Journal of Hydrology (2008) **356**, 46–55

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/jhydrol

Evaluation of two pilot scale membrane bioreactors for the elimination of selected surfactants from municipal wastewaters

Susana González [a], Mira Petrovic [a,b,*], Damiá Barceló [a]

[a] *Department of Environmental Chemistry, IIQAB-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain*
[b] *ICREA — Catalan Institution for Research and Advance Studies, Passeis Lluis Companys 23, 08010, Barcelona, Spain*

Received 11 January 2008; received in revised form 24 March 2008; accepted 26 March 2008

KEYWORDS
Membrane bioreactor;
Wastewater treatment;
Surfactants;
Ionic surfactants;
Non ionic surfactants;
Nonylphenol ethoxylates

Summary The removal of selected surfactants, linear alkylbenzene sulfonates (LAS), coconut diethanol amides (CDEA) and alkylphenol ethoxylates and their degradation products were investigated using a two membrane bioreactor (MBR) with hollow fiber and plate and frame membranes.

The two pilot plants MBR run in parallel to a full-scale conventional activated sludge (CAS) treatment. A total of eight influent samples with the corresponding effluent samples were analysed by solid phase extraction—liquid chromatography—tandem mass spectrometry (SPE—LC—MS—MS).

The results indicate that both MBR have a better effluent quality in terms of chemical and biological oxygen demand (COD and BOD), NH_4^+, concentration and total suspended solids (TSS). MBR showed a better similar performance in the overall elimination of the total nonylphenolic compounds, achieving a 75% of elimination or a 65% (the same elimination reached by CAS).

LAS and CDEA showed similar elimination in the three systems investigated and no significant differences were observed.

Introduction

There are a lot of pollutants in the aquatic environment that the conventional wastewater treatments are not able to eliminate. Among these emerging contaminants, surfactants are one of the biggest concern mainly due to the high consume (more than two million tons every year in Western

* Corresponding author. Department of Environmental Chemistry, IIQAB-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain. Tel.: +34 93 400 6100; fax: +34 93 204 59 04.

E-mail addresses: sgbqam@iiqab.csic.es (S. González), mpeqam@cid.csic.es (M. Petrovic), dbcqam@cid.csic.es (D. Barceló).

0022-1694/$ - see front matter
doi:10.1016/j.jhydrol.2008.03.023

Europe (CESIO, 2002)) and they can be found in micrograms per litre range concentrations in wastewater effluents (Petrovic and Barcelo, 2003, 2004a). Although all of them are known as primary biodegradable under aerobic conditions, ultimate biodegradation are not able in all cases and persistent biodegradation products can be formed (Petrovic and Barcelo, 2003, 2004a). Using conventional treatments and under optimised conditions more than 90—95% can be eliminated, although the percentage of elimination can vary depending on the operating characteristics of the wastewater treatment plant (WWTP) (i.e. plant size, sludge retention time (SRT), hydraulic retention time (HRT), temperature).

In order to reduce these pollutants in the wastewater effluents and improve the water quality as a possible source of drinking water, free of anthropogenic pollutants, biochemical and physical procedures are applied. Some of the most successful ones are membrane bioreactor (MBR). Basically they are a combination of the traditional biological treatment with the filtration through membranes with a pore size between ultrafiltration—microfiltration where the membrane unit replace the secondary clarifier. Among the advantages of this type of treatment can be stand out an effluent free of suspended solids and germs within compact reactor volumes. MBR also could produce good quality effluent in terms of biological oxygen demand (BOD) and chemical oxygen demand (COD) due to the retention by membranes. However, the micro and ultrafiltration membranes, which are the ones commonly used in MBRs, are not able to remove micropollutants by sieving (the molecular size of the pollutants is more than 100 times smaller than the pore size of the membrane) but they can be operated with longer sludge retention time (SRT) than the ones achieved in conventional system, which is proved to enhance the elimination of micropollutants (Clara et al., 2005a). It is well known that in MBRs can grow adapted microorganisms that can improve the elimination of these persistent pollutants present in the raw wastewater (Cote et al., 1997; Scott and Smith, 1997). Otherwise there are some studies where no clear dependency on sludge age have been found (Joss et al., 2005).

Most of the results show better or similar results applying MBR treatment to the ones obtained during the application of conventional activated sludge (CAS) treatment. A few of these studies focus on surfactants. The anionic linear alkylbencene sulphonates (LAS) are compounds known as biodegradable with removal efficiency in CAS higher than 95% (Eichhorn et al., 2000; Petrovic and Barcelo, 2004b). The degradation of these compounds in CAS systems and MBR was compared by several authors (Li et al., 2000; De Wever et al., 2004; Terzic et al., 2005; Bernhard et al., 2006; Gonzalez et al., 2007) achieving similar removal rates in both systems. Regarding the elimination of nonylphenol ethoxylates (NPEO) several studies reported that the elimination of long chain NPEO was improved by the usage of MBRs treatment (Li et al., 2000; Lubello and Gori, 2005; Terzic et al., 2005) but only in two cases the degradation products were studied. Gonzalez et al. (2007) found that the membrane treatment can improve the elimination of NPEOs and their degradation products short NPEO and nonylphenol carboxylates (NPEC), while such improvement was not significant in a study by Clara et al. (2005b).

But it has to be stand out that all the results in MBR come from laboratory scale reactor or pilot scale reactors where the parameters can be controlled better; in conventional treatment normally there are greater fluctuations on operating conditions (temperature, flow rate...) and that become more difficult to have a stable and good elimination.

In the present paper the removal of several surfactants during membrane bioreactor is studied. Two pilot scale MBRs equipped with hollow fiber and plate and frame membranes were operated in parallel to a real WWTP and the results were compared with the elimination obtained in the WWTP. The surfactants investigated were the anionic LAS and the non-ionic coconut diethanol amides (CDEA), NPEOs, octylphenol ethoxylates (OPEOs), and their degradation products: octylphenol carboxylates (OP_1EC), octylphenol ethoxycarboxylates (OP_2EC), NP_1EC, nonylphenol ethoxycarboxylates (NP_2EC), octylphenol (OP) and nonylphenol (NP).

Experimental

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). 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.

Membrane bioreactor

The two MBRs were operated in parallel to a conventional WWTP in Terrassa, (Barcelona, Spain). The WWTP of Terrassa is located approximately 21 km of Barcelona and receives water from several towns and an industrial area, it is estimated that the 80% of the receiving water is domestic and 20% industrial (mainly textile and pharmaceutical). The main characteristics of the WWTP are showed in Table 1.