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Phenol removal from industrial wastewaters: a short review

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ABSTRACT

The toxicity of phenol even at low concentrations in industrial effluents is high enough to meet its needs for separation. In this paper, a review will be carried out on the traditional techniques and recent advances in the separation of phenol from its contaminated streams. The most commonly used methods classified based on the phenol concentrations (high, medium, and low), and also, their advantages and disadvantages that should be considered in the design of industrial wastewater treatment systems will be discussed. Finally, the best methods will be suggested for each concentration range at the influent and, of course, that is allowable in the final effluent. The survey results recommended that biodegradation, chemical, electrochemical, and photocatalytic oxidation, solid phase extraction, ozonation, reverse osmosis/nanofiltration, and wet air oxidation are useful methods in low phenol concentrations, whereas liquid–liquid extraction, pervaporation, membrane-based solvent extraction, adsorption, and distillation are suggested for high phenol concentrations.

Keywords: Phenol; Wastewater treatment; Persistence organic pollutants; Membrane technologies; Emulsion liquid membrane; Adsorption; Extraction; Distillation; Ozonation; Photocatalytic oxidation; Photocatalytic membrane reactor; Concentration

1. Introduction

Phenol as a constituent of coal tar was first partially separated from coal tar in 1834 by Friedlieb Ferdinand Runge, who called it “carbolic acid” or “coal oil acid.” The French chemist, Auguste Laurent, first prepared pure phenol in 1841 and coined the name “phène” for benzene; which is the root of “phenol” and “phenyl.” In 1843, Charles Frederic Gerhardt also prepared phenol by heating salicylic acid with lime and gave it the name “phénol” [1].

Phenol is a basic raw material for various products such as herbicides, drugs, paints, cosmetics, and lubricants. Its largest use (35%) is as an intermediate in the production of phenolic resins like phenol-formaldehyde resins. Also, its conversion to a precursor of plastics, such as condensation with acetone to give bisphenol-A (BPA) for the production of polycarbonates and epoxide resins, is from its other major uses which together with the phenolic resins includes about two thirds of its general use. Condensation products of phenol or other phenol containing materials such as alkylphenols or diphenols with formaldehyde results

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in Bakelite, a synthetic thermo-setting phenolic resin. Other important chemicals which are produced from phenol are cyclohexanone, as material for the production of nylon, alkylphenols such as nonylphenol or its ethoxylated product, and nonylphenyl ethoxylate, for the production of nonionic detergents. Minor uses of phenol and its derivatives include a versatile precursor for the production of some drugs such as aspirin and pharyngitis medicines, carbolic soap, one of the constituents of industrial paint strippers in the aviation industry, and cosmetics including sunscreens, hair dyes, and skin lightening products. Therefore, phenol and its derivatives are usually present in the effluents of the relevant industries such as conversion processes, coke ovens, petroleum refineries, fiberglass production, textiles, and petrochemicals [1–5].

Phenols are present in the wastewater of various industries, such as refineries (6–500 mg/L), coking operations (28–3,900 mg/L), coal processing (9–6,800 mg/L), and petrochemical plants (2.8–1,220 mg/L). Other sources containing 0.1–1,600 mg/L phenols are pharmaceuticals, plastics, wood products, paint, pulp, and paper industries. Due to safety and environmental problems, it is very essential to collect and remove phenol from the wastes of various production units. Phenol is soluble in water, oil, carbon disulfide, and most organic solvents like alcohols, ethers, ketones, etc. It is rapidly absorbed through contact with the skin and eyes, inhalation, ingestion, and can cause skin and eye burning. In some cases, besides the corrosive effects, phenol can also cause sensitization of the skin. When the skin is wetted with phenol or phenolic solutions, it must be decontaminated immediately. In addition, phenol can affect the central nervous system such as collapse and loss of consciousness. Harmful effects of inhalation of phenolic compound vapors are dyspnea, coughing, cyanosis, and lung edema. Pouching phenol can cause caustic burns in the mouth and stomach pains. Phenol poisoning can intensely damage inner organs including kidneys, liver, spleen, lungs, and heart. When phenol poisoning is acute, neuropsychiatric disturbances will be unavoidable. The limitation of phenol's contact with the skin according to OSHA and ACGIH is less than 5 mg/L, and it is considerable that the ingestion of 1 gr of phenol is deadly for humans [2–4]. The phenol concentrations in effluents change from 0.1 to 17×10^3 mg/L, which contribute 40–80% of the total chemical oxygen demand (COD). In petroleum refinery wastes, the phenolic COD is less than 40%. The coal conversion process and coke oven effluents contain an average of 60% phenol and 30% cresols. If phenol concentration exceeds from 1 mg/L it can affect aquatic life. So usually, a stringent effluent discharge limit of less than 0.5 mg/L is imposed [3]. EPA determined a limit of less than 1 part per billion (ppb) for surface waters. The maximum allowable concentrations of phenol, which are adopted from some water supply standards, in nonchlorinated water is 0.1 mg/L (100 ppb) while that in chlorinated water is 0.001–0.002 mg/L (1–2 ppb) [1].

Phenol, with C_6H_5OH chemical formula, exists as a white solid at room temperature. Because of its high toxicity even at low concentrations, it is one of the most hazardous organic pollutants in wastewaters (Fig. 1). The presence of phenol in natural waters can also lead to formation of the substituted compounds during disinfection and oxidation processes. These compounds perform an inhibitory effect on microorganisms in the biological treatment processes, and are regarded as secondary pollutants [1].

The terms "phenols" or "total phenols" or "phenolic" in wastewater treatment are used either to denote simple phenol or a mixture of phenolic compounds in wastewaters. These compounds can directly affect the health of humans through contamination of surface and ground waters, soil, and sedimentations. Some physicochemical properties of phenol are shown in Table 1.

2. Traditional technologies for removal of phenol from wastewaters

Phenol is important in the field of environmental researches, because it has been frequently chosen as a hazardous pollutant. Hence, much data is available on its removal or destruction especially with respect to wastewater treatments. In the last decade, the treatment of aqueous effluents polluted with phenol and phenolic species has attracted much attention due to the toxicity and low biodegradability of these organic compounds. In the chemical industries, phenolic compounds are very difficult to process by conventional treatment methods such as activated sludge digestion, solvent extraction, chemical treatment, adsorption, etc. [4,5].

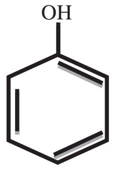


Fig. 1. The phenol chemical structure.

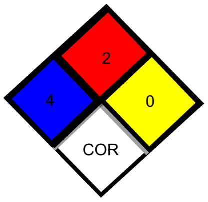
Table 1
Chemical and physical properties of phenol [1,2,6]

Reactivity=0 (normally stable)

Flammability=2 (must be moderately heated)

Health= 4 (serious temporary or residual injury)

Special COR - corrosive



Properties	Values	Units
Molecular weight	94.11	g/mol
T_{melting}	40.91	˚C
T_{boiling}	181.75	˚C
Density	1.07	g/cm^3
Flash point	79	˚C
Acidity in water (pKa)	9.89	–
Water solubility (at 20˚C)	8.3	g phenol/100 mlH_2O (wt.%)
Water solubility (at 25˚C)	8	
Vapor pressure (at 25˚C)	0.35	mm Hg

In this paper, the available technologies recently used for separating phenol from aqueous solutions are classified into two main groups: (1) traditional and (2) advanced methods. Based on the phenol concentration, traditional methods that have been used include distillation, extraction, adsorption, chemical oxidation, and biodegradation. The advanced methods are also divided into photo oxidation processes and membrane separation technologies.

