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Phenolic Compounds in Water: Sources, Reactivity, Toxicity and Treatment Methods

William W. Anku, Messai A. Mamo and
Penny P. Govender

Additional information is available at the end of the chapter

Abstract

Phenolic compounds exist in water bodies due to the discharge of polluted wastewater from industrial, agricultural and domestic activities into water bodies. They also occur as a result of natural phenomena. These compounds are known to be toxic and inflict both severe and long-lasting effects on both humans and animals. They act as carcinogens and cause damage to the red blood cells and the liver, even at low concentrations. Interaction of these compounds with microorganisms, inorganic and other organic compounds in water can produce substituted compounds or other moieties, which may be as toxic as the original phenolic compounds. This chapter dwells on the sources and reactivity of phenolic compounds in water, their toxic effects on humans, and methods of their removal from water. Specific emphasis is placed on the techniques of their removal from water with attention on both conventional and advanced methods. Among these methods are ozonation, adsorption, extraction, photocatalytic degradation, biological, electro-Fenton, adsorption and ion exchange and membrane-based separation.

Keywords: phenolic compounds, toxicity, wastewater treatment, photodecomposition, membrane-based separation

1. Introduction

There has recently been heightened concern among policymakers and scientists with regard to the effects of human and wildlife exposure to chemical compounds in the environment, particularly the aquatic environment. Phenolic compounds are among the chemicals of major concern in this regard as they tend to persist in the environment over a long period of time, accumulate and exert toxic effects on humans and animals [1]. Some phenolic compounds are

abundant in nature and are associated with the colours of flowers and fruits [2]. Others are synthesised and are used in varied aspects of mankind's everyday life.

The entrance of phenolic compounds into the aquatic environment results from natural, industrial, domestic and agricultural activities. Their presence may be due to the degradation or decomposition of natural organic matter present in the water, through the disposal of industrial and domestic wastes into water bodies and through runoffs from agricultural lands [3]. These chemicals, upon entry into the water, have the tendency of undergoing transformations into other moieties that can even be more harmful than the original compounds. This transformation is normally due to their interaction with physical, chemical and biological or microbial factors in the water [4].

Phenolic compounds have been enlisted by the United States Environmental Protection Agency (USEPA) and the European Union (EU) as pollutants of priority concern. This enlistment is due to the fact that these chemicals are noted to be toxic and have severe short- and long-term effects on humans and animals [5]. The occurrence of phenolic compounds in the aquatic environment is therefore not only objectionable and undesirable but also poses a danger as far as human health and wildlife are concerned. As a result, a number of wastewater treatment techniques have been developed and used for the removal of phenolic compounds from industrial, domestic and municipal wastewaters prior to their disposal into water bodies so as to minimise the devastating effects of these chemicals on human and aquatic lives. Some of these techniques include extraction, polymerisation, electro-Fenton process, photocatalytic degradation and so on.

This chapter presents a general overview of selected topics in relation to phenolic compounds. It dwells on the sources and reactivity of phenolic compounds in water, their toxic effects on humans and methods of their removal from water. Specific emphasis is placed on the techniques of their removal from water with attention on both conventional and advanced methods. Among these methods are adsorption, extraction, polymerisation, electro-coagulation, photocatalytic degradation, biological methods, electro-Fenton method, advanced oxidation processes, adsorption and ion exchange and membrane-based separation techniques.

2. Classification of phenolic compounds

Phenolic compounds are a class of organic compounds with a hydroxyl group(s) directly bonded to one or more aromatic rings. The first member of chemicals belonging to this category of organic compounds is called phenol, also known as carbolic acid, benzophenol or hydroxybenzene with the chemical formula of C_6H_5OH (**Figure 1**). All other members of the group are derivatives of phenol [6].

Phenolic compounds are classified into different groups based on different factors. Among these factors of categorisation are the carbon chain, basic phenolic skeleton or the number of phenol units present in the molecule, distribution in nature and location in plants.
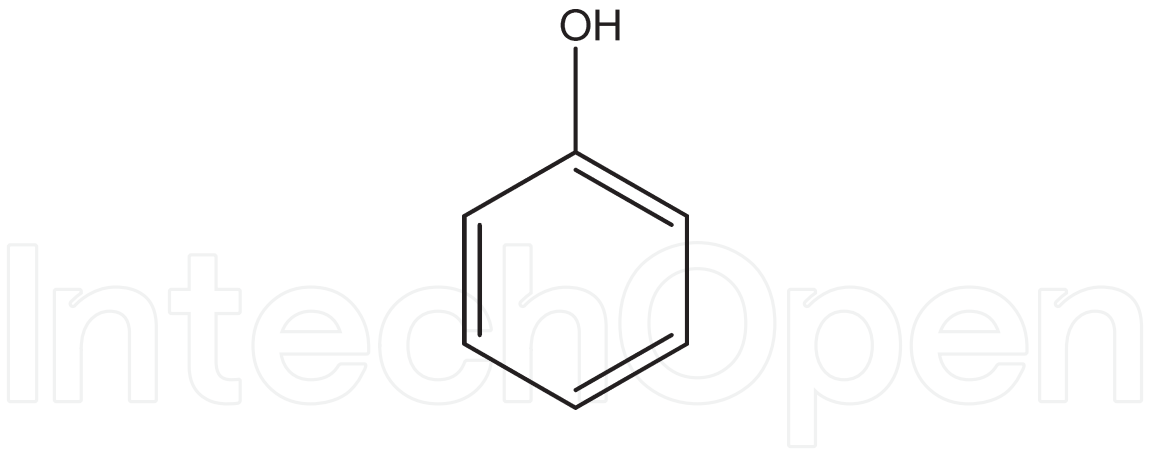
Figure 1. Structure of phenol.

