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Treatment of volatile organic compounds in pharmaceutical wastewater using submerged aerated biological filter

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HIGHLIGHTS

- Performance of SABF treating mixture of VOCs was evaluated.
- Effects of airflow rate, HRT and OLR on VOC emissions were evaluated.
- Reduced airflow rate reduced the VOC emission from SABF.
- Less contact time between pollutant and biomass reduced VOC degradation.
- Competition for the active sites affected the degradation of benzene and toluene.

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ABSTRACT

Performance of an up-flow submerged aerated biological filter (SABF), treating mixture of VOCs in pharmaceutical wastewater was evaluated. Methanol, acetone, dichloromethane, benzene and toluene were chosen as target pollutants. The effects of airflow rate, hydraulic retention time and organic loading rate on VOC emission were evaluated. During the start-up phase, SABF removed over 92% of COD, up to an organic loading rate (OLR) of 3.09 ± 0.05 kg/m^3/d at 12 h HRT. It was observed that the limited mass transfer of VOC to the gas phase at low air flow rate (0.4 L/min, with an empty bed residence time of 114 s) reduced its emission from the reactor. Performance of SABF varied with hydraulic retention time (HRT) and maximum COD removal (93%) was achieved at 10 h. Reduced contact time (less than 10 h) between pollutant and biomass affected the degradation of dichloromethane, benzene and toluene in the liquid phase. SABF exhibited effective degradation (95%) of VOCs up to an OLR of 17.45 ± 0.01 kg/m^3/d. Enzyme inactivation reduced the efficiency (72%) of the SABF for increased OLR of 20.85 ± 0.03 kg/m^3/d. Irrespective of organic loading rate, competition for the active site between the pollutants mainly affected the degradation of benzene and toluene in the liquid phase. Presence of high biomass and reduced mass transfer of VOCs to gas phase due to low air flow rate reduced VOC stripping even at higher organic loading rate. Average gas phase emission reduced to 0.075% for DCM, benzene, toluene whereas methanol and acetone was completely removed from the gas phase.

1. Introduction

Volatile organic compounds (VOC) are organic chemicals released to the atmosphere by natural and anthropogenic sources. VOCs are hazardous air pollutants and it favours formation of photochemical smog [1]. Pharmaceutical industry uses a wide range of organic solvents during chemical synthesis, formulation, extraction and product recovery. Typical solvent usage in such industry varies from 10 to 800 kg of solvent/kg of active pharmaceutical ingredient [2]. Besides in reaction process, large volume of methanol and acetone are used for cleaning purposes. As a result, waste stream generated from pharmaceutical industry consists of 75–80% of organic solvents and most of them are volatile in nature [3]. Variety of chemicals released from pharmaceutical industry include priority pollutants like benzene, toluene, and dichloromethane. EPA's toxic release inventory reported the prevalence of solvents like methanol (75.61 million kg/year), dichloromethane (25.89 million kg/year) and toluene (19.76 million kg/year) in the wastewater discharged from pharmaceutical industries [4].

Industries usually employ an array of treatment technologies. Even though anaerobic processes like anaerobic film reactors, anaerobic filters, anaerobic sludge reactors are extensively used for the pharmaceutical wastewater treatment, problems like lack

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of microbial diversity and granule deterioration due to acetate accumulation [5] and suppression of methane generation [6] were reported during the treatment. Impact of high COD wastewater on aerobic processes like activated sludge process, oxidation ditch and sequencing batch reactor were also studied. It is reported that activated sludge was not suitable for treatment of pharmaceutical wastewater with COD greater than 4000 mg/L [7].

Earlier studies on pharmaceutical wastewater treatment have focussed mainly on the COD removal. Awareness of VOC emission from biological treatment units, while treating pharmaceutical wastewater is very limited. Most of the treatment systems are open to atmosphere. Contact of organic pollutant in wastewater with the ambient air results in the VOC emission from the treatment units. VOCs like acetone (400.4 ppbv), isopropanol (22.8 ppbv) and dimethyl sulfide (641.2 ppbv) were identified in the gas phase from the wastewater treatment plant of an industrial park in Taiwan [8]. Fate of VOCs in the treatment units not only depends on their physical properties but also on design of the treatment system. It is essential to gain insight on various factors that influence the VOC emission from the treatment units. Factors like aeration, biomass adaptability, and retention time practised in the biological processes influence the VOC emission. Melcer et al. [9] reported that the surface aeration of municipal wastewater increased the stripping of 1,1,1-trichlorethane, toluene, and 1,1-dichloroethane from aeration tank when compared to diffuser type. Control of VOC emission from the wastewater treatment, is gaining importance because of the negative impact of VOCs on human being and environment.

