REMOVAL OF BENZOTRIAZOLES AND 2-OH-BENZOTHIAZOLE IN LAB-SCALE MOVING BED BIOREACTORS (MBBR) OPERATED UNDER DIFFERENT CONTINUOUS-FLOW CONDITIONS

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ABSTRACT

Benzotriazoles and benzothiazoles are two groups of polar compounds used in industries and in every day products. They are often found in the aquatic environment and they are partially removed during conventional wastewater treatment. So far, there is a lack of data for their fate and removal in Moving Bed Biofilm Reactors (MBBR). Therefore, the main objectives of this study were to investigate the removal of five BTRs (BTR, CBTR, XTR, 5TTR and 4TTR) and 2-hydroxybenzothiazole (OHBTH) in MBBR systems operating under different conditions.

For this reason two lab-scale MBBRs connected in series were used. Each bioreactor was filled with biocarriers (30% filling ratio) and was provided with aeration that kept biocarriers circulating in all parts of the tank. The system was constantly fed with real wastewater originating from the Aegean University's Campus. A startup period of some months was necessary to develop biofilm. After systems' stabilization, target micropollutants were spiked in raw wastewater at concentrations that varied from approximately 20 to 30 μg L^{-1}. Samples were collected during different days and the removal efficiency was calculated for each target compound.

In order to examine the influence of operational parameters on the removal efficiency of the system, two multiple experimental cycles were run under high and low organic loading. In order to determine the biodegradation capacity of each type of biomass developed in each experimental cycle, the mass of micropollutants removed per day was normalized to the amount of biomass in the reactor. Removal rates calculated in each case varied, while the organic loading seemed to play a crucial role, both on the development of biofilm and on the elimination of the compounds.

Keywords: micropollutants, biodegradation, attached biomass, corrosion inhibitors, biological treatment, microorganisms

1. Introduction

Moving Bed Biofilm Reactors (MBBRs) are an option for biological treatment of municipal and industrial wastewater that has been applied from the 1980s in North European countries (Barwal and Chaudhary, 2014). This technology is based on the development of microorganisms in biofilm structures on different types of carriers. Carriers are usually small plastic elements, with a high specific protected area. When referring to Moving Bed Reactors the carriers are circulating in the entire department due to aeration or mechanical stirring. Some main advantages of this type of treatment are the low hydraulic retention time (HRT) than can be applied (without biomass being washout), the avoidance of excess sludge management and the high nitrification rates that can be obtained, even at low temperatures. Nowadays, MBBRs gain interest concerning their capacity in removing micropollutants. Only few researches have been conducted but results indicate that biofilm may be an efficient solution concerning organic micropollutants removal (Edwards et Kjellerup, 2013).

Concerning Benzotriazoles (BTRs) and Benzothiazoles (BTHs), they are involved in the large group of emerging contaminates. They are used in industry applications (anticorrosion and deicing fluids, tire manufacturing ect.) as well as in everyday household products (dishwashing detergents). They occur in the environment through wastewater disposal or even rain washout (airports, roads). As they are polar compounds with a high solubility in water they persist in the water cycle and are frequently found in surface and underground water (Loos *et al*., 2009). In combination with their partial removal in wastewater treatment plants (Liu *et al*., 2012), there is need for investigation and optimization of their elimination from wastewater.

The aim of this study was to investigate the removal of a mixture of BTRs and BTHs, containing benzotriazole (BTR), 4-methyl-1H-benzotriazole (4TTR) 5-methy-1H-lbenzotriazole (5TTR), 5-chlorobenzotriazole (CBTR), xylytriazole (XTR), and 2-hydroxybenzothiazole (OHBTH) during treatment with an MBBR system. Two different organic loadings were applied and the capacity of different types of biofilm developed in removing target compounds was examined.

