WATER RESEARCH 41 (2007) 935–945

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Comparison of sulfonated and other micropollutants removal in membrane bioreactor and conventional wastewater treatment

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ARTICLE INFO

Article history:
Received 11 July 2006
Received in revised form
19 October 2006
Accepted 7 November 2006

Keywords:
Membrane bioreactors
Polar micropollutants
Trace organics
Domestic wastewater

ABSTRACT

Membrane bioreactors (MBRs) were compared with conventional activated sludge systems (CAS) for micropollutant degradation, in laboratory-scale spiking experiments with synthetic and real domestic wastewater. The target micropollutants were polar in nature and represented a broad range in biodegradability. The experimental data indicated that MBR treatment could significantly enhance removal of the micropollutants 1,6- and 2,7-naphthalene disulfonate (NDSA) and benzothiazole-2-sulfonate. 1,5-NDSA, EDTA and diclofenac were not removed in either the MBR or the CAS. The other compounds were equally well degraded in both systems. For 1,3-naphthalene disulfonate, the existence of a minimum threshold level for degradation could be demonstrated. Although MBRs could not always make a difference in the overall removal efficiencies achieved, they showed reduced lag phases for degradation and a stronger memory effect, which implies that they may respond quicker to variable influent concentrations. Finally, micropollutant removal also turned out to be less sensitive to system operational variables.

1. Introduction

Membrane bioreactors (MBR) are one of the next generation of wastewater treatment processes. Instead of a sludge sedimentation tank as in the conventional activated sludge (CAS) process, they use membranes, either submerged in, or externally mounted to a suspended growth bioreactor to separate biomass and particles from the purified water. This yields advantages such as smaller footprints and a superior effluent quality (Stephenson et al., 2000; Visvanathan et al., 2000). The latter not only allows to reach an improved discharge quality but also opens perspectives for direct and indirect reuse of industrial and municipal effluents. Although it is generally agreed that MBRs perform better than CAS for

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Abbreviation: BTSA, benzothiazole-2-sulfonate; HRT, hydraulic retention time; NDSA, naphthalene disulfonate; NSA, naphthalene monosulfonate; NS, naphthalene sulfonate; SRT, sludge retention time

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doi:10.1016/j.watres.2006.11.013

biological removal of bulk organic matter, their behavior with respect to trace pollutants is much less documented. This is however crucial to understand the full potential of this technology and to assess its applicability for water reuse.

Several mechanisms may exist through which MBRs achieve a better elimination of organic pollutants than CAS. Physical retention by the membranes and sorption to the membranes are of minor importance for trace pollutants, because their molecular dimensions are well below the pore sizes of the ultra- and microfiltration membranes applied in MBRs, and because limited membrane surface area and sorption sites are available. For apolar trace organics, sorption to the biomass and subsequent retention of the solids by the membranes will be a major removal mechanism. For polar compounds, sorption will be limited and elimination can only be achieved through biodegradation. Theoretically, several operational conditions exist in MBRs, which are in favor of enhanced biotransformation and mineralization of micropollutants. First, MBRs often operate at high sludge ages. This allows for adaptation of microorganisms in general and of potentially slow growing specialist bacteria in particular. This will establish a more diverse microbial community with broader physiological capabilities. Second, higher biomass concentrations lead to an intensification of biological processes and may increase the interaction between microorganisms and the chances of genetic information exchange. Third, because of the higher biomass concentrations, the feed to microorganism (F/M) ratio is lower which could result in more complete mineralization.

