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Kinetic evaluation and process performance of a fixed film bioreactor removing phthalic acid and dimethyl phthalate

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ABSTRACT

Phthalate esters are toxic organic contaminants which can enter into the environment through various industrial processes. In this study, a 6-liter fixed film bioreactor was used to examine biodegradation of phthalic acid (PA) and dimethyl phthalate (DMP) in synthetic wastewater. Effect on the process of two operating factors, namely hydraulic retention time (HRT) (at four levels ranging between 6 and 48 h) and initial phthalate concentrations (at six levels ranging from 10 mg to 500 mg/l), was investigated. The process was stable at all operating conditions, except for the condition with influent PA and DMP of 500 mg/l and HRT of 6 h. More than 95% removal efficiency was achieved for the conditions with HRT longer than 10 h. Remarkable amount of DMP (398 mg/kg of sludge) was adsorbed on the biomass due to its higher hydrophobicity compared to PA (171 mg/kg). The kinetic parameters (μ_m, K_s, Y and K_d) were determined and compared for both substrates, PA and DMP.

1. Introduction

Phthalates are an important class of chemicals manufactured for use, primarily, as plasticisers in polyvinyl resin, cellulosic and polyurethane polymers for manufacturing building materials, home furnishings, transportation, clothing, and for packaging of food and medical products [1]. Dimethyl phthalate (DMP) is typically used in cellulose-ester based plastics, such as cellulose acetate and butyrate, which are esters of 1,2-benzenedicarboxylic acid sharing a common structure made up of a benzene ring with two side chains. Phthalates with lower molecular weight are toxic to aquatic organisms (e.g. DMP, DEP and DBP) [2,3]. They are also used as additives in paints, adhesives, cardboard, lubricants and fragrances [4]. Phthalates have also been observed to have disrupting properties on the endocrine system [5].

Release of phthalate esters into the environment during manufacturing processes and by their wide use and disposal has caused serious concerns, since some of them are suspected to be mutagens, hepatotoxic agents and carcinogens [2,6]. Phthalate and its esters and degradation intermediates are suspected to cause cancer and kidney damage and, as a result, the US Environmental Protection Agency has added this class of chemicals to the list of priority pollutants [7]. If phthalates are not removed from sewage at a sewage treatment plant (STP), they may have toxic or endocrine disrupting effects on aquatic species in the receiving water bodies [3].

Since the rates of photolysis and chemical hydrolysis of such compounds are very slow, metabolic breakdown by microorganisms is considered to be one of the major routes for the environmental degradation of phthalate esters [8]. Several types of microorganisms were found to degrade phthalate esters including aerobic and anaerobic species [9]. A few studies have been reported on the biodegradability of DMP by bacteria [10], fungi [11], algae [12], activated sludge cultures [2,13,14] and bioreactors [15].

Phthalate esters are metabolized by both aerobic and anaerobic biological treatment methods [13,16–26]. The most common pathway for aerobic degradation of phthalate is through the protocatechuate pathway, followed by ring cleavage and complete mineralization to carbon dioxide and water [16].

These compounds have not shown any adverse effect on activated sludge systems and concentrations up to 900 mgL^{-1} could be tolerated by the system [27]. In a wastewater plant of a coke factory, PA esters, having a short hydrocarbon chain, could be removed by an activated sludge system with hydraulic retention time (HRT)

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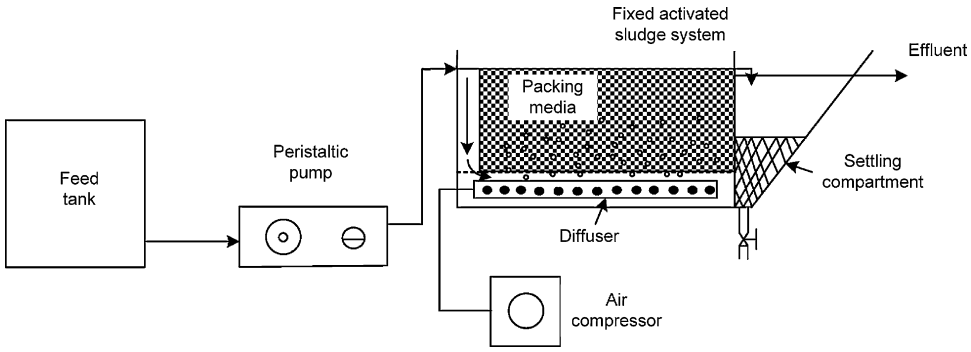

Fig. 1. Schematic diagram of the experimental rig.

from 7 to 90 d, while the removal efficiency of acid esters, having long hydrocarbon chain, is much lower at the same HRT [13].

