

DEGRADATION OF PHENOLIC COMPOUNDS BY ADVANCED OXIDATION TECHNIQUES: REVIEW

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Abstract –

Phenolic compounds are highly toxic in nature even if it is present in very low concentration. Industrial wastes from petroleum refineries, plastic manufacturing plants, coal carbonisation and pharmaceutical industries generally contains phenolic compounds which must be treated. Advanced Oxidation Process has emerged as an answer when traditional methods cannot manage degradation of phenolic compounds. In this review, different Advanced Oxidation processes such as Ozonation, Fenton, Catalytic wet air oxidation, Photocatalysis and biological treatments of waste containing phenolic compounds are discussed. Also hybrid methods for the degradation of waste water treatment have been discussed. It has been observed that the synergy in the efficiency in the combined process is due to the additional generation of hydroxyl radicals. Overall it can be said that the advanced oxidation process can be effectively used for the degradation of phenolic compounds when used as individual or hybrid process.

Key Words: phenol, advanced oxidation process, phenolic wastes, ozonation, fenton, photocatalysis

1. INTRODUCTION

Phenols are important industrial chemicals of environmental concern since they are involved in many industries such as coke, refineries, manufacture of resin, pharmaceuticals, and pesticides and can also occur in wastewater. Phenols are of widespread use for the production of other derivatives like alkylphenols, cresols, aniline and resins. Dyes, textiles and explosive industries all depend on phenol as raw material [1]. Extraction industry uses phenol in the study and extraction of bio-molecules. Phenolic compounds are chiefly used to produce epoxy resins which constitute a major ingredient for paint coatings and mouldings. Plastics, drugs like aspirin and explosives such as picric acid require phenol as raw material. Two third of total phenol is used in preparing reagents which are used in plastic manufacturing industries. Dye industry mainly relies on substituted phenols to make azo dyes. All major products of cosmetic industry like sunscreens, skin lightening creams and hair coloring solutions require phenol.

Presence of phenolic compounds in industrial wastewater, even at low concentration, directly or indirectly affects aquatic as well as human life. Phenolic compounds are present in the environment as a result of their uses and the processes in which they are implicated. Phenolic compounds enter water sources through natural, industrial, domestic and agricultural activities. Direct or indirect discharge of effluents/influents from these industrial activities into water bodies result in their pollution with phenolic compounds. The toxicity of phenol to the aquatic biota is influenced by several abiotic environmental factors, including, pH, dissolved oxygen level, salinity, water hardness, and other pollutants [2]. Therefore in recent times, the removal of Phenolic compounds has been given special consideration.

Advanced oxidation processes which are based on the generation of highly effective hydroxyl radicals can be used successfully for the degradation of phenolic compounds containing waste water. Also use of intensifying additives and/or catalyst in combination with advanced oxidation process in significant enhancement in the degradation efficiency, making it suitable technology for the degradation of the pollutants. Different operating parameters such as pH, concentration and temperature affect the rate of generation of free radicals which in turn affects the degradation of pollutants. The maximum degradation efficiency can be achieved by the optimization of operating parameters. Hence in this review different advanced oxidation processes as well as combined AOPs and addition of process intensifying additives have been discussed in detail.

2. ADVANCED OXIDATION PROCESS

Advanced Oxidation Processes (AOPs) have emerged as a solution for degradation of toxic phenolic wastes. AOPs involve reaction of recalcitrant organic matter present in wastewater with hydroxyl radical ($\cdot\text{OH}$) to degrade and mineralize them. Advanced oxidation process (AOP) can be broadly defined as aqueous phase oxidation methods based on the intermediacy of highly reactive species such as hydroxyl radicals in the mechanism leading to the destruction of the target pollutant [3]. AOPs comprise of production of OH radicals which attack target molecules breaking them into fragments followed by subsequent by $\cdot\text{OH}$ until ultimate mineralization. The significant advantage of AOPs over all existing chemical and biological processes is that they're completely "environmental-friendly" as they neither transfer pollutants from one section to the opposite (as in chemical precipitation and adsorption) nor manufacture large amounts of risky sludge [4]. The increased degradation by different AOPs of different pollutant categories has drawn attention from different research communities.

