Phenol Biodegradation: A review

[Shashi Kant Dubey, Athar Hussain]

Abstract—The release of phenolic compounds in the effluents of petrochemical, textile and coal industry has resulted in contamination of receiving environment. It is very necessary to remove these compounds before discharge of effluents as phenol is toxic to nature. Among the treatment methods biodegradation is considered as cost effective method. The paper reviews various methods used for biodegradation of phenol.

Keywords—Phenol, biodegradation, reactors, membrane bioreactor, fouling

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Abbreviations and Acronyms used

1. MBR = Membrane Bioreactor
2. CPCB = Central Pollution Control Board
3. TCP = Tri Chloro Phenol
4. FBR = Fluidized Bed Reactor
5. SBR = Sequential Batch Reactor
6. GAC = Granular Activated Carbon
7. HRT = Hydraulic Retention Time
8. SRT = Sludge Retention Time
9. COD = Chemical Oxygen Demand
10. OLR = Organic Loading Rate
11. NLR = Nitrate Loading Rate

I. Introduction

Phenol is an organic compound which is translucent and crystalline white powder. It is hygroscopic in nature and changes to red color on contact with air. It is soluble in water, petroleum glycerol and alcohol. Phenolic compounds are used for synthesis of agricultural chemicals, pesticides, dyes and pharmaceuticals. Various chemical intermediates and their uses are described below-

Bisphenol A: It is used for producing epoxy resins for paints coatings and mouldings, and in polycarbonate plastics, CDs and domestic electrical appliances

Caprolactam: It is used in the manufacture of nylon and polyamide plastics

Phenyl amine: It is used as an antioxidant for rubber manufacture, and as an intermediate in herbicides, dyes and pigments, and pharmaceuticals.

Alkyl phenols: Alkylphenols are used in the manufacture of surfactants, detergents and emulsifiers, and also in insecticide and plastics production

Chlorophenols: Chlorophenols are used in medical antiseptics and bactericides such as TCP and Dettol.

Salicylic acid: Used in the production of aspirin and other pharmaceuticals.

Phenol is a toxic chemical. It reacts to form chlorophenols during the process of chlorination. Presence of phenol inhibits or also eliminates microorganisms in municipal biological wastewater treatment plants. It has been reported that phenol in the wastewater causes inhibition (toxicity) to the biomass and results in decreased biomass specific growth rate and reduced substrate removal rate[1,2,3]. Treatment of Phenol is required before disposal of wastewater to receiving environment. In India the phenol concentration is limited to 0.001 mg/l in industrial wastewater discharges by CPCB. Various treatment technologies used for removal of phenol like adsorption, chemical oxidation, and incineration are limited by high cost of application and formation of toxic byproducts. Biological treatment is considered as cost efficient method of contaminant removal. This review will be helpful for understanding application of biological methods for phenolic waste treatment and also investigate the potential for use of membrane bioreactor for treatment of phenolic wastewater. Various sources of phenol and its concentration are given in table 1.
II. Factors affecting biodegradation of Phenol

Biodegradation is a process involving many factors [4]. These factors include temperature, pH, oxygen content and substrate concentration [4, 5, and 6]. Each of these factors needs to be optimized to achieve the maximum degradation of the desired organic compound. The optimization of the substrate concentration for biodegradation of phenols is significant as phenol biodegradation by microbes is inhibited by substrate itself, particularly at higher concentrations. Phenol can be degraded both aerobically and anaerobically, however it can inhibit the growth of microorganisms at elevated concentrations [5, 7 and 8].

Extreme pH values of the wastewater (less than 3 or greater than 9) are inhibitory for growth of microorganisms. Generally, laboratory studies on phenol biodegradation are carried out near neutral pH (pH = 7.0). Each microorganism has a specific temperature range for growth. P. putida has been reported to degrade phenol at low temperature around 10°C, while a bacterium Bacillus stearothermophilus has been used to effectively degrade phenol at 50°C[9]. Sudden exposure to temperatures higher than 35°C have detrimental effect on the bacterial enzymes that are responsible for the benzene ring cleavage. On the other hand, exposure to temperatures lower than 300°C slows down the bacterial activity.

