reported that for every m³ of waste containing 60 mg/l to 100 mg/l of phenol, 3 kg chemical would be required at a cost of approximately 4.4 c/m³ for each mg/l of phenol removed. The number of units of phenol removed per unit of potassium permanganate is shown in Fig. 2. Fig. 3 shows the relationship of reaction time to pH.

Under actual conditions on a wastewater flow of 25000 m³/day having an initial phenol concentration of 123 ppb, potassium permanganate was added at concentrations of 1, 5 and 10 mg/l. After a contact time of 20 minutes, the waste was analyzed for residual phenols. A dosage of 10 mg/l, or a ratio of
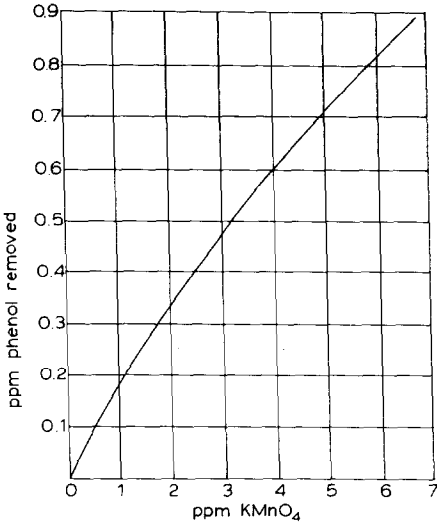
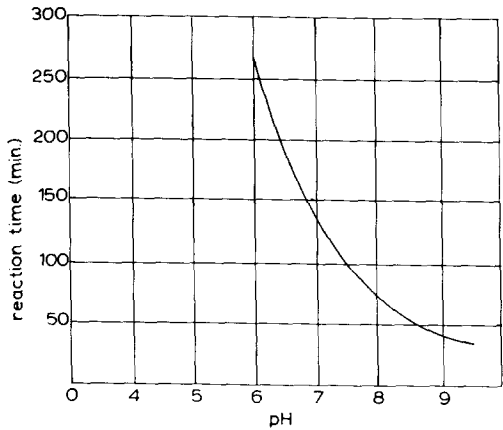Fig. 2. Removal by potassium permanganate.

Fig. 3. Potassium permanganate pH reaction.

80:1 permanganate to phenol was required to remove the phenol. Based on 1976 prices of commercial potassium permanganate in car load lots, the chemical cost to reach phenol concentrations of one ppb is 0.8 c per m^3 treated.

The initial cost of the chemical feed equipment, pH control equipment, cost of the caustic and the capital cost of the contact tanks required is not considered. Although this method of treatment is more expensive for the volume of flow in this example as compared to treatment by ozonation, it would appear to be a reasonable method of phenol treatment for smaller flows. The initial capital cost for feed and control equipment is small. However, the availability and possible price increases of potassium permanganate are concerns. Permanganate treatment is often complemented by carbon adsorption or chlorination.

Phenol removal by ozonation

Ozone has long been recognized as one of the most powerful oxidizing agents. It was in 1906 that ozone was first generated commercially. The basic ozonator configuration is shown in Fig. 4. A high voltage is imposed across a discharge gap in the presence of an oxygen-containing gas. The electrical discharge produces ozone. A glass tube serves as the dielectric, and some metal contact or coating on the glass serves as the electrode. Most ozonators are water cooled to provide optimum heat removal and thus insure the most consistent and efficient operation. Commercial units can operate on 230/460 V,
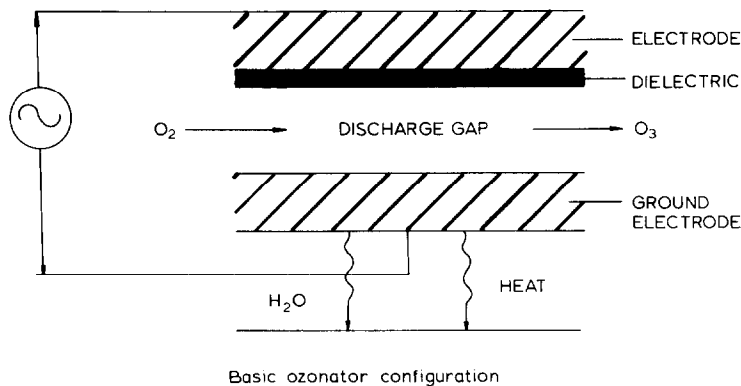
Basic ozonator configuration

Fig. 4. Basic ozonator configurations.