2.1. Separation methods

2.1.1. Separating by steam distillation

Steam distillation processes, based on the relative volatility of phenol, have been carried out for phenol removal from aqueous solutions. Phenol–water mixture has a minimum azeotrope at 9.21% (w/w) phenol [6]. Azeotropic distillation or steam stripping can purify the water from phenol impurities (Fig. 2). A simultaneous distillation-extraction process has been suggested as a pre-concentration step to measure phenols in soil and aqueous samples. Detection values of 0.01 mg/L (water) and 0.1 mg/kg (soil) were obtained by using gas chromatography analysis (150 ml water containing 400 mg phenol) [7]. In another research, extractive distillation has been applied for the catechol (CAT) separation from carbo-furan phenol (CFP) with high efficiency [8]. There is not much data on this method, because it is used for concentrated phenolic solutions (higher than 3,000 mg/L) that are not very common in wastewater treatment processes.

2.1.2. Separating by liquid–liquid extraction (LLE)

Extraction is a traditional method for the recovery of phenol from wastewaters that is still widely used. Some organic solvents such as hydrocarbons and oxygenated compounds can be used in this process. LLE is a standard procedure for phenol removal [9]. It has some advantages over other methods, especially for phenol concentrations up to 1,000 mg/L. In the production of phenol by the cumene process, the liquid resulting from caustic

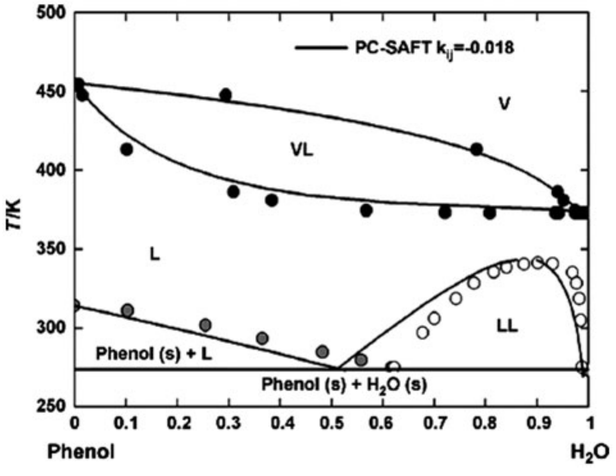


Fig. 2. Phase diagram of phenol–water system showing vapor–liquid, liquid–liquid, solid–liquid, and solid–liquid–liquid equilibrium [6].

washing of cumene and distillation of crude acetone contains 1–3% phenol. This stream can be treated by extraction, and most of its phenol can be removed. In this field, the counter-current extraction is a method that is carried out in an extraction column which uses the cumene product as an extracting agent [6]. In this process, the bottom stream leaves the column by a phenol residual concentration of 20–500 mg/L. The remaining phenol must be removed in a biological purification stage in a sewage treatment plant. All phenolic components can be almost completely recovered except partial recovery of dihydric phenols and neutral oils.

Extraction of phenol by various solvents such as a mixture of tributyl phosphate (TBP) and hexane, 2-octanol, or kerosene has been studied. The results showed that TBP has a great effect on extraction efficiency. By using TBP, phenol can be removed up to 90% with 3 min of contact time to reach extraction equilibrium [10]. Moreover, Jiang et al. [11] investigated the treatment of wastewaters containing 6,000 mg/L phenol and 5% salt in a pilot-scale LLE. They used alcohols, amines, and organic acids as extractants and reached more than 99% of phenol removal.

In a LLE work done by Hosseinzadeh et al. [12] for removal of 4-chlorophenol from water by using kerosene as the solvent, the highest extraction efficiency was found to be 77.5% under the optimum condition of pH = 1, temperature of 50°C, and initial 4-chlorophenol concentration of 100 mg/L. In a similar work by Abbassian et al. [13] for removing phenol through the LLE method and applying kerosene as the extracting solvent, the extraction efficiency up to 70% was obtained for 100 to 500 mg/L phenol concentration in the feed stream. The optimum condition in this study was pH = 6, temperature of 50°C, and initial phenol concentration of 100 mg/L. The other solvents such as toluene that were used for phenol extraction are mostly more harmful for the environment. Generally, a comparative study of processes for the recovery of phenol from aqueous effluents at concentrations higher than 50 mg/L shows that the LLE process is the most economical nondestructive one. The LLE system has advantages over treating high concentrated phenolic wastewaters (over 3,000 mg/L) [11].

2.1.3. Separating by adsorption

One of the separation processes that is used for treating wastewaters, especially diluted streams, is adsorption processes. The most common adsorbents for water purification are activated carbons (ACs) which are divided in two categories: granular activated carbons (GACs) and powdered activated carbons (PACs). The industrial practices with these two forms of ACs show that GACs are normally regenerated while PACs are discharged after use. From this point of view, GACs are preferred to PACs. The adsorption by AC is currently the most favorable method due to its good efficiency, high adsorption capacity, and low operational cost [6]. Terzyk et al. [14] distinguished three stages in the mechanism of phenol adsorption on the ACs: adsorption in the infinite dilution, filling of micropores, and adsorption in larger micropores and mesopores. The effective removal of adsorbed phenols followed by an ethanol wash leads to adsorbent regeneration and separation of the aromatic species. Generally, wastewater treatment by the conventional fixed beds has two drawbacks: one is the low efficiency of the fixed bed due to only a just fraction of adsorbent is used. The other is a new pollution problem that is caused by waste generation [15]. Otero et al. [15] tested two polymeric resins and an activated charcoal for evaluation of their adsorptive performance during the phenol removal from wastewater. The experiments were performed at three different temperatures (293, 310, and 333 K). Fixed bed and batch equilibrium

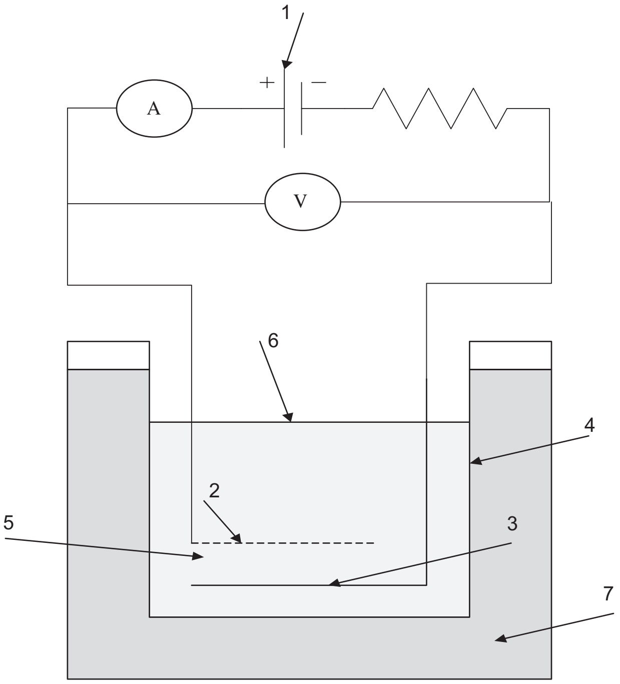


Fig. 3. Schematic view of an electrochemical system; (1) DC power supply, (2) anode, (3) cathode, (4) reactor, (5) electrode gap, (6) level of solution, and (7) water bath [36].

experiments considered under these temperature conditions to investigate the dependency of phenol adsorption on temperature for each of the adsorbents. It was observed that polymeric resins are more sensitive to temperature than ACs, and get to a high level of purification by means of thermal pumping. Among the above-mentioned traditional methods, adsorption similar to separation by distillation is suggested for high initial phenol concentration in wastewaters [8].