2.1. Classification based on carbon chain

The classes of phenolic compounds identified under this category are listed in **Table 1**. The integers attached to the carbon atoms bonded to the aromatic ring (C6) represent the number of carbon atoms directly or indirectly bonded to the aromatic ring.

Carbon chain	Number of phenolic units	Class	Examples
C6	1	Simple phenols	Catechol
C6	1	Benzoquinones	Hydroquinone
C6-C1	1	Phenolic acids	Gallic
C6-C2	1	Acetophenones	3-Acetyl-6-methoxy benzaldehyde
C6-C2	1	Phenylacetic acids	p-Hydroxypheylacetic acid
C6-C3	1	Hydroxycinnamic acids	Caffeic acid
C6-C3	1	Phenylpropenes	Eugenol
C6-C3	1	Coumarins/isocoumarins	Umbelliferone
C6-C3	1	Chromones	Cromolyn
C6-C4	1	Naphthoquinones	Plumgagin, juglone
C6-C1-C6	2	Xanthones	Mangiferin
C6-C2-C6	2	Stilbenes	Resveratrol
C6-C3-C6	2	Flavonoids	Amentoflavone
$(C6-C3)_2$	2	Lignans and neolignans	Pinoresinol, eusiderin
$(C6-C3)_n$	n > 12	Lignins	Tannic acid

Table 1. Classification of phenolic compounds based on carbon chains.

2.2. Classification based on the number of phenol units present in the molecule

Phenolic compounds can be grouped as simple, bi and polyphenols depending on the number of phenol groups present in a particular molecule. Simple phenols are phenols with only one substituted phenolic ring. In other words, they have substituted phenols. Examples of simple phenols include phenolic acid, hydroquinone, resorcinol, thymol, etc. [7]. Biphenols contain two phenolic units while polyphenols consist of multiple units of the phenolic structure. Based on the number of phenol rings present, and the type of elements binding rings together, polyphenols can be subdivided into various groups such as flavonoids, phenolic acids, tannins, stilbenes and lignans (**Figure 2**) [8].
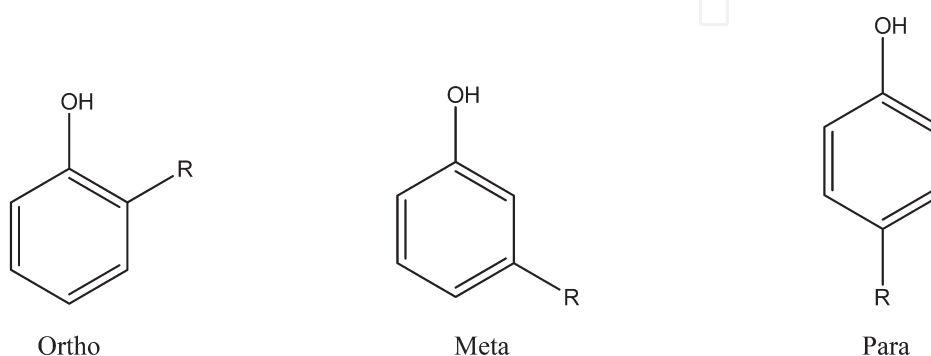

Figure 2. Structure of simple phenols.

2.3. Classification based on distribution in nature

Based on their extent of distribution in nature, phenolic compounds have been classified as being shortly distributed, widely distributed and as polymers. Widely distributed phenols are the types that are present or available in all plants, or are of high significance in specific plants. Examples include flavonoids and/or flavonoid derivatives, coumarins, phenolic acid including benzoic acid and cinnamic acid. Those that are shortly or less widely distributed are limited and include simple phenols, pyrocatechol, hydroquinone and resorcinol. Examples of the polymer class of phenolic compounds are tannin and lignin [9].

2.4. Classification based on location in plants

Phenolic compounds that are free in soluble forms in cells are categorised as being in solution while those bound as complexes in the cell wall, as insoluble. Soluble phenolic compounds include low and medium molecular weight phenolics such as simple phenol, flavonoids and tannins. Insoluble phenolics include high molecular weight tannins and phenolic acids. Other insoluble phenolics include those bound to polysaccharides in the cell walls (usually with low molecular weight), and proteins [10].

3. Sources of phenolic compounds in water

The existence of phenolic compounds in water can be attributed to natural and anthropogenic activities. Natural sources of phenolic compounds in water pollution include decomposition

of dead plants and animals (organic matter) in the water. They are also synthesised by micro-organisms and plants in the aquatic environment. Industrial, domestic, agricultural and municipal activities constitute the anthropogenic sources of water pollution with phenolic compounds. This section provides details on various sources of introduction of phenolic compounds in water bodies.

3.1. Natural sources

3.1.1. Decomposition of organic matter

The occurrence of phenolic compounds in water is sometimes due to the decomposition of dead plants and animals in the water bodies; or as a result of runoff from the land where the decomposing materials are washed into water bodies. Phenolic compounds are components of many plant species, aquatic or terrestrial. Some of these compounds are formed from amino acids, present in hemicelluloses of some plants, under ultraviolet light irradiation. For instance, willow bark is known to contain a certain amount of salicylic acid [11]. Green and red marine algae also contain macromolecules of phenolic compounds. Hydroxybenzene, for example, is produced due to decomposition of organic matter [12]. The body of humans and animals, without any external exposure, produces phenol which finally gets excreted. Thus, the metabolic waste products of humans and animals also contain phenol [13]. Phenol is produced in the gut of mammals as a result of the transformation of tyrosine in their digestive tract [14]. The compounds are also components of many food stuff including fruits and vegetables. Phenol is found to be present naturally in coal tar and creosote. It is also produced during natural fires, and through benzene degradation in the atmosphere under the influence of ultraviolet light radiation [14]. Direct decomposition of these materials in water or indirect introduction from runoffs and rainfall result in the pollution of the water bodies with these compounds.

