Progress in treatment technology of phenol-containing industrial wastewater

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Abstract. This article describes the nature and hazards of phenol-containing industrial wastewater, and summarizes the characteristics of various treatment technologies for phenol-containing wastewater. The methods for treating phenol-containing industrial wastewater include chemical precipitation method, supercritical water oxidation method, Fenton method, ozone oxidation method and extraction method. This article reviews the research status and development trend of phenol-containing industrial wastewater treatment technology.

1. Introduction
Phenol [1] is an aromatic compound that exists in large amounts in various types of wastewater. It is one of the 114 priority pollutants initially announced by the US EPA. There are many types of phenolic compounds, including phenol, chlorinated phenol, nitrophenol, alkylphenol. Among them, phenol [2] is the most prominent pollution. Phenol-containing wastewater is an industrial wastewater with a wide range of sources and serious water quality hazards in the world today. It is an important source of water pollution in the environment. Phenols are organic substances that are difficult to degrade. When discharged into water bodies, they will cause serious harm to humans, animals and plants. Phenols can damage the human nervous system and cause people to anorexia and insomnia. When the phenol content in the river is too high, it can directly cause the death of fish and aquatic plants. Irrigating crops with water with a high phenol content will reduce crop yields or even no harvest. Therefore, the prevention and control of phenol-containing wastewater pollution has attracted widespread attention from scholars at home and abroad. At present, the treatment of industrial phenol-containing wastewater includes chemical precipitation method, supercritical water oxidation method, Fenton method, ozone oxidation method, extraction method. This article reviews the progress of phenol-containing industrial wastewater treatment technology, and summarizes the development direction of wastewater treatment technology.

2. Chemical treatment method

2.1. Chemical precipitation
The precipitant is added to the wastewater to form a sulfonate material with less solubility, and the formaldehyde is condensed with urotropine to form a precipitate and be removed. Under alkaline conditions, using benzenesulfonyl chloride as a precipitating agent, and reacting for half an hour at room temperature, the phenol concentration in the wastewater can be reduced to below 4mg/L. In the
treatment of wastewater containing nitrosophenol, heating can be used to cause the nitrosophenol to undergo thermal polycondensation reaction, which in turn forms polycondensates and precipitates out of the water, which reduces phenolic pollutants while also reducing COD. At the same time, phenol and urotropine can form a phenol-urotropine precipitate. Add 4L of circulating mother liquor and 17g of urotropine to 1L of phenol-containing wastewater. The precipitate can be formed after cooling to room temperature. The mother liquor can be recycled.

2.2. Supercritical water oxidation
The supercritical water oxidation method has the characteristics of high efficiency and wide practicability, and can treat difficult-to-degrade and highly toxic pollutants. Compared with other oxidation reactions, supercritical water oxidation has the characteristics of complete reaction, short time and no new pollutants. Studies have shown that with the increase of temperature and pressure, the longer the reaction time, the better the removal of phenol. Under the conditions of a temperature of 400°C, a pressure of 30 MPa and an excess of 10 times the oxidant, the TOC degradation rate of phenol-containing wastewater is above 85%.

2.3. Fenton method
Fenton reagent requires a relatively short time to remove phenolic substances in industrial wastewater, but it takes a long time to treat very few phenolic substances, and other phenolic pollutants can achieve a higher removal rate in a relatively short time. An enterprise used Fenton oxidation method as a pretreatment method to treat phenol wastewater. The pH, oxidant, catalyst addition, time and other factors of the reaction were studied through batch experiments. The results showed that when treating 1L of phenol wastewater, the pH was 3 and the catalyst was used. When adding 8g and adding 40ml of 30% hydrogen peroxide, the biodegradability of wastewater is improved, BOD5/CODcr is increased from 0.2 to 0.6, indicating that Fenton method is suitable for the pretreatment of phenol wastewater. Under natural sunlight and artificial sun lamps, phenol can be photodegraded to form hydroquinone, but it takes a long time and cannot fundamentally remove phenolic pollutants. The research of Nadtochenko&Kiwi[3] shows that the photo-assisted Fenton oxidation method can completely decompose phenol in a short time. However, for wastewater with high pollutant content and more types, only the photo-assisted Fenton oxidation method is used for treatment. More medicaments, longer processing time and higher cost. Therefore, Fenton oxidation technology is more suitable for the pretreatment of phenol-containing wastewater to reduce the use cost.

2.4. Incineration
The incineration method can treat organic pollutants that are difficult to treat by ordinary biochemical methods. Some researchers use the incineration method to treat phenol-containing industrial wastewater. The phenolic pollutants in the wastewater can be converted into CO2 and H2O at high temperatures. Part of the generated hot waste gas undergoes heat exchange to generate steam, and the other part is discharged into the atmosphere. Treatment of phenols on the In the case of a large amount of waste water, the waste water can be concentrated before incineration, so that the pollutants can be effectively decomposed.

2.5. Ozone oxidation method
Ozone can oxidize phenolic pollutants in refinery wastewater into more easily degradable substances. When treating heavy oil cracking wastewater, adding 64.9mg/L ozone for 21.6min, the phenol content can be reduced from 2.12mg/L to 0.016mg/L, the removal rate reaches 99%, and the treatment effect is better. Unlike other treatment methods, ozone has a higher degradation efficiency for high-concentration phenol-containing wastewater, but it has a lower degradation efficiency for low-concentration phenol-containing wastewater. To remove phenolic pollutants in low-concentration industrial wastewater, It is necessary to increase the amount of ozone added to meet the effluent discharge standard.
2.6. Chlorine oxidation method
When chlorine is used to treat phenol-containing industrial wastewater, many intermediate chlorophenols will be produced and an unpleasant odor of chlorophenol will be released. The selective substitution reaction between Cl₂ and phenol produces slightly soluble chlorophenol [4], which is separated and recovered from water by means of precipitation phase separation. When using chlorine to oxidize phenol, it is necessary to add excess chlorine to make the reaction complete, so that less chlorophenol odor can be produced. Using ClO₂ as oxidant can decompose all phenols without producing odor, but the processing cost is more expensive. Studies have shown that in a solution containing 10mg/L of phenol, adding 20mg/L of chlorine, dichlorophenol appears after one hour of reaction.

