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## Chapter

# Physiochemical Properties and Removal Methods of Phenolic Compounds from Waste Waters

Yesim Gucbilmez

# Abstract

In this chapter, phenol and chlorophenols are investigated in terms of their production histories, physiochemical properties, pollution resources, and removal methods. It is seen that both phenol and chlorophenols are highly toxic compounds, produced from natural and anthropogenic sources, which are hazardous to both humans and the environment even at very low concentrations. The typical industries which produce phenol and chlorophenol pollution are petrochemical, textile, plastics, resin, dye, pharmaceutical, iron and steel, pulp and paper industries as well as the petroleum refineries, and coal gasification operations. Phenol is a highly corrosive and nerve poisoning agent. It causes harmful health effects, such as sour mouth, diarrhea, and impaired vision. It is also toxic for the ecosystem with toxicity levels ranging between 10-24 mg/L for humans, 9-25 mg/l for fish, and lethal blood concentration around 150-mg/100 ml. Chlorophenols found in natural waters or drinking water also cause serious health problems such as histopathological alterations, genotoxicity, mutagenicity, and carcinogenicity among others. Due to the aforementioned reasons, the phenolic compounds in wastewaters or drinking water must be removed using a suitable wastewater treatment method such as adsorption, extraction, electrochemical oxidation, biodegradation, catalytic wet air oxidation, or enzyme treatment among others.

**Keywords:** phenol, chlorophenols, wastewater treatment, phenolic compounds, phenolics, organic pollutants

## 1. Introduction

Due to technological advances and rapid industrial growth, water systems around the world are under threat. In general, developing countries suffer from water pollution originating from agricultural sources whereas developed countries have chemical discharge problems. In most wastewaters and drinking water, one or more of the following toxic organic pollutants may occur [1]: Organochlorines, chlorobenzenes (CBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), phenols, chlorophenols, and other phenol-derived compounds.

Phenolic compounds are phytochemicals found in nature that cannot be synthesized in the human body. They are mainly obtained from food and medicinal herbs and are present in most fruits and vegetables [2]. They are found in water systems

#### Persistent Organic Pollutants

due to the discharge streams of industrial, agricultural, and domestic activities as well as the result of natural phenomena. They cause severe and long-lasting health hazards including damage to red blood cells and the human liver. Their interaction with the aquatic ecosystem can produce new compounds, which can be as toxic as the original phenolic molecules [3].

Chlorophenols (CPs) are common contaminants that can be found in surface, ground, and drinking waters [4–8]. Thermal and chemical decomposition of chlorophenols leads to the formation of harmful compounds which cause public health problems such as genotoxicity, mutagenicity, and carcinogenicity among others. In addition, some electrophilic molecules may occur as a result of the transformation of chlorophenols, which may connect and harm the DNA or gene products [5, 6].

#### 2. History of phenol and chlorophenols

The academic and industrial chemist F.F. Runge was born in 1794 in Billwerder near Hamburg. Runge isolated phenol from coal tar in the year 1834 in an impure form and gave it the name "carbolic acid" "Karbols" aure" (carbolic acid) [7–9].

British surgeon Joseph Lister used phenol as a disinfectant for the first time in 1865 for sterilizing surgical dressings, instruments, and wounds [10]. However, the phenol sprays used during the surgeries were dangerous for the lung's mucous membrane when inhaled. Thus, by 1890, the phenol spray was abandoned by the medical community [11].

During the Boer War, England placed an embargo on phenol causing phenol shortage on the continent. This led F. Raschig works at Ludwigshafen, Germany, to produce synthetic phenol on a large scale and in 1940, Hooker Chemical Corporation built a plant based on the so called the Raschig-Hooker process for the commercial production of phenol [12, 13].

During World War I and World War II, the existing sulfonation process for the production of phenol was further improved and other processes such as chlorination process and the Raschig Process were commercialized for the first time [14]. In 1924, Dow Chemical started the commercial production of synthetic phenol using direct chlorination of benzene to chlorobenzene which was called the Dow Process [11].