2. Materials and methods

2.1. Continuous flow systems set-up and operation

A lab scale MBBR system was operated under continuous flow and aerobic conditions. The system consisted of two reactors (R1 and R2) connected in series, each one with a working volume of 4.5 L. Each bioreactor was filled with biocarriers, type K3 manufactured by AnoxKaldness, at a filling ration of 30%. The aeration in each reactor was provided by two small pipes at the bottom of the tank that ensured adequate oxygen concentration and circulation of the biocarriers in all parts of the reactor. The system was fed with real wastewater collected on a daily basis from the Aegean's university STP. The system operated for several months under stable conditions until stable biofilm was formed. Two experimental cycles were run by operating the system under two different organic loadings; 0.25 ± 0.16 kg m^{-3} d^{-1} (1^{st} experimental cycle, MBBR-A) and 0.60 ± 0.40 kg m^{-3} d^{-1} (2^{nd} experimental cycle, MBBR-B). The system was monitored for the elimination of conventional pollutants and when stable performance was achieved the target compounds were added inflow and samples were taken for the examination of their elimination through all treatment stages.

2.2. Analytical Methods

Analysis of COD, NH_4-N, NO_3-N, TSS and MLSS were performed according to Standard Methods (APHA, 1998), T, DO and pH were measured using portable instruments. The quantification of the attached biomass occurred by removing the biofim from biocarriers and measuring the dried weight difference. Microscopic observations were conducted in order to monitor biofilm development.

For the investigation of target compounds fate, samples were filtered through glass fiber filters, acidified to pH 3.0 ± 0.1 and stored at 4 ^{o}C until analysis. Analysis of target compounds included solid phase extraction (SPE) as performed in similar researches (Asimakopoulos *et al*., 2013; Mazioti *et al*. 2015). Chromatographic analysis was performed by a Shimatzu (Japan) LC20-AD prominence liquid chromatographer associated with a SPD-M20A prominence diode array detector and a SIL-20AC auto sampler. The analytical method and the chromatographic conditions are described in detail in a recently published paper (Mazioti *et al*., 2015).

3. Results

3.1. Elimination of conventional pollutants - Biofilm growth

During both experimental cycles (MBBR-A and MBBR-B), the average elimination of conventional pollutants was higher than 86% concerning the organic load reduction (expressed as COD), and higher than 95% concerning the removal of NH_4^+ (Figure 1). The pH in both reactors was stable and the average value varied in all experimental cycles from 6.8 to 7.4. In both experimental cycles the concentration of biomass was generally higher in the first bioreactor, forming a thicker biofilm on carriers due to the abundance of nutrients that favoured microorganisms development. In the second reactor the biofilm was thinner, but the nitrification rate was generally higher.

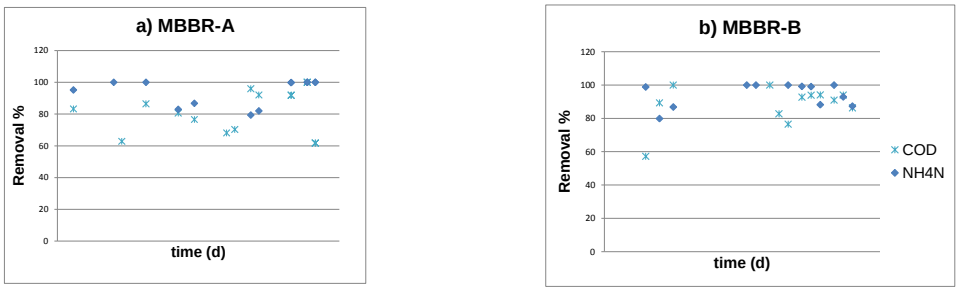

Figure 1: Percent removal of conventional pollutants in each experimental cycle.