2.1 Ozone Based AOPs

Ozonation is a chemical waste water treatment technique which involves infusing ozone in water to efficiently degrade organic and inorganic pollutants. Although ozone has been reported to oxidize both inorganic and organic pollutants but practically ozone is highly selective towards pollutants [5]. Hence ozone is considered as an electrophile with high selectivity in its reaction [6]. The target pollutants either directly react with molecular ozone (O_3) or it further transforms into oxidants like hydroxyl radicals ($OH\bullet$), hydroperoxyl radicals ($HO_2\bullet$), and species such as $O_3\bullet^-$ and $HO_3\bullet^-$ that react with target pollutants. Ozonation can simultaneously be used for disinfection and oxidation.

Olivier Chedeville et al. studied about phenolic compounds present in olive mill wastewaters and their degradation by ozonation [7]. It was found that 80% of phenolic compounds were removed with no effect on treatment due to presence of other compounds present in the waste. Kuosa et al. studied the ozonation of p-nitrophenol at pH 2, 7, and 10, using t-butanol as scavenger to ensure a direct pathway reaction [8]. Intermediates detected were hydroquinone, catechol, 4-nitrocatechol, oxalic acid, maleic acid, and fumaric acid which showed high rate of production at basic pH (pH 10) than at pH 7. The molecular ozone pathway dominated the decomposition of p-nitrophenol than the free radical ones.

The radical formation can be boosted by combinations O_3/H_2O_2 (also called peroxone-process), O_3/UV , and $O_3/catalysts$. The added hydrogen peroxide accelerates decomposition of ozone and increases the hydroxyl radical concentration. The ozone and peroxone processes are differentiated on the basis that the ozone process relies heavily on the direct oxidation of aqueous ozone while peroxone relies primarily on oxidation with hydroxyl radical. Paillard et al. studied atrazine removal in filtered water from the Seine River [9]. O_3/H_2O_2 combination showed better degradation of pesticides than ozone alone. The optimal mass ratio of H_2O_2/O_3 ranged from 0.35 to 0.45. The process performance depends on the ozone dosage, contact time, and water alkalinity.

An alternative way to speed up ozonation process is by using heterogeneous or homogeneous catalysts. A number of metal oxides and metal ions (Fe_2O_3 , Al_2O_3-Me , MnO_2 , Ru/CeO_2 , TiO_2-Me , Fe^{2+} , Fe^{3+} , Mn^{2+} , etc.) give significant increase in decomposition rates of target pollutants though mechanism of reaction remained unclear. The major advantage of a heterogeneous over a homogeneous catalytic system is the reaction media's ease of catalytic retrieval. Under operating condition, the catalyst must show the stability and durability. Leaching of the active catalytic species or poisoning of the active sites or fouling of the catalytic surface through intermediate reaction products are important factors [10]. Albin Pintar et al. studied heterogeneously catalysed liquid-phase oxidation of aqueous phenol, p-chlorophenol and p-nitrophenol solutions [11]. A complex redox and heterogeneous non-branched chain free-radical mechanism was found. It is concluded that phenols with electron-donating substituents are highly susceptible to oxidative degradation, whereas phenols with electron-withdrawing groups are more slowly destroyed. Shailesh S. Sable et al. investigated catalytic oxidative degradation of phenol using iron oxide promoted sulfonated- ZrO_2 [12]. Among all tested catalysts in this study, 4% Fe/sulfonated- ZrO_2 was found to be an effective and stable catalyst in attaining complete phenol degradation and high mineralization efficiencies. The use of a support in catalytic processes allows the catalyst to be immobilized, avoids the loss of the catalyst due to precipitation or dissolution in the wastewater, enhances the surface area and improves the adsorption. Fernando J Beltran et al. investigated the mineralization improvement of phenol aqueous solutions through heterogeneous catalytic ozonation by utilizing metal oxide-based catalysts (i.e. Ti, Co and Fe) supported onto alumina [13]. The Co / Al_2O_3 catalyst has led to the fastest mineralization rate among the catalysts tested. Bisphenol-A (BPA) at pH 10 was treated with a novel nanocomposite composed of reduced graphene oxide and sea urchin-like $\alpha-MnO_2$ nanoarchitectures (RGO/ $\alpha-MnO_2$) and manganese oxide coupled with SBA15 support ($MnO_x/SBA-15$). Almost complete degradation of 93.5% was achieved. Higher initial pH resulted in increased degradation of BPA [14].

