Journal of Environmental Management 192 (2017) 243–253

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Removal of pharmaceuticals from municipal wastewater by aerated submerged attached growth reactors

Y. Flores Velázquez [a], P. Mijaylova Nacheva [b, *]

[a] National Autonomous University of Mexico, Morelos Campus, Paseo Cuauhnahuac 8532, Col. Progreso, Jiutepec, Morelos 62550, Mexico
[b] Mexican Institute of Water Technology, Paseo Cuauhnahuac 8532, Col. Progreso, Jiutepec, Morelos 62550, Mexico

ARTICLE INFO

Article history:
Received 17 October 2016
Received in revised form
23 January 2017
Accepted 26 January 2017

Keywords:
Attached growth bioreactors
Micro-pollutants
Pharmaceuticals
Wastewater

ABSTRACT

The performance of four aerated submerged attached growth bioreactors was studied for the removal of three pharmaceutical micro-pollutants (fluoxetine, mefenamic acid and metoprolol) from municipal wastewater. Two packing materials (polyethylene tapes and polyurethane cubes) were compared and the effects of different organic loads (3.0, 6.0, 9.0 and 12 gCOD m^{-2} d^{-1}) and of the effluent recirculation were investigated. The obtained solid retention times were in the range of 4–37 d. The reactors packed with polyurethane cubes allowed 11–26% higher biomass accumulation than the ones with polyethylene tapes and higher solid retention times. The low organic loads, high solid retention times and the implementation of effluent recirculation enhanced the removal of the three pharmaceutical compounds. The highest removals were achieved at organic load of 3 gCOD m^{-2} d^{-1} and 50% of effluent recirculation, with hydraulic residence times of 3.1–4.3 h and the solid retention times of 19–32 d. At this condition, the removals of the fluoxetine, mefenamic acid and metoprolol were up to 95, 82 and 73% respectively. The reactors with polyurethane cubes showed higher removals compared with the ones packed with polyethylene tapes.

1. Introduction

Pharmaceuticals are a class of micro-pollutants that may cause acute and chronic effects on aquatic organisms in the concentration range of μg L^{-1} (Escher et al., 2011). Pharmaceuticals have been detected in municipal and hospital wastewater, surface water, groundwater, and even in drinking water (Stuart et al., 2012; Birkholz et al., 2014). Municipal wastewater treatment plants effluents represent one of the main sources of these compounds because most of these plants are not designed to remove them, as they were built with the principal aim of removing biodegradable carbon, nitrogen and phosphorus compounds (Verlicchi et al., 2012; Luo et al., 2014). For these reasons, it is necessary to improve the removal of pharmaceuticals with high environmental risk. Three pharmaceuticals from different classes of action were selected for this study, fluoxetine (psychiatric), mefenamic acid (analgesic/anti-inflammatory) and metoprolol (β-blocker). The model compounds were selected on the basis of their widespread use (Tauxe-Wuersch et al., 2005; Deblonde et al., 2011), their toxicological effects on aquatic organisms (Escher et al., 2011; Roos et al., 2012; Verlicchi et al., 2012; Mansour et al., 2016) and their concentrations in the effluents from wastewater treatment plants, and in the aquatic environment (Ternes, 1998; Miège et al., 2009; Rosal et al., 2010).

Previous studies on micro-pollutant removal in activated sludge wastewater treatment systems have indicated that high removal rates are achieved at solid retention times (SRT) higher than 10 d (Clara et al., 2005; Suarez et al., 2010. The long SRT allow an enrichment of slow growing bacteria such as nitrifying bacteria and the nitrifying activity contributes to the biotransformation of pharmaceuticals (Dawas et al., 2014; Rattier et al., 2014). Cometabolic biodegradation seems to be responsible for the initial biotransformation due to the action of ammonium monooxygenase enzyme, which catalyzes the first step of nitrification by ammonium oxidizing bacteria (Fernandez-Fontaina et al., 2012). Other experiments have indicated that the heterotrophic degradation rather than autotrophic degradation by ammonium oxidizing microorganisms was the main cause for the removal of several compounds including mefenamic acid and metoprolol (Tran et al., 2009; Majewsky et al., 2011; Maeng et al., 2013; Tran et al., 2013; Falås et al., 2016). Therefore, the nitrifying bacteria are capable to

* Corresponding author.
E-mail address: petiam@tlaloc.imta.mx (P. Mijaylova Nacheva).

http://dx.doi.org/10.1016/j.jenvman.2017.01.065
0301-4797/

enhance the biodegradation of pharmaceuticals, but the role of heterotrophic organisms must be considered.

The attached growth processes offer some advantages over activated sludge processes, such as higher biomass concentration and high SRT even operating with low hydraulic residence time (HRT), which allows the development of microorganisms with low specific growth rates, so that high nitrification rate can be achieved (Luo et al., 2014). Falås et al. (2012) showed that moving bed biofilm carriers (Kaldnes K1 and Biofilm chip) have a pharmaceutical reduction potential superior to the activated sludge one. They gave two potential explanations for the observed difference: higher quantity of slow growing pharmaceutical degrading microorganisms (because of the higher SRT in the biofilm carrier's case) and stratification of the microbial community due to the substrate and redox gradients within the biofilm. The microorganisms adapted to easily degradable organic substrates are located in the outer part of the biofilm and microorganisms adapted to the remaining and difficultly degradable organic substrates in the inner part of the biofilm. Later, Falås et al. (2013) observed clear differences between the micro-pollutant removal kinetics obtained with attached and suspended biomass in that higher removal rates were found using attached biomass for most of the studied compounds. For example, mefenamic acid was degraded faster by the attached biomass than using suspended biomass, while the degradation pattern was the opposite for metoprolol. The nitrification capacity per unit biomass was considerably higher for the attached growth biomass than for the suspended growth one. As shown, aerated submerged attached growth reactors are an alternative for the removal of pharmaceuticals, however further research is needed to enhance their performance.

