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Removal of a broad range of surfactants from municipal wastewater – Comparison between membrane bioreactor and conventional activated sludge treatment

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Abstract

Elimination of alkylphenol ethoxylates (APEO) and their degradation products (alkylphenols and alkylphenoxy carboxylates), as well as linear alkylbenzene sulfonates (LAS) and coconut diethanol amides (CDEA), was studied in a pilot plant membrane bioreactor (MBR) working in parallel to a full-scale wastewater treatment plant (WWTP) using conventional activated sludge (CAS). In the CAS system 87% of parent long ethoxy chain NPEOs were eliminated, but their decomposition yielded persistent acidic and neutral metabolites which were poorly removed. The elimination of short ethoxy chain NPEOs (NP_1EO and NP_2EO) averaged 50%, whereas nonylphenoxy carboxylates (NPECs) showed an increase in concentrations with respect to the ones measured in influent samples. Nonylphenol (NP) was the only nonylphenolic compound efficiently removed (96%) in the CAS treatment.

On the other hand, MBR showed good performance in removing nonylphenolic compounds with an overall elimination of 94% for the total pool of NPEO derived compounds (in comparison of 54%-overall elimination in the CAS). The elimination of individual compounds in the MBR was as follows: 97% for parent, long ethoxy chain NPEOs, 90% for short ethoxy chain NPEOs, 73% for NPECs, and 96% for NP. Consequently, the residual concentrations were in the low μg/l level or below it.

LAS and CDEA showed similar elimination in the both wastewater treatment systems that were investigated, and no significant differences were observed between the two treatment processes. Nevertheless, for all studied compounds the MBR effluent concentrations were consistently lower and independent of the influent concentrations. Additionally, MBR effluent quality in terms of chemical oxygen demand (COD), NH_4^+ concentration and total suspended solids (TSS) was always superior to the ones of the CAS and also independent of the influent quality, which demonstrates high potential of MBRs in the treatment of municipal wastewaters.

Keywords: Ionic and non-ionic surfactants; Nonylphenol ethoxylates; Biodegradation; Conventional activated sludge; Membrane bioreactor

1. Introduction

Surfactants are a group of compounds used daily in huge amounts mainly in household applications and as industrial cleaning agents. According to the Council of European Surfactants Producers Statistics – CESIO (CESIO, 2002) the total quantity of surfactants (without soaps) consumed in Western Europe in 2002 was more than 2.5 million tons. After their use they are discarded down the drain into municipal sewer systems and afterward treated in wastewater treatment plants (WWTP). The biodegradation of surfactants in the WWTP has been studied in numerous papers and in general most of the surfactants are well eliminated by conventional wastewater treatment. Under optimised conditions more than 90–95% can be eliminated, although the percentage of elimination can vary depending on the operating characteristics of the WWTP (i.e. plant size,

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sludge retention time, hydraulic retention time, temperature). However, despite the high elimination rates due to high influent concentrations (typically at mg/l level) they comprise a significant portion of trace organics detected in WWTP effluents and are considered as one of the most relevant organic contaminants of anthropogenic origin characterized with a very high potential to enter the environment. Additionally, all surfactant classes have been found to undergo primary biodegradation under aerobic conditions, but not all compounds are amenable to ultimate biodegradation and the formation of persistent biodegradation products can represent a serious problem.

