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A Short Review of Techniques for Phenol Removal from Wastewater

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Abstract Phenolic compounds are priority pollutants with high toxicity even at low concentrations. In this review, the efficiency of both conventional and advanced treatment methods is discussed. The applicability of these treatments with phenol and some common derivatives is compared. Conventional treatments such as distillation, absorption, extraction, chemical oxidation, and electrochemical oxidation show high efficiencies with various phenolic compounds, while advanced treatments such as Fenton processes, ozonation, wet air oxidation, and photochemical treatment use less chemicals compared to the conventional ones but have high energy costs. Compared to physicochemical treatment, biological treatment is environmentally friendly and energy saving, but it cannot treat high concentration pollutants. Enzymatic treatment has proven to be the best way to treat various phenolic compounds under mild conditions with different enzymes such as peroxidases, laccases, and tyrosinases. This review covers papers from 2013 through January 2016.

Keywords Phenol · Remediation · Wastewater · Hazardous · Treatment · Degradation

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Introduction

Phenolic compounds are present in the effluents of various industries such as oil refining, petrochemicals, pharmaceuticals, coking operations, resin manufacturing, plastics, paint, pulp, paper, and wood products [1–3]. Discharge of these compounds without treatment may lead to serious health risks to humans, animals, and aquatic systems [1]. Phenol has been designated as a priority pollutant by the US Environmental Protection Agency (EPA) and the National Pollutant Release Inventory (NPRI) of Canada [4, 5]. International regulatory bodies have set strict discharge limits for phenols for a sustainable environment [1]. For example, the EPA has set a water purity standard of less than 1 ppb for phenol in surface water [2]. The toxicity levels usually are in the range 9–25 mg/L for both humans and aquatic life [6]. Phenol possesses hazardous health effects that can be both acute and chronic. Long-term exposure can lead to irregular breathing, muscle weakness, tremor, coma, and respiratory arrest at lethal doses in humans. Human exposure to phenol results in the irritation of the skin, eyes, and mucous membranes. Chronic effects due to phenol exposure can be anorexia, weight loss, diarrhea, vertigo, salivation, and a dark coloration of the urine. Chronic exposure to phenols leads to irritation in the gastrointestinal and central nervous systems and liver, kidney, and cardiovascular tissues in animals [3, 7, 8]. Animal studies have shown fetal body weight reduction, growth retardation, and abnormal development in the offspring. Thus, there is a need to treat wastewater affected with phenolic compounds before discharge. Phenol exists in common derivatives such as Bisphenol A (BPA) [9], chlorophenols (CPs), and phenolic endocrine disrupting compounds [10]. The technologies described in this paper for removing phenols from industrial wastewater are classified as conventional and advanced methods.

Conventional methods have been applied such as steam distillation, liquid-liquid extraction, adsorption, solid-phase extraction, wet air oxidation, catalytic wet air oxidation, and biodegradation for removal of phenols.

Advanced technologies for removal of phenols include electrochemical oxidation, photo-oxidation, ozonation, UV/ H_2O_2, Fenton reaction, membrane processes and enzymatic treatment [3, 4, 6]. The time frame for this review was from 2013 through January 2016.

Distillation

Distillation technologies for removal of phenols from water are all variants of steam distillation and thus have an energy requirement to be economically met. The technologies are either destructive or non-destructive, the latter allowing for recovery of the phenolics [11]. Steam or azeotropic distillation based on the relative volatility of phenol is capable of purifying water containing phenol impurities [3]. In another study, aqueous phenol solution was directly introduced into a novel steam plasma torch (steam plasma jet treatment), and phenol was rapidly decomposed in the thermal plasma jet, by the production of hydroxyl radicals that caused oxidative degradation of organic pollutants in aqueous solutions [12]. The primary intermediates formed from phenol were pyrocatechol, hydroquinone, maleic acid, butanedioic acid, and muconic acid in the liquid phase, while the major gaseous products were H_2, CO, and CO_2. Steam thermal plasmas have high enthalpy and activity while, at the same time, they are eco-friendly, which makes them popular in the field of environmental remediation.

Olive mill wastewater (OMW) is noted for its high organic load and the presence of phenolic compounds. Sklavos et al. used a solar distillation apparatus to investigate the solar drying of OMW and the recovery of phenolic compounds with antioxidant properties in the distillate. More than 50 types of phenolic compounds have been identified in OMW of which hydroxytyrosol and tyrosol are the two most common phenolic compounds detected. These two compounds have the capability to protect low-density lipoprotein (LDL) particles from oxidative damage and have been approved by the European Food Safety Authority. Solar distillation parameters like temperature of the ambient air, vapor pressure inside the apparatus, phenolic recovery, retentate (sludge) production, and solar radiation were monitored during the experiments. Solar distillation also effected OMW dewatering within a very short time. Thus, solar distillation was suggested as an economical and eco-friendly process [13•].