One important factor that can affect the biodegradation of phenols is its chemical structure. It is determined by the number of substituents, type of substituents, position of substituents and degree of branching. The greater the number of substituents in the structure, the less biodegradable it becomes. For example, substituted phenols such as mono-, di-, tri-, and pentachlorophenol are less degradable than unsubstituted phenol. Also, o- and p-substituted phenols are more degradable than m-substituted phenols[6].

Toxicity is the factor which prevents or slows down the metabolic reactions. It depends on the type of microorganisms and the concentrations of specific toxicants. Abundance of bacteria also determines the overall efficiency of biodegradation. The biodegradation of phenol can be performed by either pure or mixed cultures. It has been reported that an application of the mixed culture permits faster phenol degradation than a pure culture [10]. The biodegradation rate of phenol can be improved by immobilizing the cells on solid support particles such as alginate, polyacrylamide, chitosan (a natural nontoxic biopolymer), diatomaceous earth, activated carbon, sintered glass, polyvinyl alcohol (PVA), and polymeric membrane to obtain the maximum degradation capability [11,12]. Immobilization of bacterial biomass for the biodegradation of phenol is effective technique that is usually employed to serve many objectives like protection of the bacteria from high phenol concentrations as well as ease of separation and reutilization of the biomass. Activated sludge processes creates problems such as solid waste disposal, while immobilized microorganisms are capable of effective treatment with little sludge formation [11, 12]. The ability of microbial communities to degrade pollutants is affected by the presence of naturally occurring carbon sources. In general, adaptation to variations in the concentration of nutrients such as glucose, yeast extract, and (NH₄)₂SO₄ enhances the ability to degrade phenols. Biodegradation of phenols increases at higher concentrations of inorganic nutrients [13].

III. Biodegradation of phenol using conventional biological processes

Treatment of phenolic compounds was reviewed using activated sludge, fluidized bed, packed bed and moving bed bioreactors [14]. Degradation of phenol was studied using packed bed reactor at a maximum rate of 18 kg m⁻³ day⁻¹ and using air stirred reactor r at a rate of 11.5 kg m⁻³ day⁻¹[15]. Rotating biological contractor has been studied for treatment of phenolic wastewater by mixed culture at 1754-3508 mg m⁻² h⁻¹ [16]. Loop airlift bioreactor with a packed bed for treatment of phenolic waste was studied and 100% phenol removal was obtained at a loading rate of 33120 mg/m⁻² h⁻¹ [17]. 100% degradation of 100 and 500 ppm phenol solutions was achieved with the help of pulse plate bioreactor [18]. GAC incorporated hollow fiber membrane bioreactor was studied for treatment of phenolic waste and removal of 1000 ppm phenol within 25 hrs has been achieved [19].

SBR was employed for phenol biodegradation and reduction of phenol by 99% was achieved [20]. The reactor was operated on a cycle of 360 minutes, out of which, 260 minutes in aerobic condition and 100 minutes in anoxic condition. Aerobic degradation of synthetic wastewater containing 5.17g/L of phenol using immobilized mixed growth in a continuous fixed bed reactor was reported [21]. Ability of mixed culture from olive pulp to degrade phenol in a pilot-scale packed bed reactor has been studied [22].

Fluidized bed reactor was compared with stirred tank reactor and higher phenol degradation efficiency of FBR has been observed [23]. Biodegradation of phenol with P. putida using continuous fluidized bed bioreactor has been reported [24]. Continuous FBR loaded with C. tropicalis immobilized onto GAC was used for efficiently removing phenol at 60 mg phenol/l.hr [25]. FBR for treatment of mixture of phenol and 4-CP at loading rate of 4.1 mg-CP/hr.L and 55 mg phenol/hr.L was also studied and 98% removal of 4-CP was reported [25].

