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Fate of hazardous aromatic substances in membrane bioreactors

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ABSTRACT

In this work, the removal of hazardous aromatic compounds was investigated in two types of membrane bioreactors (MBRs), based on cross-flow and semi dead-end filtration systems. BTEX and PAH were efficiently eliminated from wastewater during treatment via a membrane bioreactor (90–99.9%) but non-biotic processes, i.e. volatilisation and sorption, contributed significantly. The semi dead-end MBR showed slightly better removal efficiencies than the cross-flow MBR. However, non-biotic processes were more significant in the first process and, finally, degradation rates were higher in the cross-flow MBR. Higher degradation rates were explained by a higher bio-availability of pollutants. Differences in shear stress imposed in cross-flow and semi dead-end filtration systems radically modify the sludge morphology. High shear stress (cross-flow filtration) generates dispersed bacteria and larger quantities of dissolved and colloidal matter. Sorption of hydrophobic compounds (PAHs) on suspended solid was less marked in disaggregated sludge. The results suggest new strategies for improving micro-pollutant degradation in MBRs.

1. Introduction

The removal of hazardous substances from domestic and industrial wastewater is now necessary to protect water resources. At the same time, more stringent constraints concerning sludge disposal and atmospheric pollution are being imposed on treatment plants. For industrial wastewaters, membrane bioreactors (MBR) are considered as the best available technologies (BREF, 2003), the conventional activated sludge process (CAS) being insufficient to reach emission limits in some cases. Basically, membrane bioreactors achieve very good organics (COD, BOD) and nutrient removal (N, P) as well as perfect retention of suspended solids. However, the removal of hazardous aromatic compounds in MBRs has been little investigated (Bernhard et al., 2006; Cirja et al., 2007; De Wever et al., 2007; Lesjean et al., 2004; Schonerklee et al., 2009). Moreover, different MBR configurations have been proposed, based on external or internal submerged membranes, cross-flow or dead-end filtration, but there is still no comparison of the advantages or disadvantages of these options for treating specific pollutants.

This work focuses on wastewaters from the chemical, petrochemical and petroleum industries, which commonly contain the following substances: poly-aromatic hydrocarbons

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(PAH), benzene, toluene, ethylbenzene, xylene (BTEX) and phenols. In activated sludge processes, aromatic compounds are removed by three main processes: biodegradation, volatilisation and sorption. The respective contributions of these processes depend on the physical–chemical properties of the molecules. The fate of these compounds in wastewater treatment plants has been simulated with steady state models (Byrns, 2001; CEMC, 2006; Clark et al., 1995) and the concepts have been discussed for mono and poly-aromatic compounds in conventional activated sludge processes (Manoli and Samara, 2008; Wang et al., 2007). However, little attention has been paid to their operation in membrane bioreactors.

In most of the studies concerning aerobic biological processes, non-biotic transformations of aromatic compounds are generally insufficiently assessed because the authors focus on removal from the aqueous phase, evaluating the gas and solid phases only briefly (Farhadian et al., 2008). Based on the model of Byrns (2001), volatilisation of mono-aromatic compounds (whose Henry's constant is higher than 100 $Pa\,m^3\,mol^{-1}$) can reach up to 30% of the overall removal rate in activated sludge treatment. Similarly, considering the fate of hydrophobic compounds in activated sludge (example: PAHs) reveals that removal by sorption varies from 10% to 90% for molecules whose coefficients K_{ow} vary from $10^{3.5}$ to 10^6 respectively (Byrns, 2001; Manoli and Samara, 2008; Wang et al., 2007). The contribution of sorption to micro-pollutant removal in MBRs has been less studied (Joss, 2005). On the one hand, sludge sorption concepts developed for CAS can be transposed to MBR to some extent. However, on the other hand, modification of sludge properties due to shear stress and membrane retention modifies particulate and colloidal matters, and then could modify transport and partitioning phenomena. The adsorption of PAHs on dissolved and colloidal matter has been shown to improve the PAHs' bioaccessibility in an anaerobic digester and a similar phenomenon could occur in MBRs (Barret et al., 2010). In addition, concerning the concentration of PAHs in the water discharged from an MBR, it is reasonable to think that the membrane gives an advantage by retaining the small particles containing adsorbed PAHs, which would pass through a conventional settling tank. But this contribution has not been quantified in an MBR yet.