Using ultraviolet light in aqueous medium in combination with O_3 can increase $HO\bullet$ formation and concentration, thereby increasing the efficiency of degradation. H. Kusic et al. found 100 % phenol degradation in 60 mins by O_3/UV system [15]. Young Ku et al. found that the rate of decomposition of phenols by UV/O_3 increased with increased dosage of O_3 , light intensity and solution pH [16]. The order of decomposition rate was found to be 2, 4-dichlorophenol > 2-chlorophenol > 2-nitrophenol for low and neutral pH and the alkaline solution rates were almost identical.

Deysi Amado-Piña et al. studied the degradation of phenol by three different techniques namely ozonation (O_3), electro-oxidation (EO) and ozonation-electro-oxidation (O_3 -EO) coupled process. They concluded EO alone reduces 97.7% of COD and 92.1% of TOC. On the other hand, O_3 alone only reduces 63.3% of COD and 39.7% of TOC. When the coupled O_3 -EO process is used, a maximum COD reduction of 98.0% and 98.5% of TOC occurs after half of the other treatment times [17].

From the above review of ozonation process, we can conclude that ozonation is strongly affected by pH and if they are used in synergy, they give better results.

2.2. Fenton:

Another AOP capable of oxidizing aromatic pollutants is the Fenton reagent, H_2O_2 and ferrous ion at low pH. Iron (III) and hydroxyl radicals are formed when iron (II) reacts with hydrogen peroxide. Fe (II) can be regenerated back from Fe (III) acidic environment by hydrogen peroxide. The Fenton process also includes variants such as Fenton, Photo-Fenton and electro-Fenton enhancement processes.

Madani et al. explored the effect of pH, temperature, and hydrogen peroxide concentration in a Fenton process with olive mill wastewater (OMW). Optimum pH was found to be 3-4 [18]. Below 3, hydroxyl radical formation slows down while pH above 4 led to slow regeneration of iron (II) due to precipitation of ferric oxyhydroxides and slow formation of hydroxyl radicals due to formation of buffer-iron (II) complexes. Temperature slightly effected while hydrogen peroxide concentration could be a critical factor.

It is possible to use the classic Fenton process as a pre-treatment method to reduce pollutant toxicity. Another study conducted by Amor et al. investigated the combination of a Fenton process and an anaerobic biological process to treat OMW which was highly toxic to be subjected to direct biological treatment due to presence of polyphenols and high concentrations of phenolic

compounds (2 to 80,000 mg/L) [14]. Fenton pre-treatment led to removal of 82.5 % polyphenol at pH 3.5 after 8 h reaction, producing an effluent suitable for anaerobic treatment.

The photo-Fenton process is a combination of UV with Fenton or Fenton-like conditions resulting in more efficient and less pH-dependent treatment method. UV light enables hydrogen peroxide to generate hydroxyl radicals. Under UV light, iron (III) accepts a UV photon to regenerate iron (II) [19]. According to Mofrad et al., phenol removal rate was 70 % at pH 5. In photo-Fenton process, UV wavelength plays a major role. Hadjltaief et al. pointed out that UV-C ($\lambda = 254$ nm) requires less time (30 mins) than UV-A ($\lambda = 365$ nm) light (60 mins) to achieve 100 % phenol degradation [20].

Electro-Fenton process is an emerging treatment technology for water and wastewater treatment based on in situ generation of hydroxyl radicals ($\bullet\text{OH}$) in an electro-catalytic way. Inderjeet Khatri et al. evaluated the performance of electro-Fenton (EF) process for the degradation of phenol (concentration = 250 mg/L) with different operating parameters [21]. In EF experiments, maximum COD and TOC removals of 84% and 52%, respectively was achieved. DilekGümüş et al. compared Fenton and electro-Fenton processes for oxidation of phenol [22]. The results indicated that the electro-Fenton method (93.3% degradation and 87.5% mineralization) was more effective in the degradation and mineralization of phenol than conventional-Fenton process (81% degradation and 59% mineralization).