2.1.4. Solid-phase extraction (SPE)

SPE due to its benefits is considered as a proper technique for extraction of phenolic compounds such as polyphenols. Some important advantages of SPE are its simplicity, low cost, and environmentally friendly agents used in this technique. In a study by Ferri et al. [16], five adsorbent resins were applied with different physical properties such as Amberlite XAD4, XAD7, XAD16, IRA96, and Isolute ENV + and showed that the most phenol adsorption can be obtained with IRA96 polar resin in an initial phenol concentration up to 4,000 mg/L. They also tested some desorbing agents such as water, methanol, and ethanol. Adsorption of target compounds with a mixture of resins and desorbing agents was compared. The results declared that recovery of overall phenol by nonpolar ENV + resin and ethanol as the desorbing agent was the best value of about 60%. Other polymeric adsorbents such as poly methyl methacrylate (PMMA) can also be used as a good alternative to ACs for removing phenol from aqueous solutions at low concentrations [17]. The adsorption of phenol (10–90 mg/L) is an exothermic and spontaneous process in this case and higher ambient temperature leads to increasing the adsorption capacity.

Onofrejová et al. [18] studied bioactive phenolic acid adsorption from freshwater alga and food products by a new extraction technique that applies an offline combination of pressurized liquid extraction with solid phase extraction (PLE-SPE). Under the optimum condition, more than 96% of phenols present in the algae are removed.

2.2. Destruction methods

2.2.1. Total oxidation with air processes

2.2.1.1. Noncatalytic wet air oxidation. Wet air oxidation (WAO) (or wet oxidation, WO) is an important well-established technique for wastewater treatment, especially when it is too dilute to incinerate and too toxic for bio-treating. It is a low-cost operation with a minimal air pollution discharge [19,20]. In the WAO, aqueous solution containing the organic pollutants is partially oxidized into biodegradable intermediates or mineralized to carbon dioxide and water in the liquid phase at high temperatures (125–320˚C) and pressures (0.5–20 MPa) by using a gaseous source of oxygen as the oxidant. WAO has a great potential for treatment of effluents containing a high content of organic matter (about 10–100 g/L of COD) and/or toxic contaminants for which direct biological treatment is not feasible. Phenolic compounds were usually taken as model pollutants in most cases by this method of treatment [20]. According to Luck [21], typical conditions for WAO are from 180˚C and 2 MPa to 315˚C and 15 MPa. This coincides with the residence times from 15 to 120 min that leads to COD removal of about 75–90%.

WAO is an extremely clean process; because it neither uses any harmful chemical reagents nor produces any harmful final products (carbon dioxide and water are the products if a complete oxidation is achieved). However, high temperatures and pressures and the consequent residence times required to achieve a high degree of oxidation of many organic compounds are usually known as significant drawbacks of the WO process [19]. Furthermore, due to the presence of some low molecular weight oxygenated compounds (especially acetic and propionic acids, methanol, ethanol, and acetaldehyde) which are resistant to oxidation, WAO cannot completely mineralize the waste streams. Therefore, WAO is regarded as a pretreatment process of liquid wastes that requires additional treatments [21]. Aqueous oxidation can also operate at high pressure and temperature above the critical point of water (374.2˚C and 22.1 MPa), which is often referred to as super critical water oxidation (SCWO). SCWO takes advantage of the better dissolution of both organic compounds and oxygen in super critical water, which creates a single homogeneous phase for rapid oxidization of the organics [22,23].

2.2.1.2. Catalytic wet air oxidation (CWAO). CWAO is one of the most promising WAO processes. CWAO can reduce the severity of reaction conditions and decompose the refractory pollutants in mild operating conditions (temperature below 200˚C and pressures in the range 0.5–2.0 MPa) which reduce both the capital and operating costs [24]. Many recent investigations have been searching the CWAO of phenols by a variety a homogeneous/heterogeneous catalysts [19,21,25]. The widely used homogeneous catalysts for CWAO are transition metal cations, such as Cu^+ and Fe^{2+} ions. There have been industrial homogenous CWAO processes such as the Ciba-Geigy process, which work at high temperatures (300°C) and achieve high oxidation efficiencies (95–99%) [25]. To find the new catalytic materials with high activity and stability, different heterogeneous catalysts including noble metals (such as Ru, Rh, Rd, and Pt), metal oxides (such as Cu, Ni, Co, Fe, and Mn oxides with the rather lower activities than noble metals), and mixed oxides (such as ceria–zirconia and ceria–titania mixed oxides) have been prepared and tested for CWAO of phenolic model compounds and the related real wastewaters [24]. The AC can also act as a catalyst in this case, although it may be consumed by oxidation. Through the CWAO with typical reaction conditions ($T = 100–200$°C and $P_{O_2} = 0.3–3.5$ MPa, $t = 1–3$ h), phenol conversion of over 90–95% and TOC or COD removal of over 80–90% were achieved [19]. Hamoudi et al. [26] developed one of the most active mixed oxide catalysts in the mild operating conditions based on the MnO_2/CeO_2 for CWAO of phenol in terms of TOC removal. By using an oxygen partial pressure of 0.5 MPa, this catalyst achieved 80% TOC removal in 1 h at 80°C. However, the primary goal of CWAO should be to convert organics into products that are more amenable for biological treatment but it is at a challenge of being too expensive.

2.2.2. Biodegradation of phenol

Due to the toxicity of phenol for most micro-organisms at high concentrations, most of the biodegradation processes are carried out at low concentrations of phenol. Under aerobic or anaerobic conditions, phenol can be converted to harmless compounds by micro-organisms. Some aerobic bacteria and fungi use phenol as a source of carbon and energy, and degrade it [1,2]. The wastes of more industrial units contain high concentrations of phenol, so the waste treatment by micro-organisms is difficult. In a batch system, the degradation of phenol at an initial concentration of 250 mg/L was faster. Approximately, 100% degradation for phenol concentrations of 300 and 500 mg/L could be achieved. At higher concentrations of 800 and 900 mg/L, the degradation decreased to about 94 and 93%, respectively [6].

The activated sludge is known as a natural microbial consortium and due to its many advantages it is widely used in wastewater treatment processes [6,27]. This method was also used for the biodegradation of 400 mg/L phenol in a batch reactor and a rotating biological contactor (RBC) [6]. In the dual-substrate biodegradation system of phenol and *m*-cresol, it was shown that low concentrations of phenol (0–500 mg/L) could accelerate the *m*-cresol biodegradation because phenol can provide a carbon source as the first-grade substrate for the synthesis and accumulation of new cells in the dual-substrate biodegradation system. In this regard, for all the phenol and *m*-cresol concentrations, phenol is initially utilized and then the *m*-cresol [28].

In the mineralization of phenol (50 mg/L), it can biologically degrade to the concentration of 6.8 mg/L, a suitable concentration for more photocatalytic treatment to complete the process. The advantages of combined biological–photocatalytic treatment are shorter mineralization time and decomposition of intermediates or nonbiodegradable compounds. However, it requires more electric cost than the biological treatment alone [29]. As it is taken from the abovementioned, the initial concentration of phenol plays an important role in the biodegradation process, because some hydrocarbon pollutants including phenol have an inhibitory effect on the activity of the biomass. In the case of anaerobic digestion of phenols, the up-flow anaerobic sludge blanket (UASB) process is the most important operation that has been successfully used in the chemical and petrochemical companies [30]. According to the studies, it is shown that phenol and cresols are degraded with and without the dual-substrate biodegradation system in a UASB reactor. The crucial point in this case is the substrate concentration within its inhibitory range in the reactor. This will be dominated by the three methods of dilution with water, recirculation and use of co- or dual-substrates. Dilution with water, however, is not a reasonable option. In the case of effluent recirculation, it indicated that at phenol concentrations of 1,260 and 3,000 mg/L with the relevant 1:1 and 3:1 effluent recirculation ratios, the UASB reactor performance is efficient (>97% removal). The co-substrate system of phenol and glucose with the respective concentrations of 1,260 and 1,000 mg/L can be more effective with 98% phenol removal and 92% COD removal. Moreover, it is reported that *p*-cresol is completely degraded at a concentration of 650 mg/L in the presence of auxiliary carbon source such as volatile fatty acids (VFAs) as a co-substrate (*p*-cresol: VFA = 2:1 on COD basis). In the absence of VFA, only 80% *p*-cresol is removed. As previously mentioned for dual-substrate biodegradation systems of *o*- and *m*-cresol and phenol, *o*- and *m*-cresol are completely degraded in the presence of phenol [3].

