Study of Removal of Phenol by Biological Treatment Methods - with Reference to Moving Bed Biofilm Reactor & Activated Sludge Process

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Abstract: The effluent from industries such as oil refineries, paper mills, olive oil mills, wood processing, coal gasification, textiles, resins and agro-industrial wastes discharge phenols much higher than the toxic levels set for this compound. Such high concentrations of phenol pose severe health hazards to aquatic and human life. An A study was carried out for biological treatment of phenolic wastewater in moving bed biofilm reactor (MBBR) and Activated Sludge Process (ASP). Three stages were conducted in laboratory scale reactors: acclimatization of biomass with phenolic wastewater, study of COD and phenol removal in MBBR in continuous process, study of COD and phenol removal in ASP in continuous process.

Keywords: ASP, COD, HRT, MBBR, OLR

I. INTRODUCTION

During the last two decades, phenolic compounds have become the subject of intense research in the preservation of our environment. Phenol is the common name of hydroxybenzene, C₆H₅OH, an aromatic compound having one hydroxyl group attached to the benzene ring. Phenol has also been called carbolic acid, phenic acid, phenyl acid, phenyl hydroxide or oxybenzene. Phenol is produced both naturally and synthetically by chemical processes. Naturally, phenol has been extracted from coal tar distillation. Synthetically, cumene oxidation accounts for 95% of phenol production worldwide at a rate of 6.4 million metric tons produced in 2001. Despite being toxic, phenols are widely used compounds as raw materials to synthesize other industrially important chemicals.

Phenol has been selected as a model compound in this study because it is a common pollutant found in the effluent of various industrial wastes including petroleum operations, and phenol like compounds are produced in the degradation pathways of high molecular weight polycyclic aromatic hydrocarbons (PAHs). (9)

MBBR is a completely mixed and continuously operated biofilm re-actor that is designed to offer the positive aspects of biofilm process including a stable removal efficiency of toxic pollutants, compact and simplicity of operation; without its drawbacks including high head loss, medium channelling and clogging. In addition, moving bed biofilm reactors provide a better control of biofilm thickness and higher mass transfer characteristics. The concentration of biomass in MBBR can be in-creased either by raising the amount of moving media or using media with a high effective biofilm surface area that enhances resistance to toxicity and consequently improves MBBR performance. As a consequence of such advantages, MBBR process has been recently used for the removal of many toxic wastewaters including landfill leachate aniline, ammonium from saline wastewater, coal gasification wastewater, thiocyanate and antibiotic fermentation-based pharmaceutical wastewater.

OBJECTIVES

- To study COD removal efficiency of MBBR for synthetic waste water with increasing phenol concentration in batch process.
- To study COD and Phenol removal efficiency of MBBR at varying hydraulic retention time (HRT).
- To evaluate COD and Phenol removal efficiency of MBBR and ASP with increasing organic loading rate (OLR).
- To determine biomass generation and organic removal in MBBR and ASP.

LITERATURE REVIEW

Seyyed Ali Akbar Nakhli, Kimia Ahmadizadeh, Mahmood Fereshtehnejad, Mohammad Hossein Rostami, Mojtaba Safiarand Seyyed Mehdi Borghesi studied on the performance of an aerobic moving bed biofilm reactor (MBBR). It was assessed for the removal of phenol as the sole substrate from saline wastewater. The effect of several parameters namely inlet phenol concentration (200–1200 mg/L), hydraulic retention time (8–24 h), inlet salt content (10–70 g/L), phenol shock loading, hydraulic shock loading and salt shock loading on the performance of the 10 L MBBR inoculated with a mixed culture of active biomass gradually acclimated to phenol and salt were evaluated in terms of phenol and chemical oxygen demand (COD) removal efficiencies. The results indicated that phenol and COD removal efficiencies are affected by HRT, phenol and salt concentration in the bioreactor saline feed. The MBBR could remove up to 99% of phenol and COD from the feed saline wastewater at inlet phenol concentrations up to 800 mg/L, HRT of 18 h and inlet salt...
contents up to 40 g/L. The reactor could also resist strong shock loads. Furthermore, measuring biological quantitative parameters indicated that the biofilm plays a main role in phenol removal. Overall, the results of this investigation revealed that the developed MBBR system with high concentration of the active mixed biomass can play a prominent role in order to treat saline wastewaters containing phenol in industrial applications as a very efficient and flexible technology. (7)