3.1.2. Synthesis by microorganisms

The potential of microorganisms to degrade naturally occurring substrates into phenolic compounds, particularly hydroxybenzoate, is well established [15]. Debaryomyces hansenii is noted for its ability to convert ferulic acid into varied phenolic compounds in the presence of glucose and nitrogen. Debaryomyces hansenii metabolism of ferulic acid was identified by Max et al. [16] to produce 4-vinyl guaiacol, vanillic acid, acetovanillone, ferulic acid, vanillin and 4-ethylguaiacol, while Shashwati et al. [17] noted the ability of Streptomyces sannanensis to convert ferulic acid to vanillic acid. Fermentation of plant extracts by microorganisms is also known to result in the formation of different types of phenolic compounds. A study involving the use of Lentinus edodes for the fermentation of cranberry pomace identified the formation of ellagic acid [18], while fermentation of ethanolic acid (obtained from oat) by a fungus, Aspergillus oryzae, produced caffeic and ferulic acids [19].

3.1.3. Synthesis by plants

There is a vast distribution of phenolic compounds in the plant kingdom. Synthesis of phenolic compounds in plants occurs in the chlorophyll under the influence of certain external stimuli or factors including ultraviolet radiation from sunlight, chemical stressors (cations, pesticides), and microbial infections. Phenylalanine is a precursor for phenolic compound

synthesis in plants. Typically, phenylalanine is deaminated to cinnamate through phenylalanine ammonia-lysase catalysis. A hydroxylation process catalysed by cinnamate-4-hydroxylase then results in the conversion of cinnamate to coumaric acid which becomes the starting material for the synthesis of stilbenes, flavonoids and furanocoumarines including other classes of phenolics catalysed by different enzymes [20]. These compounds are stored in the leaves, roots and stems of plants. Roots and leave exudates of plants contain these phenolic compounds, which are finally introduced into the soil by the exudates. Decomposition of dead leaves, roots and plants also introduces the phenolic compounds into the soil. Runoff from land then washes these compounds into the nearby water bodies.

3.2. Anthropogenic sources

3.2.1. Industrial waste

Phenolic compounds have varied applications in the day-to-day lives of human beings. Phenol is widely used in different industries such as the chemical industry where it is used in the production of other derivatives such as alkylphenols, cresols, aniline and resins [21]. Its application in the oil and gas and coal industries is also noteworthy [1]. Phenolic resins, which are also produced from phenol, are used heavily in appliance, wood and construction industries for various purposes. Dyes, textiles and explosive industries all depend on phenol as raw material. Other phenolic compounds such as bisphenol A serves as the raw material from which non-polymer additives, polycarbonate plastics and epoxy resins are manufactured. Nylon 6 (polycaprolactam) and some fibres (synthetic) are produced using caprolactam as raw material [22]. Phenolic compounds are also constituents of some pesticides and other insecticides. Other industrial activities such as wood distillation, use of chlorine for water disinfection, cooking processes and paper production all result in the formation of chlorophenols [23]. Direct or indirect discharge of effluents and/or influents from these industrial activities into water bodies culminate in their pollution with phenolic compounds. Some of these compounds are also released into the atmosphere through vehicular activities and are finally washed into water bodies as rain water.

3.2.2. Agricultural waste

Application of pesticides, insecticides and herbicides constitutes the main source of water pollution with phenolic compounds through the agricultural source. Availability or detection of phenol and some chlorophenols such as 2-chlorophenol, 2,4-dichlorophenol and some catechols in the aquatic environment have been attributed to biodegradation of some of these pesticides. Among these pesticides are 2,4-dichlorophenoxyacetic acid, 4-chloro-2-methyl-phenoxyacetic acid, 2,4,5-richloro-phenoxy acetic acid [24, 25]. Another pesticide vastly used in the agricultural sector is pentachlorophenol which finally degrades to other chlorophenols with lower chlorine substituents [26]. These herbicides, fungicides, and pesticides with their degradation by-products are washed into the water bodies through agricultural runoff.

3.2.3. Domestic waste

Phenol is a component of many household chemicals. It is present in disinfectants, antiseptics and slimicides. Medical or pharmaceutical products including body lotions, ointments,

mouthwashes and some oral sprays meant for anaesthetic purposes or for sore throat treat-ment all contain phenol. Phenol is also present in other household products such as soaps, toys, paints, lacquers, perfumes and varnish removers [13]. Household wastewater, which invariably contains these products, is usually drained through the sinks or gutter, and finally, enter nearby water bodies contaminating them.

3.2.4. Municipal waste

Effluents and influents emanating from municipal waste treatment plants, and leachates from municipal solid waste landfill sites, are another source of phenolic compounds into water bod-ies. p-Cresols have been identified in leachates from a municipal waste landfill site and are believed to originate from incineration residues. Similarly, 2,4,6-trichlorophenol, 4-tertrabutyl-phenol and bisphenol A were also found in leachates and are believed to emanate from fly ash while combustibles were deemed to be the source of 4-tert-octylphenol in landfill leachates. Some chlorophenols, 4-nonylphenol and phenol have all been identified in municipal waste landfill sites [27]. Thus, the release of untreated leachates from landfill sites, the release of resi-dues of incineration such as solid fly ash and the release of incombustible materials into nearby water bodies result in the pollution of the aquatic environments with phenolic compounds.

4. Reactivity of phenolic compounds in aquatic environment

As a result of their high reactivity, phenolic compounds present in water have high tenden-cies of interacting or reacting with other components of the aquatic environment. Among these components are inorganic compounds and microorganisms.

