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Performance of suspended and attached growth bioreactors for the removal of cationic and anionic pharmaceuticals

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HIGHLIGHTS

- Batch studies on biodegradation and biosorption of pharmaceuticals.
- Pilot scale studies for performance evaluation of ASP, SABF and MBR.
- SRT and HRT had significant impact on performance.
- SABF performed best for removal of ciprofloxacin and gemfibrozil.
- Monod co-metabolic model could describe degradation of pharmaceuticals.

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ABSTRACT

Removal of three pharmaceuticals, namely, atenolol, gemfibrozil and ciprofloxacin in three bioreactors namely, activated sludge process (ASP), submerged attached biofilter (SABF) and membrane bioreactor (MBR) was studied. Removal efficiencies at steady state for atenolol were found to be 93%, 82% and 95% in ASP, SABF and MBR, respectively. Removal efficiencies for gemfibrozil were 75%, 90% and 85%, while those for ciprofloxacin were 84%, 95% and 93% in ASP, SABF and MBR, respectively. Nearly 20% of the ciprofloxacin was found to be sorbed on the biomass in the reactors. Reduction in sludge residence time (SRT) decreased the removal of compounds in ASP and MBR, and reduction in hydraulic residence time (HRT) caused a negative impact on the performance of all the reactors. Considerable increase in easily available carbon source reduced the removal efficiency. Sorption coefficient (log K_d) of ciprofloxacin was found to be 3.86 and sorption was negligible in case of atenolol and gemfibrozil. Monod co-metabolic model could simulate biodegradation process satisfactorily. Inhibition concentrations (K_i) of atenolol, ciprofloxacin and gemfibrozil were found to be 2.8 mg/L, 0.6 mg/L and 0.89 mg/L, respectively. Biokinetic parameters μ_{max}, K_s and $Y_{X/S}$ were 0.046 h^{-1}, 10 mg/L and 0.36, respectively. Efficiency factor (η_c) was estimated to be 0.002, 0.0006 and 0.001 mg compound/gCOD for atenolol, ciprofloxacin and gemfibrozil, respectively.

1. Introduction

Considerable attention is being paid to emerging contaminants (ECs) due to their persistence and increased toxicity. Even though concentrations of ECs are generally less, their continuous release through effluents leads to accumulation and can cause significant impact on aquatic life and humans. Among various ECs, pharmaceuticals are of significant concern because these compounds are capable of causing biological effects at very low concentrations [1]. Moreover, presence of antibiotics in trace concentrations in environment is of serious concern as it can lead to the evolution of resistant bacterial strains. Pharmaceuticals enter into the environment through various pathways and undergo different processes. Wastewater treatment plant (WWTP) effluent is identified as one of the major sources of pharmaceuticals [2] as conventional treatment plants are not effective in removing them. Hence, removal efficiencies of WWTPs have to be improved and process modifications need to be made.

Even though several studies have reported the removal of pharmaceuticals in biological treatment, further studies are needed to understand complex interactions between the pharmaceuticals. Also the effect of high COD content on the removal of pharmaceuticals has not been studied in detail. Moreover, compounds present in the surface water and wastewater are region specific and are dependent on the consumption pattern. Among various

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pharmaceuticals, ciprofloxacin, atenolol and gemfibrozil are widely used in India and are included in national list of essential medicines. Ciprofloxacin is a commonly used antibiotic which belongs to the quinolone derivatives. Its presence has been detected in domestic, hospital and industrial wastewater and surface water in India in the range of μg/L to mg/L [3–5]. Atenolol is one of the most commonly prescribed cardio selective β-adrenergic blockers, used in treatment of hypertension [6]. Gemfibrozil is a fibrate drug used as a lipid regulator. It is used in the treatment of hypertriglyceridemia and hypercholesterolemia. Presence of gemfibrozil and atenolol were detected in the range of ng/L to μg/L in wastewater [7,8]. At neutral pH, ciprofloxacin is present in zwitter ionic form whereas atenolol and gemfibrozil are present in cationic and anionic forms, respectively. Only limited number of studies are available on the laboratory scale biodegradation of atenolol [6,9–11], ciprofloxacin [12–14] and gemfibrozil [15].

Several studies have been conducted to understand the removal of pharmaceuticals in wastewater [11,14–20]. Membrane bioreactor (MBR) is an advanced technology for treating wastewater and is known to remove most of the organic contaminants. Moreover, quality of effluent coming out of MBR treatment is superior to effluent from other treatment methods [16]. Some studies have shown that fine membrane processes such as nano filtration (NF) and reverse osmosis (RO) are efficient in removing ECs [16,17]. Although several studies on the removal of pharmaceuticals in ASP and MBR are available, there is no comparative study on the performance of suspended and attached growth treatment systems. Previous studies on hybrid activated sludge process (ASP) and moving bed biological reactors (MBBR) [18] reported that the chances of pharmaceutical removal by attached growth biomass is higher as it contains diverse bacterial community and offers removal in different zones such as aerobic, anoxic and anaerobic. Most of the earlier studies focused only on the influent and effluent concentration of the target compounds and did not consider the presence of intermediate compounds in the treated water [19]. Also, as demonstrated in several earlier studies, the compound could be present in sludge and thus reach the environment because of bio-sorption, even though it is not detected in the effluent [12,20–23]. Only a few studies have modeled the biodegradation of pharmaceuticals in detail [9,13,22,24], in which substrate degradation, biomass growth and pharmaceutical degradation are interrelated and dependent on each other. Most of these studies assumed first order degradation of pharmaceuticals, which was then coupled to a biokinetic model. There is a need for evaluating the efficiency of these models for predicting the biodegradation of different pharmaceutical compounds, other than those used in developing these models.

