Biodegradation of pharmaceuticals in a pilot-scale staged Moving Bed Biofilm Reactors (MBBRs)

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Abstract The amount of pharmaceuticals that hospital wastewater can contribute directly into a sewage is significantly high while conventional activated sludge (CAS) sewage wastewater treatment plants (WWTPs) provides insufficient removal of these pharmaceuticals. Therefore, a pilot-scale MBBR was built at Skejby hospital with the aim to investigate the possibility to reduce the pharmaceuticals load in the wastewater. A batch and a continuous flow experiment were conducted to assess the pilot plant. In general, antibiotics (azithromycin, ciprofloxacin, clarithromycin and trimethoprim), sulfonamides (sulfadiazine, sulfamethizole and sulfamethoxazole) and X-ray contrast media (diatrizoic acid, iohexol, iomeprol, iopamidol and iopromide) showed higher degradation rate constants (k_{bio}) and removal than other treatment systems including a CAS treatment system. In particular, removal of more than 50% has been determined as compared to treatment systems utilizing activated sludge. Besides, diclofenac was measured to have a total removal of up to 80% over the treatment train.

Keywords: Biodegradation; diclofenac; hospital wastewater; pilot-scale MBBR

1. Introduction

The load of pharmaceuticals contributed by hospital wastewater to municipal WWTPs is remarkably high in which they are typically being treated together. Municipal WWTPs usually operate on CAS treatment in which the capability in degrading pharmaceuticals proves to be relatively low (Joss *et al.*, 2006; Ternes *et al.*, 2004). Consequently, an on-site hospital wastewater treatment has been taken into consideration in industrialized and developing countries as a solution to reduce pharmaceuticals input entering WWTPs.

Although many technologies including fungal fluidized-bed bioreactors and lab-scale MBBRs have been tested to degrade diclofenac, trimethoprim and X-ray contrast media to a higher extent than CAS (Escolà Casas *et al.*, 2015a; Falås *et al.*, 2012; Hapeshi *et al.*, 2013), pilot-scale MBBRs for treating hospital wastewater have not been explored. Degradation as well as rate constants determined in the laboratory are usually higher due to the fact that laboratory-scale reactors have a more straightforward manipulation. Therefore, in order to simulate a full-scale treatment plant, a system using 0.9 m^3 reactors were built to experiment on the capability of MBBRs to remove pharmaceuticals.

Since MBBRs have been studied extensively and they have been proven to be robust and efficient in removing pharmaceuticals, this study aims to test to which extent MBBRs in a larger pilot-scale degrade pharmaceuticals. Besides, the performance in which this pilot-scale can be used to treat hospital wastewater independently is explored as a solution for the coming future. Batch, as well as, continuous flow experiment have been conducted in evaluation of the capability of the pilot-scale MBBR.

2. Material and Methods

A six-staged MBBR composed of four 900 L and two 500 L reactors in series, namely M1, M2, M3A, M3B, M4 and M5, respectively, was built. The MBBR was operated with a filling ratio of 50% where approximately 150000 and 80000 AnoxKaldnesTM K5 carriers (AnoxKaldnes, Lund, Sweden) were in the 900 L and 500 L reactors respectively. The set-up is illustrated in Figure 1 where M1, M2, M3A and M3B are 900 L reactors and the latter two, M4 and M5, are 500 L reactors. The biofilm in reactor M3A and M3B is fed intermittently in which the flow of the pilot plant follows either the black path or the gray path (Figure 1), each lasts for 12 hours. The flow rate was 800 L h^{-1} for the 900 L reactors (M1, M2, M3A and M3B) before the return flow while a flow of 300 L h^{-1} was achieved for 500 L reactors (M4 and M5) after the return flow. The wastewater was pumped from a reservoir tank (influent) and recirculated after the fourth reactor at 300 L h^{-1} and 500 L h^{-1}, respectively.