Biodegradation of phenol was faster in airlift bioreactor than in bubble column [26]. It has been also reported that internal loop airlift bioreactor has preferred for phenol biodegradation to conventional type of reactors, due to better mixing, intimate contact between phases, and faster oxygen transfer rate. Phenol and 2,4-dichlorophenol biodegradation was studied using internal loop airlift bioreactor packed with honeycomb-like ceramic as the carrier to immobilize the culture [27].
Pulsed plate bioreactor for the biodegradation of phenol has been studied and 100% degradation of phenol at a conc. of 500 mg/l has been reported [18]. Phenol degradation was reported to increase with the increase in frequency and amplitude of pulsation. Table 2 shows the advantages and disadvantages of commonly used biological reactors.

iv. **Membrane bioreactor technology**

Membrane bioreactor (MBR) has been extensively used for treatment of various types of industrial wastewater like food processing, pulp and paper, textile, tannery, landfill leachate, pharmaceutical, oily and petrochemical wastewaters. Membrane bioreactor processes, use membrane filtration units to replace the secondary clarifier.

Membrane bioreactor is an attractive solution for the treatment and clarification of high-strength, complex industrial waste streams [28]. MBR has some advantages over the conventional processes such as excellent effluent quality, good disinfection capability, higher volumetric loading, reduced footprint and sludge production, process flexibility toward influent changes, and improved nitrification [29]. Membrane bioreactor is quite effective in removing organic and inorganic pollutants as well as microorganisms from wastewaters [30]. Submerge membranes bioreactor configuration with the advantage of lower operating cost and decreased cost of membrane has been studied [31].

Membrane bioreactors consist of membrane unit responsible for physical separation of solids, and biological reactor for degradation of pollutants in wastewater. These systems can be divided into two main configurations external/side-stream configuration and submerged/immersed configuration in which submerged configuration is mostly used.

External configuration, involves the recirculation of the mixed liquor through a membrane module that is outside the bioreactor. It employs high cross-flow velocity along the membrane surface to provide membrane driving force and also to control membrane fouling. It has been reported that external configuration provides more control of membrane fouling and have the advantages of easier membrane replacement and high fluxes but requires more energy [32]. However in submerged configuration, membrane is placed in the mixed liquor. The driving force across the membrane is achieved by creating negative pressure on the permeate side. Advantages of submerged MBRs are lower energy consumption and less rigorous cleaning procedures [33, 34]. Figure-1 shows the membrane bioreactor configuration.

v. **Membrane bioreactor: operating Conditions**

A. **Hydrodynamic Conditions**

Better hydrodynamic conditions are achieved by increasing aeration in submerged MBRs and the flow velocity of mixed liquor in external MBRs. By increasing aeration or flow velocity energy cost is increased and also it disrupts sludge flocs, which releasing more extracellular polymeric substances (EPS) to speed up membrane fouling [35]. A decrease in biological performance due to negative effect of high shear conditions over microbial activity has been observed [36, 37 and 38].

B. **Hydraulic retention time, sludge retention time and biomass concentration**

On using MBR for anaerobic treatment of municipal wastewater HRT is generally longer than 8 hr, while it requires 4-8 hours for aerobic treatment [32]. Typical anaerobic and aerobic HRTs for Industrial waste treatment using membrane bioreactor have been reported as 2–10 days and 0.5–3 days, respectively [39]. MBR needs to be operated with long SRTs and low food to microorganisms (F/M) ratio for reduced production of sludge. However, increasing the HRT will increase mixed liquor suspended solids (MLSS), and sometimes, the soluble microbial products (SMP) will be accumulated in mixed liquor. The relationship between SRT and membrane fouling is complex. SRT for MBR should be kept at 20–50 days [40]. MLSS values for submerged MBR in the range of 12–15 g/L and for external MBR up to 30 g/L has been reported for industrial wastewater treatment [41].