Adsorption and Extraction

Adsorption and extraction technologies for removal of phenols from water are effective from trace concentrations to percent concentrations, depending on the economics (including energy) of using and recycling the required secondary material, adsorbent, or extractant. Activated carbon is the most used and a highly efficient adsorption method. It is expensive but has been shown to be effective for removal of trace organic compounds [14, 15•]. Therefore, new options are being developed including chemical modification of the activated carbon, impregnation with nanoparticles, different sources of carbon, different activation methods, as well as substitution with low-cost biosorbents, such as lignocellulose and chitin/chitosan, which are promising alternatives to remove phenolic compounds [15•, 16–19]. Nadavala et al. studied the adsorption of phenolic compounds using pine bark, a lignocellulosic waste from forestry. The optimal pH was 6, reaching biosorption equilibrium in 120 min, with a total biosorption capacity for phenol of 143 mg/g [17]. Another possible option is the combination of activated carbon with a biosorbent. For example, Huang et al. used a composite of activated carbon and chitosan (ratio of 1:1) to remove phenol as well as chromium (VI), achieving up to 95 % removal of both, reaching equilibrium in 40 min [20]. A chemical modification of activated carbon was developed by Carvajal-Bernal et al., in which activated carbons of two different types, granular and pelletized, were impregnated with phosphoric acid or potassium hydroxide. Both impregnations modified the surface area, micropore volume, and the volume of mesopores due to reaction with superficial oxygen groups. Phosphoric acid promoted better adsorption of 2,4-dinitrophenol. On the other hand, potassium hydroxide did not show a benefit on the adsorption process [19]. Substances like natural organic matter (NOM) can interfere in the removal of phenolic compounds such as Bisphenol A (BPA). For example, Park et al. impregnated powdered activated carbons (PACs) with different types of iron oxide nanoparticles (IONPACs) to enhance the removal of BPA in the presence of organic matter. The adsorbents were PAC, ferrihydrite/PAC, magnetite/PAC, and hematite/PAC. Electron-microscopic analysis showed that the iron was impregnated in the PAC inner pores not on the surface at 12.6–17.4 mg-Fe/g-PAC. Equilibrium for BPA and NOM on these IONPACs was reached at 150 min. Adsorption of BPA was similar by all the adsorbents used; but for NOM, adsorption was better with the IONPACs. The Freundlich isotherms for both compounds showed greater adsorption for IONPAC adsorbents than for PAC. For example, the Freundlich isotherm coefficient (K_F; which corresponds to the adsorption capacity at unit equilibrium BPA concentration) for PAC was 94.1 and for IONPACs they were in the range 119–270, which means a greater sorption capacity for IONPACs than for bare PAC. It was also found that if the concentration of NOM increased, the

BPA absorbed onto PAC was decreased; however, in the IONPAC, the adsorption capacity was nearly the same in the presence of large amounts of NOM, making it more stable in the presence of organic matter and enhancing the removal of both NOM and BPA [15•].

Liquid-liquid extraction, also known as conventional solvent extraction, is a standard, non-destructive process for treatment of phenolic compounds, suitable over a wide range of phenol concentrations [21]; it is cost-effective in some circumstances. Liu et al. investigated the efficiency of using cumene as extractant for phenol in wastewater. The experiment was carried out with 100 mg/L phenol aqueous solution and three parameters (temperature, pH, and extraction time) were studied. On the one hand, the extraction time did not have much effect on the phenol removal, whereas a change of temperature had an impact on the extent of phenol removal, for example, the phenol removal can increase 5 % with a 30 °C temperature raise. The cumene extraction process was pH-dependent, since phenol ionizes at high pH. The method performed well over a wide range of phenol concentrations (50–2200 mg/L) [22].

Cloud-point extraction (CPE) is based on surfactants separating into two phases (coacervate and bulk aqueous solution) when the solution reaches a certain temperature, known as the cloud point. The phenolic compound will gather in the coacervate and can be separated from the surfactant by pH changes. El-Abbassi et al. used CPE to remove phenolic compounds from pretreated olive mill wastewater. With Triton X-100 as a surfactant, it was found that phenol removal was dependent on both the surfactant concentration and temperature. At a certain temperature above the cloud point (67 °C), the phenol removal extent relied less on surfactant concentration when Triton X-100 concentration was higher than 5 % (w/w). However, increasing temperature achieved a higher removal, for example, when the temperature was raised from 70 to 90 °C, the removal increased 20 % at the same Triton X-100 concentration, due to the phenol solubility change. Phenol removal of 66.5 % (initial phenolic content is 9150 mg/L) was observed using 10 % Triton X-100 at 90 °C [23].

Phenol Removal by Membrane Processes

Membrane technologies are reliable and economically feasible to treat phenol and have many advantages such as low power consumption, high quality effluent, small footprint, and easy scaling up with membrane modules. However, consideration must be given to membrane fouling which can occur due to particles and colloids present in the feed streams [3, 9]. The most important membrane technologies used to remove phenols from wastewater are extractive membrane bioreactors and hollow fiber membranes; photocatalytic membrane reactors; high-pressure membrane

processes such as nanofiltration, reverse osmosis, and pervaporation; and membrane distillation [3, 9, 24].