Two experiments were conducted to investigate the efficiency of the pilot-scale in degrading pharmaceuticals

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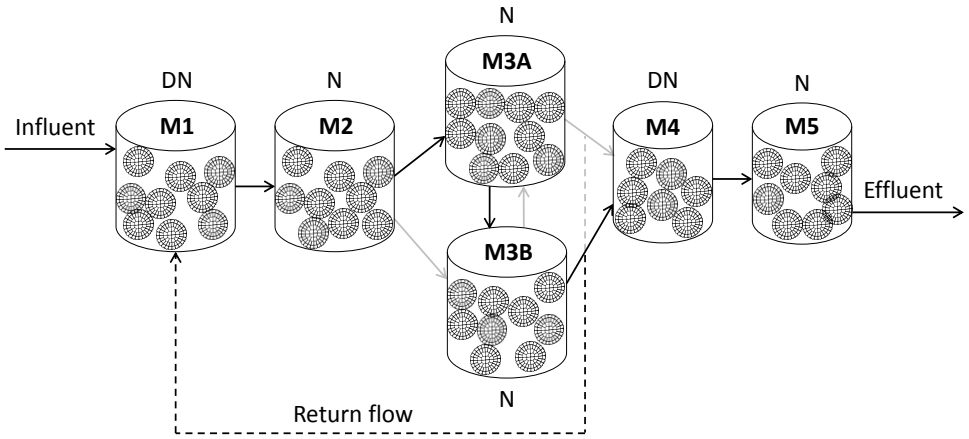

Figure 1. Overview of the pilot plant for treating hospital wastewater. DN denotes denitrification processes while N denotes nitrification processes.

First experiment was a batch experiment in which pharmaceuticals were spiked into each reactor that the flow between reactors was stopped and reaction kinetics was observed. The second experiment was a continuous flow experiment in which the pilot-scale MBBR was operated under indigenous concentration in hospital wastewater while samples were taken according to the hydraulic retention time (HRT) in each reactor. The samples obtained were centrifuged and added with internal standard and analyzed by HPLC-MS/MS.

Results and Conclusions

The pilot-scale MBBR showed stable operations for treating hospital wastewater. The performance of this pilot-scale staged MBBR has been a breakthrough in which antibiotics (azithromycin, clarithromycin and trimethoprim), sulfonamides (sulfadiazine, sulfamethizole and sulfamethoxazole) and X-ray contrast media (iohexol, iomeprol and iopromide) show a higher degradation rate constant (k_{bio}) than a lab-scale MBBR determined by Escolà Casas *et al*., 2015 (Table 1 and Figure 2).

In fact, antibiotics, for example, azithromycin showed removal up to 90% in the batch experiment as compared to 26% removal in fungal fluidized-bed bioreactors. Besides, sulphonamides, for instance, sulfadiazine and sulfamethoxazole showed a much higher removal (of >50%) when comparing with removal by membrane bioreactor (MBR) treatment, keeping in mind that these bioreactors have proved to have a higher removal than CAS.

Additionally, X-ray contrast media (diatrizoic acid, iohexol, iomeprol, iopamidol and iopromide) are used extensively in hospitals in which these compounds remain persistent through wastewater treatment systems can be removed to up to 60% in this pilot-scale MBBR as compared to a highest removal of 31% (iopromide) in an MBR in which the removal of the other X-ray contrast media was negligible. Besides, a low removal rate (ranging from 0 to 44%) in general was observed for X-ray contrast media in other treatment systems. Therefore, the capability in degrading these compounds in MBBR suggests a future perspective in using MBBR as a solution to treat hospital wastewater.

More importantly, diclofenac was removed to up to 50% in the batch experiment while in the continuous flow experiment, diclofenac was removed almost entirely (Figure 2A). An explanation for the distinctive results compared to previous studies may be that MBBR promotes the development of a more viable and robust biofilm degraders than the typical suspended bacteria found in activated sludge. This MBBR shows a high capability for treating hospital wastewater and removing pharmaceuticals. Therefore, MBBR is an interesting option for treating hospital wastewater before discharging directly or to WWTP.

