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Degradation of Phenolic Compounds Through UV and Visible-Light-Driven Photocatalysis: Technical and Economic Aspects

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Additional information is available at the end of the chapter

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Abstract

Phenolic compounds are found in surface and groundwater as well as wastewater from several industries. It is necessary to eliminate phenols and phenolic compounds from contaminated water before releasing into water bodies due to their toxicity to human beings. Photocatalytic degradation seems to be a promising technology for the degradation of several phenolic compounds. Complete mineralization of phenol and phenolic compound has been achieved with TiO₂-based photocatalysts under both UV and visible-light irradiation. This chapter will evaluate the conventional processes and advanced oxidation processes for the degradation of phenol and phenolic compounds. The process economics and efficiencies of different advanced oxidation processes will also be discussed. The main focus of the chapter is photocatalytic degradation processes under UV and visible light along with a detailed review of several factors affecting degradation of phenol and phenolic compounds. Photocatalytic degradation process is governed by reactions with hydroxyl radical or superoxide ion. The extent of degradation depends on light sources (UV, visible, and solar), the type of photocatalyst, and experimental conditions (pH, photocatalyst dosage, initial concentration of phenolic compounds, light intensity, electron donor concentration, etc.). Visible-light-active photocatalysts are applied by several researchers to exploit sunlight and to make the photocatalysis process sustainable. In the future, using sunlight in place of UV could make photocatalysis economically more efficient.

Keywords: AOPs, dye sensitization, photocatalyst, phenol, TiO₂, UV, visible

1. Introduction

Phenol and phenolic compounds (chlorophenols, nitrophenols, etc.) detected in water and wastewater are toxic in nature and treated as primary water pollutants as per different countries' regulations. Phenol is one of the first compounds included in the US EPA list of priority pollutants [1]. Chlorophenols and nitrophenols are even more toxic than phenol itself. The exposure, health effects, and regulatory limits of phenols are mentioned in **Table 1** [2]. High concentration of phenolic compounds is present in the effluents from different industries, such as textiles, plastics, paint, paper, petroleum refining, coal processing, wood products, pharmaceuticals, and steel manufacturing [3]. Phenols can be removed by conventional techniques such as (i) physicochemical processes and (ii) biological processes. A comparative study of different phenol degradation methods is presented in the following section. Because of several limitations of the conventional phenol degradation processes, researchers are now relying on advanced oxidation processes (AOPs) for the complete mineralization of phenols. AOPs provide much faster degradation rate with the participation of hydroxyl radical (HO^\bullet), and phenols are mineralized to CO_2 and water instead of transferring the pollutants from one phase to another [4]. Heterogeneous photocatalysis process became very popular among the AOPs, and it requires mainly three components such as (i) semiconductor photocatalyst, (ii) light energy (UV or visible or solar), and (iii) electron donor or hole acceptor. When semiconductor photocatalyst is illuminated with light energy greater than the band gap of the photocatalyst, charge carriers (i.e., electron-hole pair) are produced which ultimately generate hydroxyl radicals (HO^\bullet) in the system. Recently, photocatalytic degradation of phenol and phenolic compounds in wastewater has been extensively studied by several research groups [4–13]. Titanium dioxide (TiO_2) photocatalyst is frequently used in the degradation of phenols under ultraviolet light [14–16]. TiO_2 is nontoxic, photostable, insoluble under most conditions, and inexpensive and has exceptional chemical and biological inertness [17]. There are few other photocatalysts such as ZnO , CuO , and $\beta\text{-Ga}_2\text{O}_3$ which are also used for phenol degradation under UV light. TiO_2 shows highest efficiency among the photocatalysts [6]. However, the use of UV light is neither feasible nor economical for the degradation of a larger volume of industrial effluent containing phenols. Again, sunlight contains only a small fraction of UV light (4% of solar spectrum) in comparison to visible light (46% of solar spectrum) [18]. For this reason, visible-light-active photocatalyst development is necessary to utilize sunlight in photocatalytic degradation of phenols. There are two approaches to achieve the visible-light-active photocatalysts: (i) modifying existing photocatalysts (via techniques such as doping, composite semiconductor, and dye sensitization) and (ii) developing novel undoped single-phase mixed oxide photocatalysts [19]. Phenol degradation is achieved successfully under visible light with doped- TiO_2 photocatalysts, where different dopants such as iodine [20], nitrogen [21], sulfur [12], praseodymium [22], and iron [23] are used to expand their photoresponses into the visible spectrum. In the case of a composite semiconductor, a large band gap semiconductor is coupled with a small band gap semiconductor with a more negative conduction band level. Therefore, the conduction band electrons can be injected from the small band gap semiconductor to the large band gap semiconductor providing a better charge carrier separation [24]. There are few composite photocatalysts such as $\text{Co}_3\text{O}_4/\text{BiVO}_4$ [19], TiO_2 /multiwalled carbon nanotubes [13], and coke-containing TiO_2 [25] that are

reported for the degradation of phenols under visible light. In dye-sensitization process, electron injection occurs from the excited dye into the conduction band of the semiconductor photocatalyst, followed by interfacial electron transfer [7]. Dyes are naturally visible light active, and upon light illumination, they get excited. Vinu et al. [11] used eosin Y and fluorescein as sensitizers of TiO_2 to degrade 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol under visible light. Chowdhury et al. [7] used eosin Y-sensitized Pt-loaded TiO_2 for phenol degradation. Qin et al. [8] applied N719 dye-sensitized TiO_2 for the degradation of 4-chlorophenol. Degradation of 4-nitrophenol is studied with Cu(II)-porphyrin and Cu(II)-phthalocyanine sensitized TiO_2 under visible light [26].