3. Advanced methods for phenol separation or reduction

Several advanced methods mainly based on the oxidation processes have been widely investigated in order to complete destruction of phenolic compounds.

Electrochemical oxidation, photo oxidation processes, and oxidation with chemical oxidants are in this category. Membrane separation processes such as nanofiltration (NF) and reverse osmosis (RO) are also considered as another state of the art technology in this context [31,32]. Phenol concentration plays a crucial role to perform a fast, economical, and suitable advanced process [4,33].

3.1. Electrochemical oxidation

3.1.1. Indirect electro-oxidation

Chlorine and hypochlorite generated anodically, the electrochemically generated hydrogen peroxide (H_2O_2), and the metal ion mediators are used adequately for indirect electro-oxidation of pollutants. The indirect electro-oxidation technique using high chloride concentration can efficiently oxidize many organic and inorganic pollutants [34]. The electrochemically generated H_2O_2 can also degrade the pollutants by applying a proper cathode/anode system. Adding the Fe^{2+} salts into the wastewater makes an electro Fenton reaction. The advantage of the electro Fenton process is to allow a better control of hydroxyl free radical production [3]. Metal-ion mediated electro-oxidation is another indirect electro-oxidation process. Metal ions as mediators are oxidized in a cathode/anode system, which in turn attack organic pollutants directly, and may also produce hydroxyl free radicals that promote destruction of the organic pollutants. This process usually needs to operate in acidic media to prevent the metal from hydroxide precipitations. In addition, there is a secondary pollution due to the addition of heavy metals [34]. A schematic view of an electrochemical system which is used by Abdelwahab et al. is shown in Fig. 3 [35].

3.1.2. Direct anodic oxidation

Direct (or anodic) oxidation is another electrochemical oxidation process. Oxidation of pollutants directly occurs on the anode by physically adsorbed (hydroxyl radicals, $^\bullet OH$) or chemisorbed (oxygen in the oxide lattice, MO_{x+1}) “active oxygen.” Generally, chemisorbed active oxygen is more effective than the physical one. The anodic oxidation has some advantages compared to the other electro-oxidation processes. It does not need the addition of many chemicals to the wastewater or feeding O_2 to cathodes which in turn, no secondary pollutions are produced and the fewer accessories are required [34]. Boron-doped diamond (BDD) is a specific electrode material that shows an increased activity in the oxidation of aromatic compounds [36,37]. Applying BDD at high anodic potentials, total mineralization of phenol may occur without anode deactivation. The combustion efficiency of phenol on BDD electrodes is independent of the concentration. According to studies, BDD electrodes have better performances in mineralization of phenols with respect to others such as SnO_2, PbO_2, and IrO_2 [6,36,37].

3.2. Photo-oxidation processes

3.2.1. Catalytic photo-oxidation

Phenol oxidation activity under the UV irradiation may strongly increase when photocatalysts are present. In the photocatalytic method, when the photocatalyst immobilizes on a support, the active surface may lead to significant reduction in the photoactive capacity of photocatalysts; whereas using the catalyst as a suspension state has a much greater active surface than others [38]. Among several materials with some photocatalytic activities, photo catalysis with TiO_2 has been intensively investigated for the destruction of environmental toxic pollutants. Hidalgo et al. [39,40] found a complete conversion of phenol (50 mg/L) with TiO_2 (1 g/L) by using a medium pressure of 400 W mercury lamp (under the wavelength of 270 nm) after a 90 min illumination. Copper may also favor photo activity of TiO_2 towards phenol degradation especially in conjunction with sulfate radicals [41]. Vione et al. [42] have observed that the degradation of phenol may depend inversely on the radiation that scatters from the photocatalyst, due to its particle size, and is increased by using surfaces fluorinated with TiO_2. Reactors operating photo catalytically use semiconductors such as TiO_2 in different ways, e.g. in suspension as a fluidized bed or internally supported as a fixed bed [41,42]. In the fixed bed catalytic reactors, the sol–gel procedure is used to deposit the catalyst from its solution on the internal reactor walls, and the subsequent elimination of the solvent [43]. Transition metal-containing mesoporous materials (MCMs) like MCM-22 and MCM-41 exhibited an excellent capability in adsorbing phenol compared to SiO_2 and ZSM-5 [6]. In the work carried out by Sun et al. [41], MCM-22 was used as a support for ZnO to prepare a catalyst for photocatalytic degradation of phenol. Moreover, they used peroxydisulphate (PDS) and peroxymonosulphate (PMS) to provide sulfate radicals in order to carry out chemical oxidation. It was found that the adsorptive property of the supports played an important role in photochemical and photocatalytic oxidation. The MCM-22 supported ZnO catalyst exhibited a strong adsorption (68% of phenol removal in a 25 ppm solution) in comparison with the 0.0% for unsupported ZnO. In the photocatalytic degradation system under low UV irradiation, the phenol removal efficiency in ZnO (10%)/MCM-22/UV/PDS at 90 min and 60 $\mu W/cm^2$ was 79%.

A combination of biological and photocatalytic mineralization of phenol (50 mg/L) was conducted by Suryaman et al. [29] in a flow-type membrane bioreactor (MBR) combined with a batch-type TiO_2-suspended photocatalytic reactor. Phenol was first treated biologically in the MBR up to the concentration of 6.8 mg/L and then photo catalytically in a photoreactor to complete mineralization of phenol. Kashif and Ouyang [44] investigated the effect of initial concentration of phenol in the range of 0.128–0.784 mmol/L at photocatalytic degradation by TiO_2: 200 mg/L and pH: 5. They showed that the degradation rate increases up to a certain limit (herein 0.25 mmol/L) and then decreases because the light absorbed by phenol in high initial phenol concentrations is more than that of TiO_2. The best performance of photodegradation of phenol was obtained by photo-deposited gold on TiO_2 support at low light intensities [45]. The gold deposition at low light intensity can be controlled through an effective deposition, aggregation, and oxidation state by changing the deposition time that enables a feasible method of tailoring Au–TiO_2 for a high photocatalytic activity.

Royaee and Sohrabi [46] utilized a new configuration for photo irradiations named the photo-impinging streams reactor (PISR) for degradation of phenol (110 mg/L) by illuminating it from UV light in the presence of TiO_2 suspension. This leads to elimination of both the photon and mass transfer limitations as well as higher efficiency of phenol degradation.

The kinetics of phenol decomposition under UV irradiation on Fe-loaded carbon-coated TiO_2 (Fe–C–TiO_2) photocatalyst in the presence of H_2O_2 was investigated by Tryba et al. [47]. They showed the H_2O_2 could change the pathway of phenol oxidation to another intermediate, the CAT, which is mineralized faster than the two more known intermediates of hydroquinone (HQ) and benzoquinone (BQ). CAT forms dihydroxybenzenes (1,2-HQ and 1,4-HQ) which can reduce Fe^{3+} to Fe^{2+} and accelerate the rate of phenol decomposition. Mohammadi [48] showed that without H_2O_2, and also, by applying nonsupported TiO_2 under the UV irradiation, a continuous-circulating system with the phenol initial concentrations of 100 and 200 mg/L after a long period (~50 h) of operation reaches only 80 and 70% phenol removal, respectively.