4.1. Interaction with microorganisms

In the aquatic environment, certain bacteria are known to degrade non-ionic surfactants into other phenolic compounds such as alkylphenolic compounds, most of which tend to be more toxic or harmful compared to the original compounds. For example, bacterial deg-radation of nonylphenol polyethoxylate surfactant results in the formation of nonylphenol. There is also evidence of microbial degradation of nonylphenoxyacetic acid into nitrophenol. Bacteria conversion of nonylphenol polyehoxylaes into other intermediate forms is also iden-tified to occur under certain specific environmental and chemical conditions. Nonylphenol polyehoxylaes are converted to nitrophenols under anaerobic conditions [28], and additional conversion of nitrophenol by iso-substitution occurs under aerobic conditions [29]. Microbial interaction with 4-chlorophenoxyacetic acid results in the production of 4-chlorophenol. Pentachlorophenol degradation by bacteria produces tetrachlorocatechol which can undergo further degradation to form chlorinated catechols. Chlorocatechol was also identified to be the microbial degradation product of chlorobenzenes [30].

4.2. Interaction with inorganic compounds

Ultraviolet radiation from the sun initiates a reaction between phenol and nitrite ions in the aquatic environment resulting in the formation of 2-nitrophenol and 4-nitrophenol [31]. In a

similar manner, the interaction between hydroxyl radical and phenol in water produces 2-nitrophenol [32]. Conversion of phenol to nitrophenol also occurs with the availability of nitric ions. Photolysis of phenol in the presence of charge transfer complexes results in the formation of hydroquinone, while the formation of chlorophenol occurs through chlorination of aromatic compounds in water [33]. Some phenolic compounds also coordinate with metal cations of water enhancing their ionisation with the subsequent increase in their solubility in water [34].

5. Toxic effects of phenolic compounds on humans

Most phenolic compounds can easily penetrate the skin through absorption and can readily be absorbed from the gastrointestinal tract of humans. Once in the system, they undergo metabolism and transform to various reactive intermediate forms particularly quinone moieties, which can easily form covalent bonds with proteins, resulting in their ability to exert toxic effects on humans [35].

Chlorophenols, aminophenols, chlorocatechols, nitrophenols, methylphenols and other phenolic compounds have all been characterised as exerting toxic influence on humans [36]. Bisphenol A and some alkylphenols have been identified to exert endocrine disrupting effects on humans by altering the development of mammary glands in exposed animals [37]. Similar work also discloses the tendency of bisphenol A to delay the onset of puberty in girls [38]. Consumption of liquids, including drinking water, containing a high concentration of phenol results in problems with the gastrointestinal tract and muscle tremor with difficulty in walking. Application of products containing a high concentration of phenol to the skin causes blisters and burns on the skin; heart, kidneys, and liver damage may occur with exposure to high levels of phenol [39]. Because of their tendency to readily oxidise to quinone radicals, which tend to be more reactive, catechols have the tendency to cause DNA damage or arylation, destroy some proteins in the body and disrupt transportation of electrons in energy transducing membranes [35]. Caffeic and dihydrocaffeic acids, in the presence of copper, also cause damage to DNA [40]. Chlorophenol poisoning causes mouth burning, throat burning and necrotic lesions in the mouth, stomach and oesophagus. It also induces abnormal temperature and pulse fluctuation, weak muscles and convulsions [41]. Other effects of chlorophenol poisoning include damage to the liver, kidneys, lungs, skin and the digestive tract [42]. Hydroquinone also damages chromosomes. Para-cresol and 2,4-dimethyl phenol have been classified as a chemical with the potential of inducing carcinogenic effects [43].

6. Techniques for the removal of phenolic compounds from water

Recovery of phenolic compounds from the aquatic environment is a mandatory requirement in order to safeguard the life of humans and aquatic organisms through possible contamination of these toxic chemicals. Deployment of appropriate technologies for effective removal of these compounds will not only eliminate problems of possible harm associated with pollutants, as well as waste disposal problems, but also allow the attainment of value-added

phenolic compounds as by-products. This section, therefore, discusses various techniques being employed to effectively eliminate phenolic compounds from wastewater prior to their final discharge into water bodies.

6.1. Photocatalytic degradation of phenolic compounds

Photocatalytic degradation is the use of metal oxide catalysts to degrade pollutants where the catalyst is usually activated by absorption of a photon of appropriate energy and is capable of speeding up the reaction without being used up [44]. Photocatalytic properties of metal oxide catalysts are due to the fact that excitation of electrons from the valence to the conduction band of the catalyst occurs upon its irradiation with a light of appropriate wavelength. Promotion of the electrons (e^-) creates positive charges or holes (h^+) on the valence band, and accumulation of electrons on the conduction band of the catalyst. Generation of these charge carriers (e^- and h^+) initiates the photocatalytic degradation process. The valence band holes attack and the oxidised surface absorbs water molecules to form hydroxyl radicals ($OH^\bullet$). Conduction band electrons reduce oxygen molecules and produce oxygen radicals or superoxide radicals ($O_2^\bullet$). These highly reactive radicals then attack and convert the pollutants to harmless products such as carbon dioxide and water [45, 46].

Photocatalytic degradation is regarded as an efficient technique for the elimination of pollutants from polluted water as a result of its ability to completely degrade the pollutant instead of their transformation into other products. The degree of effectiveness of the degradation process is known to rely heavily on the catalyst dose, exposure time, solution pH and light intensity [47].