Phenol and phenolic compounds	Use/exposure	Health effects	Human health for the consumption of water and organism (maximum contaminant levels) [2]
Phenol	(i) Used in the production of aniline, phenolic resins, cresols, alkylphenols, dyes, pesticides, synthetic fiber, disinfectant, and antiseptic; (ii) found in industrial effluent from different industries such as pulp and paper, food processing, textile, pharmaceuticals, coal gasification, and petroleum refining	Headache, skin irritation, kidney damage, liver damage	4 mg L ⁻¹
Chlorophenols	(i) Used in antiseptics and pesticide production, (ii) produced in chlorine-bleaching process during paper making, (iii) produced via chlorination of humic matter during the chlorination of drinking water, and (iv) also produced in textile, chemical, and pharmaceutical industry	Burning pain in the mouth, headache, lung damage, affects the digestive tract and immune system	2-Chlorophenol (0.03 mg L ⁻¹), 3-methyl-4-chlorophenol (0.5 mg L ⁻¹), 2,4-Dichlorophenol (0.01 mg L ⁻¹), pentachlorophenol (0.03 µg L ⁻¹), 2,4,6-Trichlorophenol (1.5 µg L ⁻¹)
Nitrophenols	(i) Formed via reaction of phenol and nitrite ions in water under light (UV or solar), (ii) also produced during production and degradation of pesticides, (iii) produced from metallurgic and electronic industry, and (iv) used in solvents, dyes, and plastic production	Weakness, muscles pain, anorexia, kidney damage	2,4-Dinitrophenol (0.01 mg L ⁻¹)

Table 1. Exposure and regulatory limits of phenol and phenolic compounds [1, 2].

In the first part of this chapter, conventional treatment methods for the degradation of phenol and phenolic compounds are presented, followed by the application of AOPs for such treatment. The process economics and efficiencies of different AOPs are also discussed for the degradation of phenolic compounds.

In the second part of the chapter, we focus on the photocatalytic degradation processes concerning different areas such as (i) basic principle of photocatalysis, (ii) experimental details of photocatalytic degradation of phenols, (iii) photocatalysis reaction mechanism for the degradation of phenols, and (iv) effect of different experimental parameters on degradation of phenol and phenolic compounds.

Finally, we demonstrate a dye-sensitized method to improve the photocatalytic activity and visible-light response of TiO₂-based photocatalyst to perform visible-light-driven phenol degradation.

2. Degradation methodologies of phenol and phenolic compounds

It is of utmost importance to treat wastewater containing phenols before disposal to the environment in order to save the aquatic life. Physical/chemical treatment methods such as activated carbon adsorption, ion exchange, liquid-liquid extraction, chlorine oxidation, chlorine dioxide oxidation, and hydrogen peroxide oxidation are mostly applied for the removal of phenols. However, these methods are expensive and produce hazardous by-products. On the other hand, biological treatment methods for phenol degradation are superior in the above aspects, but these are applicable only for low concentration of phenols [3]. AOPs normally produce hydroxyl radicals (HO•) as active species which have very low selectivity and can drive phenol degradation through complete mineralization [27]. A review of the conventional and advanced degradation methods of phenol and phenolic compounds is presented in **Table 2**.

No.	Technology	Target compound	Process details and significant factors	Experimental results	References
1.	Chemical oxidation with sulfatoferrate (VI)	Phenol	Solution pH 9, stirring for 1 h, Fe ^(VI) O ₄ ²⁻ to phenol molar ratios (1:1, 10:1, and 15:1), phenol initial conc. 30 ppm	(i) Phenol oxidation follows a second-order reaction kinetics; (ii) at Fe(VI)/phenol of 10:1, phenol degrades 100%, TOC decreases 57%, and COD decreases 82%; (iii) oxidation reaction follows a radical pathway to undergo ring opening forming intermediates such as phenoxyphenol and benzoquinone	[32]
2.	Chemical oxidation with potassium permanganate	Phenol and bisphenol A (BPA)	Solution pH (4–8.5), initial conc. of BPA 0–16.8 μM, phenol initial conc. 10 μM, permanganate conc. 181 μM	(i) Oxidation follows a second-order reaction kinetics; (ii) oxidation of both phenol and BPA improve under mildly acidic conditions (pH 4–6); (iii) oxidation of phenol delays at pH range 7.5–8.5; (iv) manganese intermediates such as Mn(V) and Mn(VI) form during the reactions	[33]
3.	Chemical oxidation with ozone (O ₃)	BPA	O ₃ concentration, solution pH, bicarbonate concentration, initial conc. of BPA 35 μM	(i) BPA oxidation with aqueous O ₃ follows a second-order rate equation at pH 7; (ii) O ₃ conc. and solution pH show a significant effect on BPA removal	[34]
4.	Adsorption	BPA	Adsorbent: powdered activated	(i) Reach adsorption equilibrium in 150 min; (ii) adsorption follows a Freundlich isotherm; (iii) iron oxide impregnation improves BPA removal	[35]

No.	Technology	Target compound	Process details and significant factors	Experimental results	References
			carbons impregnated with iron oxide nanoparticles		
5.	Reverse osmosis	Phenol	Polyamide thin-film composite reverse osmosis membrane, pH (3–12), phenol conc. (50–1000 ppm), ionic strength (NaCl conc. 0.1–0.001 molL ⁻¹), transmembrane pressure (5–15 bar)	(i) Phenol retention depends on transmembrane pressure, feed concentration, solution pH, and ionic strength; (ii) phenol mainly diffuses through the membrane; (iii) phenol retention exceeds 85% at alkaline pH; (iv) electrostatic repulsion plays a more important role than size exclusion process	[36]
6.	Nanofiltration	Phenol	Composite polyamide nanofiltration membrane, transmembrane pressure, pH, recovery rate, volumetric cross flow rate, phenol initial conc. 132 ppm	(i) 97% phenol and 96% COD removal take place by cross flow nanofiltration; (ii) nanofiltration membrane successfully removes coke-oven wastewater containing phenol, oil and grease, cyanide, and ammonia	[37]
7.	Solvent extraction	Phenol	Cumene is the extractant, pH range for extraction 1–7, phase ratio between 0.5 and 4, extraction temperature (from 25 to 55°C), phenol initial conc. 500–5000 ppm	(i) Stripping efficiency for phenol is more than 99%; (ii) cumene shows excellent extraction performance on phenol in acidic solution	[38]
8.	Biodegradation by activated sludge	BPA	Operating temperature 20°C, DO 4 ppm, pH 7.5, sludge age 30 or 45 days, hydraulic retention time 48 h, BPA initial conc. 40 ppm	(i) Metabolic intermediates are 4-hydroxyacetophenone, 4-hydroxybenzaldehyde, and 4-hydroxybenzoic acid; (ii) biodegradation kinetics is influenced by the sludge age, BPA concentration, and the acclimation process	[39]

