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Integration of photocatalytic and biological processes for treatment of pharmaceutical effluent

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ABSTRACT

This paper aims to investigate integration of biological process with photocatalytic oxidation for treating pharmaceutical wastewater characterized by simultaneous presence of biodegradable and refractory compounds. An integrated lab-scale biological system with a photocatalytic reactor (containing Degussa P25 TiO_2 in slurry mode) was operated in batch mode to treat simulated wastewater containing 10 mg/L of the model compound, Atenolol (ATL). Biodegradability (BOD_5/COD ratio) increased from 0.23 to 0.42 after 4 h of photocatalytic treatment (1.5 g/L TiO_2) with COD removal of 69.7% when using a solar simulator. In the independent biological treatment, the amount of sludge was varied as 2, 5, 10 and 15% in simulated wastewater, to optimize sludge concentration at three different temperatures of 20, 27 and 37 °C. The maximum BOD and COD removal of 46.3% and 46.2% respectively was achieved with 5% activated sludge at 37 °C for 48 h at natural pH of 6.9 under continues aeration. By employing 4 h of photocatalytic treatment using TiO_2 (1.5 g/L) followed by 48 h of biological treatment (37 °C, 5% Sludge concentration) resulted in 90.5% and 80.8% removal of COD and BOD, respectively. The study shows integration of the two processes can be a promising technology.

1. Introduction

Pharmaceuticals are considered as harmful pollutant among various emerging contaminants because they have endocrine disrupting properties. Biological treatment has lower operating cost when compared to other alternatives because these are natural processes and convert complex substances into simpler substances.

Based on type of wastewater, compounds involved and its concentrations, the integration of Advanced Oxidation Processes (AOPs) and biological processes could be considered in various alignments. To enhance the biodegradability and to detoxify effluents, coupling of AOPs with biological treatments have been considered [1–3]. In general, the removal efficiency of pharmaceutical compounds could be improved by coupling the biological treatment with advanced oxidation technologies such as ozonation, Fenton process and photocatalyst treatments [4]. Bandara et al. [5] employed photo Fenton as pre-treatment method followed by biological method for the removal of para-nitro-toluene-ortho-sulfonic acid. The intermediary formed in the photocatalytic treatments were identified as biodegradable. Horsch et al. [6] studied degradation of stilbene-based fluorescent whitening agents by combination of advanced oxidation and biodegradation processes. AOPs boost the biodegradability of low biodegradable of such wastewater generally by reducing the COD load [7,8]. Reddy et al. [9] assessed degradation of Pyrazinamide drug by employing photocatalysis using TiO_2 as photocatalyst followed by biological treatment and found 91% removal of COD in 44 h of treatment.

Similarly, pre-treatment by photocatalysis can be employed to enhance the biodegradability of pollutants and to reduce its toxicity [10]. Similarly, Oller et al. [11], showed the degradation of α-methyl-phenylglycine at pilot scale, by combining Fenton process with a biological reactor. In this study, the degradation attained by the combined process was assessed in terms of dissolved organic carbon and was perceived to reach values up to 95%. Degradation of α-methyl-phenylglycine, Alachlor, Atrazine, Chlorfenvinphos, Diuron, Isoproturon using photo fenton along with biological treatment showed 90% degradation of compound [11,12]. Sangave et al. [13] assessed the efficacy of a combination of US/ozone treatment in refining the aerobic degradation of distillery wastewater and reported a COD reduction of 45%. Integrated treatment showed higher COD removal, when compared to single treatments. Varatharajan and Kanmani [14] investigated the treatability of wastewater from a pharmaceutical industry by combined solar photo-fenton oxidation with activated sludge process and obtain BOD and COD removal of 93 and 95%, respectively. Sirtori et al. [15] assessed the efficiency of photo-fenton process and biological treatment

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for degradation of Nalidixic acid and attain 95% degradation of which 33% correspond to the solar photochemical process (190 min) and 62% to the biological treatment. Fenton reaction sequential with membrane bioreactor (MBR) was employed for the treatment of the waste water from an integrated dyeing wastewater treatment plant and biodegradability was assessed, both after coupling Fenton with MBR system and the Fenton treatment alone [16].

The sequential photocatalytic/biological treatment of a contaminated groundwater from an industrial site was studied using a corrugated plate photoreactor and observed that optimal pre-treatment time of photocatalysis significantly enhance the extent of biological nitrification [17]. Yahiat et al. [18] studied degradation of Tetracycline and Tylosin by employing photocatalysis as pre-treatment followed by activated sludge process resulting in significant decrease in COD. Integrated biological and advanced oxidation process employing TiO_2 has been evaluated for the degradation of Carbamazepine (CBZ) drug which showed 95% removal of CBZ [19]. The effect of coupling of AOP and biological treatment has been studied on degradation of wastewater from chemical process industries by applying Fenton treatment along with varied concentration of H_2O_2. Similarly effect of integration of biological and photocatalytic processes for degradation of bio-recalcitrant compounds from pulp and paper mill effluent has been investigated and sequential treatment was found to possess higher degradation efficiency than the independent treatments [20]. Kumar et al. [21] treated the pharmaceutical waste water by coupling photo-Fenton process with an aerobic sequential batch reactor (SBR) and obtain 90% COD removal after 60 min of photocatalytic treatment at optimum conditions followed by biological treatment.