There have been a number of reports where photocatalytic degradation techniques have been utilised effectively to degrade phenol and its derivative from the water. Natural clinoptilolite zeolite and FeO-based nanoparticles were used by Mirian and Nezamzadeh-Ejhieh [48] in photocatalytic degradation of phenol in polluted water under simulated solar light irradiation. The results confirmed that using zeolite as a support for FeO enhanced its photocatalytic degradation efficiency. The improved photocatalytic activity of the FeO-zeolite composite was attributed to the fact that the zeolite prevented agglomeration of the FeO nanoparticles and minimised the charge carrier recombination rate. In their study, Shahrezaei et al. [49] explored the photocatalytic degradation ability of TiO_2 in the degradation of phenolic compounds present in wastewater from a refinery. Highest degradation efficiency of the phenol and its derivatives was identified at an optimum temperature of 318 K, pH 3 and 100 mg/l catalyst concentration. A 90% degradation efficiency of phenol was achieved within 2 hours at these optimum conditions. Photocatalytic degradation of phenolic compounds from wastewater has also been demonstrated by many researchers using various catalysts including TiO_2/reduced graphene [50], ZnO [51], Fe_2O_3 decorated on carbon nanotubes [52] and CuO [53].

6.2. Ozonation

Ozone (O_3) is formed naturally when ultraviolet (UV) rays from the sun enter the earth's atmosphere. It is also formed whenever lightning strikes during a thunderstorm. Under

these conditions, oxygen molecules (O_2) split to form highly reactive oxygen radicals ($O^{\bullet}$), which in turn react with O_2 to form ozone. Ozone has a very high oxidising potential (-2.74 V) which is much higher than that of hypochlorite ion (-1.49 V) and chlorine (-1.36 V) [54] which are all employed as oxidants for pollutant removal from water. This high oxidation potential forms the basis of the use of ozone as an oxidant for removal of organic pollutants from water.

Ozonation process begins with the formation of ozone through corona discharge simulation of lightning, or the use of UV-type ozone generator for simulation of ultraviolet radiation from the sun, by passing clean and dry air through high voltage ozone generators. The waste-water is then allowed to flow along a venture throat, which generates a vacuum and pulls the ozone into the wastewater, or the ozone is simply bubbled up through the wastewater. The ozone then oxidises and decomposes the pollutants leading to their elimination from the water. UV ozonation is mostly used for small-volume wastewater treatment while the corona discharge method is employed in large-scale wastewater treatment processes. Some advantages of ozonation include [55]:

(1) The process is completely natural with no inclusion of chemicals and produces no chemical waste.

(2) High microorganism elimination efficiency with the microorganisms having no potential to developing resistance against ozone.

(3) The process is self-sustaining as the main source of ozone is oxygen from the air.

(4) Ability to remove organic, inorganic, microorganism and improve taste and odour of the water.

Based on the above advantages, several research works have been performed on the use of ozonation technique for phenolic compounds removal from wastewater. Treatment of olive mill wastewaters containing garlic, p-hydroxybenzoic and p-coumaric acids based on ozonation was studied by Chedeville et al. [56]. They identified that the highest ozonation process was attained when the gas-liquid contractor was adopted to HaN_3 regime. The gas/liquid contractor used permitted a comprehensive removal of the phenolic compounds within a short time. A maximum of 80% of the pollutants was eliminated with up to 95% ozone mass transfer. Ozonation was also used to treat ethylene glycol containing wastewaters with emphasis on the impacts of pollutant dose, process time, and pH on the decontamination efficacy. After 180 min, ethylene glycol removal efficiencies were 93.31, 89.96 and 85.01% at 10, 20 and 50 mg/l pollutant concentrations, respectively. Removal efficiency was observed to be highest in alkaline medium [57].

6.3. Extraction method

Among the techniques used for removal of phenolics from water is extraction using polar organic solvents. The extraction method of phenolics removal from wastewater can be categorised as liquid-liquid extraction and solid phase extraction.

6.3.1. The liquid-liquid extraction method

This technique separates compounds on the basis of their solubilities in two immiscible liquids. The compounds are normally separated from one liquid phase to another. The immiscible liquids usually consist of water and an organic solvent.

The liquid-liquid extraction method was used by Rao et al. [58] to remove phenol from sebacic wastewater. The experiment was performed using batch, and serial approaches through the application of different solvents such as Aliquat-336, 1-hexanol, 1-octanol, 1-heptanol and castor oil. The extinction experiment which involved shaking and allowing for phase separation resulted in 75–96% extraction of phenol with the different solvents, where the solvent and the wastewater were mixed in a ratio of 5:250. The extraction efficiency was observed to vary according to the ratio of the solvent used. The best solvent for phenol extraction was Aliquat 336. Liu et al. [59] also used cumene to extract phenol from water. Cumene showed excellent extraction performance on phenol in acidic solution. The distribution coefficient was observed to be directly proportional to the temperature but decreased with increasing pH value.

6.3.2. Solid phase extraction method

Despite the efficiency of liquid-liquid extraction method of removal of chemicals from wastewater, the technique comparatively consumes a lot of time and is expensive with possible associated injuries from the large quantity of organic solvents (some toxic) used in the process. Solid phase extraction technique, which requires minimal time and organic solvents, highly selective and environmentally friendly, is therefore regarded as an appropriate alternative for liquid-liquid extraction method [5].

Solid phase extraction system consists of a syringe containing a merged silica fibre, which is coated with an immobilised phase. The aqueous solution containing the analyte is exposed to the fibre with the subsequent accumulation of the analyte on the stationary phase. The fibre is then removed from the aqueous solution followed by desorption of the extracted analyte in a column injector or gas chromatography. Polydimethylsiloxane is normally used as the stationary phase for removal of halogenated and polycyclic aromatic hydrocarbons and polychlorinated biphenyls [60].