In terms of patent literature, since the middle of the twentieth century, researchers have mainly tried to improve the existing processes rather than developing new ones. One such example was the 1989 European patent of Mitsui Petrochemical Limited which used a recycle loop to reduce the amount of the side product acetone [15, 16].

Presently, phenol is used in the manufacture of phenolic and epoxy resins [17, 18], plastics [19], plasticizers [20], polycarbonates [21], nylon [22], dyes [23, 24] disinfectants [25], herbicides [26], polymers, drugs, pesticides [27] wood preservatives [28], and fungicides [29].

Chlorophenols (CPs) are produced by the electrophilic halogenation of phenol with chlorine. There are five basic types and 19 different CPs. CPs are mostly used as pesticides, herbicides, antiseptics, and disinfectants [30]. They are very toxic and their presence is dangerous for humans as well as aquatic life. They are found in the wastewaters of textile, pharmaceutical, petrochemical, pesticide, paper, and other industries [31].

The processes given in **Figure 1** have been mainly used in the industry for the production of phenol up to date [10, 32–35] and among them, only the Hock and Toluene Oxidation Processes are important for the phenol industry, the others have been discarded for economic reasons [10].



Processes used up to date for the industrial production of phenol [10, 32–35].

The global phenol market reached a value of 23.17 billion US Dollars (USD) in the year 2020. The phenol market is further expected to grow at a compound annual growth rate (CAGR) of 5.3% between the years 2021 and 2026 to reach a value of about 30 billion USD by the year 2026 [36].

In the case of CPs, their production and usage have caused the presence of persistent toxic components into the water systems which are resistant to biological degradation. However, microorganisms exposed to these pollutants have obtained the ability to biologically degrade some of them and the biodegradation routes were seen to depend on the physicochemical and biological properties of the particular wastewater system under question. Understanding the genetic basis of catabolism of CPs may increase the efficiency of naturally occurring microorganisms or help to raise new microorganisms which can degrade CPs successfully [37].

## 3. Physiochemical properties of phenol and chlorophenols

Phenol is an odorous chemical compound, found either as a colorless liquid or white solid at room temperature, and maybe highly toxic and corrosive. Phenols are similar to alcohols but form stronger hydrogen bonds. The presence of stronger hydrogen bonds makes them more water-soluble than alcohols and their boiling points higher than those of alcohols [38]. They are widely used as raw materials in the manufacture of phenolic resins, automotive parts, nylon, epoxy resins, polycarbonate engineering thermoplastics, wood preservatives, heavyduty surfactants, pharmaceuticals, disinfectants, tank linings, and coating materials among others. They are also widely used in household products; for instance, phenol-derived *n*-hexylresorcinol, is used in cough drops and other antiseptic applications and butylated hydroxytoluene (BHT) is a common antioxidant in foods. Also, in the dye industry, substituted phenols are used to make intensely colored azo dyes [38, 39].

CPs, produced by chlorinating phenol or hydrolyzing chlorobenzenes, contain the benzene ring, the OH group, and chlorine atoms. All CPs, except 2-CP, are solids with melting points in the range of 33–191°C. They are weakly acidic and their acidity is slightly lower than that of phenols. In reactions with alkaline metals in water solutions, they yield highly soluble metal salts. Their level of toxicity depends on the chlorination degree and the place of the chlorine atoms with respect to the hydroxyl group [40].

## 4. Sources of phenol and chlorophenol pollution

The presence of phenolic compounds in wastewaters stem from two main sources: Natural and human-based activities. Natural activities include the decomposition of dead plants and animals, synthesis by microorganisms and plants in the aquatic ecosystem. Human activities, on the other hand, include industrial, domestic, agricultural, and municipal activities [10].

Phenol enters water systems in effluents from major industries, such as petrochemical, textile, plastics, resin manufacturing, dye, pharmaceutical, iron and steel, pulp and paper as well as petroleum refineries, and coal gasification operations. It is very important to remove phenols and aromatic compounds from industrial streams before discharging them because of their toxicity to aquatic organisms [41, 42].