Extractive Membrane Bioreactors (EMBR) and Hollow Fiber Membranes

An EMBR combines an aqueous-aqueous extractive membrane process and biodegradation to show high potential in treating phenol in wastewater. Loh et al. prepared composite hollow fiber membranes with different levels of polydimethylsiloxane (PDMS) intrusion by coating a layer of PDMS on a polyetherimide (PEI) hollow fiber substrate for phenol removal [24]. Praveen and Loh investigated removal of phenol from wastewater by hollow fiber membranes impregnated with trioctylphosphine oxide (TOPO), which was immobilized in the hollow fiber membrane for removal of phenol. Advantages of this process include compact design and flexible equipment configuration that makes it popular in the field of environmental engineering [25].

Photocatalytic Membrane Reactors (PMRs)

PMRs are hybrid reactors in which photocatalysis is coupled with a membrane separator that acts as a simple barrier for the photocatalyst and, at the same time, a selective barrier for the molecules to be degraded. It is necessary to remove the photocatalyst particles from treated water after degradation [3]. In other work, Vaiano et al. studied the degradation of organic matter present in tannery wastewater by means of an undoped commercial TiO_2 catalyst, Degussa P25, and N-doped titania nanoparticles under UV or visible light irradiation, respectively. It was observed that P25 was only active in the presence of UV light whereas N-doped titania was potent in treating tannery wastewater in the presence of visible light emitted by LEDs [26].

Reverse Osmosis (RO) and Nanofiltration (NF)

RO is a membrane-based demineralization technique that is used to separate dissolved solids, especially ions, mostly from aqueous solutions whereas NF is widely used for removing organic pollutants, inorganic salts, color, and hardness from aqueous solutions [3]. NF is suitable to use in front of an RO unit in order to decrease RO pressures associated with organic matter [27]. Sun et al. investigated pretreatment by microfiltration (MF) or ultrafiltration (UF) membranes prior to NF or RO systems to avoid fouling of membranes [1]. Mnif et al. studied removal and adsorption of phenol from aqueous solutions using a polyamide thin film composite RO membrane. The effects of parameters such as feed concentration, ionic strength, transmembrane pressure, and recovery on the elimination of phenol were studied [28]. Khazaali et al. studied

Bisphenol A (BPA) removal from aqueous solutions using a low-pressure RO system, an improvement over conventional RO, consuming less energy, having a lower pressure requirement, good rejection, and higher water flux [9].

Kumar et al. studied phenol removal from coke-oven wastewater by cross-flow nanofiltration membranes. Four different types of composite polyamide commercial products (Sepro, USA) were tested under different operating conditions such as transmembrane pressure, pH, and recovery rate. It was concluded that nanofiltration had improved efficiency in phenol removal from industrial wastewater [29].

Pervaporation (PV)

In recent times, PV has attracted attention as an alternative means of removal of low volatility organics from wastewater. The characteristic features of PV include minimal energy consumption, no secondary contamination, high efficiency, and easy operation. Generally, water and volatile organic compounds are localized at the feed and permeate side of the membrane, respectively, with simultaneous evaporation of the permeate compound. Membranes like PDMS, urethane polymers, and poly(ether block amide) (PEBA) membranes have been used for phenol removal. Previous research also suggested that PV using a PEBA 2533 membrane can be an alternative way for retrieving phenol from wastewater streams. This membrane showed good selectivity for phenol compared to PDMS and zeolite-filled PDMS membranes [3, 30].

Membrane Distillation (MD)

The MD process is a non-isothermal, membrane-based separation competing with other technologies like RO, which suffer from osmotic pressure limitations [31]. In other work, Mohammadi et al. have studied phenolic wastewater treatment by vacuum membrane distillation (VMD) using the Taguchi optimization approach. A polytetrafluroethylene (PTFE) membrane with a pore size of 0.22 μm was used for the process [32]. Membrane fouling and pore wetting are the major drawbacks of the MD process [31].

Chemical Oxidation

Chemical oxidants provide destructive treatments of aqueous phenols. The processes have low reagent and energy costs, operating under mild conditions (temperature and pH) most commonly in the parts per million range and higher. Ozone, chlorine, chlorine dioxide, chloramines, ferrate [Fe (VI)], and permanganate [Mn (VII)] are the most common chemicals applied in oxidative treatment of wastewater. Permanganate and ferrate have been widely studied and used due to their high reduction potentials $\left(E^{\circ}_{(KMnO_4)} = 1.68\,V, E^{\circ}_{(K_2FeO_4)} = 2.2\,V\right)$. Ferrate has the ability to oxidize various contaminants over a wide range of pH. It reduces to ferric hydroxide which has coagulation/flocculation properties, thus providing better efficiency. On the other hand, permanganate is relatively cheap, easy to handle (including the manganese dioxide sludge produced), stable, and does not form chlorinated or brominated by-products [33–35]. Peings et al. investigated the oxidation mechanism of phenol by sulfatoferrate (VI) and compared it with permanganate and hypochlorite. The experiment was carried out with 30 mg/L of phenol in alkaline solution (pH 9) to avoid ferrate degradation. Complete transformation of phenol was achieved only with excess oxidant. For example, a molar ratio of 10 (oxidant to phenol) decreased TOC by 57 % for K_2FeO_4, 70 % for permanganate, and 61 % for $Ca(Cl0)_2$. The reaction of ferrate (VI) and phenol followed first-order kinetics with respect to both reactants and was not influenced by the presence of impurities. Data from a spin-trapping study confirmed formation of phenoxy radical and hence a radical reaction pathway. In the case of hypochlorite, various amounts of chlorophenolic by-products were observed depending on reactant molar ratio [36].