India has large pharmaceutical industries, but there is no monitoring of effluent characteristics. It has been found that high concentrations of pharmaceuticals in effluents from these industries is increasing the extent of contamination [3]. Thus, there is a need to understand the removal of these compounds in biological systems, at environmentally relevant and high concentrations. Even though comparison of biological systems in WWTPs have shown the dependence of various operational parameters on pharmaceutical degradation, lab scale studies conducted by varying the operational parameters in a controlled manner are few [25–27], and further studies are needed. Present study investigated the biodegradation kinetics of three pharmaceuticals, namely, atenolol, ciprofloxacin and gemfibrozil. Biodegradation of pharmaceutical compounds when they are present as part of a mixture could be very different from the biodegradation when they occur as single pollutants due to complex interactions. Therefore, in the present study, experiments were conducted for the target pharmaceutical compounds when they occur individually and also when they occur in a mixture. It was demonstrated that inhibition constant for a particular compound estimated from the single pollutant degradation study can be incorporated into a multiple compound degradation model. Separate experiments were conducted using inactive biomass to determine the effect of sorption onto biomass. Also, removals of these compounds in ASP, submerged attached biofilter (SABF) and MBR are studied. SABF is a packed bed reactor, which represents the degradation of ECs in a biofilm. Moreover, comparison of performances of these reactors would help in understanding the fate of pharmaceutical compounds in different bacterial communities.

2. Materials and methods

2.1. Materials

Standards for atenolol, ciprofloxacin and gemfibrozil were supplied by Sigma Aldrich (USA). Stock solutions were prepared in millipore water. HPLC grade acetonitrile was purchased from Merck (India). HPLC grade potassium dihydrogen phosphate was procured from Fisher Scientific (India). All other chemicals used were purchased from Rankem, India.

2.2. Microbiological consortia

The bacterial consortium used in this study were previously isolated and enriched by Priya and Philip [28] for the degradation of VOCs in pharmaceutical wastewater. All bacterial strains were grown in aerobic conditions in minimal salt medium (MSM). The list of compounds used in preparing MSM is given in units of g/L in parentheses: $Na_2HPO_4{\cdot}2H_2O$ (3.5), KH_2PO_4 (1), $(NH_4)_2SO_4$ (0.5), $MgCl_2{\cdot}6H_2O$ (0.1), $Ca(NO_3)_2{\cdot}4H_2O$ (0.05)and trace elements (1 mL). Trace elements' solution contained: $ZnSO_4{\cdot}7\ H_2O$ (0.1), $FeSO_4{\cdot}7H_2O$ (0.2), and $Na_2MoO_4{\cdot}2H_2O$ (0.03). Organic carbon source in the form of dextrose at a concentration of 500 mg/L was added initially to attain rapid bacterial growth. Acclimatization was carried out in 1L flask containing 300 mL of media. The microbial suspension was kept in a magnetic stirrer (Remi) at 200 rpm under aerobic conditions. The bottle was loosely capped to allow air diffusion into the system. All three pharmaceutical compounds were added at a concentration of 5 mg/L after adequate growth of biomass. It was considered that 5 mg/L concentration of the compound was sufficient to induce the specific enzymes required for the degradation of these compounds. In order to get the microbes accustomed to the new conditions, the medium was refreshed on alternate days. This was carried out by separating bacterial pellet by centrifugation and re suspending it in fresh medium and maintaining volume as 300 mL. This procedure was continued for 7 days. Then onwards, the degradation of pharmaceuticals was monitored. The medium was refreshed and compounds were added again whenever the TOC of the system dropped below 20 mg/L. This process was continued for three months in order to acclimatize microbes to compounds. The degradation rate of pharmaceuticals slowly increased with time. Mixed consortia were used for batch experiments only after more than 80% of compounds were removed from the system for several consecutive cycles. After acclimatization, pharmaceutical concentrations were reduced to 1 mg/L before conducting batch experiments.

2.3. Analysis of target compounds

Selected compounds were analyzed using HPLC (Dionex, USA) with UV detector. Reverse phase Acclaim C-18 column (4.6×250 mm; 5 μm) was used for separation of compounds. Ciprofloxacin was analyzed using the method reported by