3.2.2. Noncatalytic photo oxidation

Microwave (MW) irradiation has attracted much attention in wastewater treatment due to its significant ability in pollutant degradation. Some advantages of MW technology in wastewater treatment are (1) reducing the reaction time, (2) increasing the selectivity of reaction, (3) decreasing the activation energy, (4) improving the reaction rate, (5) reducing the equipment size and waste, (6) providing ease of control, and (7) increasing the yield and purity of products [49]. Applying MW irradiation (2.5 GHz) in a UV/H_2O_2 system can improve the oxidative decomposition of phenol. Both the phenol conversion and the TOC removal efficiency increase up to 50% by MW irradiation. In this case, in order to produce many OH radicals, more than a stoichiometric amount of H_2O_2 is crucial to ensure the mineralization of aqueous solutions. In addition, MW irradiation can accelerate the degradation rate of intermediates [50,51]. Khokhawala and Gogate [52] have investigated the effect of ultrasonic (US) irradiation and also its combination with UV irradiation for the degradation of phenol. From a comparison between US and UV in an individual mode of operation, they concluded that UV has more efficiency than US especially considering the power dissipation into the reactors. However, the combined UV/US system resulted in a better efficiency as compared to the individual operations due to the synergistic effect between the two methods.

Tawabini and Zubair [53] presented a combined UV and ozone (O_3) process to phenol removal from its contaminated sources. Through the combined UV/O_3 continuous process at 1 L/min and by the addition of 1.5 ppm ammonia for adjusting the pH below 6, they could completely remove phenol.

Manganese oxides individually have a weak ability to degrade phenol in dark conditions, while in the presence of UV–vis light irradiation a photochemical reaction occurred due to excitation of the occupied electrons on O-2p of the manganese oxide to the unoccupied orbits (mainly Mn-3d). This could significantly cause an increase in phenol degradation. There are three possible mechanisms for photochemical degradation of phenol in the presence of manganese oxides: direct photolysis of phenol, oxidation by manganese oxides, and photocatalytic oxidation assisted by manganese oxides. Among these, photocatalytic oxidation is the dominant one [54].

Based on a research for conducting a system for simultaneous utilization of UV irradiation and electrolysis with Fenton's reagent (photo-electro-Fenton process), a better result was obtained for phenol destruction by the photo-electro-Fenton process compared to that of the sonolysis assisted one, the sono-electro-Fenton process. Both of the processes have complete degradation of 200 mg/L phenol, whereas the photo-electro-Fenton showed a superiority in case of its shorter required times of performance [55].

3.3. Oxidation with chemical oxidants

Different chemical oxidants have been reported to be active in the total wet oxidation of phenol in aqueous solutions. The most applied chemical oxidants are O_3 and H_2O_2 [50,56–63].

3.3.1. Oxidation with O_3 (ozonation)

O_3 with environmentally safe oxidizer and disinfector characteristics can oxidize organic and inorganic compounds present in wastewaters. Ozonation can effectively detoxify harmful chemicals [50]. In the presence of catalysts or in combination with UV or H_2O_2, the ozonation process would be more efficient in the degradation of organic compounds. There are also some disadvantages for using O_3 to remove pollutants from water, which limit its application in wastewater treatment. Some of these are high O_3 generation cost, its low solubility in water, and low oxidation rate towards stable organic compounds such as phenols. In addition, the rate of pollutant removal is slow through the ozonation process, which requires high O_3 dosages [50,55,64]. Using O_3 and various salts or their coupling with UV radiation or H_2O_2 are typical homogeneous catalytic oxidation [26,52,53,64–67]. Heterogeneous catalytic ozonation dating back from the 1970s [56] is now attracting attention once more. In the case of Al_2O_3 supported transition metal oxide catalysts [64], the high oxidation activity in the presence of ozone has been attributed to the high content of these agents. Dong et al. [59] synthesized ZnO particles of 200 nm through a hydrothermal method and applied them in the degradation of phenols with the increase in removal efficiencies of up to 23.7%. Chang et al. [60] applied the $CeO_2/\gamma\text{-}Al_2O_3$ catalyst as a feasible alternative to CeO_2 for the catalytic wet air oxidation of phenol. After 2 h, approximately 100% phenol conversion and 80% total organic carbon (TOC) removals were obtained at 180°C in an initial phenol concentration of 1,000 mg/L and 3.0 g/L of catalyst. At higher phenol concentrations, both catalyst loading and O_2 partial pressure should be increased to maintain performance. In another work, a dose of 4 g/L zeolite in H-form (HZSM-5 (with SiO_2/Al_2O_3 ratio of 80)) catalyst was applied for 100 mg/L of phenol concentration and resulted in 50.5% removal after 80 min [50].

3.3.2. Noncatalytic oxidation with H_2O_2

H_2O_2 has effective oxygen content with low cost, safe storage, and operational methods, and more importantly, it is environmentally friendly in nature. This implies that there is a strong oxidant in both acidic and basic solutions. The reactivity of H_2O_2 is generally low and largely incomplete [63] because of the kinetics being much enhanced by homogeneous and/or heterogeneous catalysts, especially in acidic media.

3.3.2.1. Conventional homogeneous Fenton reaction. In conventional Fenton reaction, H_2O_2 is combined with Fe^{2+} at acidic pH to produce ferric ions and hydroxyl radicals, which can oxidize organic compounds. The zero-valent iron metal can then reduce the ferric ions down to ferrous (so the reaction rate increases) or indeed may interact with hydroxyl radicals resulting in oxidation of hydroxide ions, so it limits the reaction rate. Also, Fe^{3+} at acidic pH reacts with H_2O_2 in the so-called Fenton-like reaction, producing $\cdot HO_2$ radicals and causing the catalyst to be generated. This action is frequently done that causes the process to be sustainable. Fenton's reaction may be recommended as a pretreatment process to increase later microbial transformation that lowers the operational costs. Due to the simplicity of equipment and mild operational conditions, Fenton reaction has been postulated as the most economic oxidation alternative. Kang et al. [67] performed a kinetic modeling of Fenton oxidation of phenol and mono-chlorophenols. Based on Zazo et al. [68] the chemical pathway of phenol oxidation by Fenton's reagent may be much more complex than what was expected.

3.3.2.2. Heterogeneous Fenton reaction. The application of conventional homogeneous Fenton reaction becomes complicated by the typical problems of homogeneous catalysis, such as catalyst separation, regeneration, etc. [69,70]. Thus, Fenton-like heterogeneous catalysts, i.e. solids containing transition metals (mostly iron ions) have been developed and tested. One of the most popular metal cations is Fe-MFI zeolite [69], which is very active but may suffer from diffusion limitation because of the relatively small size of its pores. The mesoporous materials containing transition metal, like MCM-41 type, are considered as perspective catalysts due to a larger pore size. They are able to increase diffusion of reagents as compared to microporous materials which are used as catalysts for wet phenol oxidation with H_2O_2 under mild reaction conditions ($pH = 3.5$, $P = 1$ atm, $T = 353$ K). Using copper/MCM-41 as catalyst, it was revealed that both the phenol conversion and the final TOC removal level were 90% after 10 min. However, these materials suffer from destruction of the mesopore orders, iron agglomeration, and leaching (from 6 to 100 wt.%) [65].