Möder et al. [61] used a polyacrylate-coated fibre as a solid phase extractant for phenolic compound elimination from wastewater. Effects of humic acid and surfactant concentrations on the extraction efficiency were analysed. They attributed the successful extraction of naphthols, alkylated phenols and Tetra-ols from the wastewater to the fact that the polyacrylate coating demonstrated high specificity for polar hydroxylated aromatic compounds. Non-polar molecules hardly interacted with the extractant within the optimum 45 min extraction time. Another experiment on solid-phase extraction of phenols from wastewater was carried out by Tavallali and Shiri [62]. Their study involved the use of iron oxide nanoparticles modified with activated carbon as the solid adsorbent. They demonstrated that development of solid phase extraction method based on magnetised activated carbon prior to their spectrophotometric determination is an appropriate technique. Their result showed 98% removal of phenol from water, indicating the effectiveness of the iron oxide nanoparticle modified activated carbon solid adsorbent.

6.4. Biological method

Biological method of phenolic compound removal from wastewater is subdivided into microbial and enzymatic methods. The microbial method involves the deployment of bacteria, yeast and fungi in breaking down the phenolics into harmless products such as carbon dioxide and water. This method of phenolics removal is feasible as a result of the fact that some microorganisms are known to depend on aromatic compounds, including phenolics, as their source of carbon or nutrient [63, 64]. It has the advantage of a comparatively low operational cost. Microbial removal of phenolic compounds occurs through either aerobic or anaerobic processes and begins with hydroxylation (introduction of hydroxyl groups) of the aromatic ring [65]. Hydroxylation through aerobic degradation involves two steps with catechol being the end product [66]:

(1) Reduction of one of the molecular oxygen to water under the influence of a hydrogen donor (reduced pyrimidine nucleotide), and devouring of the other oxygen atom.

(2) The second step of the hydroxylation process occurs in the presence of dioxygenase enzyme with the subsequent formation of catechols.

Cleavage of the catechol aromatic rings then passes through various stages with specific enzymes, based on the type of microorganisms, resulting in the conversion of the phenolic compounds to compounds such as carbon dioxide and water [67]. Anaerobic degradation occurs whenever oxidising agents such as sulphates, nitrates and CO_2, or light are present. This process is believed to be initiated by carboxylation of phenol to 4-hydroxybenzoate [68].

In general, the aerobic process is known to be better suited for the degradation of phenolics with minimal substituents consisting of halogens. On the other hand, the anaerobic process is mostly appropriate for reduction of chlorinated phenolic compounds [69]. The anaerobic system produces methane in addition to carbon dioxide and water. A major advantage of the anaerobic system of degradation is the absence of aeration cost, recovery of methane and minimum excess biomass generation [70].

Kukadiya et al. [71] studied the effectiveness of using a moving bed biofilm reactor for phenolic compounds removal from wastewater. The laboratory scale model moving bed biofilm reactor was observed to be effective against the removal of phenol with about 98% efficiency. In their experiment, Sinha et al. [72] studied the p-chlorophenol and phenol microbial degradation as a single and mixed substrates by using *Rhodococcus* sp. RSP8 bacteria strain. The experiment was performed with a liquid mineral salt medium in a shake flask experiment at a neutral pH and a temperature of 37 °C. The two compounds (p-chlorophenol and phenol) served as the main source of carbon and energy for the cells and were consumed completely as individual solutions by the cells. The two pollutants, however, repressed each other's degradation by the cells in the mixed substrate experiment.

The enzymatic method of degradation, however, employs enzymes (biological catalysts). Enzymes can be used effectively to selectively eliminate pollutants in water since they catalyse specific reactions under modest temperature, pH and ionic strengths [73]. In addition, the enzymatic reaction is known to occur at much faster rates compared to other types of reactions [74]. As an advantage over the microbial system of pollutant degradation, the

enzymatic system of pollutant removal can occur under conditions, which are unfavourable or toxic to bacteria. This system can operate under different pollutant concentration (high or low), eliminates the time requirement for biomass acclimatisation, involves no shock loading effect and with no generated biomass [74]. This method receives a high level of consideration due to its high pollutant removal efficiency, operation in wide temperature and pressure ranges and formation of harmless end products [75, 76]. The enzyme with a high promise for dephenolisation of phenolics in water is tyrosinase (KF1.14.18.1). This enzyme oxidises the phenolics to quinones, which are further broken down into the non-toxic intermediate product. The intermediate products are then removed through the addition of binding agents [77].

There has been a series of reported research works where enzymes have been used for the removal of phenolic compounds from wastewater [78, 79]. Among these reports is the work done by Shesterenko and co-workers [79]. They used tyrosinase isolated from *Agaricus bisporus* and immobilised it on polymer carriers, and inorganic coagulants to remove phenols from water. Peroxidase extracted from horseradish, hydrogen peroxide and polyethylene glycol (PEG) was also used to catalyse phenol removal from simulated wastewater [80]. Optimum degradation of 1 mM phenol (80%) was attained at 0.3 U/ml horseradish peroxidase and 3.0 mM hydrogen peroxide concentrations at pH 7 and 273 mg/l of PEG.

6.5. Adsorption

Adsorption is considered as one of the appropriate techniques for removal of phenolics from water because the technique is easy to design and operate. The technique produces no toxic wastes. The spent sorbent can serve as a source fuel to produce power [81]. Adsorption process involves the accumulation of the pollutant on the adsorbent's surface (usually solid material). An appropriate adsorbent must be porous with large surface area, possess high hydrophobicity and have the ability to selectively accumulate the pollutant from water onto its surface. Efficiency of the adsorption process is governed by [82]:

(1) Adsorbent's properties, i.e. its functional group composition, the size of its surface area together with the distribution of the pore size and the extent of its ash content.

(2) The solution chemistry including its pH, temperature, degree of polarity, availability of other solutes competing for the adsorbent surface area and the concentration of the adsorbate.

(3) Nature of the adsorbate. This includes its degree of solubility in water, hydrophobicity, size and molecular weight.