C. **pH and Temperature**

Generally Membrane bioreactors are operated at near neutral pH. However, bringing the pH of wastewater to neutral pH requires excessive use of chemicals because some industrial wastewaters may have extreme pH values. Equalization can be practiced to avoid use of excessive chemicals for neutralization.

Generally aerobic membrane bioreactor are operated at ambient temperatures around 20–30°C, whereas anaerobic MBR are usually operated at elevated temperatures of 30–40°C. Pulp and paper and textile industries, mostly generate high-temperature wastewaters. Several researchers [42, 43, 44,45,46,47 and 48] studied use of aerobic and anaerobic MBRs operated at hemophilic (50–55°C) temperatures for industrial wastewater treatments.
vi. Phenol biodegradation using membrane bioreactor

The membrane bioreactor (MBR) is effective in the treatment of municipal wastewater and industrial effluents with toxic contents. MBR has several advantages. MBRs are compact provides high effluent quality. It produces little sludge [49, 50 and 51]. Hollow fiber membrane bioreactor for degradation of phenol in the range of 1000-2000 mg l\(^{-1}\) has been studied [52]. Membrane bioreactor (hollow fiber module) was used for the biodegradation of phenol by activated sludge [23]. Phenol biodegradation under continuous operation in an immobilized-cell hollow fiber membrane bioreactor using P. putida has been reported [53].

Tubular ceramic membrane bioreactor can be an effective wastewater treatment option [54]. It can be backwashed effectively providing high resistance to fouling, abrasion, and corrosion. Wastewater containing phenol up to 948 mg l\(^{-1}\) can be treated in MBR using ceramic ultra filtration membrane to produce effluent containing phenol in the range of 20 mg l\(^{-1}\) [55]. MBR is more stable than activated sludge process [56]. It also reported that maximum COD loading rate of the MBR was 28 kg COD m\(^{-3}\) d\(^{-1}\). However for activated sludge process it is 15 kg COD m\(^{-3}\) d\(^{-1}\).

Fouling is the main disadvantage associated with the use of membrane bioreactor. The nature and extent of fouling in membrane is affected by three factors: biomass characteristics, operating conditions, and membrane characteristics [57]. Ceramic membrane bioreactor with HRT of 4 hours and SRT of 30 days can be used to treat synthetic wastewater containing phenol up to 600 mg l\(^{-1}\) with 72% removal efficiency [58].

Due to the more stringent in effluent discharge standards in most of the countries, the MBR technology has become an attractive alternative to conventional activated sludge systems, which is possible to be used for expansion and upgrading of the existing systems [59].

For external MBR, cross-flow membranes are used and the membrane module is located apart from the activated sludge reactor. This can ideally control the fouling by reducing the deposition of foulants on the membrane surface [34]. However, the external MBR usually consumes more energy and requires larger footprint. Furthermore, the tubular membrane used in the cross flow MBR has lower packing density and is more expensive. Owing to this, mixed liquor is pumped into the tubular membrane module to obtain the required high shear stresses to reach high permeate flux values [60]. Consequently, high circulation velocity is always needed in the tubular membrane that contributes eventually to high head loss and high energy consumption [61].

On the contrary, low cost capillary and hollow fiber membranes are common in most submerged MBR. This kind of membranes has higher packing density and can be operated at lower transmembrane pressure (TMP). As a result, the operation flux can be reduced and energy consumption is less. Furthermore, the coarse bubbles generated from the aeration in the reactor are utilized to maintain sufficient oxygen for the microorganism metabolism, and create shear stress to suppress the deposition of foulants on the membrane surface. This eliminates the requirement of high rate circulation pump as in external MBR [33]. Besides, submerged MBR has lower tendency towards fouling, and contributing to less cleaning and replacement of membrane [62, 63]. In view of the low energy consumption, together with less fouling tendency of the membrane, submerged MBR is more popular in the application in domestic and industrial wastewater treatment.