3.4. Membrane processes

Membrane processes are applied in different industries such as water and wastewater treatment to remove some organic pollutants. Recently, this technology has been commonly investigated for the phenolic compound removals. Low energy consumption, low operating cost, and easy scale up by membrane modules are the main advantages of these technologies while it the limited lifetime of the membranes must be given attention because of membrane fouling due to particles and colloids present in the feed streams [71–73]. The most important membrane technologies used to remove organics from wastewater are membrane-based solvent extraction (MBSE) (known as liquid membranes), NF/RO, pervaporation (PV), and membrane distillation (MD) [74–78]. MBRs and photocatalytic membrane reactors (PMRs) are the other related techniques that will be explained in the "hybrid systems" section.

Membrane processes are categorized based on the driving forces. Liquid membranes are driven by means of the concentration difference of donor and receiving phases. NF, RO, and PV are carried out with transmembrane pressure difference. MD is a thermal-driven separation in which only vapor should be passed through the membrane pores [79–95].

3.4.1. Separating by MBSE

The membrane extraction technique is a very attractive alternative to conventional extraction methods for sample preparation, because the analyses can be isolated in a continuous fashion [96,97]. A MBSE process couples the principles of solvent extraction with the high compactness and interfacial exchange area that is offered by the hollow fiber membrane contactors. In this case, the membrane mainly acts as a physical barrier between the aqueous feed and the organic solvent without significant effect on the selectivity. It is easy to immobilize the water–solvent interface at the pores' entrance of the membrane by applying a slight transmembrane pressure difference. The extraction is driven by a concentration gradient and the transfer operation is not dependent on the transmembrane pressure [95].

Recently, the phenol–water mixture separations using membrane processes have been vastly studied, most of which were interested in using hollow fiber modules. For this purpose, Kujawski et al. [98] applied some organic solvents (extractants) such as methyl terbutyl ether (MTBE), cumene, and a mixture of hydrocarbons in a polypropylene (PP) membrane. They found that MTBE as an extracting agent can be more superior to hydrocarbons, because of its higher polarity and the possibility of constituting H-bonds with phenol. In this regard, Reis et al. [99] found that polydimethylsiloxane (PDMS) is more suitable for the operations under strong base conditions. In further investigations, the experimental results showed that the phenol removal efficiency increased 99.9% in less than 10 min, under the conditions of 2.0 l/d feed flow rate, phenol concentration of more than 5 g/L, and temperature of 298 K [4].

3.4.1.1. Emulsion liquid membrane (ELM) technique. One of the suitable and widely used membrane methods for phenol removal from aqueous solution is the ELM, which has attracted more scientists and engineers because of its preferred advantages in comparison with the other methods (Fig. 4) [79]. Li [100] first proposed the ELM technique in 1968 for separating hydrocarbons. All compounds, except for hydroquinone, can be treated by the ELM process under optimum conditions to result in high extraction efficiency (more than 96%) [101–103]. In the ELM process, two main operations, the extraction and stripping, occurs simultaneously in one stage. Commonly, the ELM consists of an organic phase, an internal phase, emulsifier, and in some cases a chemical carrier [104,105]. In addition, a high interfacial area for extraction and kinetics of stripping, especially due to the small size of the internal droplets are favored [106,107]. Unfortunately, the instability of the emulsion globules against fluid shear has limited this process. Releasing internal phase to the external phase due to rupture of emulsion globules could cause an unsuccessful extraction process [104,106]. Juang et al. [108] found that conversion of the membrane phase from Newtonian to a suitable non-Newtonian fluid would enhance emulsion globules stability without considerable reduction in extraction efficiency. Also an amount of stabilizing surfactant is needed that affects mass and chemical reaction rates at the interfaces and also decreases the swelling problem. Internal droplets get smaller because of low apparent viscosity which increases the mass transfer area. Non-Newtonian conversion modifies permeability and transport through the membrane phase. Park et al. [109] studied emulsion liquid membranes for extracted benzoic from aqueous solution that were stabilized by non-Newtonian conversion in the Taylor–Couette flow. Investigation of leakage rate for emulsion globules was done in their study which

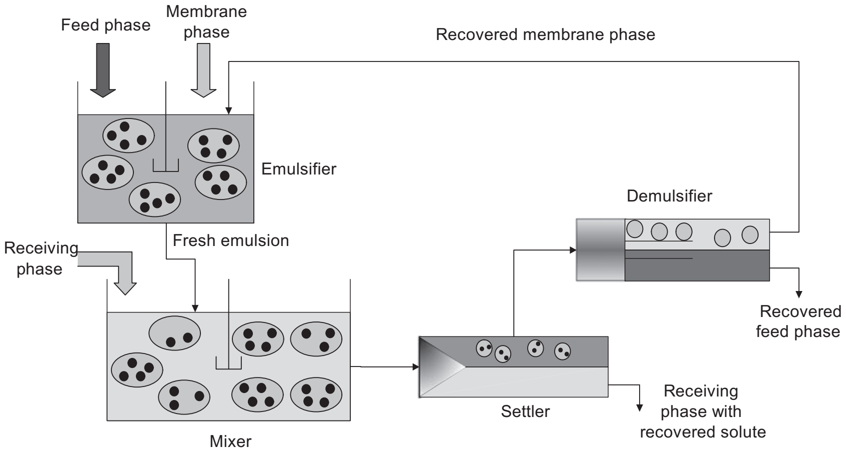


Fig. 4. Schematic view of the ELM [79].

is related to rotation rate. Leakage rate will be increased by increasing the rotation rate. Mortaheb et al. [110] used a new polyamine-type surfactant that was synthesized for emulsion phase stabilization. By using this new surfactant, due to the stable emulsion globules and increasing the amount of internal phase which consequently enhances the driving force, removal efficiencies increased up to 98%. However, this study declared that high concentration of the internal phase leads to swelling and increasing in hydrolysis of the emulsifier. Investigations of Ng et al. [111] and Juang et al. [112] founded that the breakage of emulsion globules increases by increasing the concentration of surfactant.

3.4.1.2. Supported liquid membrane (SLM). In the supported liquid membrane (SLM) technique a microporous polymeric or inorganic film is filled with the membrane liquid and lies between two aqueous solutions. The desired substance dissolves in membrane pores, and transports from the feed to strip phase. SLMs are prepared in various configurations such as flat sheet, hollow fiber, and spiral wound (Fig. 5) [71]. One of the SLM applications is the separation of organic compounds [113]. Some studies have been carried out for separating phenol. In this regard, kerosene is used as an organic solvent, NaOH as stripping agent, and TBP and tri-n-octyl phosphine oxide (TOPO) as carriers. The results showed that SLM systems based on the TOPO are more stable than TBP-SLM systems. It was also indicated that using the hollow-fiber SLM (HFSLM) system can be more favorable due to the higher membrane surface area [114]. Venkateswaran and Palanivelu [115] used a flat sheet SLM containing vegetable oil as the membrane's liquid, and poly-tetrafluoroethylene (PTFE) and PP as solid membrane supports which resulted in the phenol removal efficiency of 95%. Other carriers such as organosiloxane dodecane and 1-n-alkyl-3-methylimidazolium salts have been used in the SLM structure. In these systems, NaOH was utilized as the stripping agent which resulted favorable efficiencies [115–118].