Reference [82] found phenol adsorption process to be solely dependent on the initial pollutant concentration and speciation, which in turn depends on pH of the solution. Adsorption of pollutants from water is believed to be based on the following steps [83]:

(1) Movement of the pollutant molecules towards the adsorbent across the external boundary layer.

(2) Movement of the pollutant molecules to the adsorbent's active surface sites.

(3)   Adsorption of the pollutants on the active surface sites.

(4)   Migration of the adsorbed pollutants through diffusion onto the pores' surfaces.

Various researchers have studied phenol adsorption from polluted water with different types of adsorbents. Phenol adsorption efficiency of different adsorbents including bagasse ash, activated carbon and charcoal from wastewater was studied by [84]. The adsorption efficiency was assessed based on the influence of pH, concentration of EDTA, anions and adsorbent dose. Their result showed 98, 90 and 90% phenol removal efficiencies by activated carbon, wood charcoal and bagasse ash systems, respectively. Removal efficiency was observed to increase with a decrease in the pH of the system. Effects of EDTA and nitrate ion content of the solution were identified as the factors that influenced the adsorption process. Chloride ion, on the other hand, exerted a significant adverse effect on the efficiency of bagasse ash system. Film diffusion was noted to control the adsorption efficiencies of all the adsorbents used. Similarly, the use of sugarcane bagasse-based activated carbons for effective phenol adsorption from aqueous medium was assessed by Akl et al. [85]. The result of the study proposed sugarcane bagasse-based activated carbon (SCBAC) as a viable adsorbent for phenol elimination from water. The pollutant eradication process depended solely on its concentration, solution pH and temperature.

6.6. Membrane-based separation method

A membrane is a specific type of a barrier that enables the separation of species in a gas or liquid through various mechanisms such as diffusion, sieving or sorption. The selective separation occurs as a result of the semipermeable nature of the membranes. This is the ability of the membrane to allow the passage of certain substances through it while it prevents the passage of others based on their sizes and/or molecular weights. Thus, in membrane-based separation method of water purification, the water usually passes through the membrane while the suspended pollutant, usually with comparatively larger sizes and molecular weights, is unable to pass through the membrane. They get retained in the medium or on the membrane and later removed.

Membrane separation is a general term used to encompass different types of separation processes that are characteristically the same or similar since they all use membranes. The difference lies in the pore size of the membranes and the driving force involved in the separation process. The driving forces for separation may include high pressure application, the creation of concentration gradient and the use of electric potential [86]. These processes are categorised as microfiltration, ultrafiltration, nanofiltration and reverse osmosis [87]:

- Microfiltration: The membrane's pore size of this technique ranges from 0.1 to 1.0 μm. It is normally used to filter suspended particles or colloidal solutions with large particles and bacteria.

- Ultrafiltration: The pore diameter of this type of membrane ranges from 0.01 to 0.1 μm and can be used for filtration macromolecules such as polymers and proteins from solution.

- Nanofiltration: The pore size range of this type of membrane is 1–10 nm. It is used for brackish water desalination and removal of micropollutants or metal ions.

- Reverse osmosis: This refers to a membrane with pore diameters in the range of 0.0001–0.0001 µm and may be used for filtration of solutions of polymer chains, ultrapure water production and desalination of sea and brackish water.

An ideal membrane system must have good fluxes and be highly selective. It must have excellent thermal, chemical and mechanical stability with low tendency of foul formation. Some advantages of membrane system of water purification include the following [87]:

(1) It has comparatively low energy requirements.

(2) It is simple, easy to use with low maintenance requirements.

(3) It is highly selective to the material to be separated.

(4) It is environmentally friendly as the system works without the addition of chemicals.

The technology is also not without disadvantages. Some of these disadvantages include [88]:

(1) Many membranes composed of polymeric materials can decompose, or swell or become weak under harsh conditions, thereby weakening the selectivity, and shortening the lifespan of the membrane.

(2) Some of the membranes based on polymeric material have temperature limitation as most of these polymers are unable to maintain their properties at temperatures above 100°C.

(3) Membrane fouling also occurs and interferes with the permeability of the membrane.

Phenol has been separated from water with membrane-based separation technique by using non-modified, and ionically, and covalently cross-linked ethylene methacrylic acid copolymer-based membranes [89]. They found out that the total flux increased with increasing phenol content in the feed while the enrichment factor decreased. They, however, observed lesser fluxes and higher enrichment factors when non-modified membrane containing a higher amount of methacrylic acid monomer was used. Ionic cross-linked membrane proved to be the most efficient membrane against the feed containing a high concentration of phenol.

Use of ionic liquids in the form of bulk liquid membranes for the elimination of phenol from water has also been studied by Ng et al. [90]. High hydrophobic ionic liquids including 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide and 1-butyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate were used for the experiment. The stability, membrane loss and phenol elimination efficiency of these liquids were compared. Their results identified 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide as the best performing liquid in terms of phenol elimination and stripping efficiencies. This liquid exhibited phenol extraction efficiency of 96.21% and stripping efficiency of 98.10%. These values were attained at optimum conditions of 225 and 135 rpm aqueous and membrane stirring speed, respectively.

This solvent was identified to possess higher hydrogen bonding, basicity and low viscosity compared to the other two solvents used.

6.7. Electro-Fenton method

Fenton reaction is a reaction between iron (II) and hydrogen peroxide resulting in the formation of hydroxyl radicals (OH$^\bullet$), a non-selective and strong oxidising agent [91]. As a result, this process has been used to oxidise organic pollutants in aqueous solution to carbon dioxide and water. However, Fenton process has the disadvantage of the high cost of procuring the reactants (hydrogen peroxide and iron (II)) and sludge generation. An improved technique, electro-Fenton process, which is capable of overcoming the above-mentioned hindrances and permits improved control of hydroxyl radical generation [92], has therefore been devised. Electro-Fenton process involves cathodic reduction of iron (III) in solution to iron (II) with a potential of E^o = 0.77 V/SHE. This process, often referred to as electrochemical catalysis, produces the iron (II) at a faster rate and thus promotes the production of hydroxyl radical for enhanced pollutant oxidation process [92].