The results obtained from a pilot scale study using activated sludge showed removal efficiency of 79–97% for PA esters with inlet amount of 100 $\mu g L^{-1}$ [28]. In another experiment, under the same conditions, the removal efficiency obtained was 71–91%. In plastic and paint industries the concentration of PA esters has been reported to be about 10–100 $mg L^{-1}$ [29].

The applicability of a fixed activated sludge system consisting of an aeration tank with a packing bed and a settling tank is developed to a higher level because of its high efficiency in removing organic compounds from urban and industrial wastewater [30,31]. Biodegradation of DMP in a immobilized cell reactor with high DMP loading and removal rates, using an acclimatized mixed bacterial culture isolated from activated sludge, was studied [32]. It showed very high removal efficiency at phthalate-loading rate of 560 g/m^3 h, indicating high affectivity of this approach in deterioration of phthalate compounds.

In the present research, the performance of a fixed film bioreactor for removing PA and DMP at various operating conditions was studied. Kinetic parameters (μ_m, K_s, Y and K_d) for both PA and DMP biodegradation processes were also determined using a mass balance model.

2. Materials and methods

2.1. Experimental setup

The schematic diagram of the experimental setup is shown in Fig. 1. An integrated system including a fixed activated sludge bioreactor and settling tank with total volume of 6 and 3 l, respectively, was designed and fabricated. The bioreactor working volume was determined 5 l. In order to provide high surface for growing the biofilm, the aeration tank was packed using PVC pieces with a specific surface area of 700 $m^2 m^{-3}$. An air compressor was applied for aerating the wastewater through a perforated column placed at the bottom of the reactor.

2.2. Feed

A synthetic wastewater solution was prepared with different concentrations of PA and DMP (Merck Co., Germany) including 10, 20, 50, 100, 200, and 500 mg/l. Nitrogen and phosphorous sources were supplied from ammounium nitrate (NH_4NO_3) and potasium dihydrogen phosphate (KH_2PO_4) (Merck Co., Germany), respectively, with a ratio of COD:N:P = 100:7:1.

2.3. Operation conditions

All experiments were carried out at lab temperature (28–32 °C). After a one-month start-up period, the bioreactor was initially operated at HRT of 48 h so that the HRT was stepwise decreased to 6 h. At each HRT, the bioreactor was fed by various concentrations of the substrates ranging from 10 to 500 mg/l. Each step was continued to a steady state condition where the variations in effluent parameters maintained constant. During the experiment, the process was continuously monitored by taking samples from influent, effluent, and sludge.

2.4. Analytical methods

The following parameters were analyzed according to Standard Methods [33]: pH, alkalinity, total suspended solids (TSS), volatile suspended solids (VSS), BOD and COD. Sodium hydroxide sollution (1 M) was used to adjust pH when pH dropped to less than 6 due to the high concentration of PA. To measure PA and DMP concentrations, a HPLC-UV system (2000 Eurochrom, Knuer Co., Germany) equiped with a column (C8, 15 cm × 46 mm) (Waters Co., USA) with packing size of 5 μm was used. The mobile phase consisted of methanol–water (65:35 v/v), so that water used contained 0.5% phosphoric acid. The flow rate of the mobile phase was adjusted at 1 ml/min. The analysis was carried out at ambient temperature. At each injection, 100 μl of the sample was taken. The limit of detection and quantity of detection were 5 and 50 μl, respectively. Methylen chloride was used to extract PA and DMP from the sludge [33]. Dissolved oxygen (DO) and temperature were monitored using a portable DO meter (B50, YSI Co., USA).

In order to determine the evaporation rates of PA and DMP, the bioreactor was operated at different HRTs and substrate concentrations in biomass-free conditions. In these experiments, the concentrations of PA and DMP at influent and effluent were periodically measured. The eliminated amounts of the compounds indicated the evaporated fraction.

2.5. Inoculum solution

In order to prepare a suitable inoculum solution, some sludge was taken from a working wastewater treatment plant (Shoosh, Tehran). The sample was then acclimatized with PA and DMP in a batch experiment. After a one-week acclimatization phase, the sample was prepared to be inoculated into the bioreactor.

3. Mathemathical modeling

The substrate utilization rate in biological systems can be modeled with the following expression for soluble substances [34]

$$r_{su} = -\frac{dS}{dt} = \frac{kSX}{K_s + S} \quad (1)$$

where r_{su} is the rate of change in the substrate concentration due to utilization, g/m^3 d, k is maximum specific substrate utilization rate,