No.	Technology	Target compound	Process details and significant factors	Experimental results	References
9.	Enzymatic process	Phenol (in refinery effluent)	Packed bed bioreactor, biocatalyst weight 135 g, effluent pH 7, temperature (20–32°C), flow rate (3–6 ml min ⁻¹), H ₂ O ₂ conc. (1–9 mM), phenol initial conc. 100 ppm	(i) 97% phenol degradation is attained; (ii) H ₂ O ₂ concentration, temperature, and flow rate have a positive effect on phenol degradation; (iii) immobilized enzyme shows better stability at broad pH range and at high temperature	[40]
10.	Advanced oxidation with UV, O ₃ , and TiO ₂	Phenol	A low-pressure mercury lamp (λ , 184.9 and 253.7 nm), circulation flow rate for phenol 1000 ml min ⁻¹ , phenol initial conc. 50–200 ppm	(i) Phenol degradation follows a pseudo-first-order kinetics; (ii) O ₃ -UV-TiO ₂ process achieves complete degradation of phenol within 2 h; (iii) formic acid, acetic acid, propionic acid, and fumaric acid are the reaction intermediate	[41]
11.	Advanced oxidation by Fenton process	Phenol	Concentration of iron (II) sulfate 0.001 mol L ⁻¹ , flow rate of H ₂ O ₂ (0.075, 0.15, and 0.3 mol per 30 min), pH 3, temperature 30°C, phenol initial conc. 0.012 mol L ⁻¹	(i) About 94% organic degradation possible in 2 h; (ii) excess iron(II) is responsible for the lower efficiency of Fenton process; (iii) higher H ₂ O ₂ flow rate provides best results	[42]
12.	Photocatalysis with UV-TiO ₂	4-Nitrophenol (4-NP)	Initial concentration of 4-NP, light intensity, partial pressure of oxygen, photocatalyst concentration, pH, chloride ion, and temperature	(i) Degradation rate of 4-NP follows pseudo-first-order kinetics with respect to its concentration; (ii) Cl ⁻ ion shows a negative effect on the degradation	[14]
13.	Photocatalysis -visible-light BiVO ₄	Phenol	Chelating agents (ascorbic acid or citric acid), solvent volumetric ratio, electron scavenger	(i) Three-dimension ordered macroporous (3D-OM) bismuth vanadates successfully remove phenol (94% removal) from wastewater under visible light; (ii) Bi(+V)/chelating agent optimum molar ratio is 2:1	[43]

No.	Technology	Target compound	Process details and significant factors	Experimental results	References
			(H ₂ O ₂), phenol initial conc. 0.1–0.4 mmol L ⁻¹		
14.	Photocatalysis -visible-light-S-doped TiO ₂	Phenol	Thiourea to TiO ₂ mass ratio, photocatalyst calcination temperature	(i) Photocatalyst activity depends on the doping amount of S; (ii) maximum activity is observed when the photocatalyst is calcinated at 600°C with the mass ratio of thiourea/TiO ₂ of 1:1	[12]
15.	Photocatalysis -visible-light-multiwalled carbon nanotubes (MWNT)-TiO ₂ composite	Phenol	MWNT/TiO ₂ ratio, MWNT surface area, photocatalyst preparation method, phenol initial conc. 50 ppm	(i) MWNT-TiO ₂ composite photocatalysts are synthesized via modified sol-gel method; (ii) the increase of MWNT/TiO ₂ ratio from 5 to 20% favors the enhancement of the synergetic effect on phenol disappearance	[13]
16.	Photocatalysis -visible-light-dye-sensitized TiO ₂ /Pt	Phenol	pH, photocatalyst loading, triethanolamine concentration, Pt loading on TiO ₂ , visible solar light intensity, phenol initial conc. 20–100 ppm	(i) Superoxide ion is the active species for phenol degradation; (ii) complete phenol degradation is achieved in 1 h with initial phenol concentration of 20 ppm (pH 7.0, light intensity 100 mWcm ⁻²)	[7]
17.	Photocatalysis -visible-light-dye-sensitized TiO ₂	Phenolic compounds	Concentration of sensitizing dye	(i) Degradation order of the different phenolic compounds: chlorophenol > trichlorophenol > dichlorophenol > phenol	[11]

Table 2. Different treatment methods for removal/degradation of phenol and phenolic compounds.

There are two major constraints that need to be considered for industrial applications: (i) technical feasibility and (ii) economic feasibility. The overall costs of the processes are calculated by summing up the capital cost, operating cost, and maintenance cost [28]. In the following section, we compare the costs associated with different advanced oxidation methodologies. The treatment costs of the AOPs are ranked on a 0–5 scale, 0 being the most expensive and 5 being the least. In between 0 and 5, the ranking is evaluated based on Eq. (1) [29]:

$$Rank_{cost, i} = \left(\frac{Cost_{max} - Cost_i}{Cost_{max} - Cost_{min}} \right) \times 5 \quad (1)$$

where $Rank_{cost,i}$ is the cost rank of AOP, i . $Cost_{max}$ is the most expensive AOP, and $Cost_{min}$ is the least expensive AOP.