As non-biotic processes compete with biotic transformations, assessing and predicting the biodegradation rate of a specific aromatic compound is finally a critical task. The solids retention time (SRT) is considered as the most suitable design parameter to evaluate micro-pollutant removal in CAS and MBR (Byrns, 2001; Clara et al., 2005; Joss, 2005; Lesjean et al., 2004). As micro-pollutant degradation is generally considered to increase with increasing SRT, MBRs may have an advantage because they can work at higher SRT than CAS for a similar footprint. Additional specificities should be considered in MBRs: aeration with coarse bubbles, hydrodynamic constraints due to liquid circulation, total retention of small particles and accumulation of colloids. Consequently, various amounts of dispersed bacteria and extracellular polymeric substances are generally observed in MBR sludge. These specificities vary with the MBR configuration and operation. Basically, membranes can be submerged in the bioreactor or operated in an external element (side-stream configuration). In the latter case, the system can be operated with cross-filtration (high liquid velocity is then imposed at the membrane surface) or semi dead-end filtration with submerged membranes (coarse bubble aeration is then used to control fouling). Both systems generate shear stress which reduces the floc size to a greater or lesser extent (Kim et al., 2001; Stricot et al., 2010). This phenomenon reduces mass transfer resistance, which improves the accessibility of bacteria to pollutants and modifies the apparent biokinetic parameters (Fenu et al., 2010). But the relation between sludge structure and biokinetics is complex and still controversial. Most aromatic compounds become toxic at a given concentration and aggregation is also a microbial protection from this. For example, based on short-term experiments Sponza (2002) and Henriques et al. (2005) observed that floc disaggregation increased the inhibition of biomass for a given inhibitor concentration. However, there is still no information on the long-term consequences of disaggregation in MBR as acclimatisation of the microbial population plays a major role in resistance development and biodegradation kinetics for xenobiotic compounds (Rezouga et al., 2009).

Consequently, the aim of this study is to evaluate the fate of hazardous aromatic compounds in two MBR configurations, one using a submerged membrane in an external reactor (semi dead-end filtration), which generates low shear stress, the other an external cross-flow filtration unit which generates high shear stress. Specific attention is paid to the contribution of non-biotic phenomena as well as biodegradation and inhibition.

2. Materials and methods

2.1. *Experimental set-up*

Two lab-scale pilots were operated in parallel. Both MBRs provided a permeate rate of $1\,L\,h^{-1}$ but different configurations led to differences in terms of liquid velocity and aeration. The first membrane bioreactor worked with a cross-flow filtration unit, using a tubular ceramic membrane (inside/out ultra-filtration membrane Novasep/Carbosep 40, total surface area $0.01\,m^2$). It was operated in a side-stream loop with a high liquid velocity ($5\,m\,s^{-1}$) which induced a strong shear stress ($72\,N\,m^{-2}$). A mean filtration flux of $100\,L\,m^2\,h^{-1}$ was maintained by imposing a trans-membrane pressure (TMP) of 2 bar. The second MBR was a semi dead-end filtration system using hollow fibres submerged in an external cell (outside/in polysulphone membrane, external diameter 1.4 mm, mean pore diameter 0.1 μm, total surface area $0.1\,m^2$, Polymem®). The sludge recirculation flow rate was equal to the reactor feeding flow rate, which induced low liquid velocity and low shear stress ($0.07\,N\,m^{-2}$). Aeration was applied under the membrane bundle to prevent fouling (flow rate of $200\,NL\,h^{-1}$). The filtration flux was fixed at $10\,L\,m^2\,h^{-1}$ by a suction peristaltic pump. The hydrodynamic characterisation of these processes is detailed in Stricot et al. (2010). Both bioreactors, similar in volume (18 L), were continuously fed with synthetic wastewater, the composition of which was inspired by the analysis of a petrochemical wastewater. It was composed of readily biodegradable compounds on the one hand (methanol,