Formation of brominated polymers by Mn (VII) was evaluated during treatment of water containing bromophenols (BrPs) by Jiang et al. A kinetic study on micromolar BrP solutions with $[MnO_4^{2-}]/[BrP] = 15 - 40$ exhibited a bell-shaped pH dependence of the second-order rate constant [37••], consistent with formation of products following the mechanism demonstrated by Du et al., for chlorophenols [38]. Product analysis suggested C–O and C–C coupling between bromophenoxyl radicals formed through one-electron oxidation of BrPs by Mn (VII) [37••]. The effect of ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)) as a catalyst or mediator on oxidation of substituted phenols by Mn (VII) was studied by the same group. The reaction happens through a one-electron transfer mechanism producing $ABTS^{\bullet+}$ and Mn (VI). $ABTS^{\bullet+}$ quickly oxidizes phenol with a greater rate than that of Mn (VII). ABTS also accelerated Fe (VI) kinetics with phenol but had no effect on milder oxidants such as HOCl due to a lower degree of $ABTS^{\bullet+}$ generation [39].

Oxidation by permanganate has been reported to be very effective in removing endocrine disrupting chemicals like Bisphenol A (BPA). Over 99 % of 5 μM BPA was degraded using 100 μM $KMnO_4$ at pH 7. The reaction rate showed strong dependence on temperature and pH. The proposed reaction pathway was similar to that of BPA ozonation, with the benzene ring being the reaction site in the early stages of oxidation [40].

Electrochemical Oxidation

Electrochemical oxidation is an alternative destructive treatment of aqueous phenols which has no reagent requirement and cost, but does incur equipment and energy costs. As previously reviewed by Martinez–Huitle et al. and Tasic et al., electrochemical oxidation techniques are divided into direct and indirect oxidation. Direct or anodic treatment happens through adsorption of the pollutants onto the anode surface. Various anode materials are used with Pt, PbO_2, SnO_2, IrO_2, and BDD (boron-doped diamond) being the most investigated ones. Parameters such as current density, pH, anode material, and electrolytes used influence treatment efficiency. Degradation of phenol follows pseudo first-order kinetics and the effectiveness of the process is indicated by apparent current efficiency, electrochemical oxidation index, or instantaneous current efficiency. Indirect oxidation takes advantage of intermediary redox reagents to effect electron transfer between electrode and pollutant, thereby preventing electrode fouling by contaminants. The presence of chloride ions enhances removal of phenolic compounds through the formation of Cl_2 or ClO^- in a process called electrochemical oxidation of active chlorine [41, 42•].

Rabaaoui et al. investigated the electrochemical oxidation of *o*-nitrophenol at a BDD electrode, which has the highest potential value for oxygen evolution among other conventional electrodes. In nitrophenols, regardless of the relative position of $-OH$ and $-NO_2$ groups, after 8 h, 96 % mineralization was achieved with all samples at 60 mA cm^{-2} and pH 3. The group found *o*-nitrophenol degradation was the fastest in the presence of Na_2SO_4 in comparison with NaCl and KCl and is more efficient in acidic medium. Based on ion-chromatographic data, the group suggested a mineralization pathway through carboxylic acids by hydroxyl radicals (OH•) and total transformation of organic nitrogen to NH_4^+ and NO_3^- ions [43].

Gupta et al. studied interaction of the most influential parameters on degradation of 2,4-dinitrophenol in both batch and continuous-flow reactors using a PbO_2 electrode coated on steel. Their statistical optimization found pH 6.59, NaCl concentration of 1.12 g/L, and current of 1.44 mA/cm^2 predicted 94.2 % chemical oxygen demand (COD) removal in a batch reactor, which was confirmed by obtaining 93.9 % COD removal experimentally. A continuous-flow reactor showed the same COD removal trend using 0.5 g/L of electrolyte with 500 mL/h flow at a current density of 58 mA/cm^2 [44]. Hurwitz et al. designed a photo-assisted electrochemical (UVEL) reactor with BDD and ruthenium oxide on titanium (DSA-Cl_2) as anodes to study the effect of an advanced oxidation process (AOP) and electrochemical hybrid techniques on phenol treatment. The experiment was conducted in the presence and absence of chlorine for 6 h at a current density of 20 mA/cm^2. DSA-Cl_2 showed higher free-chlorine generation and TOC removal than BDD. In the absence of chloride, BDD led to 71 % TOC removal using UVEL whereas DSA-Cl_2 showed only 43 %. Addition of chloride enhanced TOC removal in DSA-Cl_2 up to 96 % but had no effect with BDD. UVEL had a synergic effect on removal of phenol TOC with both DSA-Cl_2 and BDD [45]. Based on the results of Chu et al., the electro-Fenton oxidation process can enhance biodegradability of *m*-cresol using Ti/SnO_2-Sb_2O_5-IrO_2 as anode, and a porous carbon PTFE composite as cathode. *m*-Cresol decay depended on (OH•) generated in bulk solution through Fenton reaction as well as that formed at the anode. Total destruction of 100 mg/L *m*-cresol was achieved at pH 3 with 22.4 mg/L of Fe^{2+} in 2 h [46].