The CPs are among the most important environmental pollutants. They are mostly used in the production of paper and pesticides and also as intermediate materials in the production of dyes, plastics, and pharmaceuticals [43–45]. These industries often cause wastewater and groundwater pollution. In addition, as a result of tap water chlorination treatment, CPs have also been detected in drinking water [46].

#### 5. Removal methods of phenol and chlorophenols

Phenol is a nerve poisoning agent and it is highly corrosive. It causes health hazards, such as diarrhea, sour mouth, and impaired vision. It is also toxic for fish and the toxicity levels are in the range of 10–24 mg/L for humans and 9–25 mg/L for fish while the lethal blood concentration is around 150-mg/100 ml [47].

The available removal methods used for phenol can be separated into two main groups: Traditional and advanced. Traditional methods include steam distillation, extraction, adsorption, ion exchange [42] and advanced methods include wet air oxidation, catalytic wet air oxidation, ozonation, membrane processes, electrochemical oxidation, biological processes/biodegradation, and enzymatic treatment among others [42, 48].

Using the relative volatility of phenol, steam distillation can be carried out in order to remove phenol from aqueous mixtures. The phenol–water mixture forms a minimum azeotrope at 9.21% (w/w) phenol [42, 49–51]. Using this property, azeotropic distillation or steam distillation can be used to treat phenol wastewaters to obtain effluent concentrations as low as 0.01 mg/L [48].

Liquid–liquid extraction is a commonly employed technique used for the removal of phenolic compounds. It can be used for a wide range of phenol concentrations and is economical in some cases. Benzene and butyl acetate have been popular as solvents in this process in the past, however, presently, the most used solvent is di-isopropyl ether, which is used in the phenosolvan process [50, 51]. For the extraction process, the solubility of the preferred solvent in water should be tolerable so that further purification steps will not be necessary. The selectivity of the solvent depends mainly on the type of the solvent, the system temperature, and the amount of phenol in the wastewater [50].

The adsorption method has been found to be successful for the removal of phenols from wastewaters for a large concentration scale, depending on the adsorbent, recycling, and economics. Among the used adsorbents, activated carbon (AC) is the most preferred one in the industry. It is expensive but has been shown to be efficient for the removal of even very low amounts of organic pollutants [51–53].

Chemical oxidation processes can turn phenolic compounds into smaller molecules that are less toxic and easier to process or mineralize [54, 55]. Among the chemical oxidation processes, advanced oxidation processes (AOPs) such as the Fenton process, ozonation, photolysis, or their combinations are recommended for low-concentration wastewaters. Incineration, on the other hand, is suitable for wastewaters for which the COD values are higher than 100 g/L, however, it is no more commonly used since it is not an eco-friendly process [56].

Wet air oxidation (WAO) is a very clean technology since no additive is added to cause secondary pollution. The reaction is carried out at moderate temperatures (175–320°C) but at high pressures (2.17–20.71 MPa); the organic pollutants in the wastewater are oxidized into small organic acid molecules which are likely to biodegrade [57]. This method can be used for the treatment of wastewaters with initial COD values in the concentration range of 20–200 g/L [58].

Catalytic wet air oxidation (CWAO) offers an alternative path to treat refractory wastewaters. CWAO gained a lot of interest over the past 20 years due to its ability to oxidize toxic wastewaters and complete their mineralization [59–63]. In addition, it is a heterogeneous process, thus, an extra catalyst separation step is not necessary in most cases making the process more economical to apply [64].

Many researchers have studied the electrochemical oxidation of phenolic compounds [65, 66]. In this process, the electrode should be electrochemically stable, economically viable, and very efficient for the removal of organic pollutants [67]. There are different researches carried out using several anodic materials like Ti = SnO<sub>2</sub>, Pt [68], vitreous carbon [69], and PbO<sub>2</sub> [70]. Among them, PbO<sub>2</sub> electrodes have been successfully applied due to their high electrical conductivity values, strong oxidizing properties, and low costs [71, 72].