2.3. Photocatalysis

Photocatalytic degradation is the use of metal oxide catalysts to degrade pollutants from the water. Here, the catalysts are usually activated by absorption of photon of suitable amount of energy. 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 happens because of its irradiation with a light of suitable wavelength. Generation of positive charges or holes on the valence band and accumulation of electrons on the conduction band of the catalyst starts the photocatalytic degradation process. Highly reactive radicals such as hydroxyl radicals ($\text{OH}\bullet$) and oxygen radicals or super-oxide radicals ($\text{O}_2\bullet$) formed during the process attack and convert the pollutants to non-toxic products such as carbon dioxide and water [23]. The photocatalytic activity of catalyst depends on surface and structural properties of the semiconductor. In heterogeneous catalysis, particle size of catalyst is of primary importance because it is directly related to a catalyst's efficiency by defining its specific surface area. H. Dewidar et al. researched photocatalytic degradation of phenol solution using Zinc Oxide/UV [24]. The results showed that most of phenol degradation occurs nearly at the first 90 min, and then any further increase in time will result in a mild increase in degradation rate. Priya and Madras compared the photocatalytic degradation of nitrophenols using two different catalysts, namely, combustion synthesised nano-TiO₂ and Degussa P-25 [25]. Results revealed that the photodegradation kinetics was first order and combustion synthesized TiO₂ offered higher degradation rates than P-25. The position of substitution affected the rate of degradation. The efficiency of three commercial catalysts Degussa P25 (20 nm), TiO₂-A1 (160 nm) and TiO₂-A2 (330 nm) available in anatase form, and ZnO for the degradation of phenol was compared by Salah et al. [26]. The order of efficiency was found to be ZnO > P25 > TiO₂-A1 > TiO₂-A2. V. Vaianoa et al. used ZnO modified with Ag for removal of phenol from aqueous solutions [27]. Ag/ZnO photocatalysts were synthesized through photodeposition method and the highest photocatalytic phenol removal from aqueous solution was obtained by using 1% Ag/ZnO.

The intensity of light determines the extent of light absorption at a given wavelength by the photocatalyst. The initiation rate for electron - hole formation in the photochemical reaction relies heavily on the light intensity. Puma and Yue investigated the effect of light wavelength on 2-Chlorophenol (2-CP) photocatalytic degradation using UV - A alone and simultaneously with UV - A, B, and C radiation [28]. The rate of degradation and mineralization of 2-CP were significantly improved as the photon flux with UV-ABC was found to be 1.56 times higher compared to UV-A radiation alone. Venkatachalam et al. compared the efficiency of 4-CP mineralization using 365 nm and 254 nm wavelength lamps over TiO₂ [29]. It is reported that the mineralization rate at 365 nm is slightly higher than 254 nm. As the band gap excitation of electrons in TiO₂ with 254 nm can promote high kinetic energy electrons to the conductive band, they can easily reach the solid - liquid interface, suppressing the recombination of electron - hole compared to 365 nm.

In UV/H₂O₂ method, UV light has a particular wavelength which helps in photolyzing hydrogen peroxide into hydroxyl radicals. These radicals react rapidly with phenolic compounds. The rate of degradation by this process is 5 times faster than photocatalysis and UV alone. The purpose served by H₂O₂ is to accelerate the decomposition of phenolic compounds. Mineralization of carbon to carbon dioxide and water can be completely possible by this method.

Maurizio Carotenuto et al. studied degradation kinetics and toxicity effects of Nonylphenol ethoxylated (NP) by UV/H₂O₂ [30]. Removal rates of NP-10 solution (initial concentration 100 mg/L) in deionized water was found to be 88%, 97% and 98% for 10, 20 and 100 mg/L of H₂O₂ respectively after 80 min of treatment whereas in wastewater, it was found to be 84%, 98% and 99%, respectively. Akin Karci et al. studied comparison action of H₂O₂/UV-C oxidation and UV-C photolysis for two compounds named as 2, 4-dichlorophenol (2, 4-DCP) and nonylphenol decaethoxylate (NP-10) [31]. After 90 min treatment of both compounds subjected to UV-C photolysis, there was 72% removal (10% TOC removal) of 2, 4-DCP and 75% removal (9% TOC removal) for NP-10 whereas in case of H₂O₂/UV-C, there is complete degradation of both the compounds with 95% and 78% TOC removals for 2, 4-DCP and NP-10 respectively. In terms of TOC removal and degradation, H₂O₂/UV-C was superior method as compared to UV-C photolysis.