Advanced Oxidation Processes (AOPs)

AOPs are an array of techniques having the common feature that they form hydroxyl radical (OH•) in situ and this free radical is capable of mineralizing most organics, including phenolics. The AOPs covered below, UV/H_2O_2, Fenton, wet air oxidation, and ozone, are variously applicable across a wide concentration range of the phenolic target compounds.

Phenol Removal by UV/H_2O_2 Treatment

Microwave (MW) irradiation is a useful adjunct for UV/H_2O_2 wastewater treatment, leading to shorter reaction time, reduction in the activation energy, smaller equipment size, greater ease of operation, and high product yield. For example, a MW irradiation at 2.5 GHz combined with a UV/H_2O_2 system improved the oxidative decomposition of phenol. Although a greater amount of H_2O_2 was needed for mineralization in aqueous solution, conversion of phenol and the TOC removal efficiency increased up to 50 % [3]. In another study, Karci et al. studied degradation and detoxification of industrially important phenol derivatives in water by a direct UV-C photolysis and by a UV-C/H_2O_2 process. 2,4-Dichlorophenol (2, 4-DCP) and the non-ionic industrial surfactant nonylphenol decaethoxylate (NP-10) were compared in the two processes with respect to changes in parent pollutant, total organic carbon (TOC), oxidation products, and acute toxicity to the marine photobacterium *Vibrio fischeri*. The UV-C/H_2O_2 process was better than direct UV-C photolysis in terms of parent compound and TOC removals. It was further observed that UV-C/H_2O_2 treatment for 90 min led to complete degradation of the parent compound and achieved 95 and 78 % TOC removals for 2,4-DCP and NP-10, respectively [47]. Another study was conducted by Zhang and Li for the removal of phenolic endocrine disrupting compounds (EDCs) such as steroid estrogens, 17β-estradiol, estriol, 17α-ethinylestradiol, phenolic xenoestrogens (such as 4-nonylphenols, 4-NP), and Bisphenol A (BPA) from waste activated sludge (WAS) using

UV, H_2O_2, and UV/H_2O_2. It was observed that the combined UV/H_2O_2 process was more efficient in degrading organic micropollutants and WAS solubilization in water, than UV irradiation or H_2O_2 oxidation alone, due to photolysis of H_2O_2-generating hydroxyl radicals [10].

Fenton and Fenton-Like Treatment

The Fenton reagent, H_2O_2 and ferrous ion at low pH, is an AOP capable of oxidizing aromatic pollutants. The iron (II) reacts with hydrogen peroxide to form iron (III) and hydroxyl radicals. Iron (III) is regenerated back to Fe (II) by hydrogen peroxide in an acidic environment. Also, the Fenton process has variants, such as Fenton-like, photo-Fenton, and electro-Fenton processes for enhancement [48, 49•, 50–53].

The classic Fenton process can be used as a pre-treatment method to reduce the toxicity of pollutants. Amor et al. investigated the combination of a Fenton process and an anaerobic biological process to treat olive mill wastewater (OMW). The OMW was too toxic for direct biological treatment, due to the presence of polyphenols and high concentrations of phenolic compounds (2 to 80,000 mg/L). With a Fenton pretreatment method, they removed 82.5 % polyphenol at pH 3.5 after 8 h reaction, producing an effluent suitable for anaerobic treatment [48]. In another study done by Madani et al., pH, temperature, and hydrogen peroxide concentration were investigated in a Fenton process with OMW. The suitable pH was 3–4; if pH was lower (<3), some iron (II) would be present in the Fe $(OH)^{2+}$ which form and slow the formation of hydroxyl radicals; when the pH was higher (>4), the regeneration of iron (II) was slowed by the precipitation of ferric oxyhydroxides and the formation of buffer-iron (II) complexes which slowed the formation of hydroxyl radicals [49•]. Temperature only had a slight effect while hydrogen peroxide concentration could be a critical factor, depending on the iron salt concentration. In both studies using a Fenton process to treat OMW, it was found that when the H_2O_2/Fe^{2+} molar ratio was at around 15, the process reached optimum removal in both COD and total phenol concentration [48, 49•].

The Fenton-like process uses iron (III) as catalyst to turn the reaction from homogeneous to heterogeneous and is cheaper and more efficient compared to the classic Fenton process while having a similar mechanism [50, 51]. According to Pariente et al., with a Santa Barbara Amorphous-15 (SBA-15) silica-supported iron oxide (Fe_2O_3/SBA-15) as catalyst, nearly 99 % of phenol can be removed using this process at 160 °C in an acidic environment. They also found that iron leaching was reduced as reaction temperature increased [50]. In other research, Kuan et al., using FeO_x/TiO_2 as catalyst for 4-chlorophenol (4-CP) treatment, suggested that although the catalyst was in heterogeneous form, the reaction actually occurred in

homogeneous solution. After a 6.5-h reaction in acidic environment, the concentration of Fe ions increased from 0.8 to 30 μM, the concentration of 4-CP decreased from 0.4 mM to nearly 0 [51].

