Phenol Removals

Subjects: Environmental Sciences

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Phenol acts as a pollutant even at very low concentrations in water. It is classified as one of the main priority pollutants that need to be treated before being discharged into the environment. If phenolic-based compounds are discharged into the environment without any treatments, they pose serious health risks to humans, animals, and aquatic systems.

Keywords: phenol removal ; technology advances ; catalytic ozonation ; zeolite

1. Overview

Phenol acts as a pollutant even at very low concentrations in water. It is classified as one of the main priority pollutants that need to be treated before being discharged into the environment. If phenolic-based compounds are discharged into the environment without any treatments, they pose serious health risks to humans, animals, and aquatic systems. Several technologies have been developed to remove phenol to prevent environmental pollution, such as biological treatment, conventional technologies, and advanced technologies. Among these technologies, heterogeneous catalytic ozonation has received great attention as an effective, environmentally friendly, and sustainable process for the degradation of phenolic-based compounds, which can overcome some of the disadvantages of other technologies. Recently, zeolites have been widely used as one of the most promising catalysts in the heterogeneous catalytic ozonation process to degrade phenol and its derivatives because they provide a large specific surface area, high active site density, and excellent shape-selective properties as a catalyst. Rational design of zeolite-based catalysts with various synthesis methods and pre-defined physiochemical properties including framework, ratio of silica to alumina (SiO_2/Al_2O_3), specific surface area, size, and porosity, must be considered to understand the reaction mechanism of phenol removal. Ultimately, recommendations for future research related to the application of catalytic ozonation technology using a zeolite-based catalyst for phenol removal are also described.

2. Phenol

At present, about 80% of all wastewater is discharged into the world’s waterways, wherein it creates health, environmental, and climate-associated hazards [1]. Phenol and phenolic compounds are found in several industrial wastewater processes such as refineries, coking operations, coal processing, petrochemicals, pulp, paper, etc., as shown in **Figure 1**. In addition, phenolic-based compounds (cresols, xylenols, etc.) are also found in wastewater of biomass gasification plants due to the formation of tar (a group of organic compounds) in the process, especially if wet scrubbers are an effective method of removing tar from the syngas stream [2].

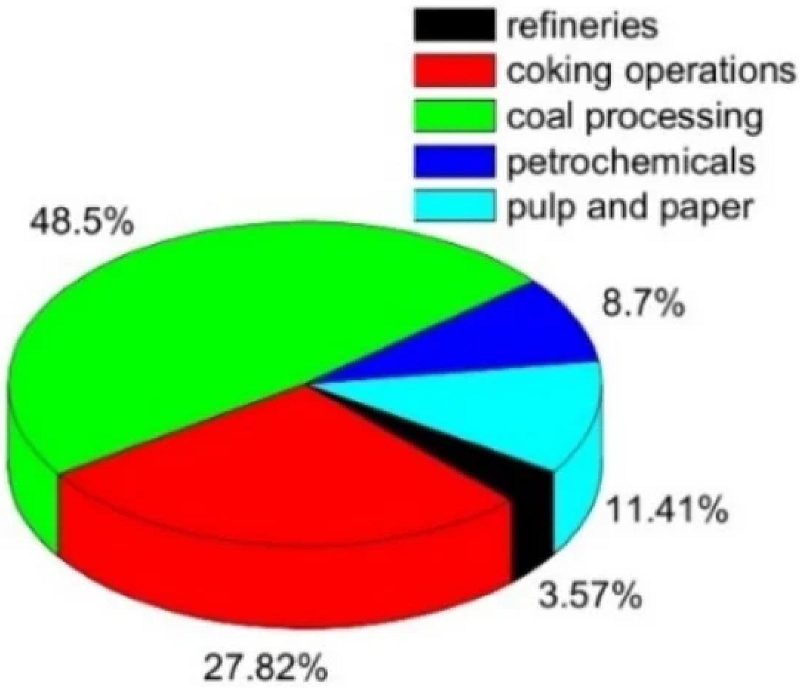

Figure 1. Phenol concentration (%) in the effluent of various industries. Reproduced from ref. [3]. Copyright 2019 Elsevier.

