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# Removal of emerging contaminants from secondary effluents by micellar-enhanced ultrafiltration

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ABSTRACT

The removal of 11 selected emerging contaminants (ECs, acetaminophen, metoprolol, caffeine, antipyrine, sulfamethoxazole, flumequine, ketorolac, atrazine, isoproturon, 2-hydroxybiphenyl and diclofenac) by micellar-enhanced ultrafiltration (MEUF) has been investigated. Anionic sodium dodecylsulfate (SDS), non-ionic surfactants Triton X-100 (TX-100) and Tween 20 (TW-20), and cationic surfactants cetylpyridinium chloride (CPC) and cetyl trimethyl ammonium bromide (CTAB) were used. The retention coefficients of the selected compounds were determined in order to evaluate the separation efficiency of ECs from surfactant micelles. It was found that cationic surfactants were more appropriated for the removal of negatively charged and hydrophobic ECs. However, the presence of surfactant decreased the permeate flux due to the concentration polarization and membrane fouling. Among surfactants, the best results in terms of lower membrane fouling and higher retention of ECs were obtained with CPC. In addition, the effects of the MWCO of UF membranes and the water matrix on ECs and CPC removal and on membrane fouling were also evaluated. The increase of the feed CPC concentration improved the removal of ECs, although the permeate flux decreased. The removal of ECs and CPC was not affected by trans-membrane pressure. According to these results, solubilisation of ECs in the micelles and retention of the micelles by the membrane govern the overall retention process.



## 1. Introduction

The continuous daily use of an increasing amount of organic contaminants is leading to the increased occurrence of a considerable group of organic contaminants in urban wastewater system. Thus, in the last two decades, many reports have demonstrated that pharmaceutically active compounds (PhACs), personal care products (PCPs) and endocrine disrupting compounds (EDCs) are ubiquitous contaminants in wastewater effluents at low concentrations [1–3]. Many of these compounds, as well as other organic contaminants (such as pesticides, fuel additives, plasticizers, disinfection by-products), are included in the so-called category of "emerging contaminants" (ECs). Most of these ECs are recalcitrant/not completely removed during conventional wastewater treatments and they have been found in surface receiving waters that serve as sources for drinking water [2,3]. The presence of these substances in the aquatic environment is a cause for concern since these compounds have endrocrine disrupting activity and/or are potentially carcinogenic and mutagenic substances [4,5].

New technological alternatives such as advanced oxidation processes, activated carbon adsorption or membrane filtration are being explored as tertiary treatment in wastewater treatment plants (WWTP). Membrane separation processes, mainly in the range of nanolfiltration (NF) and ultrafiltration (UF), are increasingly used in the field of water and wastewater purification and for the elimination of ECs, microorganisms and organic matter in general [5–8]. NF technique has been successfully applied to remove PhACs and PCPs from different natural waters and wastewaters, although high transmembrane pressure (TMP) must be applied, increasing the energy requirements. UF membrane is characterized by relatively large pore sizes, which allows the use of lower TMP. However, the retention of low molecular weight organic contaminants, such as ECs, with UF membranes is rather low, which constitutes one of the critical limitations of UF for water and wastewater treatments [7,9]. In order to improve the removal efficiency, the effective size of a low molecular weight contaminant can be increased by binding it to a larger entity; this approach forms the basis of micellar-enhanced ultrafiltration (MEUF) [10]. In effect, MEUF has been proved to be an effective removal technique for a variety of trace contaminants in wastewater, including dyes, phenols, and some PhACs [9–12]. This technique is based on the tendency for surfactants in water to

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spontaneously aggregate to form micelles at concentration above the critical micellar concentration (CMC). The internal core is the hydrophobic region of the micelle and can solubilize hydrophobic and less polar molecules. The external polar or charged layer of the micelle (in the case of polar surfactants) can interact with oppositely charged ions and molecules with strong dipoles. Micelles have larger size than the pores of UF membrane and therefore can be easily retained together with bound contaminants. Hence, highly purified permeate can be obtained by using MEUF.

Specifically for the removal of ECs by MEUF, Exall et al. [9] have investigated the elimination of sulfonamide antibiotics using both, synthetic and real wastewater effluent. The presence of micellar concentration of a cationic surfactant (cetyl trimethyl ammonium bromide (CTAB)) increased the removal of sulfonamides compared to single UF, demonstrating that MEUF is a viable technique for improving the removal of PCPs from wastewater. Sarker et al. [13] determined binding of sulfonamide antibiotics to CTAB micelles using semi-equilibrium dialysis and found that there was a weak correlation between binding and log $K_{OW}$, and a stronger correlation with $pK_{a2}$ for these compounds. According to these publications, the effectiveness of contaminant uptake by surfactant micelles is affected by several parameters such as surfactant charge, micelle composition, water matrix, and the nature of contaminant. To the best of our knowledge, the removal of other groups of ECs, and the differences of separation of ECs in various surfactants micellar solutions (anionic, cationic, non-ionic) have not yet been investigated.