A change of catalyst in a Fenton-like process can reduce its pH dependence. Kuan et al. also studied $CuFe_2O_4$ as a catalyst in 4-CP treatment. With the addition of copper, 4-CP removal after 30 min reaction at pH 7.4 was 99 %. They suggested that neutral pH allows Cu^{2+} and Fe^{3+} leaching from the catalyst, which then convert 4-CP homogeneously. However, they indicated that in the buffer system used, this leaching was not a problem for the effluent since the metal ion concentration would decrease after the degradation of 4-CP. They suggested that the H^+ generated from 4-CP degradation was the cause for Fe and Cu ions' dissolution; when 4-CP was fully degraded, the H^+ concentration decreased and caused a reverse dissolution reaction of $CuFeO_2$, which in an unbuffered system cannot happen [51].

The photo-Fenton process, a combination of UV with Fenton or Fenton-like conditions, is a more efficient and less pH-dependent treatment method. Hydrogen peroxide can generate hydroxyl radicals under UV light and iron (III) can accept a UV photon to regenerate iron (II) [52]. According to Mofrad et al., the photo-Fenton reaction was less pH-dependent than the Fenton process; the phenol removal rate was 60 % at pH 2 and 70 % at pH 5 [52]. UV wavelength also plays an important role in photo-Fenton process. Hadjltaief et al. pointed out that using both UV-C ($\lambda = 254$ nm) and UV-A ($\lambda = 365$ nm) can achieve 100 % phenol degradation, but UV-C was more efficient than UV-A since the reaction time of UV-C was 30 min and UV-A was 60 min. Catalyst leaching was not significant in this experiment; the concentration of metal ion was only 0.5 ppm in the effluent [53].

Wet Air Oxidation (WAO) and Catalytic Wet Air Oxidation (CWAO)

Wet air oxidation (WAO) can be used to treat toxic organic wastewater, which is recalcitrant to biological treatment, with only high temperature and high pressure (WAO) or with a combination of high temperature, high pressure, and catalysts (CWAO). In this process, oxidizable organics, like phenol and phenolic compounds in water, are mixed with gaseous oxygen (normal air or oxygen alone) at temperatures from 150 to 400 °C and pressures from 2 to 40 MPa [54]. The concentration of oxygen in water is much higher than at atmospheric pressure, and the water remains in the liquid phase. The oxidation reactions in WAO turn phenolic compounds into less toxic end products, such as carboxylic acids, carbon dioxide, or other harmless small molecular weight products [55].

WAO is a temperature-dependent process. Weber et al. found out that resorcinol removal in wood processing wastewater was increased from 27 to 97.5 % when the temperature was

raised from 150 to 230 °C [55]. Chen and Cheng used both WAO and CWAO to treat refinery wastewater (volatile phenols concentration was 36.8 g/L). For example, at an air pressure of 2 MPa in a mixed reactor, WAO only achieved phenolic compound conversions of 13 and 42 % at 150 and 200 °C, respectively. With a MnO_x-CeO_x/γ-Al_2O_3 catalyst under the same conditions, phenolics removal improved from 42 to 74 % [54].

Two types of catalysts are used in CWAO, transition metal oxides and supported noble metals. Espinosa de Los Monteros et al. investigated TiO_2-CeO_2 supported noble metals (Ru, Pt) in a CWAO process for phenol at 190 °C and 0.2 MPa oxygen pressure. The Pt-based catalyst had nearly 50 % more phenol conversion in 20 min than the Ru-based one on the same support, which they believed was affected by the number of Lewis acid sites on these two metals. However, the amount of CeO_2 on the support had a larger negative impact on the Pt-based catalyst than the Ru-based one, due to changes in the oxygen storage capacities (OSC) of the support. It was suggested that as the amount of CeO_2 increased, the OSC increased and caused polymerization of the phenol, thereby poisoning the catalysts [56].

In another study, Tu et al. investigated iron oxide supported on sewage sludge-derived carbon (FeSC) as catalyst in CWAO for 2-chlorophenol (2-CP) degradation. They observed an additional 80 % 2-CP removal in the presence of FeSC compared to just sewage sludge-derived carbon. Also, the FeSC showed 20 % more 2-CP conversion than the classical Ru/ZrO_2 catalyst after 5 h reaction. However, the FeSC suffered some leaching, in effect turning the heterogeneous reactions into homogeneous ones. Their CWAO process created an acidic environment (pH 2) resulting in 7 wt.% iron being leached. Buffering the pH at 4.5 resulted in only 0.2 wt.% iron being leached; however, the 2-CP removal dropped from 100 to 42 % [57].

Ozone

Ozonation involves either direct reaction between molecular ozone (O_3) and the dissolved compounds or further transformation of O_3 into oxidants such as ($OH^\bullet$), hydroperoxyl radicals ($HO_2^\bullet$), and species such as $O_3^{\bullet-}$ and $HO_3^\bullet$, which then react with the target compounds [58].