The different process costs are compared by few authors. Saritha et al. [30] compare UV, UV/TiO₂, UV/H₂O₂, UV/Fenton, Fenton, and H₂O₂-based AOPs for the degradation of 4-chloro-2 nitrophenol (4C-2-NP). Based on the overall costs, we find that AOP carried out using H₂O₂ and Fenton are least expensive having ranks of ~5, while UV is the most expensive, assigned a rank of 0. **Figure 1** shows the cost ranking of the different AOPs for the degradation of 4C-2-NP. Esplugas et al. [31] compare UV, O₃/H₂O₂, O₃/UV, O₃/UV/H₂O₂, UV/H₂O₂, and O₃ processes for phenol degradation. Again, based on the overall costs, the different O₃-based AOPs are least costly, while UV is the most expensive, as evident from **Figure 2**. We can infer from the cost comparison that incorporating a photocatalyst such as TiO₂ with UV lowers the overall cost by one-third [30]. In the future, using sunlight in place of UV could make AOPs economically more efficient.

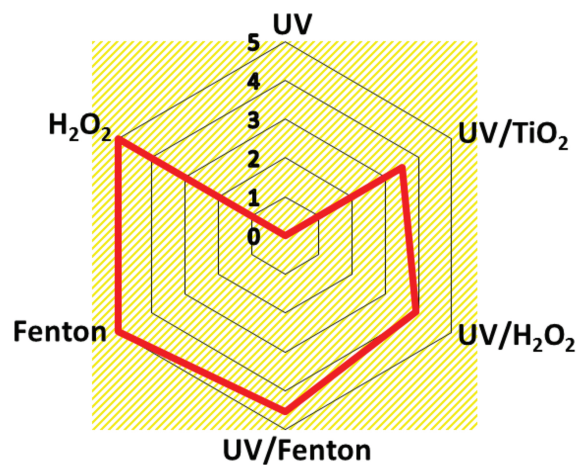


Figure 1. Cost comparison on AOPs for the degradation of 4C-2-NP.

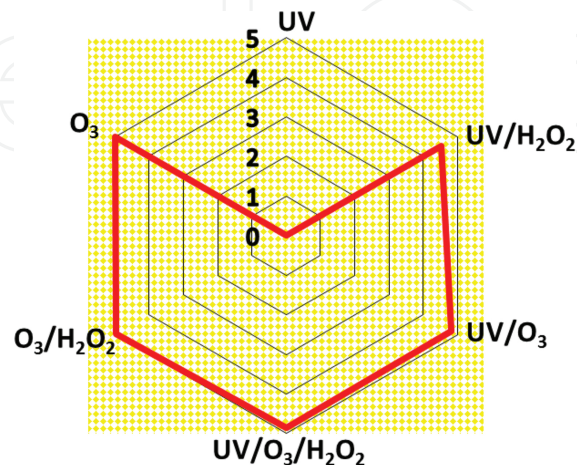


Figure 2. Cost comparison on AOPs for the degradation of phenol.

3. Photocatalytic degradation of phenol and phenolic compounds

3.1. Basic principle of photocatalysis

The precise definition of heterogeneous photocatalysis is a tricky one; particularly as in many cases, the complete mechanism of the reactions is uncertain [27]. In photocatalytic reactions, liquid or gas phase reactants and/or products come into contact with the light-absorbing semiconductor photocatalyst [44]. The semiconductor material can be activated by photons with sufficient energy equal to or greater than the band gap energy (E_g) between the conduction band and valence band of the material [45]. A photocatalytic reaction initiates with the formation of electron-hole pairs followed by oxidation and reduction reactions [46]. In the presence of hole scavenger, the reduction reactions become predominant, whereas in the presence of electron scavenger, the oxidation reactions are the key reactions. However, there are some unwanted reactions such as recombination of electron-hole pairs which reduces the photocatalysis efficiency [47]. **Figure 3** provides a detailed mechanism of photocatalytic reactions.

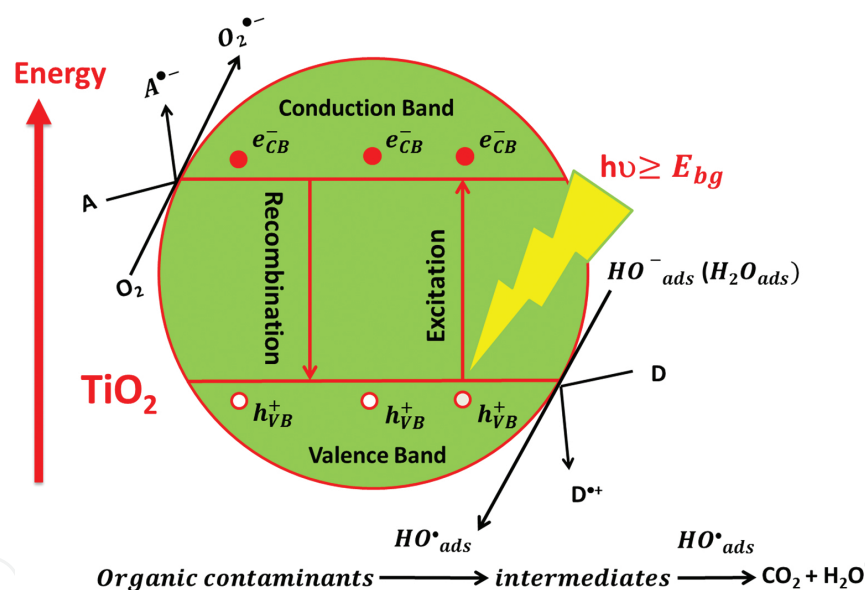


Figure 3. Schematic diagram of photocatalytic reactions for the degradation of organic contaminants.