Biological treatment or biodegradation is the most widely employed method for the removal of phenols from water systems. The treatment is inexpensive, simple to design and maintain, and transforms the phenolic solutions into simple end products. Phenolic molecules such as Bisphenol A (BPA) can also be successfully treated with biological treatments such as activated sludge [73–75].

CPs, on the other hand, can be removed from wastewaters by a variety of methods including biological treatment [14], advanced oxidation processes [76], and adsorption [77–79].

Although various traditional and advanced methods are possible to apply for the removal of phenol from wastewaters; the two important parameters which define the suitable method are the initial and final phenol concentrations as seen in **Table 1** [42].

| Initial<br>Concentration<br>(mg/L) | Method       | Initial<br>Concentration<br>(mg/L) | Method                                 | Final<br>Concentration<br>(mg/L) | Method                      |
|------------------------------------|--------------|------------------------------------|--|----------------------------------|-----------------------------|
| Over 3000-<br>6,000 or 20-500      | LLE          | ~ 50                               | Photocatalytic<br>Oxidation            | <10                              | Bio-degradation             |
| Up to 4,000 or<br>300-3000         | Adsorption   | ~ 50                               | Chemical-<br>Electrochem.<br>Oxidation | Very low                         | Adsorption                  |
| ~ 3,000                            | Distillation | <50                                | Bio-<br>degradation                    | Very low                         | Photocatalytic<br>Oxidation |

#### Table 1.

Initial and Final Phenol Concentrations of Waste Waters and Corresponding Removal Methods (Modified from [42]).

# 6. Comparison of different methods for the removal of phenol and chlorophenols

Researchers still extensively focus on phenol removal methods from wastewaters, considering both traditional methods such as adsorption and steam distillation and advanced processes, such as wet air oxidation and biodegradation. The traditional methods mostly have the drawbacks of low efficiency and high operational cost which can be cured by using low-cost adsorbents or increasing the surface area of the existing adsorbents. In the case of advanced methods, enzymatic treatment which uses different peroxidases seems to be an efficient method with removal efficiencies above 95% [49].

As for CPs, adsorption, biodegradation, and oxidation by AOPs seem more widely used than other methods [76–79]. AOPs involve the formation and use of hydroxyl ions (OH<sup>-</sup>) through chemical, photochemical, or photocatalytic methods [77]. Adsorption has been reported to be one of the most successful methods for CP removal from wastewaters since it is a simple method with a low-maintenance cost, high efficiency, and less toxic by-product generation [79].

## 7. Conclusions

Phenols and CPs are important compounds used in the manufacture of epoxy resins, plastics, polycarbonates, nylon, dyes, disinfectants herbicides, drugs, pesticides, wood preservatives, and fungicides among others. However, they are quite toxic chemicals, even at low concentrations, causing harmful effects ranging from sour mouth, diarrhea, and impaired vision to histopathological alterations, genotoxicity, mutagenicity, carcinogenicity, and death. Thus, wastewaters containing phenol and CPs have to be treated thoroughly before being discharged into water systems. The water treatment processes used in industry depend on the type of wastewater and initial and final concentrations of the phenol and CPs. Traditional methods such as adsorption and distillation or advanced methods such as wet air oxidation and biological treatment can be used to remove phenol and CPs from wastewaters. For the removal of phenol from wastewaters, among traditional methods, the adsorption method is efficient on a large scale of concentrations, depending on the economics, recycling, and the adsorbent properties. Among advanced methods, on the other hand, the inexpensive and simple to design biological treatment is the most commonly applied method and the enzymatic treatment yields more than 95% phenol removal efficiency using different peroxidases. Finally, for the removal of chlorophenols from wastewater systems, the most used methods are adsorption, biological treatment, and advanced oxidation processes.

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# **Author details**

Yesim Gucbilmez Department of Chemical Engineering/ESTU, Eskisehir, Turkey

\*Address all correspondence to: ygucbilmez@eskisehir.edu.tr

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