2.5. Wet Air Oxidation And Catalytic Wet Air Oxidation

Wet air oxidation (WAO) can be used to treat recalcitrant toxic organic wastewater with only high temperature and high pressure (WAO) or with a combination of high temperature, high pressure, and catalysts (CWAO) [32]. The phenolic compounds are converted to less toxic products, predominantly carbon dioxide, some biodegradable carboxylic acids or other harmless small molecular weight products. Inorganic constituents such as sulphides and cyanides are converted to non-reactive inorganic compounds. Efficiency of WAO depends on temperature. Weber et al. discovered that resorcinol removal from wood processing water showed an increase from 27 to 97.5% as temperature was elevated from 150 °C to 230 °C [33].

CWAO method is a promising method of AOP capable of degrading organic pollutants in which an oxidant (usually air) is mixed with the effluent stream and is then passed through over catalyst at high temperature and pressure. Chen and Cheng treated refinery wastewater with volatile phenols concentration 36.8 g/L using both WAO and CWAO [34]. In a mixed reactor with air pressure 2MPa, WAO showed degradation of 13% and 42% at 150 and 200 °C, respectively. When MnOx-CeOx/ γ -Al₂O₃ catalyst was used under the same conditions, phenolics removal increased from 42 to 74%.

2.6. Biological Treatment

Microbial degradation is a useful strategy for eliminating organic compounds and detoxifying wastewater and contaminated environments. Phenols occur extensively in environment which is utilized by both aerobic and anaerobic microorganisms as the sole carbon and energy source. Athar Hussain et al. carried out kinetic study for aerobic treatment of phenolic wastewater [35]. It was observed that phenol removal efficiency was maximum up to medium phenol concentration (500–1500 mg L⁻¹), beyond which it started to decrease and finally accumulation of substrate occurred showing substrate inhibition. The ability of activated sludge acclimatized to 2500 mg L⁻¹ of influent phenol concentration declined drastically, which may be attributed to the phenol toxicity which retarded the activity of activated sludge towards biodegradation. Chakraborty et al. used native microorganisms isolated from coke-oven wastewater to study the degradation of phenols [36]. The initial concentration of 200 mg / L phenol was administered as the sole source of carbon. Phenol removal at optimum conditions was 76.76 percent. Adding glucose to a specific low concentration could improve the rate of degradation, but at higher concentrations it impeded the process of degradation.

Anaerobic treatment is less advanced than aerobic treatment. However anaerobic treatment is more energy efficient than aerobic treatment. Anaerobic biological degradation of phenols offers the advantages of no oxygen requirement, low waste biomass production, and generation of a valuable waste product, methane gas [37]. Azbar et al. used anaerobic hybrid reactor to study phenol removal. The efficiency of phenol removal ranged from 39% to 80% under different conditions. During this process, biogas was obtained [38].

3. CONCLUSION

Phenols are important and extensively used industrial chemicals of environmental concern. But, presence of phenolic compounds even at low concentration in industrial wastewater adversely affects aquatic as well as human life directly or indirectly. Hence, it is of at most importance that these phenolic wastes are removed from water sources. So, the removal of phenolic compounds has been given special consideration. Advanced Oxidation Processes (AOPs) have emerged as a solution for degradation of toxic phenolic wastes. The review clearly discusses about various AOPs that has been extensively used for waste water treatment. The efficiency of each treatment varied according to the process parameters. So far photocatalysis, ozonation and Fenton's reactions have been extensively used for the removal of phenolic compounds. The key factors affecting the removal processes are the initial concentration of the target compounds, the amount of oxidizing agents and catalysts, the light intensity, the irradiation time and the nature of the wastewater's solution (pH, presence of solids and other ions).

Efficiency of Ozonation can be improved by using nano-catalysts. Loss of catalysts can be avoided by using catalyst supported on substrates. Fenton can be used as pre-treatment method. Photo-fenton and Electro-fenton are emerging as new technologies. From the review, we could deduce that photocatalysis is highly dependent on light intensity. Ways to achieve effective degradation by replacing UV source by solar energy must be explored to obtain economic savings. WAO and CWAO are costly as they require high temperature and pressure conditions. The biological treatments are time consuming and demand strict maintenance of operating conditions.

Synergetic systems offer the advantage of better degradation rate, complete mineralization and flexibility. More research on synergetic systems is needed, to exploit its benefits. The main challenges for use of AOPs in wastewater treatment in future is the development of efficient and inexpensive materials that foster adequate treatment, utilization of renewable energy sources, targeting new pollutants and revising these processes to use it beyond laboratories.

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