Phenol biodegradation by mixed culture was studied in a membrane bioreactor over a period of 285 days [64]. The acclimatized activated sludge allowed significant phenol degradation (95% average COD removal efficiency and greater than 99% phenol removal efficiency) without supplemental reagent addition. Excellent effluent quality was obtained regardless of the extremely short SRT (5 – 17 days). This work shows the potential of MBR for toxic chemical elimination, charged effluents treatment and process stability.

When phenol and 2,4-DCP were used as a carbon source in MBR system, 98.99% of phenol, 2,4-DCP, TOC and COD removal could be obtained when organic loading was increased from 1.80 to 5.76 kg/m\(^{3}\).d COD. Removal of chemical oxygen demand (COD) and phenol in submerged membrane bioreactor (MBR) has been reported up to 85 % and 90 %, respectively, even though at high concentration of 600 mg/L phenol [65].

Vii. Conclusion

Effective treatment of various kinds of industrial wastewaters is of growing concern to industries. Conventional biological treatment of industrial wastewater encounters difficulties due to the high organic strength or the presence of toxic or inhibitory pollutants like phenol. MBR technology appears to be a solution for such industrial wastewater treatments. The commercial application of the MBR technology for industrial wastewater treatments has been in rapid research and development. The application areas cover a wide range of industrial wastewaters, which include food processing, pulp and paper, textile, tannery, landfill leachate, pharmaceutical, oily and petrochemical, and other types of industrial wastewaters. Fundamental aspects studied in academic research involve aspects related to membrane fouling, microbial characterization, and optimizing operational performance. MBR systems can be used for treatment of inhibitory waste waters.
TABLE 1. Phenol concentration in various industrial effluents and discharge standards

<table>
<thead>
<tr>
<th>Industry</th>
<th>Concentration of Phenol (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Mining</td>
<td>1000-2000</td>
</tr>
<tr>
<td>Lignite transformation</td>
<td>10000-15000</td>
</tr>
<tr>
<td>Gas Production</td>
<td>4000</td>
</tr>
<tr>
<td>Petrochemicals</td>
<td>50-700</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>1000</td>
</tr>
<tr>
<td>Oil refining</td>
<td>2000-20000</td>
</tr>
<tr>
<td>CPCB (Drinking water standard)</td>
<td>0.001</td>
</tr>
<tr>
<td>Discharge limit</td>
<td>1 (surface discharge)</td>
</tr>
<tr>
<td></td>
<td>5 (Sewer discharge, Oceans)</td>
</tr>
</tbody>
</table>

Table 2: Conventional Biological Reactors

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Reactor Type</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sequencing Batch Reactor</td>
<td>- Flexibility of cyclic phasing, operational modes</td>
<td>- Expensive aeration - May require more no. of reactors</td>
</tr>
<tr>
<td>2.</td>
<td>Trickling Filter</td>
<td>- Simple in operation</td>
<td>- Problems of sludge disposal - Less control</td>
</tr>
<tr>
<td>3.</td>
<td>Rotatory Biological Contractors</td>
<td>- Easier to handle shock loading - Better DO levels</td>
<td>- Degradation rate controlled by mass transfer</td>
</tr>
<tr>
<td>4.</td>
<td>Packed Bed Reactor</td>
<td>- High efficiency</td>
<td>- Difficulty of maintenance and cleaning</td>
</tr>
<tr>
<td>5.</td>
<td>Fluidized bed reactor</td>
<td>- No clogging</td>
<td>- Detachment and washout of sludge</td>
</tr>
<tr>
<td>6.</td>
<td>Pulsed plate reactor</td>
<td>- Enhanced mass transfer</td>
<td>- Commercial use not reported</td>
</tr>
</tbody>
</table>
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