3.2. Experimental details of photocatalytic degradation of phenols

3.2.1. Photoreactors

Photocatalytic degradation of phenols is performed with either slurry or immobilized photoreactors [15]. Slurry photoreactors provide a high photocatalytic surface area to reactor volume ratio but require filtration after the reaction. On the other hand, immobilized photoreactor can be used continuously without any photocatalyst separation step. However, immobilized reactors suffer from mass transfer limitations and high light scattering [10]. Slurry

photocatalyst provides much higher phenol degradation efficiency than immobilized photocatalysts [15]. Our research group used few different types of photoreactors for the degradation of phenol and phenolic compounds. Chen and Ray [14] used two-phase monolithic-type photoreactor for the photodegradation of 4-nitrophenol under UV light. Sengupta et al. [48] used a Taylor vortex reactor (TVR) for the degradation of phenol under UV light. Chowdhury et al. [7] used slurry photoreactor with dye-sensitized photocatalyst, and Malekshoar et al. [5] used slurry photoreactor with graphene-based photocatalyst for phenol degradation under solar light. Studies by other researchers reported degradation of phenols with (i) TiO₂-coated-fiber-optic cable reactor [16], (ii) tubular photoreactor [49], (iii) continuous flow photoreactor [50], and (iv) solar photoreactor (CPC modules and flat reactor) [51].

3.2.2. Light sources

Photocatalysis process efficiency largely depends on photocatalyst surface area and incident photons. Ray [17] combined these two factors and came up with a parameter called illuminated photocatalyst surface area (κ , m² m⁻³) which mainly represents the illuminated photocatalyst inside the photoreactor to undergo the photocatalysis process. Therefore, distribution of light inside the photoreactor is a crucial factor. In majority cases of phenol degradation, photoreactors use an external light source (UV or solar) with a slurry reactor. Chen and Ray [14] used 125 W high-pressure Hg vapor lamp (Philips) in a swirl-flow reactor. However, such external-type photoreactors are limited by the low value of κ , and thus scale up is not possible. Sengupta et al. [48] used a TVR with immersion-type lamp and immobilized photocatalyst for phenol degradation and achieved a κ value of 80 m² m⁻³. In such case, photoreactor, scale up is possible with larger reactor volume [52]. Chowdhury et al. [7] used a solar simulator (1000 W Xe arc lamp with AM 1.5 G filter) in an external-type slurry photoreactor for dye-sensitized phenol degradation under solar-visible light. Gimenez et al. [51] studied the photocatalytic degradation of phenol and 2, 4-dichlorophenol under natural sunlight using compound parabolic collectors (CPCs) and the flat reactor (cylindrical tank). CPCs showed higher phenol degradation efficiency, but it is technologically more complicated than the flat reactor.

3.2.3. Photocatalysts

Degussa P25 TiO₂ (DP25) is the most common photocatalyst used for phenol degradation under UV light. Some other commercial TiO₂ photocatalysts such as Hombikat UV100, TTP, and PC500 are also used for the same. Among them, DP25 provides the highest photocatalytic activity due to slow electron-hole recombination during photocatalysis [53]. Several visible-light-active photocatalysts such as eosin Y-sensitized TiO₂/Pt [7], dye-sensitized TiO₂ [11], MWNT-TiO₂ composite [13], S-doped TiO₂ [12], and BiO₄ [43] are also used for degradation of phenol and phenolic compounds.

3.2.4. Experimental procedure

Aqueous solutions of target compounds (phenol and/or phenolic compounds) are prepared at a desired initial concentration. Solution pH is adjusted with HCl or HNO₃ or NaOH solutions. In some cases, buffer solutions are used to maintain the solution pH. In the case of

slurry photocatalyst, the powered photocatalysts are dispersed in the solution with ultrasonication and then mixed with a magnetic stirrer. Sometimes the photocatalyst slurry is circulated through a peristaltic pump. Appropriate electron acceptor or hole scavenger is used in the reaction mixture. At first, the dark reaction is performed to study the adsorption behavior of phenols over the photocatalyst. Then photocatalytic reactions are performed under illuminated conditions, and aqueous samples are collected at regular time interval to check the residual concentration of phenols [7, 14].

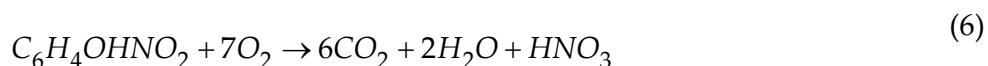
3.2.5. Analyses of phenols

Chowdhury et al. [7] used high-pressure liquid chromatography (HPLC) to quantify the concentration of phenol and phenolic compounds in aqueous medium. The instrument is equipped with a column oven and a diode array detector. AC18 column (5 $\mu\text{m} \times 150 \text{ mm} \times 4.6 \text{ mm}$) and a mobile phase of methanol and water (67/33% v/v) at a flow rate of 0.5 ml min^{-1} are used. The temperature of the column oven is kept at 25°C throughout the analysis. The wavelengths of analyses for phenol and reaction intermediates catechol, hydroquinone, and 1,4-benzoquinone are done at 270, 290, 275, and 255 nm, respectively.

3.3. Photocatalysis reaction mechanism for the degradation of phenols

Here we are discussing the photocatalysis reaction mechanism for TiO_2 photocatalyst only. The first step in the photocatalytic degradation is the formation of electron-hole pairs within the TiO_2 photocatalyst. Most of the electron-hole pairs are recombined producing heat energy. However, hydroxyl radicals (HO^\bullet) are formed in the presence of electron acceptor (dissolved O_2) while hole (h^+) oxidizes water or TiO_2 surface active $-\text{OH}$ group. Dissolved O_2 reacts with the electron (e^-) and generates superoxide ion ($\text{O}_2^{\bullet-}$). Finally, the HO^\bullet reacts with either phenol or phenolic compounds until complete mineralization. Photodegradation mechanism of 4-nitrophenol (4-NP) under UV light is presented as follows [14]:





Overall reaction stoichiometry shows complete mineralization of 4-NP with the involvement of HO^\bullet (Eq. (6)). Devi and Rajashekhar [9] described the possible degradation mechanism for phenol under natural sunlight/UV light using nitrogen-doped TiO_2 . Phenol mineralization went through the formation of dihydroxybenzene (catechol or resorcinol), pent 2-enedioic acid, and oxalic acid. In a parallel reaction path, benzoquinone and maleic acid were formed during the mineralization (**Figure 4**).