2.7. Electrocatlytic oxidation
Electrocatalytic oxidation is a new wastewater treatment method that replaces the traditional process. Electrochemical oxidation can effectively oxidize phenolic pollutants in phenol-containing wastewater [5]. Studies have shown that using Ti electrodes as anodes [6-7], phenol can be oxidized to maleic acid. If there are sufficiently strong oxidizing free radicals, maleic acid can be directly oxidized to oxalic acid and then oxidized to carbon dioxide. The structure and operation of the electrocatalytic device are simple, and it is a relatively economical treatment technology. Electrolytic method is used to treat phenol-containing wastewater. Graphite is generally used as anode to oxidize phenol to quinone or acid, and salt is added to the electrolytic cell. The addition amount is generally 20g/L. This is to increase the Cl⁻ concentration and reduce the solution system Resistance to reduce power consumption while improving current efficiency [8]. The current density of the electrolytic cell is generally 3A/dm², and the electrolysis time is 30min. The mass concentration of phenol can be reduced from about 400mg/L to about 2mg/L.

3. Physical and chemical treatment methods

3.1. Adsorption method
The adsorption method treats pollutants that are difficult to oxidize with ordinary oxidants. Activated carbon is usually used to adsorb phenols and other organic matter in industrial wastewater. The adsorption method can decolor and deodorize wastewater while removing phenolic pollutants. A certain factory uses a fixed-bed adsorption device to remove phenol from sodium chloride solution with activated carbon. The adsorbed phenol can be desorbed with lye. After activated carbon is regenerated, it can be reused to reduce processing costs. L.Vaoques [9] and others used activated carbon to adsorb phenol in coking wastewater. Studies have shown that the larger the particle size, the greater the adsorption capacity of activated carbon for phenol, so activated carbon with a relatively large particle size can be selected to treat wastewater.

3.2. Extraction method
As shown in Figure 1, the extraction and dephenolization process. At present, many treatment plants use extraction methods to treat phenol-containing wastewater, and then use lye to recover phenol. Diesel can be used to extract phenol from wastewater, or coal tar extraction, and the extracted tar can be distilled to recover phenol oil. The extraction method is a process in which organic pollutants are separated from waste water using an extractant. First, the extractant and wastewater are mixed, and the extract is transferred from the wastewater to the extractant by shaking. After standing for stratification, the extract phase is separated from the water phase. The contaminants in the extract phase can be separated to obtain useful by-products. The extractant is reused. The condensate discharged from some chemical plants contains a higher concentration of phenol. The wastewater after extraction treatment can be diluted for biochemical treatment, and the water after biochemical treatment can be used in the production process, or discharged. Studies have also shown that when processing high-concentration phenol-containing wastewater, an emulsion system configured with active agents can be used for
extraction. After multiple countercurrent liquid membrane extractions, the concentration of phenol can be reduced to less than 0.5mg/L, and the treatment effect is better. High-concentration phenol-containing wastewater can be recovered by distillation and extraction, and low-concentration phenol (5-500 mg/L) can be effectively treated by biodegradation [10]. Petrochemical plants usually use pulsed sieve plate extraction to remove phenol. When the ratio of wastewater: extractant is 1:1, the removal rate of phenol in wastewater can reach more than 80%. At the same time, the extract can be alkali washed and regenerated for reuse. Sodium phenolate can be recovered at the bottom of the tower.

![Figure 1. Extraction and dephenolization process.](image)

4. Biological method
Many microorganisms can participate in the degradation reaction of phenolic compounds. It is proved by experiment (Table 1) that in the initial aeration system, after about 5 hours of aeration treatment, phenol can be basically removed. When the biological method treats phenol-containing wastewater, it is usually treated in an anaerobic manner. However, when anaerobic biotechnology treats high-concentration phenol-containing industrial wastewater, the degradation rate is slow and the effect is not ideal. It needs to domesticate anaerobic microorganisms suitable for the treatment of phenolic pollutants. Desulfitobacterium chlororespirans and Syntrophorhabdus [11] are anaerobic microorganisms that degrade chlorophenol compounds and phenolic compounds, respectively, and they exist in anaerobic biological treatment wastewater. There are also denitrifying bacteria, which use phenolic compounds as the main carbon source to meet their own growth needs while degrading phenolic pollutants. Generally, the ability of denitrifying bacteria to degrade phenolic compounds is improved by increasing the content of nitrate.

| Time/d | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Water ingress (mg/L) | 579 | 568.6 | 597.6 | 576 | 502 | 502 | 569 | 504 | 625.6 |
| Initial aeration effluent (mg/L) | 0.7 | 2.3 | 0 | 0 | 5.2 | 0 | 2.2 | 1.7 | 7.78 |
5. Conclusion
Phenol-containing industrial wastewater was highly toxic and causes severe pollution. Although there are many treatment methods for phenol-containing wastewater, only one water treatment technology cannot meet the discharge standard, and multiple methods need to be used together for treatment. The development of a new type of phenol-containing wastewater treatment technology to achieve the discharge of wastewater up to standards will be the trend of current social development.

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