Evaluation of the electro-Fenton process as an appropriate substitute technique for elimination of phenol from a phenol simulated wastewater was conducted by Abdelaziz et al. [93]. They used a sacrificial iron anode as the source of iron (II), added hydrogen peroxide to the system externally and used nitrogen gas sparging to stir the batch reactor. They also examined the influence of some factors on the effectiveness of the electro-Fenton process. Their results revealed 97% overall COD reduction of 50 mg/l pollutant concentration at optimum conditions of pH 3, the superficial gas velocity of 1.18 cm/s, current density (1.7 mA/cm^2) and hydrogen peroxide concentration of 1500 mg/l. They observed that COD removal percentage increased with increasing current density, hydrogen peroxide concentration and sodium chloride concentrations but started decreasing, in all cases, beyond their respective optimum values. In addition, consumption of energy and iron decreased as the initial pollutant (phenol) and sodium hydroxide concentrations were increased, but increased with an increase in the current density.

In their study, where they investigated the effectiveness of the electron-Fenton process for removal of COD from paper mill wastewater, Un et al. [94] concluded that electro-Fenton process is effective for removal of COD from tissue paper waste water. They achieved a COD removal efficiency of 80% within 60 min at 20 mA/cm^2 current density with 0.1 M hydrogen peroxide concentration at pH 2. They noticed that though increasing the current density caused a corresponding increase in the COD removal, it also resulted in increasing energy consumption. Similarly, Rahmani et al. [95] have effectively applied the electro-Fenton technique to degrade phenol from aqueous solution. In this study, they applied a disposable iron anode as the source of ferrous iron and added the hydrogen peroxide manually. Highest degradation efficiency of 100% was obtained within 30 minutes at pH 3, 100 mg/l hydrogen peroxide concentration and 5 mA/cm^2 optimum conditions.

6.8. Adsorption and ion exchange

In an ion exchange process, an interchange of ions between two phases, usually a solid and a liquid phase, occurs. The ion change resin forms the solid phase while the sample under

consideration is normally in the liquid phase. A typical ion exchange resin comprises a cross-linked polymer network with its surface covered with a uniform distribution of ions. Ions with charges similar to that of the resin are exchanged once the solution containing the ions comes into contact with the ion exchanger. The degree to which the ions are exchanged is governed by the concentration of the ions in solution (ions to be exchanged with the resin) and their degree of affinity for the ion exchange resin. The ion exchange process is reversible and is deemed as one of the unique technologies for wastewater treatment because of its high degree of recyclability and environmentally friendly nature [96]. The use of polymer-based anionic resins can allow successful elimination of phenolic compounds from polluted water through adsorption in conjunction with ion exchange. The ions of the resin provide sites for ion exchange while the porous nature permits adsorption through hydrophobic interaction [97].

The efficiency of phenol exclusion from polluted water involving the use of Amberlyst A26 and Amberlite IRA-67 as strong and weak base ion exchangers, respectively, has been conducted. As an observation, phenol removal efficiency of both the strong and weak base ion exchange resins decreased significantly with increased initial phenol concentration from 99.6% (1 mg/l phenol concentration) to 74.2% of 200 mg/l (strong base), and from 65.7% 1 mg/l phenol concentration to 22.1% of 200 mg/l phenol concentration (weak acid). The strong base ion exchange (Amberlyst A26) was considered to be a better ion exchange medium for phenol removal compared to Amberlite IRA-67 [98].

The use of Amberlite IRA-420, a strong base ion exchange resin, for the removal of phenol from water was also carried out by Carmona et al. [99]. Both theoretical and empirical approaches were used to identify the parameters that governed the rate at which the Amberlite IRA-420 removed phenol from the solution. According to their results, the phenol elimination process with Amberlite IRA-420 occurred in the acidic medium through adsorption, and in the alkaline medium through both adsorption and ion exchange. The process increased with increasing pH values from 9 to 14. Ahmed et al. [100] also compared the phenolic compound removal effectiveness of four different ion exchange resins, namely, Ameberlite XAD-4, Ameberlite XAD-7, Ameberlite IRA-94 and Ionac AFP-329, and observed that the effectiveness of the degradation process depended on the size of the resins' surface area and temperature. Ionac AFP-329 was the most efficient sample. However, Ameberlite XAD-4 demonstrated the highest desorption ability with almost complete pollutant recovery at 60 °C.

7. Conclusion

The rapid increase in industrial and domestic activities as a result of the desire to meet the demands of the ever-increasing human population creates the possibility of phenolic compounds introduction into water bodies. Extensive research has been performed on these compounds resulting in the elucidation of their structure or classification, their sources of entry into the aquatic environment and their reactivity or interaction with other components of the aquatic environment. Research has also unveiled the significant toxic effects that these compounds exert on humans and wildlife upon exposure. Significant efforts have been made

for the total elimination of phenolic compounds from water before use. This resulted in the development of water treatment technologies including the conventional methods such as activated carbon adsorption, solvent extraction and advanced technologies such as electro-Fenton method, membrane-based separation method, photocatalysis and so on, which have all been successfully used for removal of phenolic compounds from water.

Author details

William W. Anku, Messai A. Mamo* and Penny P. Govender*

*Address all correspondence to: messaim@uj.ac.za and pennyg@uj.ac.za

Department of Applied Chemistry, University of Johannesburg, Doornfontein, Johannesburg, South Africa

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