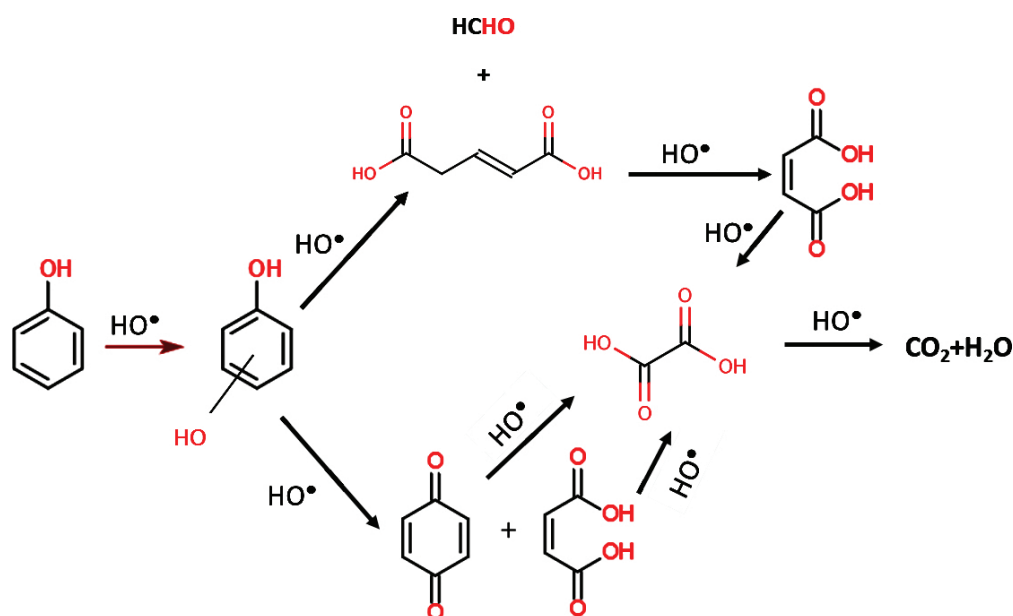


Figure 4. Phenol degradation mechanism (adapted from Ref. [9]).

3.4. Effect of different experimental parameters on degradation of phenol and phenolic compounds

Different parameters such as solution pH, light intensity, initial concentration of target compounds, photocatalyst concentration, and electron acceptors play a significant role on photocatalytic degradation of phenol and phenolic compounds. The following section will provide a review of recent studies on the degradation of phenol and phenol derivatives.

3.4.1. Effect of solution pH

Solution pH plays a vital role in the photocatalytic degradation of phenol and phenolic compounds since it influences two surface properties of the photocatalyst: (i) band edge position and (ii) surface charge. TiO_2 P25 shows a point zero charge at pH 6.8. Thus at $pH < 6.8$, TiO_2 surface attains positive charge and can easily adsorb anionic species at the photocatalyst surface [54]. Again, the protonation and deprotonation of phenols greatly depend on solution

pH. Different phenolic compounds show different optimum pH during photodegradation. Venkatachalam et al. [55] studied the photocatalytic activity of Mg^{2+} and Ba^{2+} -doped TiO_2 nanoparticles for the degradation of 4-chlorophenol (4-CP). In the acidic pH (pH 5), 4-CP was well adsorbed on the photocatalyst surface and showed higher degradation rate than alkaline pH. Lathasree et al. [56] reported the photocatalytic degradation of phenol and chlorophenols with ZnO under UV light. Significant phenol degradation was achieved at neutral and mildly acidic pH. The zero point charge for ZnO was 8, and at alkaline pH, chlorophenols exist as negatively charged chlorophenolate anion. Thus the photodegradation rate was higher at acidic pH (pH < 8).

3.4.2. Effect of light intensity

Photodegradation rates of different organic compounds improve with increasing light intensity. At high light intensity when mass transfer limitation is low, the reaction rate is found to be proportional to the square root of light intensity. However, at the low-intensity level, the photodegradation rate is directly proportional to the light intensity [14, 54]. Al-Sayyed et al. [57] observed a similar rate shift from first order to half order in intensity while they studied photocatalytic degradation rate of 4-CP in the light intensity range of 2–50 mW cm^{-2} . Chen and Ray [14] correlated 4-CP degradation rate constant (k) with light intensity (I): $k \propto I^{0.84}$ indicating that the degradation was independent of mass transfer limitation.

3.4.3. Effect of initial concentration of phenols

As the effect of phenol concentration is of importance in the process of treatment of phenolic wastewater, it is necessary to investigate its dependence. Different concentration profiles can be seen during phenol degradation at different initial concentrations. The degradation rates at same concentration with different initial concentrations are different. However, all the concentration profiles could be correlated with an exponential function as follows [14]:

$$C = C_0 \exp(-kt) \quad (7)$$

where C_0 and C , respectively, are the initial concentration and concentration of phenol at time t and k is the apparent rate constant. Chen and Ray [14] studied the photocatalytic degradation of 4-nitrophenol (4-NP) with varying initial concentration between 10 and 120 ppm. The degradation rate mainly followed a pseudo-first-order kinetics with respect to the initial concentration 4-NP.