Kuosa et al. studied the ozonation of p-nitrophenol at pH 2, 7, and 10, using t-butanol as scavenger at pH 2 to ensure a direct pathway reaction. The intermediates hydroquinone, catechol, 4-nitrocatechol, oxalic acid, maleic acid, and fumaric acid were detected. At a basic pH (pH 10), production of the intermediate oxalic acid was fast, while at pH 7 it was slower. It was also found that the decomposition of p-nitrophenol was carried out more by the molecular ozone pathway than the radical ones and it was practically the same at pH 7 and 10 [58]. Ozone consumption was a function of p-nitrophenol decomposed and it was highest when t-butanol is used at 2.25 μM. Felis and

Miksch determined the effectiveness of several advanced oxidation processes (UV, UV/H_2O_2, O_3, and UV/O_3) for nonylphenols (NPs). The O_3 and UV/O_3 processes were done as homogeneous aqueous reactions in a flow system. In both processes, the decomposition efficiency was dependent on the initial ozone concentration. During the homogeneous ozonolysis, the initial concentration of NP was 10 mg/L and the ozone doses were 0.8, 1.0, and 2.0 mg/L, achieving NP removals of 45, 52, and 60 %, respectively, with 3 min' reaction. For the UV/O_3 system with the same three ozone concentrations, the removals were 60, 62, and 75 %, respectively [59]. Harufmi et al. also used an AOP (O_3-UV-TiO_2) for the degradation of phenol in water. The ozone was generated by UV irradiation of the oxygen in the air (wavelength 175–242 nm), allowing for energy saving. In an O_3–UV process, phenol decomposition was achieved by irradiating the sample solution with UV light as well as feeding ozone. On the other hand, in an O_3–UV–TiO_2 process, the removal of phenol was achieved by coating the inside of the outer quartz glass tube with TiO_2, and feeding ozone while irradiating with UV light. The decomposition of 50 mg/L and 100 mg/L phenol were reached within 120 and 240 min, respectively, using the O_3-UV-TiO_2 process, and COD removal reached 100 % within 240 min. Furthermore, 200 mg/L phenol decomposition reached rate was 84.3 % after 240 min [60].

Biological Treatment

Biological treatment is the most commonly applied treatment for aqueous phenols and, as such, is the baseline or reference method against which the other methods covered here are often compared. The treatment is an inexpensive method, simple to design and maintain, for transforming phenolic solutions into simple end products. Jalayeri et al. investigated phenol removal in a batch system using small amounts of acclimatized activated sludge. They also studied the effects of several factors such as volume of inoculant, pH, temperature, and initial concentration of phenol. The initial mixed liquor suspended solids (MLSS) was 2000 mg/L, pH values were from 3 to 11, temperatures in the range 25 to 40 °C, phenol concentrations from 400 to 1500 mg/L as well as 1, 3, and 5 mL of acclimatized activated sludge; for all samples the total volume was 100 mL (including the sludge). At phenol concentrations of 100, 200, and 400 mg/L, the optimal inoculant volume was 5 mL at 30 °C. Optimal removal was at pH 7 (6 h reaction) for 200 mg/L of phenol at 30 °C; other pHs increased the removal time. The maximum phenol removal was at 30 °C. The microorganism showed an inhibition stage when using 1500 mg/L phenol due to the toxicity of phenol. Using an acclimatized activated sludge, 1500 mg/L of phenol was removed in 80 h compared to non-acclimatized activated sludge which required more than 200 h [61, 62]. In another

study, Rafiei et al. used hybrid membrane reactors (H-MBRs) to treat synthetic phenolic wastewater (1000 mg/L) in a hydraulic retention time of 13 h. H-MBRs are membrane bioreactors (MBRs; also see "Phenol Removal by Membrane Processes" section, above) combined with carriers; they mitigate membrane fouling which is the principal drawback of conventional membrane processes and increase the operation life times. In this study, the authors immobilized acclimatized activated sludge on polypropylene (BF-MBR) or polyurethane carriers (BE-MBR); they used passive immobilization (bio-film on surface) and entrapment (cell trapping in polyurethane foam). For a conventional MBR, in 5 days (time of membrane fouling at 0.6 bar), final concentrations of phenol and COD of 301 mg/L (71 % removal of phenol) and 822 mg/L were detected, respectively. For the BF-MBR, the membrane fouling time was 9 days with 258 mg/L of phenol and 700 mg/L COD concentrations detected, meaning a 73 % phenol removal. For BE-MBR, the membrane fouling time was 21 days, the phenol concentration was 3 mg/L (99 % removal) and the COD was 200 mg/L. Also, BE-MBR was tested under phenol shock loading finding a complete recovery of phenol removal after elimination of shocks [63].

Other compounds such as Bisphenol A (BPA) have been efficiently removed with biological treatments such as activated sludge [64–66]. For example, Zielińska et al. studied BPA removal using a mixed consortium of immobilized microorganisms in a nitrifying system. This system which is dominated by heterotrophic bacteria could be an effective method for BPA removal. The removal of BPA was more than 92 % from an initial 10 mg/L initial concentration with 1.5 h of hydraulic retention time. It was also found that higher BPA concentrations resulted in a decrease in nitrification activity [66].