The main objective of this study was to assess the feasibility and advantages of the integrated approach for the treatment of pharmaceutical wastewater. So, independent photocatalytic and biological reactors were set up. Finally, integrated treatment involving sequential photocatalytic-biological process was employed for the degradation of simulated pharmaceutical wastewater and optimal time required in each process of the integrated treatment was assessed.

2. Experimental section

2.1. Materials

Atenolol (Fig. 1) were purchased from Sigma–Aldrich and was used without further purification. Simulated pharmaceutical effluent was prepared by dissolving Sodium acetate (16.3 g), methanol (11.8 g), potassium dihydrogen phosphate (11.7 g) and Ammonium chloride (9.48 g) in 1000 ml distilled water and Atenolol (10 ppm) was added as model pharmaceutical compound, purchased from sigma Aldrich. Such concentrations, although considerably greater than those typically found in waters, were chosen to allow (i) the evaluation of efficiency of process within a measurable time scale, and (ii) the precise estimation of left over concentrations with the various analytical techniques used in this work. Commercially available TiO_2 was employed by Aeroxide P25.

Simulated effluent was subjected to independent solar induced photocatalytic, biological as well as sequential photocatalytic-biological (Photo + Bio) treatments.

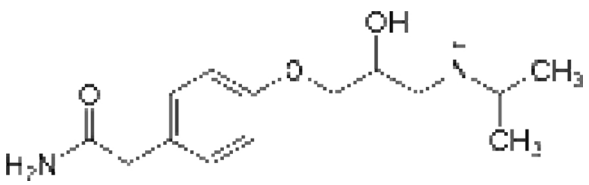

Fig. 1. Structure of Atenolol.

2.2. Biological treatment

For Biological experiments, 1000 mL of effluent was taken and activated sludge was added in varying proportions (2–15%) at natural pH of 6.9. The flasks were incubated at different temperatures (20 °C 27 °C, 37 °C) at 120 rpm for 48 h to study the degradation of effluent. Samples (10 ml each) were drawn after every 3 h and centrifuged at 10,000 rpm for 5 min. at 27 °C.

Photocatalytic–biological (Photo + Bio) treatment was applied to evaluate the efficiency of the sequential treatment in comparison to independent treatments. In integrated approach, individual simulated effluent samples (1000 ml) treated by photocatalysis under optimized conditions with time duration of 0.5–5.0 h was subjected to biological treatment upto 48 h at 37 °C. For instance, 0.5 h of photocatalytic followed by 48 h of biological treatment; 1 h of photocatalytic and 48 h of biological treatment and so on. Sample was withdrawn after the application of photocatalytic as well as biological treatment for assessing the degradation of simulated effluent in terms of Biochemical Oxygen Demand (BOD) & Chemical Oxygen Demand (COD). Mineralization was also assessed in terms of Total Organic Carbon (TOC) for the optimized set of experiments.

2.3. Photocatalytic measurement

Simulated effluents were subjected to independent solar induced photocatalytic, biological as well as sequential photocatalytic-biological (Photo + Bio) treatments. Photocatalytic experiments were carried out in slurry mode in specially designed glass reaction vessels placed in solar simulator. To optimize the time of photocatalytic process, the experiment was carried under solar simulator for different time duration ranging from 0.5 to 5.0 h in which the dose of TiO_2 was kept at 1.5 g/l (optimum) determined through pre-conducted experiments [22]. Aeration was facilitated through the aqueous suspension. At each time interval of 1 h, aliquots were collected using syringe filter and degradation efficacy was assessed. All the tests were carried out in triplicate for reproducibility of results.

2.4. Analytical procedures

2.4.1. Chemical oxygen demand (COD)

COD is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. The degradation efficiency of effluents was expressed with reference to the decrease in COD (Chemical oxygen demand) measured by closed reflux method (spectrophotometric) using standard protocols [23]. Test solution (2 ml) was pipetted into the COD Vials containing standard amount of potassium dichromate oxidizing mixture and digested at 150 °C for two hours. The intensity of the resultant coloured solution was measured by COD meter against blank sample.

2.4.2. Biological oxygen demand (BOD_5)

BOD_5 measurements were done by HACH BOD meter (HQ40d multi). To analyse the BOD, Firstly, nutrient preparation was done by filling the BOD water tank with 15 L distilled water and further 5 mL of each of the 4 nutrients were added: $MgSO_4.7H_2O$ (22.5 g/L), $FeCl_3.6H_2O$ (0.25 g/L), Phosphate buffer (54.3 g/L K_2HPO_4), $CaCl_2$ (27.5 g/L), then the mixture was Aerated overnight (24 h). The resultant water obtained is called as the Nutrient water. Further Bacterial preparation was carried out in which 500 mL of the above solution (nutrient water) was taken out and one capsule of polyseed (only the powder inside the capsule) was added. Followed by aeration for 3–4 hours (Never more than 6 h, 4 h is optimum). This is called the seed water. After aerating Sample preparation and BOD measurement was carried out.