3.4.2. RO and NF

Regardless of great rejecting salt levels, membrane processes often have low rejecting levels for many small organic molecules. Therefore, their use in combination with adsorption processes has been developed. RO is a membrane-based demineralization technique that is used to separate dissolved solids, such as ions, mostly from water-based solutions. In general, membranes act as perm-selective barriers, allow some species such as water to selectively permeate through them while other dissolved species such as ions,

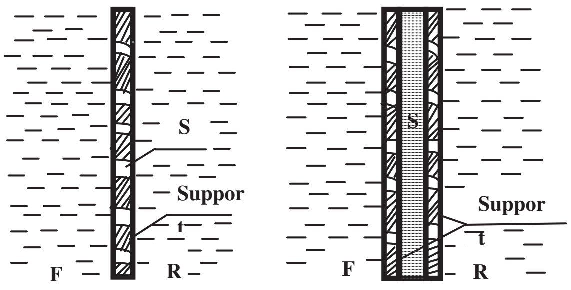


Fig. 5. Schematic view of the SLM [79].

retained selectively [119,121]. Bódalo et al. [121] studied phenol removal from aqueous solutions by three different RO membranes and obtained low rejection percentage in all cases (up to 40%). They concluded that by increasing the pressure, the rejection values decrease. Furthermore, they examined three NF membranes (NF-97, NF-99, and DSS-HR98PP) for changing these anomaly results. A rejection percentage of approximately 80% was obtained by DSS-HR98PP with the same pressure conditions used for RO membranes.

NF is one of the widely used techniques for removing natural and synthetic organic pollutants, inorganic salts, color, and hardness from aqueous solutions. Results that were recently achieved on the improvement of membranes showed profitably and economically viable use of NF membranes for the separation of organics, but much effort is required to fully understand the roles of all the factors that affect it. For achievement of the total elimination of such pollutants, the combination of advanced oxidation and RO processes is one of the effective procedures that are used. In addition, both NO and RO have been used as good treatment methods for removal of organic pollutants in order to produce purified water [122]. Agenson et al. [122] used five membranes for removing alkyl phenols with 0.05 mg/L initial concentration and obtained more than 90% removal. At a constant operating pressure, volume flux reduced with a decrease in solute retention. Also, the volume flux increased at higher pressures while retention increased up to a limiting value. Solute size and functional groups also affected the retention. Significant differences in the retention values of phenolic compounds in the commonly used NF membranes, NF-270 and NF-90 were clearly evident [123]. Arsuaga et al. [124] also used a thin-film composite NF membrane (NF-90) for phenol removal with the feed concentration of 100–500 mg/L, temperature of 20–41 °C, and pH = 2.8–5.3. They observed that operating pressure and organic concentration affect the permeate flux. The permeate flux increases by increasing pressure and decreasing organic concentration. In addition, they found that temperature had no considerable effect, but pH noticeably affected the phenol removal. Actually, because of the molecular form of phenol at a low pH, its removal is more than high pH. Increasing the concentration, they also reached an increase in percentage of removed phenol up to 50–60%.

In case of RO for removing phenol from aqueous solutions using different experimental conditions (phenol concentration, pressure, and pH) and different membranes, polyamide membranes have shown suitable results [122]. Ozaki and Li used the ultra-low pressure reverse osmosis (ULPRO) membrane for removing phenol and some phenolic components such as chloro- and nitrophenols [125]. They reported that with an initial concentration of 10 mg/L, the percentage of removal of the phenolic component increases by increasing pH. It demonstrated that nitrophenols are removed more than 90% while it is more than 60% for chlorophenols at pH = 9. Srinivasan et al. [126] studied separating dimethylphenol from aqueous solution by using polyamide RO membranes. They showed the variation in pressures between 2 to 12 atm and the feed concentrations from 85 to 750 mg/L resulting in the rejection coefficient values to increase from 92 to 97%.

In order to retain the intermediate products of phenol chemical oxidation in aqueous solution López-Muñoz et al. [31] examined the performance of NF and RO membranes (NF-90 and TFC-HR). They reported that by using the TFC-HR membrane with a 100 mg/L initial feed concentration, 46% removal of phenol was obtained, higher than that for the NF-90. They showed that this is in relation to the more porous, rough, and hydrophobic active layer of NF-90. One of the important results was about pure water permeability where for NF (NF-90) it was four times higher than RO (TFC-HR). Their results also showed that steady relative fluxes of NF-90 are lower for solutes compared to the TFC-HR membrane.

3.4.3. PV

PV is a technique that recently attracted researcher's attention for removal of low volatile organic compounds (VOCs) from aqueous solution. No addition of an entertainer, no secondary contamination, minimal energy consumption, and no regeneration needed are some benefits of PV [127]. Generally, in this technique, water and VOCs are, respectively, separated at the feed and permeate side of the membrane where it is simultaneous with evaporating the permeate compound. Some attempts have been made for removing phenol by PV. By using a polyurethane membrane Hoshi et al. [128] observed a lower phenol concentration in the permeate solution rather than the feed stream. With a rise in temperature, phenol flux increased due to enhancing the solubility of phenol in the polyurethane membrane. Also, it was founded that by increasing concentration of phenol in the feed phase its flux also increases, but it decreases with downstream pressure. Kujawski et al. [129] investigated the application of a series of composite membranes based on the polyether-block-amide (PEBA), PDMS, and zeolite-filled PDMS for PV of water–acetone and water–phenol mixtures. The PEBA membrane showed the best selectivity. Since the PEBA membrane is not available on a commercial-scale, others might have a more practical use. Finally, they claimed that hybrid systems containing PV and adsorption could be used to obtain the higher decomposition efficiency of phenol in effluents of the cumene oxidation process. In this connection, the dense and porous hydrophobic polyurethane urea (PUU) membrane was used for PV separation of phenol and better results for porous PUU were observed. The separation of phenol could be carried out with separation factors ranging from 570 to 1,760 at total permeate fluxes of 7.7–14.1 kg/m^2 h over feed concentrations of 1,000–4,000 ppm at 30˚C. In addition, it has been reported that the phenol flux increases remarkably by applying the porous membranes while it could not increase the separation factor [130].

3.4.4. Hybrid systems

3.4.4.1. MBRs. One of the new technologies in biodegradation of pollutants is the use of membrane MBRs (Fig. 6) [1]. MBR is a combination of the activated sludge process with micro- or ultrafiltration membrane separation that was widely used as an effective method for industrial wastewater treatment due to its high product water quality and low footprint. In fact, a wastewater treatment process was characterized by a suspended growth of biomass, and with a micro- or ultrafiltration membrane system. The biological units can biodegrade the waste compounds and the membrane module is responsible for the physical separation of the treated water from the feed solution [131–133]. When the wastes contain a considerable value of minerals, their treatment with MBRs can be problematic. In fact, when the acid and saline quantities are high enough, the use of biological methods are instantly avoided [134,135]. Liu [136] had carried out a study on a system that treated acidic streams including 2,4-dichlorophenol (DCP). His system applied an extraction unit, which used a water insoluble organic solvent in order to separate the organics from wastewaters. Stripping units transferred the organic pollutants to an alkaline aqueous solution. A ceramic hydrophilic membrane separates the formed emulsion in the stripping unit, and then the organic phase is returned to the stripping unit. While the aqueous phase is fed into the bioreactor, a second membrane leads to separating the biomass from the treated water, which is circulated in order to dilute the pollutant content in the wastewaters. This system is very attractive for the treatment of DCP containing streams. During 14 of continuous operation, 98.7% of DCP and 86.5% of the total organics were degraded.

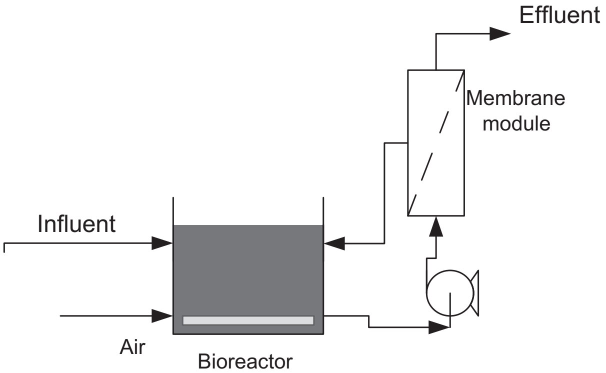


Fig. 6. Schematic diagram of a MBR with external membrane module [132].