3 phase current, and can produce ozone in the range of 0—3% from atmospheric air, or 0—6% from oxygen. The range of operating pressures is 0—1 kg/cm^2. Units with higher operating pressure are available. Smaller units have a generation capacity of 1—10 kg per day from air and 2—20 kg of ozone generation from pure oxygen. Large scale units can produce ozone in quantities of 22—220 kg per day from dry air and 44—440 kg per day from oxygen or from oxygen enriched air (40% O_2).

In the test work that was done by Envirex Inc. on a foundry complex, handling an annual flow of 9 million m^3, the waste was presettled using an anionic polyelectrolyte for removal of suspended solids, and decanted for treatment with ozone. The phenol concentration in the raw waste after pretreatment was 110 ppb. The temperature of the waste was 24°C, and the contact time in the reaction cell was 5 minutes. Table 2 shows that the minimum dosage of 1.24 mg/l of ozone was not sufficient for complete removal of phenol, although an 87% reduction was effected. At all other dosages, complete removal of phenol was accomplished. Only at the highest dosage of 25.5 mg/l of ozone was a trace of residual ozone detected, which indicates that compounds other than phenol are oxidized after the phenol reaction is complete.

TABLE 2

Removals by ozonation

O_3 dosage (mg/l)	Ozone: phenol ratio	Residual O_3 (mg/l)	Phenol concentration (ppb)	
			Initial	Final
1.24	11:1	0	110	14
5.32	48:1	0	110	n.d.*
11.6	101:1	0	110	n.d.
25.5	200:1	Trace	110	n.d.

* Non detectable.

An ozone to phenol ratio of approximately 50:1 would be required for complete oxidation of the phenols.

Based on a power cost of 3 c/kWh along with the cost of cooling water pumpage, the yearly power cost to treat 9 million m^3 annually would be from $ 6,000 to $ 13,500, depending upon phenol influent concentrations. The initial cost of capital equipment including installation based on 1976 prices would be $ 125,000. There is the possible need of injecting ozone under slight pressure to increase its solubility, and to prevent the loss of the costly, toxic, and corrosive ozone/air mixture. The costs associated with this arrangement have not been investigated. It should be cautioned that ozone may be irritating or toxic depending upon exposure. Direct and extended contact with ozone should be avoided. Care should be taken to protect against the output of the ozone generator being discharged into areas where human beings are present. Piping should be checked for leaks before placing in ozone generator into operation.

Conclusion

Table 3 shows the comparative costs on the four methods that have merit in removing phenols. Any of these four methods will achieve low level phenol concentrations of less than 1 ppb. For flows of substantial magnitude, in excess of several million gallons per day, ozonation would appear to be the least

TABLE 3

Comparative costs

Comparative costs of phenol removal to reduce foundry effluent from 3 sources of 2.89 MGD, 1.3 MGD and 2.4 MGD to 1.5 ppb; based on 1974 prices

Chlorination:

    Initial cost of chlorinators and contact tanks $ 125,000
    Yearly cost of chlorine $ 40,000

Potassium permanganate:

    $ 65,000/year

Hydrogen peroxide:

    $ 75,000/year

Ozonation:

    $ 80,000–125,000 initial cost
    Power cost $ 4,000 to $ 9,000/year, based on 2c/kWh and cooling water pumpage cost, depending upon phenol influent concentrations

Carbon adsorption:

    9 million dollars initial capital cost
    Operational costs $ 1,100/year

costly method. However, for smaller flows, a cost comparison between ozonation and potassium permanganate or hydrogen peroxide should be made. The cost effectiveness of reducing phenols to concentrations of less than 200 ppb is also subject to question based on aquatic life standards and dilution factors available in receiving waters. The removal cost increases markedly below 200 ppb in actual practice.

One of the most influential parameters in oxidation reactions is pH, and it should be carefully monitored and/or controlled in chemical oxidation processes for phenol removal.

Phenol removal to almost any low level concentration is obtainable by a variety of means, and the cost effectiveness to meet requirements should be thoroughly investigated.

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