According to these considerations, a study was designed for the elimination by MEUF of 11 ECs: acetaminophen (ACET), metoprolol (MET), caffeine (CAF), antipyrine (ANT), sulfamethoxazole (SUL), flumequine (FLUM), ketorolac (KET), atrazine (ATR), isoproturon (ISOP), 2-hydroxybiphenyl (HYD) and diclofenac (DIC). Most of these ECs have been found in different aquatic environments at concentrations in the range of ng $L^{-1}$ to μg $L^{-1}$ [3]. The elimination of these compounds was previously investigated by using single UF and NF processes in batch concentration mode [14], and by the combinations constituted by powdered activated adsorption and/or coagulation pre-treatments followed by UF [15]. As a continuation, the main objective of this work was to study the elimination of these selected 11 ECs from a WWTP effluent (secondary effluent, SE) by applying MEUF with different head group surfactants. Specifically in this research, anionic sodium dodecylsulfate (SDS), two non-ionic surfactants, Triton X-100 (TX-100) and Tween 20 (TW-20), and cationic surfactants cetylpyridinium chloride (CPC) and CTAB were used. As the best results were obtained with CPC, this surfactant was used to compare the removal of selected ECs in the SE with those obtained in ultrapure (UP) water and with single UF. In addition, the effect of several operating parameters such as feed CPC concentration, molecular weight cut-off (MWCO) of UF membranes, and applied TPM was also established.

## 2. Materials and methods

### 2.1. Emerging contaminants, secondary effluents and surfactants

The selected ECs (ACET, MET, CAF, ANT, SUL, FLUM, KET, ATR, ISOP, HYD and DIC) were purchased from Sigma-Aldrich (Germany) and were of 99% purity or higher. Some relevant physico-chemical properties of these ECs are summarized in Table 1. These substances were simultaneously dissolved in UP water (18.2 MΩ cm, purified by a Milli-Q Academic (Millipore)) or in a SE collected from a municipal WWTP that employed an activated sludge process in Ciudad Real (Spain). This effluent was previously filtered by Whatman filter paper No. 1 to remove suspended matter and stored at 4 °C until use. The main quality parameters of this effluent were: pH = 7.9 ± 0.2; turbidity = 1.2 ± 0.3 NTU; chemical oxygen demand (COD) = 23.1 ± 2.0 mg $L^{-1}$, total nitrogen (TN) =4.5 ± 0.3 mg $L^{-1}$, total phosphorus (TP)=0.17 ± 0.2 mg $L^{-1}$, and UV absorbance at 254 nm (UVA)=0.22 ± 0.2 $cm^{-1}$.

Selected surfactants (SDS, TX-100, TW-20, CPC and CTAB) of the highest available purity were obtained from Sigma-Aldrich (Germany). The properties of these surfactants are listed in Table 2. These chemicals were used without further purification.

### 2.2. Experimental equipment and membranes

The filtration experiments were conducted in the laboratory membrane equipment (CM-CELFA, model P-28) described in detail in a previous publication [16], which operated in cross-flow mode. Basically, it was constituted by a 500 $cm^3$ pressurized storage ves-

**Table 1**
List of compounds and physico-chemical properties.

| Name | Use | MW, g $mol^{-1}$ | $pK_a$ | log $K_{OW}$ | Charge at pH 8 |
|---|---|---|---|---|---|
| Acetaminophen (ACET) | Analgesic, antipyretic | 151.17 | 10.2 | 0.46 | Neutral |
| Metoprolol (MET) | β-blocker | 342.41 | 9.6 | 1.72 | + |
| Caffeine (CAF) | Psichoactive stimulant | 194.19 | – | −0.45 | Neutral |
| Antipirine (ANT) | Analgesic, antipyretic | 188.23 | 1.3 | 0.54 | Neutral |
| Sulfamethoxazole (SUL) | Antibiotic | 253.28 | 1.8; 5.7 | 0.86 | – |
| Flumequine (FLUM) | Antibiotic | 261.25 | 1.3; 6.1 | 1.31 | – |
| Ketorolac (KET) | Anti-inflamatory | 255.27 | 4.0 | 2.15 | – |
| Atrazine (ATR) | Herbicide | 215.69 | 1.7 | 2.52 | Neutral |
| Isoproturon (ISOP) | Herbicide | 206.29 | – | 2.22 | Neutral |
| Hydroxybiphenyl (HYD) | Biocide | 170.21 | 9.8 | 3.27 | Neutral |
| Diclofenac (DIC) | Analgesic | 318.14 | 4.3 | 4.29 | – |

**Table 2**
Characteristics of selected surfactants.

| Name | MW, g $mol^{-1}$ | CMC, mM | MW of micelle, g $mol^{-1}$ | HLB[a] |
|---|---|---|---|---|
| SDS | 288 | 8.0 | 23,040 | 40 |
| TX-100 | 625 | 0.24 | 87,500 | 13.5 |
| TW-20 | 1227 | 0.07 | – | 16.7 |
| CPC | 358 | 0.90 | 34,010 | 26 |
| CTAB | 364 | 0.96 | – | 15.8 |

[a] HLB means hydrophile-lipophile balance [12].