M. Rajani Rani, D. Sreekanth, V. Himabindu reported the feasibility of aerobic treatment of wastewater having mixed Phenolic compounds (phenol, 2,4-dinitrophenol, 2,4-dichlorophenol, 4-chlorophenol, 4-nitrophenol) by using 9L lab scale Activated Sludge Process (ASP) at HRTs (Hydraulic Retention Time) varying between 3.0, 2.5, 2.0, 1.5 and 1 day. Continuous monitoring of parameters like pH, Oxidation Reduction Potential (ORP), Chemical Oxidation Demand (COD), compound reduction is used to assess the treatment efficiency of ASP. The highest percentage COD removal and percentage compound reduction of 98% and 99.3% of phenol was observed at 3.0 d HRT respectively. After treatment pollutants are removed in the order of phenol > 4chlorophenol (4CP) > 4nitrophenol (4NP) > 2,4-dichlorophenol (2-4DCP) > 2,4-dinitrophenol (2,4DNP). The dissolved oxygen concentration and pH in the activated sludge reactor was found to be 1-3 mg/L and 7-8 respectively. The optimum biomass concentration was 2500-3000 mg/L, whereas the corresponding SVI was found to be around 70mL/g. The morphological characterization of aerobic granules was carried out by using SEM. Thus the results obtained indicate that ASP could be used efficiently for the treatment of wastewater containing mixed phenols. (3)

II. MATERIALS AND METHOD

A. Treatment Of Phenolic Wastewater By Moving Bed Biofilm Reactor.

Development of biomass over media of MBBR

For the development of biomass over MBBR media, following steps were taken. 3 L of Mixed Liquor and 5 L of raw sewage (outlet of grit chamber) were taken from existing sewage treatment plant and aerated in a glass jar with 6-7 lpm of air supply. During aeration, Glucose and Tryptone were added as nutrients to the jar. Contents of the jar were replenished by replacing 2 L of supernatant with raw sewage every day. Microscopic observations of aerated biomass were carried out on daily basis. Microscopic observation showed presence of free swimming ciliates in the reactor indicating stable system.

After 10 days of such aeration 100 numbers of plastic media of size 16mm length, 16mm diameter & specific surface area 339m2/m3 were introduced in the aeration jar for development of biofilm over the media. Gradual increase in number of media was carried out by addition of 100 media over every 2-3 days. Gradually total numbers of plastic media in the jar were increased to 1008 numbers.

Literature on MBBR treatment recommended 30 – 70 % volumetric filling of plastic elements in empty reactors. Selection of 60% of reactor volume was done randomly in this range. Media was observed under the microscope for development of biofilm. It took 20-25 days for development of biofilm on plastic media.

Contents of the jar including plastic media with biofilm were transferred to a flexi glass laboratory scale model of MBBR (Aerobic bio reactor) of 8 L capacity.

Acclimatization Of Biomass With Phenolic Waste Water

For acclimatization of biomass with phenol, synthetic waste water was prepared using Laboratory grade phenol added to primary settled sewage in desired concentrations.

Biomass attached to media as well as in suspension was acclimatized within the feed. Acclimatization was initiated with 50 mg/L of phenol concentration and gradually increased to 500 mg/L in the increment of 50 mg/L. After addition of each 50 mg/L phenol, mixing of feed to reactor contents was achieved to have uniform concentration of phenol throughout the reactor volume.

Both initial sample (influent) & final samples after hydraulic retention time of 24 hours were analysed for COD. COD was taken as an evaluation parameter 1 mg/L phenol contributes 2.3 mg/L COD. At different phenol concentrations & at 24 hours HRT COD were measured. This COD value is Total COD i.e. COD due to phenol and COD due to influent sewage.