Table 1. Comparison of biomass normalized rate constants (k_{bio}).

k_{bio} [L h^{-1} g^{-1}]								
Compounds	Present study					Staged MBBR (Escolà Casas *et al*., 2015b)		
	M1	M2	M3	M4	M5	Reactor 1	Reactor 2	Reactor 3
Atenolol	4.2×10^{-3}	9.5×10^{-2}	**2.5×10^{-1}**	9.4×10^{-2}	8.5×10^{-2}	8.2×10^{-2}	1.8×10^{-1}	1.4×10^{-1}
Azithromycin	4.4×10^{-2}	1.1×10^{-1}	1.9×10^{-2}	**2.0×10^{-1}**	7.5×10^{-3}	1.0×10^{-2}	2.3×10^{-2}	3.1×10^{-2}
Ciprofloxacin	4.7×10^{-17}	2.8×10^{-3}	2.5×10^{-3}	7.1×10^{-17}	2.9×10^{-3}	3.0×10^{-3}	8.0×10^{-3}	**2.1×10^{-2}**
Clarithromycin	3.9×10^{-2}	8.7×10^{-2}	1.6×10^{-1}	**2.0×10^{-1}**	2.2×10^{-2}	2.6×10^{-2}	5.9×10^{-2}	8.5×10^{-2}
Diatrizoic acid	7.8×10^{-17}	5.2×10^{-5}	3.0×10^{-3}	4.1×10^{-3}	8.4×10^{-4}	1.9×10^{-3}	4.1×10^{-3}	**1.9×10^{-2}**
Diclofenac	6.1×10^{-17}	1.4×10^{-14}	7.5×10^{-3}	1.4×10^{-3}	4.4×10^{-17}	2.6×10^{-2}	**5.7×10^{-2}**	1.5×10^{-2}
Ibuprofen	4.0×10^{-3}	5.1×10^{-1}	6.5×10^{-1}	3.2×10^{-2}	2.5×10^{-1}	1.3×10^{0}	**2.9×10^{0}**	4.8×10^{-1}
Iohexol	4.7×10^{-17}	4.4×10^{-2}	**3.4×10^{-1}**	2.8×10^{-3}	5.0×10^{-2}	3.0×10^{-2}	6.7×10^{-2}	9.1×10^{-2}
Iomeprol	5.9×10^{-17}	3.6×10^{-2}	**2.4×10^{-1}**	2.4×10^{-3}	3.4×10^{-2}	2.5×10^{-2}	5.6×10^{-2}	6.7×10^{-2}
Iopamidol	8.1×10^{-4}	4.0×10^{-5}	6.3×10^{-3}	1.7×10^{-3}	1.3×10^{-3}	3.9×10^{-2}	8.6×10^{-2}	**1.1×10^{-1}**
Iopromide	1.5×10^{-1}	8.6×10^{-2}	**4.6×10^{-1}**	3.7×10^{-3}	5.9×10^{-2}	3.0×10^{-3}	6.7×10^{-3}	2.0×10^{-2}
Metoprolol	7.8×10^{-17}	2.3×10^{-2}	2.8×10^{-2}	1.1×10^{-3}	4.5×10^{-3}	2.3×10^{-2}	5.2×10^{-2}	**3.0×10^{-2}**
Phenazone	6.2×10^{-17}	**4.9×10^{-2}**	1.6×10^{-2}	6.3×10^{-17}	1.5×10^{-3}	8.6×10^{-3}	1.9×10^{-2}	3.6×10^{-2}
Propranolol	1.3×10^{-2}	5.0×10^{-2}	1.0×10^{-2}	1.2×10^{-2}	4.3×10^{-3}	7.6×10^{-1}	**1.7×10^{0}**	1.3×10^{-1}
Sotalol	5.6×10^{-4}	1.4×10^{-2}	1.3×10^{-2}	5.6×10^{-4}	5.7×10^{-3}	2.6×10^{-2}	**5.8×10^{-2}**	3.1×10^{-2}
Sulfadiazine	5.9×10^{-17}	5.0×10^{-3}	5.1×10^{-2}	7.9×10^{-17}	**1.0×10^{-1}**	3.9×10^{-3}	8.7×10^{-3}	3.7×10^{-3}
Sulfamethizole	1.0×10^{-2}	2.5×10^{-2}	**3.0×10^{-1}**	4.1×10^{-3}	2.1×10^{-1}	9.6×10^{-3}	2.1×10^{-2}	2.9×10^{-2}
Sulfamethoxazole	2.6×10^{-3}	7.5×10^{-3}	6.5×10^{-2}	7.2×10^{-3}	**1.1×10^{-1}**	7.9×10^{-3}	1.8×10^{-2}	1.1×10^{-2}
Trimethoprim	**1.4×10^{-1}**	4.5×10^{-3}	1.4×10^{-2}	1.9×10^{-2}	5.8×10^{-3}	2.8×10^{-2}	6.3×10^{-2}	2.9×10^{-2}
Venlafaxine	5.9×10^{-17}	6.2×10^{-3}	7.6×10^{-3}	3.9×10^{-3}	1.5×10^{-3}	4.0×10^{-3}	8.9×10^{-3}	**1.5×10^{-2}**