3.4.4. Effect of photocatalyst concentration

Photocatalyst concentration is a crucial parameter that has been widely studied for photocatalytic processes. The optimum photocatalyst concentrations usually vary between 0.15 g l^{-1} and 8 g l^{-1} for different photocatalyst systems and photoreactors. A large difference in optimum photocatalyst concentration (0.15–2.5 g l^{-1}) was reported even for the same photocatalyst (DP25). Chen and Ray [15] expressed the photocatalytic degradation rate as follows:

$$r_i = K[1 - \exp(-\epsilon\beta C_{\text{photocat}}H)] \quad (8)$$

$$\text{again, } K = \frac{k_1 A f(C_i) I_0^\beta}{\epsilon\beta} \quad (9)$$

where k_1 is a proportionality constant, A is the illuminated area of the photoreactor window, C_{photocat} is the photocatalyst concentration, ϵ is the light absorption coefficient of the photocatalyst, I_0 is the incident light intensity, and β is a constant. They reported β values of 0.84, 0.72, and 0.82 for the degradation of 4-NP, 4-CP, and phenol, respectively.

3.4.5. Effect of electron acceptor

Photocatalytic degradation reaction requires the use of electron acceptor to reduce the charge carrier recombination. Oxygen is the most common electron acceptor because of its availability, higher solubility, and nontoxic nature. The partial pressure of oxygen is adjusted by mixing the oxygen stream with nitrogen stream by maintaining the total flow rate of gas at a constant value. The photocatalytic reaction of phenols will terminate if sufficient oxygen is not available in the solution [15]. Chen and Ray [14] showed the improvement of 4-NP photodegradation rate with increasing oxygen partial pressure. The photodegradation rate constant reached approximately 70% of its maximum value at oxygen partial pressure of 0.2 atm. The effect of oxygen partial pressure on the photodegradation of 4-NP is described by a noncompetitive Langmuir kinetic equation as follows:

$$k_p \propto \frac{K_{O_2} p_{O_2}}{1 + K_{O_2} p_{O_2}} \quad (10)$$

where k_p is the kinetic constant for 4-NP degradation, K_{O_2} is the adsorption constant of dissolved oxygen on photocatalyst, and p_{O_2} is the partial pressure of dissolved oxygen.

4. Dye-sensitized photocatalytic degradation of phenol and phenolic compounds

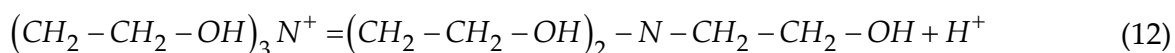
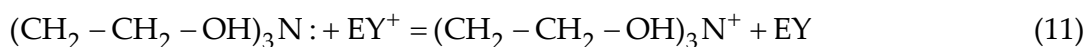
4.1. Theory of dye sensitization

The process of expanding the spectral sensitivity of semiconductor materials with a dye to the visible spectra is known as dye sensitization. Dye is typically adsorbed onto the semiconductor surface by chemical adsorption process. Chemisorbed dye molecules act as spectral sensitizer that upon excitation with visible light inject an electron into the conduction band of the semiconductor [27]. To undergo successful electron injection, the dye molecule should include few basic properties regarding energy levels, ground-state redox potential, and surface anchoring group. Carboxylic and phosphoric acid groups form strong covalent bonds with semiconductor and provide fast electron transfer rate [58]. Recent studies mention the use of a group of sensitizers such as poly(aniline), poly(thiophene), porphyrins, coumarin, phthal-

cyanines, eosin Y, alizarin red S, and carboxylate derivatives of anthracene [11, 26, 27]. Among the photosensitizers, transition metal-based sensitizers have shown best results in dye-sensitization process. Transition metals such as Fe (II), Ru (II), and Os (II) form d^6 complex and undergo intense charge transfer absorption across the entire visible range [59]. However, metal-based sensitizers are not environment friendly, and thus researchers are now focusing on the use of natural dyes as an alternative for dye-sensitization process [59–62]. Several semiconductor photocatalysts have been studied for dye sensitization including TiO_2 , $SrTiO_3$, ZnO , SnO_2 , and Cu_2O [63, 64]. Among them, TiO_2 is the best photocatalyst in terms of (i) cost, (ii) availability, (iii) toxicity, (iv) stability against photocorrosion, and (v) electronic energy band structure [65, 66].

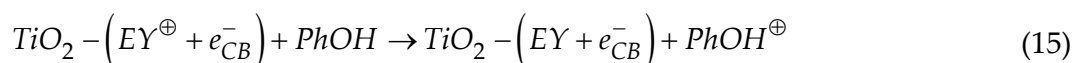
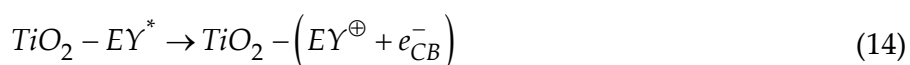
4.2. Dye-sensitized photocatalytic phenol degradation mechanism

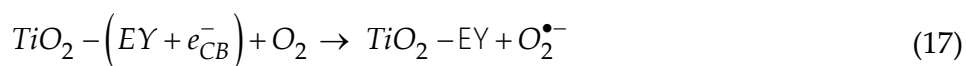
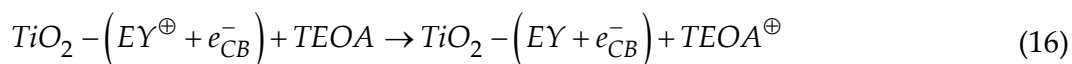
Dye-sensitized photodegradation of phenol under visible light began through excitation of the dye molecule from its ground state to the excited state, which then assists the electron transfer to the conduction band of the semiconductor. The oxidized dye molecule (dye^+) can interact with either phenol or an electron donor to return back to its ground state [7]. Chowdhury et al. [67] used eosin Y (EY) as the sensitizer which provided TiO_2/Pt a significant visible-light activity via dye sensitization. Eosin Y contains both hydroxyl and carboxyl end groups, which actually assists the dissociative surface adsorption of eosin Y onto the surface hydroxyl ($Ti-OH_2^+$) sites of EY-sensitized TiO_2/Pt [11]. Triethanolamine (TEOA) was used as an electron donor, which was consumed through an irreversible oxidation by extending the lifetime of eosin Y during phenol degradation (Eqs. (11) and (12)) [7].