Presence of high active biomass for biodegradation can be considered as an important key aspect during the selection of a treatment technology to reduce VOC emission [10]. Biological fixed film reactor is effective in retaining large quantity of biomass within the inert media. The packed column has been reported to be more effective in reducing VOC emission when compared to CSTR [11] and among several fixed film bioreactors, submerged aerated biological filter has proven its capability to reduce VOC emission during the wastewater treatment. Presence of high biomass in the biological aerated filter enhances the degradation of VOC in the wastewater and reduces its emission to atmosphere. Cheng [12] reported a VOC emission of 0.97 ± 0.2 ppmv from an aerated biological filter while treating wastewater from multiple layer capacitor plant with an organic loading of 2.76 $kg/m^3/d$. They also reported that the high biomass in BAF effectively degraded the isopropanol in the wastewater, thereby reducing its air phase emission to less than 0.1%. Ramos et al. [13] reported a complete removal of phenol (1 g/L) from the industrial wastewater with high salinity (30 g/L) using submerged fixed film reactor. They reported that the aerobic submerged fixed film reactor adapted well to the high phenol concentration and the presence of high biomass in the fixed film reactor resulted in the complete removal of phenol. However, most of the above cited studies focussed on the degradation of one or two combination of VOC in the wastewater. It is essential to evaluate the performance of SABF to treat mixture of VOCs from pharmaceutical wastewater. Moreover the effect of various operational parameters like hydraulic retention time (HRT) and organic loading rate (OLR) on VOC emission is an area to explore.

In the present study, an attempt was made to optimise the operational parameters and to evaluate the performance of a submerged aerated biological filter in treating pharmaceutical wastewater. The effects of air flow rate hydraulic retention time, and organic loading rate on the VOC emission were investigated. Most frequently found pollutants in pharmaceutical wastewater include methanol, acetone, dichloromethane, toluene and they contribute to more than 80% of pollutant load in wastewater. Hence, these pollutants were selected as the target pollutants for the present study. They are true representatives of hydrophilic and hydrophobic compounds with different physical and chemical properties that are encountered in the pharmaceutical wastewater.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

Methanol (Thomas Baker, India, 99.8%) acetone (Rankem, India, 99.8%), benzene (Rankem, India, 99.8%), toluene (Rankem, India, 99.5%), dichloromethane (Rankem, India, 99.8%) were utilised in this study. All the chemicals were of high performance liquid chromatography (HPLC) grade.

2.1.2. Microorganism and culture media

The submerged aerated biological filter was initially inoculated with the mixed consortia previously utilised for the biodegradation of different groups of VOCs (alcohol, aromatics, chlorinated and ketone) by Priya and Philip [14]. Some of the strains identified by 16S rDNA technique in the mixed consortia were *Bacillus cereus* and *Burkholderia kururiensis*. The composition of the minimal salt media (MSM) used for this study was (the parentheses denote the quantity of chemicals in g/L): Na_2HPO_4 (1); K_2HPO_4 (1), $(NH_4)_2SO_4$ (0.5); $Ca(NO_3)_2{\cdot}4H_2O$ (0.05). The initial pH in the reactor was 7 ± 0.2.

2.2. Experimental studies

2.2.1. Experimental setup

Submerged aerated biofilter (SABF) was fabricated using a column made up of 3 mm thick plexi glass with an outer diameter of 9.0 cm and height of 60 cm. The reactor was packed with the open pore spirals (supplied by Fujino spirals, India), made of polyvinylchloride with average size of 50 mm, and a surface area of approximately 350 m^2/m^3 [15]. The number of spiral used to fill the SABF was 100 and the initial porosity of the packed column was 0.83 ± 0.005. The bed height was 35 cm and the packed media were completely immersed in water. The sampling ports were placed at 10 cm interval along the height of the bed. 10 L glass chamber fitted with an air tight Teflon septa was used as an influent tank for the synthetic wastewater. The synthetic wastewater prepared using the minimal salt media and the target pollutants were pumped by the peristaltic pump (PP30, Miclins, India) to the inlet port placed at a distance of 20 cm from the bottom of the reactor. The effluent port was at a distance of 3 cm from the top layer of the packed media. The liquid samples were collected daily from both the inlet and outlet ports for the analysis. Air sampling port was at a distance of 5 cm above the effluent port. Air was supplied by an air pump to the diffuser provided at the bottom of the reactor. Air flow rate was measured using an air flow meter (Placka Instrumentation, India). The circular base plate with perforations was provided at the bottom of the column to support the media. U-tube manometer filled with water was used to measure the pressure drop across the bed. The schematic of the reactor is given in Fig. 1.

2.2.2. Start up and performance evaluation of SABF

Most prevalent VOCs in pharmaceutical wastewater such as methanol, acetone, benzene, toluene and dichloromethane are chosen as target compounds. Performance of submerged aerated biological filter was evaluated in terms of VOC removal efficiency (RE%) in liquid phase and also on the emission rate for different organic loading rate (OLR). Organic loading rate as VOCs, applied to the reactor was estimated using Eq. (1):