Few papers report on micropollutant removal during MBR treatment. Some point to an improved removal efficiency compared to CAS treatment for nonylphenols and nonylphenol ethoxylates (Petrovic et al., 2003; Gonzalez et al., 2006), for several acidic pharmaceuticals (Lesjean et al., 2004; Kimura et al., 2005; Quintana et al., 2005), for diclofenac, mecoprop and sulfophenylcarboxylates (Bernhard et al., 2006) and for benzothiazoles (Kloepfer et al., 2004). De Wever et al. (2004) showed that not only the removal of easily degradable linear alkylbenzene sulfonates was slightly better. MBR effluents also contained lower amounts of the more recalcitrant sulfophenylcarboxylate metabolite. Other authors conclude that removal rates in MBR and CAS are comparable for selected pharmaceuticals, fragrances, endocrine disrupting compounds, naphthalene sulfonates and benzothiazole-2-sulfonate (Reemtsma et al., 2002; Clara et al., 2005a; Joss et al., 2005). Increasing the sludge retention time (SRT) above 15 d was found to improve micropollutant removal in all biological processes. Hence, when MBR and CAS were operated at comparable SRT, no difference in micropollutant removal was detected (Clara et al., 2005b).

It is clear from the above that literature on micropollutant removal by MBR is as yet limited and to some extent contradictory. In an attempt to compare and evaluate trace organics removal potential in MBRs and CAS, we performed comparative tests on municipal wastewater spiked with model substances. These were selected based on three criteria: (1) The substances are ubiquitous in the environment and occur in municipal and industrial effluents as well as in surface waters (Alonso et al., 2005; Kloepfer et al., 2005; Reemtsma et al., 2006). (2) Their biodegradability in CAS varies from easily to poorly degradable. (3) They are polar and will not be removed by sorption. This allows to evaluate whether differences in removal rates are really due to improved biodegradation. Experiments were performed at laboratory-scale for an optimal control of operational parameters. A first test run used synthetic domestic wastewater to ensure a constant influent composition. In a second test run, the matrix was real domestic wastewater and the range of target compounds was further enlarged.

2. Materials and methods

2.1. Reactor description

All reactor systems consisted of an aerobic zone only, and were inoculated with activated sludge from a municipal wastewater treatment plant in Belgium. The influent was kept at 4 °C throughout the test runs. The reactors were operated at room temperature and at oxygen concentrations between 1 and 2 mg/l (unless specified otherwise). Due to nitrification reactions, the pH showed a tendency to decrease and was corrected to neutral with 10% NaOH. The MBR was of the internal type and had an active volume of 21 l in which Kubota microfiltration membrane plates (Solis Engineering, the Netherlands, 0.4 mm nominal pore size) were submerged. Suction was applied for permeate collection. Coarse bubble aeration was provided under the membranes to create turbulence along the membrane surface. The CAS consisted of a 4.2 l bioreactor and 2 l decanter, respectively.

2.2. Trace organics

The technical mixture of 2 naphthalene monosulfonates (NSA) and 6 disulfonates (NDSA) was a gift from a manufacturer. Diclofenac (sodium salt) was purchased from Sigma (Belgium), and the disodium salt of ethylenediamine tetra acetate (EDTA) from Acros Organics (Belgium). Benzothiazole-2-sulfonate (sodium salt, BTSA) was a kind gift from Bayer Antwerpen NV (Antwerp, Belgium).

2.3. Experimental setup

In the first test run the MBR and CAS were operated in parallel on a synthetic domestic wastewater (skim milk, 333 mg/l, NH_4Cl, 120 mg/l, KH_2PO_4, 13.4 mg/l, $NaHCO_3$, 583 mg/l) spiked with a technical mixture of naphthalene sulfonates, which are industrial chemicals. Because 1,5-naphthalene disulfonate (1,5-NDSA) was present in very low concentrations in the technical mixture, it was added separately to achieve the desired concentration level. A new batch of synthetic wastewater was prepared every 2 d. Operational variables such as HRT and micropollutant concentration are given in Table 1. The calculated sludge age was always above 100 d. The coarse bubble aeration resulted in an oxygen concentration close to saturation in the MBR. Therefore, the aeration in the CAS was adjusted to achieve similar oxygen concentrations. To avoid membrane clogging, the influent to the MBR was prescreened at 0.75 mm, as opposed to the CAS. Measurements confirmed that micropollutant concentrations before and after the sieve