3.2. Elimination of micropollutants

The elimination of target compounds was calculated by measuring concentration inflow and outflow. The percent elimination of target compounds is shown in Table 1. Four micropollutants (BTR, 4TTR, 5TTR and OHBTH) were eliminated at a higher rate during the first experimental cycle (in MBBR-A), whereas the organic loading was lower. Concerning 4TTR and 5TTR, they were not eliminated when a higher organic loading was applied. On the other hand, both CBTR and XTR were eliminated at the same rate in both experimental cycles.

Table1: Average removal (%) of target compounds in both experimental cycles

	BTR	4TTR	5TTR	CBTR	XTR	OHBTH
MBBR-A	76 ± 6	69 ± 8	53 ± 10	42 ± 15	43 ± 10	97 ± 3
MBBR-B	43 ± 12	8 ± 16	0	44 ± 12	43 ± 16	86 ± 8

In order to compare all types of biofilm developed during each experimental cycle, concerning micropollutants elimination, the specific removal rate was calculated. The total mass of micropollutants removed per day was normalized to the mass of biomass in each reactor. Results indicated that the specific removal was approximately the same in both experimental cycles for CBTR, XTR and OHBTH, varying from 4.4 μg g^{-1} d^{-1} (XTR, MBBR-B) to 11.5 μg g^{-1} d^{-1} (OHBTH, MBBR-A and MBBR-B). On the other hand, specific removal was higher for BTR, 4TTR and 5TTR in MBBR-A (11.3, 9.9 and 10.9 μg g^{-1} d^{-1} respectively).

When comparing the two different biofilms developed in each reactor it can be seen that in MBBR-A both types of biofilm from R1 and R2 had generally a similar potency in removal. In MBBR-B there was a difference between two biofilms concerning three compounds (BTR, 4TTR and 5TTR), with the thinner biofilm in R2 being more effective. When comparing all four types of biofilm between them, it seems that the biofilms developed under poor organic loading conditions (R1 and R2 MBBR-A and R2 MBBR-B) had a stronger capacity to eliminate micropollutants, implying that low organic loading results in the development of a more competent biofilm, able to utilize different types of carbon source.

4. Conclusions

Removal of conventional pollutants was adequate and stable during wastewater treatment with the MBBR, under both organic loadings applied. The MBBR system was able to remove all target compounds partially when operated at low organic loading, while 4TTR and 5TTR were not eliminated when a high organic loading was applied. The biofilm developed under poor organic loading had a greater capacity in removing micropollutants.

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REFERENCES

1. APHA (1998), Standard methods: for the examination of water and wastewater, American Public Health Association, 20th edition
2. Asimakopoulos A.G., Ajibola, A. Kannan, K. and Thomaidis N.S. (2013), Occurrence and removal efficiencies of benzotriazoles and benzothiazoles in a wastewater treatment plant in Greece, Sci. Total Environ., **452/453**, 163-171.
3. Barwal A., Chaudhary R. (2014), To study the performance of biocarriers in moving bed biofilm reactor (MBBR) technology and kinetics of biofilm for retrofitting the existing aerobic treatment systems: A review. Reviews in Environ. Sci. Biotechnol., **13** , 285-299.
4. Edwards S.J., Kjellerup B.V. (2013), Applications of biofilms in bioremediation and biotransformation of persistent organic pollutants, pharmaceuticals/personal care products, and heavy metals. Appl. Microbiol. Biotechnol. **97**, 9909-9921.
5. Liu Y.-S., Ying G.-G., Shareef A., Kookana R.S. (2012), Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant. Environ. Pollut. **165**, 225–232.
6. Loos R., Gawlik B.M., Locoro G., Rimaviciute E., Contini S., Bidoglio G. (2009), EU-wide survey of polar organic persistent pollutants in European river waters. Environ. Pollut. **157**, 561–568.
7. Mazioti A.A., Stasinakis A.S., Gatidou G., Thomaidis N.S., and Andersen H.R. (2015), Sorption and biodegradation of selected benzotriazoles and hydroxybenzothiazole in activated sludge and estimation of their fate during wastewater treatment, Chemosphere **131**, 117-123.