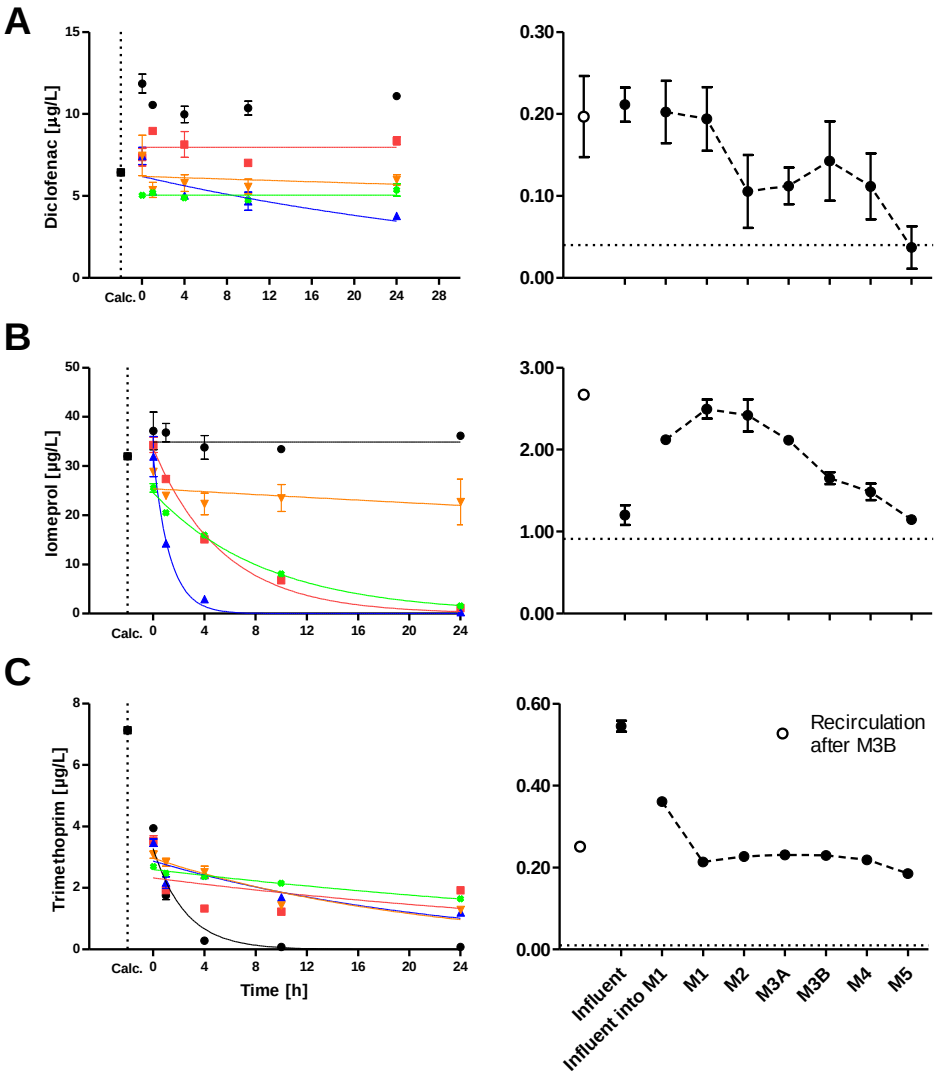

Figure 2. First-order kinetics fitted curve for the batch experiment (left) and a continuous fitting for the continuous flow experiment (right).

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