For those reasons and in order to reduce the concentration of surfactants and metabolites in the wastewater effluents new technologies are being applied. Membrane bioreactor (MBR) treatment is an emerging technology based on the use of membranes in combination with the traditional biological treatment. MBRs are considered as promising technologies to achieve further removal of micro-pollutants in comparison to conventional WWTP. This is due to two characteristics of MBRs, (a) the low sludge load in terms of biological oxygen demand (BOD) that can be expected to force bacteria to mineralize also poorly degradable organic compounds and (b) the high sludge age that gives the bacteria time to adapt to these substances (Ghyoot and Verstraete, 2000; Wei et al., 2003). High sludge concentration is due to the higher retention of particles and microorganisms compared with conventional activated sludge (CAS) systems (vanDijk and Roncken, 1997; Jeffrey et al., 1998). This leads also to an increased microbiological concentration in reactor that gives the bacteria time to adapt to the treatment-resistant substances (Cote et al., 1997; Scott and Smith, 1997). However, there are only a few papers regarding the behaviour of polar pollutants during MBR treatment (Buenrostro-Zagal et al., 2000; Li et al., 2000; Wintgens et al., 2002; Clara et al., 2004; De Wever et al., 2004; Wintgens et al., 2004; Terzic et al., 2005), and most of them report no significant differences between MBR and CAS systems. A few of these studies focus on surfactants. Li et al. (2000) compared the conventional treatment with the membrane assisted biological wastewater treatment, showing that the membrane treatment can improve the elimination of nonylphenol ethoxylates (NPEOs) but can not entirely stop their discharge in the permeate. Other studies (Wintgens et al., 2002, 2004) reported 70–99% removal of nonylphenol (NP) from a waste dump leachate plant in different systems using nanofiltration or reversed osmosis membranes, where the elimination mechanism was size exclusion or in combination with a biological treatment using MBR. The degradation of linear alkylbenzene sulfonates (LAS) in CAS system and MBR was compared by De Wever et al. (2004) achieving over 97% of removal in both systems. Terzic et al. (2005) compared the degradation of LAS, NPEOs and their degradation products in a CAS system and MBR based on hollow fiber membranes, and obtained higher elimination rates using the MBR.

The objective of this work was to assess the viability of MBR operating under aerobic conditions in the treatment of relatively low strength wastewaters in municipal applications. The specific objective was to assess the efficiency of MBR in the elimination of a broad range of surfactants of various chemical type like NPEOs, octylphenol ethoxylates (OPEOs), and their degradation products: nonylphenol monoethoxylates (NP_1EO), nonylphenol diethoxylates (NP_2EO), octylphenol carboxylates (OP_1EC), octylphenol ethoxycarboxylates (OP_2EC), nonylphenol carboxylates (NP_1EC), nonylphenol ethoxycarboxylates (NP_2EC), octylphenol (OP) and NP, as well as LAS and coconut diethanol amides (CDEA) and to compare its performance with a CAS treatment. To achieve these objectives a MBR pilot plant has been operated in parallel to a full-scale WWTP. To our knowledge such a detailed study on the biodegradation of a broad variety of surfactants in WWTP using two different treatments had not been reported earlier.

2. Experimental

2.1. Materials and standards

All solvents (water, acetonitrile and methanol) were high performance liquid chromatography (HPLC) grade and were purchased from Merck (Darmstadt, Germany).

The standards used in this study were of the highest purity available. High purity (98%) 4-*tert*-OP and 4-NP were obtained from Aldrich (Milwaukee, WI, USA). NP_1EO, NP_2EO, OP_1EC, OP_2EC, NP_1EC and NP_2EC were synthesized according to the method described elsewhere (Diaz et al., 2002). Additionally, technical mixture of NPEOs containing chain isomers and oligomers with an average of 10 ethoxy units (Findet 9Q/22) was from Kao Corporation (Barcelona, Spain).

Commercial LAS with low dialkyltetralinsulfonate content (<0.5%) were supplied by Petroquimica Española S.A. in a single standard mixture with the proportional composition of the four homologues of: C10: 3.9%, C11: 37.4%, C12: 35.4%, C13: 23.1%.

The mixture of CDEA was kindly supplied by H. Fr. Schröder. The proportional composition of the five homologues is: C7: 7%, C9: 7.5%, C11: 60.9%, C13: 18%, C15: 6.6%.

4-NP_1EO-d_2 and 4-*n*-NP-d_8 which were used as the internal standard were obtained from Dr. S. Ehrenstorfer (Augsburg, Germany).

Stock solutions (1 mg/ml) of individual standards and standard mixtures were prepared by dissolving accurate amounts of pure standards in methanol. Working standard solutions were obtained by further dilution of stock solutions with methanol.

2.2. Membrane bioreactor

The pilot MBR was installed at WWTP Rubí, located about 20 km outside of Barcelona (Spain) and it was oper-