Due to its high toxicity and poor biodegradability, phenol acts as a pollutant even in very low concentrations. According to the United States Environmental Protection Agency (USEPA) and the National Pollutant Release Inventory (NPRI) of Canada, phenol is classified as one of 129 priority pollutants [4][5][6][7]. It is toxic, carcinogenic, mutagenic, teratogenic, and when the concentration in wastewater is higher than 50 mg/L, it can inhibit the rate of biodegradation [7][8]. As a result, if phenolic compounds are discharged into the environment without any treatment, they can cause serious health risks to humans, animals, and aquatic systems. It can cause irregular breathing, muscle weakness, tremors, coma, and breathing cessation at lethal doses in humans with prolonged exposure. The level of toxicity of phenol for humans varies between 10 to 24 mg/L, and the lethal blood concentration is approximately 1.5 mg/mL [8]. In addition, exposure to phenolic compounds can cause eating disorders, weight loss, diarrhea, vertigo, salivation, and dark stools, as well as irritation of the ducts and the central nervous systems and liver, kidneys, and vascular tissues in animals. Therefore, phenol compounds must be removed from wastewater before being discharged into the environment to meet the maximum allowable phenol limit in wastewater stream, which is less than 1 mg/L (1 ppm). The levels of phenol concentration in some industrial wastewaters are shown in **Table 1**.

Table 1. The reported levels of phenol in industrial wastewater. Adapted from ref. [9]. Copyright 2006 Elsevier.

Industrial Sources	Phenol Concentration (mg/L)
Paint manufacturing	1.1
Rubber industry	3–10
Leather	4.4–5.5
Ferrous industry	5.6–9.1
Pulp and paper industry	22
Petroleum refineries	40–185
Fiberglass manufacturing	40–2564
Wood preserving industry	50–953
Textile	100–150
Petrochemical	200–1220
Coke ovens (without dephenolization)	600–3900
Phenolic resin	1270–1345
Phenolic resin production	1600

Industrial Sources	Phenol Concentration (mg/L)
Coal conversion	**1700–7000**
Biomass-based gasification	**772–4630**

Various treatment techniques have been applied to remove phenol and phenolic compounds from aqueous effluent, including biological treatment, conventional treatments, and advanced treatments. **Figure 2** shows the number of publications related to various conventional and advanced technologies for phenol removal. This review article provides a comprehensive summary of effective and potential methods for removing phenol from wastewater.

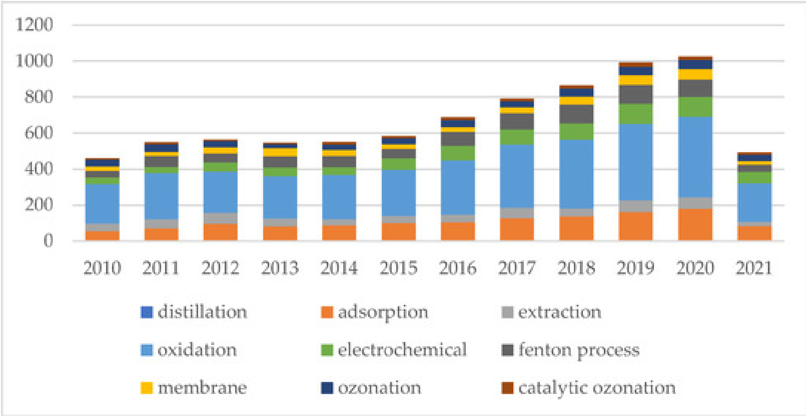

Figure 2. The number of annual publications related to various methods to degrade phenol in 2010–2021. Indexed by Scopus (TITLE-ABS-KEY (terms); terms: distillation, adsorption, extraction, oxidation, electrochemical, Fenton process, membrane, ozonation, catalytic ozonation phenol degradation) [10].

3. Phenol Compounds in Wastewater

Wastewater is polluted water that contains physical, chemical, and biological pollutants caused by human use and has a negative impact on the environment. Domestic wastewater from households, municipal wastewater from communities, and industrial wastewater are some types of wastewaters that are all around us. Phenol is an important organic chemical intermediate and raw material in wastewater. The main application of phenol is in the production of phenolic resin, bisphenol A, and caprolactam [11]. Due to its high harmful effect, phenol is classified as a pollutant even at very low concentrations. It can be found in several wastewater treatment industries, such as oil refining, petrochemicals, and pharmaceuticals industries.