(acid-base equilibrium of TEOA)

Eosin Y-sensitized phenol degradation mechanism under visible light is described below [7, 68]:





4.3. Dye-sensitized photocatalytic phenol degradation kinetics

In dye-sensitized photodegradation under the visible light, the dye molecule is first activated by visible light ($\lambda > 420$ nm) and then injects electrons into the conduction band of the semiconductor. Chowdhury et al. [7] described the kinetics of phenol degradation using eosin Y-sensitized TiO_2/Pt with a modified Langmuir-Hinshelwood equation as follows:

$$-\left(\frac{dC_{Ph}}{dt}\right) = \frac{W(k_r K_A C_{ph})}{V(1 + K_A C_{Ph0})} \times I^{\beta} \quad (21)$$

where W is the mass of photocatalyst, C_{ph} is the phenol concentration at time t , C_{ph0} is the initial phenol concentration, V is the volume of the reaction mixture, K_A is the adsorption equilibrium constant, k_r is the kinetic rate constant, I is the light intensity, and β is a constant. The apparent kinetic constant as is defined as follows:

$$K_{app} = \frac{W}{V} (k_r K_A) \quad (22)$$

Combining Eqs. (21) and (22), they obtained Eq. (23) as follows:

$$-\left(\frac{dC_{Ph}}{dt}\right) = \frac{K_{app} C_{Ph}}{1 + K_A C_{Ph0}} \times I^{\beta} \quad (23)$$

Eq. (23) was used to predict the kinetic parameters of phenol photodegradation at different irradiation intensities (range, 25–100 mW cm⁻²). Based on a parameter estimation using the experimental data, the values of K_{app} , K_A , and β were obtained for the degradation of phenol. The values of K_{app} was 8.02×10^{-6} min⁻¹, K_A was 0.13 L mg⁻¹, and β was 2.15 [7].

4.4. Application of dye-sensitized photocatalyst for the degradation of phenols

Dye-sensitized photodegradation of phenol and phenolic compounds showed promising results under visible-light irradiation [7, 11, 26, 69–71]. Vinu et al. [11] reported degradation of phenol, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol using eosin Y and fluorescein-sensitized combustion-synthesized nano TiO_2 under visible light. Eosin Y-sensitized photocatalyst showed better performance than fluorescein-sensitized photocatalyst. Phenol degradation rate was slowest among the phenolic compounds. Chowdhury et al [7] used eosin Y-sensitized TiO_2/Pt for the degradation of phenol under the visible solar light in the presence of triethanolamine as an electron donor. About 93% phenol degradation (initial concentration 40 ppm) was achieved within 90 min using eosin Y-sensitized TiO_2/Pt photocatalyst under optimum experimental conditions (pH 7.0, photocatalyst concentration of 0.8 g L^{-1} , triethanolamine concentration of 0.2 M, 0.5% Pt loading on TiO_2 , visible solar light intensity of 100 mW cm^{-2}). Mele et al. [26] studied photocatalytic degradation of 4-nitrophenol with polycrystalline TiO_2 impregnated with functionalized Cu(II)-porphyrin or Cu(II)-phthalocyanine. Cu(II)-based sensitizers provided better results for the degradation of 4-nitrophenol in comparison with metal-free sensitizers. Iliev [69] studied photooxidation of phenol with phthalocyanine-modified TiO_2 and Al_2O_3 under visible light. The degree of photodegradation of phenol in the presence of phthalocyanine-modified TiO_2 is much higher than phthalocyanine-modified Al_2O_3 . Superoxide ion was considered as the active species during photodegradation. Grandos et al. [70] used Co(II) and Zn(II) tetracarboxyphthalocyanine (TcPcM)-sensitized TiO_2 for the degradation of phenol under visible light. The photodegradation efficiencies were reported to be 4.3 and 3.3% for TcPcCo/ TiO_2 and TcPcZn/ TiO_2 , respectively. Ghosh et al. [71] demonstrated the photocatalytic degradation of 4-chlorophenol with coumarin-sensitized TiO_2 under visible LED light. The degradation rate followed a first-order kinetics and moved toward a limiting value at a photocatalyst concentration of 0.3 g L^{-1} .

5. Conclusions

Phenol and phenolic compounds are considered as priority pollutants by US EPA because of their high toxicity. They impose severe short-term and long-term health problems to human beings. In this review, we discussed different phenol degradation methods such as physical treatments, biological treatments, and advanced oxidation processes (AOPs). AOPs provide much faster degradation rate than conventional treatment methods and undergo complete mineralization instead of transferring the pollutants from one phase to another.

Heterogeneous photocatalysis is such an AOP that limits the use of oxidizing chemicals (e.g., ozone and hydrogen peroxide) and only utilizes light (UV or solar) and photocatalyst to generate hydroxyl radicals (HO^\bullet). Several photoreactors are used with UV lamp, namely, swirl-flow reactor, Taylor vortex reactor, and two-phase monolithic-type reactor for the photocatalytic degradation of phenolic compounds. In UV-light-driven photocatalysis, hydroxyl radicals are the active species which react with either phenol or phenolic compounds until complete

mineralization. Different parameters such as solution pH, light intensity, initial concentration of target compounds, photocatalyst concentration, and electron acceptors play a significant role on photocatalytic degradation of phenol and phenolic compounds. However, our economic assessment indicates that the use of UV light significantly increases the overall process cost.

Visible-light-active photocatalysts are developed to utilize the most abundant sunlight to make the photocatalysis economically feasible. Compound parabolic collectors (CPCs) are commonly used for solar photocatalytic degradation of phenol and phenolic compounds. Photocatalysts are modified via doping, dye sensitization, and coupling method to expand the photoresponse to the visible region. Among these, dye-sensitized photocatalysis is shown to be an efficient method for phenol degradation under the visible solar light. The process involves electron transfer to the conduction band of semiconductor initiated by dye sensitization under the visible solar light. Dye-sensitized photocatalysis processes are shown to be Efficient methods for the degradation of phenol and phenolic compounds under the visible solar light.

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