3.4.4.2. PMRs. As previously mentioned, it is necessary for photocatalytic wastewater treatment to separate photocatalyst particles from treated water after degradation. PMRs are a very promising method for solving the problems which are involved in separating photocatalysts, products and by-products of photodecomposition. PMRs are hybrid reactors in which photocatalysis is coupled with a membrane separator that the membrane can help as a simple barrier for the photocatalyst and a selective barrier for the molecules to be degraded (Fig. 7). Some additional operations, such as coagulation, flocculation, and sedimentation that are necessary in conventional photoreactors to remove the catalyst from the treated solution in the PMRs have been avoided. In the PMRs, similar to the classical photoreactors, the catalyst should immobilize on/in a membrane or it can suspend in the reaction mixture. With respect to conventional photoreactors, PMRs have many advantages such as the control of residence time of molecules in the reactor and a continuous process with simultaneous catalyst and product separation from the system [38].

Recently, the photodegradation of organic compounds from wastewaters with TiO_2 as a photocatalyst has frequently been reported. In photocatalytic reactors, TiO_2 is suspended in the reaction medium or fixed on a carrier material such as glass, quartz, titanium metal, zeolites, etc. PMRs with photocatalytic MF/UF membranes have been applied for removing different pollutants, such as BPA, chlorophenol, and 4-nitrophenol [39]. PMRs with NF membranes have also been used for removing 4-nitrophenol [39]. Chin et al. [137, 138] used a continuous submerged membrane photocatalytic reactor (SMPR), consisting of a borosilicate glass photoreactor and a hollow fiber membrane module submerged in the reactor, for removing BPA from water. They showed that by

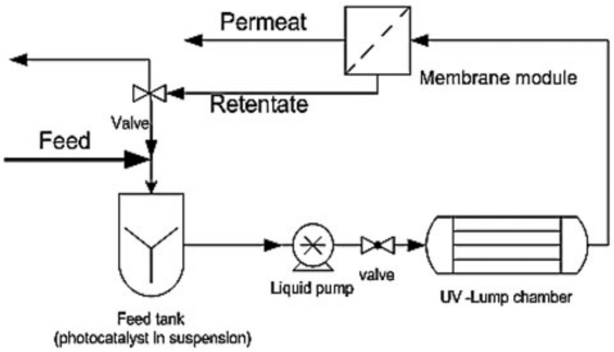


Fig. 7. Schematic view of a PMR with photocatalyst in suspension [48].

using this SMPR system, 97% of BPA (10 ppm) under photodegradation after 90 min, and more than 90% by photomineralization after 120 min of UV illumination could be removed. In addition, it was found that pH at low values affected degradation of BPA because of its better adsorption on the catalyst. The efficiency of photocatalytic degradation was a function of aeration rate and it increased with an increase in aeration rates. Generally, they concluded that SMPR operation can be worthwhile at high feed flux and also with the low membrane fouling. Mohammadi [48] applied a RO membrane separator in a PMR system using the two commercially available nanosized TiO_2 photocatalysts, the Degussa P-25 and Riedel-DeHäen. For a typical condition (initial phenol concentration of 100 ppm and pH = 5), it was demonstrated that this UV/TiO_2/RO

Table 2
Categorization of phenol removal methods based on the initial concentration

Influent phenol concentration					
High		Medium		Low	
Technique	Concentration (mg/L)	Technique	Concentration (mg/L)	Technique	Concentration (mg/L)
Thermal decomposition	As high as 15,000	LLE	20–500	Chemical- electrochemical oxidation	~50
Distillation	~3,000	Adsorption	300–3,000	Photocatalytic oxidation	~50
LLE	Over 3,000–6,000	WAO	–	SPE	10–90
Membrane PV	Up to 10,000	ELM	300–3,000	Biodegradation	Less than 50
MBSE	Over 5,000	CWAO	–	Ozonation	~50
Adsorption	Up to 4,000			RO/NF	0.5–750

Table 3
Categorization of phenol removal methods based on the final concentration

Effluent phenol concentration					
High		Medium		Low	
Technique	Concentration (mg/L)	Technique	Concentration (mg/L)	Technique	Concentration (mg/L)
Distillation	–	Membrane-base solvent extraction	–	Biological degradation	Less than 10
LLE	–	PV	~300	Photocatalytic oxidation	Very low
		CWAO	–	Adsorption	Very low
				WAO	Very low
				CWPO-Fenton oxidation	–
				Ozonation	Very low

hybrid system could approximately remove 50% of phenol within one hour of continuous operation.

Finally, as a brief summary, all the traditional techniques and recent advances for phenol removal are given in Tables 2 and 3 based on the influent and effluent phenol concentrations.

4. Conclusions

Various traditional techniques and the relevant advances for treatment of phenolic wastewaters were reviewed. It is concluded from the investigations that two fundamental parameters should be considered to design an appropriate process in this case: initial and final phenol concentrations. It must be noted that in either case, the level of phenol concentration (low, medium, and high) is the key factor for appropriate selection of the methods (Tables 2 and 3).

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Nomenclature

ACGIH	—	American Conference of Governmental Industrial Hygienists
ACs	—	activated carbons
AOPs	—	advanced oxidation processes
BDD	—	boron-doped diamond
BPA	—	bisphenol-A
BQ	—	benzoquinone
CAT	—	catechol
CFP	—	carbo-furan phenol
COD	—	chemical oxygen demand
CWAO	—	catalytic wet air oxidation
CWO	—	catalytic wet oxidation
CWPO	—	catalytic wet peroxide oxidation
DCP	—	dichlorophenol
ELM	—	emulsion liquid membrane
EPA	—	environmental protection agency
GAC	—	granular activated carbon
H_2O_2	—	hydrogen peroxide
HQ	—	hydroquinone
IRA96	—	name of a special resin
LLE	—	liquid–liquid extraction
MBRs	—	membrane bioreactors
MBSE	—	membrane-based solvent extraction
MF	—	microfiltration
MTBE	—	methyl-ter-butyl ether
NF	—	nanofiltration
OSHA	—	Occupational Safety and Health Administration
P	—	pressure, bar or psi
PAC	—	powdered activated carbon
PCBs	—	polychlorinated biphenyls
PDMS	—	polydimethylsiloxane
PDS	—	peroxydisulphate
PEBA	—	polyether-block-amide
PISR	—	photo-impinging streams reactor
pKa	—	acid dissociation constant
PLE	—	pressurized liquid extraction
PMMA	—	poly methyl methacrylate
PMRs	—	photocatalytic membrane reactors
PMS	—	peroxymonosulphate
POPs	—	persistent organic pollutants
PP	—	polypropylene
ppb	—	part per billion
ppm	—	part per million
PTFE	—	poly-tetrafluoroethylene
PUU	—	polyurethane urea
RBC	—	rotating biological contactor
RO	—	reverse osmosis
SBBR	—	spouted bed bioreactor
SCWO	—	super critical water oxidation
SLM	—	supported liquid membrane
SMPR	—	submerged membrane photocatalytic reactor
SPE	—	solid phase extraction
T	—	temperature, °C
$T_{boiling}$	—	boiling temperature, °C
TBP	—	tri butyl phosphate
$T_{melting}$	—	melting temperature, °C
TOC	—	total organic carbon
TOPO	—	tri-n-octyl phosphine oxide
UASB	—	up flow anaerobic sludge blanket process
UF	—	ultrafiltration
ULPRO	—	ultra-low pressure reverses osmosis
US	—	ultrasonic
VFA	—	volatile fatty acid
VOC	—	volatile organic compound
WAO	—	wet air oxidation
Water solubility	—	g phenol/100 ml H_2O
WPO	—	wet peroxide oxidation

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