Enzymatic Treatment

Enzymatic treatment, taking inspiration from biological treatment, uses a biocatalyst, an enzyme, to carry out a transformation on phenolic compounds that leads to their removal from water. The process can have significant advantages (including cost-effectiveness) over conventional biological and chemical treatments, as long as the enzyme in question is available as a commodity at the right price [67•]. In the early 1980s, Klibanov and co-workers started enzymatic treatment of aromatics using horseradish peroxidase (HRP). This technique can be applied as a primary treatment or in combination with a biological unit. Ease of control, reduced sludge volume, effectiveness over wide ranges of substrate concentration, pH, and salinity, short contact time, and no limitation due to shock loading are the major advantages of this method. Among all enzymes, oxidoreductases like laccases, tyrosinases, and peroxidases have the ability to catalyze removal of phenolic pollutants [68]. In contrast to biological treatment, the strategy involves polymerization of the target compounds, not breakdown, until the products reach their solubility limits and precipitate. In all cases, enzyme concentration is specified as standard units of activity (U) per volume.

Tyrosinases and laccases are copper-containing enzymes. Tyrosinases catalyze o-hydroxylation of monophenols to o-diphenols followed by oxidation of o-diphenols to o-quinones. Non-enzymatic polymerization of the quinones forms insoluble products. Immobilizing tyrosinase covalently on nylon membrane, magnetic, or siliceous supports can enhance stability and industrial application of the enzyme [68, 69].

Laccases are activated by molecular oxygen (four electrons), while heme-protein peroxidases are activated by hydrogen peroxide (two electrons). They each then carry out successive one-electron oxidation of reducing substrates like phenols to form the corresponding phenoxy radicals, and these radicals couple non-enzymatically to form dimers. Additional enzymatic cycles with these dimers lead eventually to polymers [70].

Although HRP is the most studied heme-protein peroxidase, soybean peroxidase (SBP) has received lots of attention because of numerous advantages over HRP. SBP has proven to be an effective enzyme to remove phenol [70, 71]. Immobilization techniques such as support- or carrier-binding through physico-chemical interaction, encapsulation which traps enzyme inside the pores of the support, or covalent cross-linking of enzyme functional groups have been investigated to enable large-scale enzymatic treatment [70].

Rezvani et al. immobilized SBP in a semi-permeable alginate membrane in a packed-bed bioreactor and studied the effect of different factors such as the flow rate, temperature, and H_2O_2 concentration on phenol removal. For an initial phenol concentration of 1 mM and 2.25 U/mL enzyme, the optimal conditions obtained for a 97 % removal were 56 °C, 14 mM H_2O_2 and 5.5 mL/min flow rate [72].

A drawback in enzymatic treatment is inactivation of the enzyme, and one of the approaches to limit this is the use of additives. For example, Torres et al. studied the influence of the additives polyethylene glycol and Triton X-100 on the removal of phenol and other compounds from coffee-processing wastewater using soybean and turnip peroxidases. There was only an effect on the removal of phenol in the presence of the additives (a change in phenol oxidation of 50 %) at pH 7 using turnip peroxidase. At pH 3 with turnip peroxidase, only Triton X-100 showed an effect in the oxidation of caffeic acid with a 22 % increase. However, there was no influence on the oxidation of other phenolic compounds in the presence of these additives using SBP because previous work has shown that the additives inhibit enzyme deactivation by adsorption to solid polymeric products and in this process no precipitate formed; consistent with the proposed adsorption mechanism for inactivation [71, 73]. Recent work from this lab has further characterized the Triton X-100 effect and turned it to advantage, on the one hand, through recycling of

precipitates carrying active SBP [74], while on the other hand, exploiting the adsorption for concentrating SBP from a dilute hull extract as a route to cost-effective production of SBP for wastewater treatment applications [75].

Another plant peroxidase, from potato pulp has been successfully used by Kurnik et al. to remove over 90 % of phenol from a manufacturing industry wastewater in a 2 h reaction, with 2.59 mM H_2O_2, for phenol in the range 0.02–0.1 mM. The reaction was done over a wide range of pH (4–8); however, the phenol removal efficiency decreased sharply when the reaction was done at pH 10. In addition to pH, several concentrations of enzyme, phenol, and H_2O_2, were studied as well as range of temperatures [76].

Conclusions

Extensive research continues to be carried out on phenol removal from water, from conventional methods like adsorption on activated carbon to new technologies such as enzymatic treatment. Improvements to overcome low efficiencies and high operational costs of conventional techniques provide attractive alternatives, for example low-cost adsorbents, chemical modification on the adsorbents to increase surface area, hybrid systems like electro-Fenton to increase the efficiency of phenol removal, achieving total destruction of diverse phenol compounds. Enzymatic treatment has proven to be an effective method with more than 95 % phenol removal using different peroxidases such as soybean and horseradish. New developments in the use of additives substantially mitigate enzyme inactivation, hitherto the most important drawback in industrial application of enzymatic treatment.

Compliance with Ethical Standards

Conflict of Interest   On behalf of all authors, the corresponding author states that there is no conflict of interest.

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