Plastic media are the most frequently used material for biofilm support in aerated attached growth reactors. The selection of packing materials for this study was based on previous work by Mijaylova et al. (2008) which studied the performance of aerobic submerged packed bed reactors for the treatment of domestic wastewater using seven different kinds of packing materials with specific areas in the range of 760–1200 m^2 m^{-3}. The study concluded that the highest SRT (until 39 d) was obtained in the reactors with polyethylene tapes and polyurethane cubes, and both reactors presented almost 99% NH_4-N removal. Mijaylova and Moeller (2010) reported that the biofilm developed in the reactors with polyethylene tapes was thin and this favored the diffusivity and mass transfer in the biofilm, while Guo et al. (2010) indicated that the biomass on polyurethane cubes is retained in two different forms: biofilm developed onto the cube surfaces and biomass deposited or entrapped within the cubes' void spaces. A distinctive dissolved oxygen gradient occurred within the cubes' inward depth, resulting in anaerobic conditions in the space deep inside the cube. The objective of this study was to assess the removal of fluoxetine, mefenamic acid and metoprolol from municipal wastewater by aerated submerged attached growth reactors, comparing the performance of two biomass support materials (polyethylene tapes and polyurethane cubes). The effects of different organic loads and of effluent recirculation were evaluated.

2. Material and methods

2.1. Experimental set-up and packing materials

The experiments were performed using four aerated submerged attached growth reactors. Each reactor had a cylindrical packed bed zone, a peripheral settling zone and a conical bottom for the extraction of accumulated sludge. Biomass support materials were placed into the cylindrical zone with 0.15 m diameter and a bed height of 0.8 m. Two reactors (PU1 and PU2) were packed with 3250 polyurethane cubes of 1.5 cm edge length and 10 pores per inch; the other two (PE1 and PE2) were packed with 3300 polyethylene tapes of a 5 cm length and 3 cm width. The tapes were supported by a vertical shaft of stainless steel. The specific areas of both packing beds were almost 700 m^2 m^{-3}. The schematic diagram of the experimental setup is presented in Fig. 1. The reactors were continuously fed with municipal wastewater, the wastewater passed down-flow through the packed bed and up-flow in the peripheral settling zone. The effluent was collected from the upper part of the settling zone and the sludge accumulated in the conic zone was periodically extracted. The aeration was provided by porous stone diffusers installed at the bottom; the dissolved oxygen levels were kept higher than 3 mg L^{-1}.

2.2. Experimental procedure and analysis

The immobilized biomass was developed by supplying municipal wastewater to all the bioreactors at an organic load (OL) of 3 gCOD m^{-2} d^{-1}, without any special inoculation. The addition of the pharmaceutical compounds began after the process stabilization (80% COD and NH_4-N removal). The concentrations of the pharmaceuticals in the wastewater were selected according to the reported concentrations in influents to wastewater treatment plants. Tauxe-Wuersch et al. (2005) measured up to 4.54 μg L^{-1} of mefenamic acid in municipal wastewater treatment plants in Switzerland. Deblonde et al. (2011) reported 4.9 μg L^{-1} of metoprolol in influents from wastewater treatment plants. Rosal et al. (2010) reported 1.827 μg L^{-1} of fluoxetine in urban wastewater, while Al Aukidy et al. (2014) reported 2.3 μg L^{-1}. Thus, the pharmaceuticals were added to wastewater to obtain almost 2 μg L^{-1} of fluoxetine and 5 μg L^{-1} for mefenamic acid and metoprolol. Pharmaceutical compounds were purchased from Sigma-Aldrich, the CAS numbers were: fluoxetine hydrochloride (56296-78-7), mefenamic acid (61-68-7) and metoprolol tartrate (56392-17-7). The stock solutions were prepared containing one pharmaceutical compound; the correction due to the purity of the compound was taken into account. The mefenamic acid and metoprolol were dissolved in methanol and the fluoxetine in acetone, stirring the solutions during 5 min at 25 °C to create a stock solution of 1000 μg mL^{-1}, the solutions were stored in amber vials at 4 °C and used to spike into the municipal wastewater.

The effect of different organic loads on the reactor performance and pharmaceutical compounds removal was evaluated: 3.0, 6.0, 9.0 and 12 gCOD m^{-2} d^{-1}. The operational parameters for each experimental phase are presented in Table 1. The effect of 50% effluent recirculation was assessed for all organic loads. Each experimental phase was evaluated for 60 d. The variation of the organic load was performed by increasing the flow rate of the influent to the reactors, thus a decrease of HRT occurred when the organic load was increased.

The changes in the microbial community of the immobilized biomass can show the conditions that benefit the removal of pharmaceuticals in municipal wastewater. The study consisted of five phases, phase 1 (start-up of the reactors) and during the phases 2–5 different organic loads were applied to favor different microbial consortia. The low loaded biofilm processes tend to favor the development of slow growing autotrophic bacteria, such as nitrifying bacteria, which seems promising for the pharmaceutical removal (Falås et al., 2012). The high load condition favor the development of heterotrophs, which grow faster than autotrophs, as a result, the autotrophic nitrifiers can be overgrown by heterotrophs, which cause the nitrification efficiency to decrease (Bassin et al., 2011). According to a previous study, when applying the organic loads of 3 and 6 gCOD $m^{-2}d^{-1}$, high solid retention times (higher than 10 days) are expected and therefore the development