3.1. Chemical Structure and Properties of Phenol

Several types of phenolic compounds in nature, such as eugenol, thymol, pyrogallol, guaiacol, or pyrocatechol, occur naturally. However, some are formed as byproducts of industrial, agricultural, and human activities that can pose serious environmental risks. Phenol with a chemical structure of C_6H_5OH represents an aromatic compound with one or more hydroxyl groups (-OH) connected directly to an aromatic system (e.g., phenyl, naphthyl). Moreover, all the carbon atoms that make up aromatic rings are sp^2 hybridized. Therefore, phenyl has a hexagonal planar structure with all bond angles of 120° and delocalized electrons distributed over the ring. Thus, Csp^2–Osp^3 forms C–O and O–H bonds made from Osp^3–H1s, and unattached electron pairs occupy the other two oxygen atomic orbitals. As shown in **Figure 3** the hydroxyl functional group of C–O–H has a bent shape that is close to a tetrahedral bond perspective with a bond angle of 109.5°. Both C–O and O–H are polar because oxygen is more electronegative than carbon and hydrogen [12].

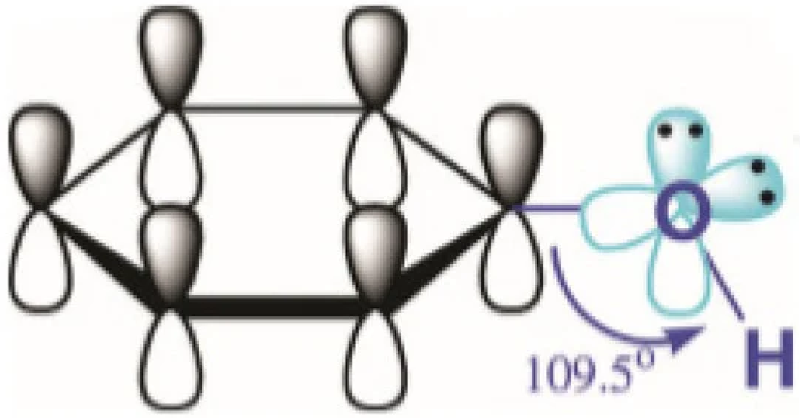

Figure 3. The chemical structure of phenol. Reproduced from Ref. [12]. Copyright 2017 IntechOpen.

Phenol has a cross-sectional area of 4.20×10^{-10} m, a volume of 87.8×10^{-6} m^3/mol, a saturated concentration in water of 912 mol/m^3, and pKa of 9.99 [13]. Phenol is classified as an acid that is weaker than carbonic acid (pKa of carbonic acid is 6.4) but stronger than water (pKa of water is 15.7). Substituted phenol derivatives do not dissolve well in water (solubility does not exceed 30 g/L), but unsubstituted phenols are relatively soluble in water (83 g/L). Alkyl and halogen groups can be used as substituents to increase the hydrophobicity of the aromatic ring (decrease its solubility in water). Adsorption or extraction of phenolic compounds is challenging at very low concentrations because phenols have a large variety of physicochemical properties, especially the electron density of the aromatic ring that affects the solubility of phenol compounds in water [13]. The physiochemical properties of phenol are shown in **Table 2**.

Table 2. Chemical and physical properties of phenol. Adapted from ref. [14]. Copyright 2015 Taylor & Francis Online.

Properties	Value	Units
Reactivity	**0 (normally stable)**	**-**
Flammability	**2**	**-**
Health	**4 (serious temporary or residual injury)**	**-**
Special COR	**Corrosive**	**-**
Molecular weight	**94.11**	**g/mol**
$T_{melting}$	**40.91**	**°C**
$T_{boiling}$	**181.75**	**°C**
Density	**1.07**	**g/cm^3**
Flash point	**79**	**°C**
Acidity in water (pKa)	**9.89**	**-**
Water solubility (at 20 °C)	**8.3**	**g phenol/100 mL H_2O (wt.%)**
Water solubility (at 25 °C)	**8**	**g phenol/100 mL H_2O (wt.%)**
Vapor pressure (at 25 °C)	**0.35**	**mmHg**

3.2. Phenol Toxicity

Phenol is one of the top priority contaminants and also a potentially carcinogenic pollutant [13]. Phenol is a toxic, carcinogenic, mutagenic, and teratogenic substance that can inhibit the rate of biodegradation at concentrations of more than 50 mg/L in wastewater [7]. For human and aquatic life, the levels of toxicity vary between 9 and 25 mg/L. Exposure to phenolic compounds can cause eating disorders, weight loss, diarrhea, vertigo, salivation, and dark coloration of feces [15]. According to the Health Protection Agency (HPA), there is about 60–88% of phenol exposure through inhalation and followed by oral and dermal exposure [16]. The toxicological properties of phenol have been contributed mainly by the formation of organic species and free radical species and their hydrophobicity. The structure of phenol itself shows its reactivity, which leads to its properties such as persistence in the environment, toxicity, and possible carcinogenicity to living organisms [17]. The presence of phenol in wastewater during disinfection and oxidation processes can also form substituted compounds and toxic intermediates as secondary pollutants that can inhibit microorganisms in biological treatment processes [14]. Therefore, the removal and mineralization of phenolic compounds from wastewater is necessary before being discharged into the environment. Consequently, wastewater treatment with phenol species has attracted a lot of attention due to the toxicity and low biodegradability of phenolic compounds.