% reduction in COD was observed in the range of 52 % to 60% up to phenol concentration of 300 mg/L. At 400 - 450 mg/L, % reduction decreased to 19 - 15%. Therefore restoration of biomass was carried out by adding Glucose and Tryptone. Acclimatization once again started with 100 mg/L phenol concentration and continued up to 650 mg/L, where very low % reduction in COD (i.e. 23.22 %) was observed.
Reactor was aerated in order to provide oxygen for degradation & to keep carrier in constant movement. In Batch treatment, higher phenol concentration i.e., more than 650 mg/L may cause shock loading during application of phenolic load, therefore it was thought to switch the reactor over continuous mode.

PH in the reactor was measured around 8. In aerobic process BOD: N: P was maintained in the ratio of 100:5:1. To avoid the nutrient deficiency Urea & KH2PO4 were added in the reactor. All the parameters were analysed by using Standard Methods for Examination of water and waste water.

**Study of COD removal efficiency of MBBR in continuous process**

In continuous process phenol concentration was increased from 700 mg/L gradually to 1500 mg/L in MBBR and % reduction in COD in 72 hrs. HRT was determined. Microscopic observations of reactor showed presence of ciliates indicating the aerobic system.

**Effect of OLR on removal efficiency of phenol**

At 1500 mg/L phenol concentration, MBBR was operated at variable organic loading rate (OLR). Variations in OLR were carried out by varying influent flow rate with the peristaltic pump. Each OLR was operated for 3 cycles to have steady state condition in the reactor. The steady state condition is defined as the period during which the effluent quality was relatively constant at a constant loading with regard to the parameter of COD & SS.

**III. RESULTS & DISCUSSION**

The Effect of OLR on COD & Phenol Reduction are shown in Table 1 & Table 2 for MBBR & ASP respectively

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Initial COD (mg/L)</th>
<th>Flow Rate (ml/min)</th>
<th>OLR (g/d)</th>
<th>Final COD (mg/L)</th>
<th>% Reduction (COD)</th>
<th>Residual Phenol (mg/L)</th>
<th>% Reduction (Phenol)</th>
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<td>66.22</td>
<td>528</td>
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<tr>
<td>5</td>
<td>3800</td>
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<td>32.83</td>
<td>1926</td>
<td>49.31</td>
<td>640</td>
<td>57.33</td>
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</table>

Following graph shows % reduction in COD at various hydraulic retention time (HRT) for phenol concentration of 1500 mg/L. With decrease in HRT decrease in % reduction was observed. At about 27 h HRT % reduction in COD was 98.2 with residual phenol concentration of 30 mg/L at 9 h HRT % reduction in COD decreases to 57 % with residual phenol concentration 640 mg/L.

Graph showing relationship of % reduction in COD v/s HRT for MBBR
The initial phenol concentration obviously influenced the COD removal. From the tests with the increasing COD, there were excessive substrate for the biomass culture resulting in decreasing in the COD removal efficiencies.

From the experiments, it is observed that COD removal efficiency decreased as organic loading rate increased. The same results are observed for the phenol removal efficiency. The removal performance significantly decreased while the phenol concentrations increased. This phenomenon was self-inhibition typically found in organic biodegradation. Moreover, the compound, phenol, is a toxic substance; therefore, this growth substrate (phenol) at high concentration (1500 mg/L) could be toxic to biomass resulting in lower phenol removal efficiency.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>OLR (g/d)</th>
<th>% COD Reduction</th>
<th>Phenol loading (g/d)</th>
<th>% Phenol Reduction</th>
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<td>5</td>
<td>32.83</td>
<td>49.31</td>
<td>12.96</td>
<td>57.3</td>
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</table>

The Effect of Organic Loading Rate & Phenol Loading Rate on COD & Phenol removal efficiency are shown in Table 3 & Table 4 for MBBR & ASP respectively.

Table 2 Effect of OLR on COD & Phenol Reduction in ASP

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Initial COD (mg/L)</th>
<th>Flow Rate (ml/m in)</th>
<th>OLR (g/d)</th>
<th>Final COD (mg/L)</th>
<th>% Reduction (COD)</th>
<th>Residual Phenol (mg/L)</th>
<th>% Reduction (Phenol)</th>
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<td>6</td>
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<td>1766</td>
<td>54.62</td>
<td>760</td>
<td>49.33</td>
</tr>
</tbody>
</table>

Graph showing relationship of % reduction in Phenol v/s Phenol Loading for MBBR

Table 4 Effect of Organic Loading Rate & Phenol Loading Rate on COD & Phenol removal efficiency in ASP

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>OLR (g/d)</th>
<th>% COD Reduction</th>
<th>Phenol loading (g/d)</th>
<th>% Phenol Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.22</td>
<td>63.91</td>
<td>4.32</td>
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<tr>
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</tr>
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</table>

Graph showing relationship of % reduction in COD v/s OLR for MBBR
Phenol and organic matter in sewage were the substrate in which sewage organic matter is readily biodegradable. The difference between COD equivalent of measured phenol and COD measured in the effluent could be explained by accumulation of organic intermediates (metabolites) that were generated during the partially phenol biodegradation caused by inhibitory effect of high phenol concentration in wastewater. (7)  

IV. CONCLUSION

Treatment of Phenolic Wastewater In Moving Bed Biofilm Reactor

- Time period required to develop biofilm on plastic media was about 20 to 25 days after introduction of media to the well developed bio culture.
- Acclimatization study of phenolic waste water with phenol concentration of 100 – 600 mg/L in batch process in laboratory scale model of MBBR gives COD reduction in the range of 50 – 70% at 24 hours hydraulic retention time.
- Continuous flow process in laboratory scale model of MBBR with phenol concentration of 700 – 1500 mg/L results in COD reduction of 91 – 98% in 72 hours hydraulic retention time.
- With 1500 mg/L influent phenol concentration and low organic loading rate of 10.02 g/d, COD reduction obtained as 98.02 % with outlet value of COD 63 mg/L. As organic loading rate increased stepwise to 32.83 g/d, COD reduction decreased to 49.3 % with outlet COD value of 1926 mg/L.
- With 1500 mg/L influent phenol concentration and increasing phenol loading rate from 4.32 to 12.96 g/d reduction in phenol concentration decreased from 98 to 57.33%.

Treatment Of Phenolic Wastewater In Activated Sludge Process

- At 1500 mg/L influent phenol concentration and organic loading rate of 10.22 g/d, reduction in COD obtained as 64 %. As organic loading rate increased stepwise to 32.83 g/d, reduction in COD decreased to 54 %.
- At 1500 mg/L influent phenol concentration and phenol loading rate of 4.32 g/d, reduction in phenol concentration obtained as 69 %. As phenol loading rate increased to 12.96 g/d, reduction in phenol decreased to 49 %.
- Comparison of MBBR with ASP at 1500 mg/L influent phenol concentration shows that for low organic loading rates i.e. 10, 15 and 20 g/d, MBBR is more efficient than ASP for COD and phenol reduction. At higher organic loading rates i.e. 26 and 33 g/d efficiency of ASP was found higher than MBBR.
- In MBBR reactor concentration of biomass was remarkably higher when biomass was transferred from batch acclimatization stage to continuous. Then after biomass concentration was in the range of 3800-4600 mg/L. In ASP system biomass concentration was found increasing with increase in organic loading rate.

- The average COD applied for VSS unit was 0.815 g/gVSS for MBBR system & 3.49 g/gVSS for ASP. The average COD removals referred to the biomass unit was 0.6 g/gVSS for MBBR & 2.14 g/gVSS for ASP. Thus if removal is referred to the biomass unit in the reactor its value can be compared in the two systems: 73.6% for MBBR & 61.3% for ASP.
- The volatile suspended solids production rate in an MBBR is higher than that for ASP practicing phenol removal. The MBBR generated 1.70 g of volatile suspended solids for every g of COD removed. This is higher than the 0.62 g volatile suspended solids/g COD removed calculated for activated sludge process that practice phenol removal.(16)  

V. REFERENCES

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