4. Conclusions

Phenol acts as a harmful pollutant even in very low concentrations in water. Several methods have been developed to remove phenolic compounds from wastewater. Chemical adsorption and oxidation are the most common methods, but they still have some drawbacks including requiring higher energy consumption, maintenance (corrosion, sediment, and scale), high operating cost, and being unsustainable. As an alternative, ozone-based technology has been widely used to degrade organic pollutants because ozone has a high oxidizing ability. However, single ozonation exhibits very low efficiency, requires a large amount of ozone, low solubility in water, low reaction rate with organic compounds, and slow mineralization rate. Therefore, to overcome this problem, the involvement of a catalyst in the ozonation process is able to increase the degradation efficiency and reduce the use of ozone because there are reactive oxygen species formed from the decomposition of ozone involved in the reaction (i.e., hydroxyl radicals).

Catalytic ozonation consists of homogeneous catalytic ozonation and heterogeneous catalytic ozonation. Heterogeneous catalytic ozonation has the tremendous advantage of no secondary pollutant produced and an easier catalyst regeneration process than homogeneous catalytic ozonation. The degradation of phenol in solution using heterogeneous catalytic ozonation processes has been developed by many researchers. Of the various types of catalysts that have been developed, zeolite has the potential to be a promising catalyst in the catalytic ozonation process for the degradation of phenol waste. Zeolites have a large specific surface area, good thermal and chemical stability, and controllable hydrophilic/hydrophobic properties. Several parameters need to be reviewed to produce an ideal zeolite for the catalytic ozonation process of phenol waste removal, namely the Si/Al ratio, suitable pore size for adsorption of phenolic compounds, morphology, acidity level, and specific surface area. Furthermore, with a large surface area and short diffusion path length, nano-sized zeolites provide an active site that is more accessible to the pollutants so that the production of nano-sized zeolites is currently being developed.

There is still a lack of research with regard to the use of heterogeneous catalytic ozonation for phenol removals. Thus, to fulfill this research gap, the following strategies can be set for the future directions:

(i) Necessities of standardized performance evaluation.

In the literature, the choice of reactor type configuration is well reported to play a role in determining phenol removal efficiency. In fact, the number of parameters such as operating testing conditions (pH, ozone concentration and flow rate, temperature, and pressure) and reactor configuration greatly affect the catalytic performance. As a result, we propose the necessity of a standardized performance evaluation technique so that the different catalysts developed for phenol removal can be appropriately compared.

(ii) Development of zeolite-based catalyst for phenol removal

Most research in heterogeneous catalytic ozonation for phenol removal has been to develop metal oxides-based catalysts. Furthermore, developing an advanced synthetic method, that is, ultrafast synthesis using continuous flow to synthesis various types of zeolites in the order of seconds, provides great potential to facilitate the large-scale production of zeolite.

(iii) Elucidation of active sites in zeolite-based catalyst

Besides the mass production of zeolite, the understanding of fundamental reaction mechanisms, in particular, the catalytic active sites in heterogeneous catalytic ozonation are not fully understood. Thus, the utilization of in situ and operando characterizations will be beneficial to fully understand the active sites especially in zeolite-based catalysts for phenol removal.

(iv) Application of artificial intelligence (AI) for catalyst development

The development of an ideal catalyst for heterogeneous catalytic ozonation for phenol removal is still an important issue. An automatic machine learning framework based on artificial intelligence is advocated to allow the development of high-throughput catalysts with desired physiochemical properties for phenol removal in large-scale applications.

(v) Techno-economic evaluation of heterogeneous catalytic ozonation

After finding the most optimum catalyst and suitable synthetic methods as well as reactor configuration process, techno-economic evaluation is necessary to be conducted in order to analyze the economic performance of the implementation of an industrial process. Ultimately, heterogeneous catalytic ozonation technology supported with the ease of the recovery and reuse of catalyst will lead to the creation of green, sustainable, environmentally friendly technology and will be the embodiment of the circular economy concept.

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