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Impact of selected wastewater constituents on the removal of sulfonamide antibiotics via ultrafiltration and micellar enhanced ultrafiltration

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HIGHLIGHTS

- Ultrafiltration alone removed 15–20% of the sulfonamides from synthetic wastewater.
- MEUF generally improved sulfonamide removal, with rejections ranging from 20 to 74%.
- Environmental solids can further increase sulfonamide removal in UF and MEUF.
- Dissolved organic matter does not appear to influence rejection of sulfonamides.
- MEUF processes can be designed for the selective removal of sulfonamide antibiotics.

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ABSTRACT

To better understand the environmental mobility of sulfonamide antibiotics and develop improved processes for their removal during wastewater treatment, stirred cell ultrafiltration (UF) experiments were conducted using both synthetic and real wastewater effluent. The interactions between selected sulfonamides (sulfaguanidine, sulfathiazole and sulfamerazine), solids and dissolved organic matter were systematically explored. The further impact of micellar enhanced ultrafiltration (MEUF), a process in which surfactants are added at micellar concentrations to enhance removal of various trace contaminants from aqueous streams, was then explored by using a cationic surfactant, cetyltrimethylammonium bromide (CTAB). Ultrafiltration of sulfonamides in the absence of other materials generally removed only 15–20% of the antibiotics. The presence of micellar solutions of CTAB generally improved removal of sulfonamides over UF alone, with rejections ranging from 20 to 74%. Environmental solids (sediment) further increased retention of sulfonamides using both UF and MEUF, but the presence of DOM did not influence rejection. Similar trends were observed on UF and MEUF of real effluent samples that had been spiked with the sulfonamides, confirming the environmental relevance of the observed interactions between sulfonamides, surfactant, and wastewater constituents. The results demonstrate that MEUF processes can be designed for the selective removal of such trace contaminants as sulfonamide antibiotics.

1. Introduction

Over the past few decades, various pharmaceuticals and personal care products (PPCPs) have been detected in effluent from municipal wastewater treatment plants, as well as in groundwater and surface waters that serve as sources for drinking water (e.g., Monteiro and Boxall, 2010; Heberer, 2002; Daughton and Ternes, 1999). Sulfonamide antibiotics have been frequently detected at low concentrations, <1 ppb (Zhang and Li, 2011; Kümmerer, 2009; Miao et al., 2004); the presence of these substances in the aquatic environment is a cause for concern due to their potential for chronic toxicity to other organisms and promotion of antibiotic resistance (Monteiro and Boxall, 2010; Kümmerer, 2009; Daughton and Ternes, 1999).

The behavior of many trace contaminants of concern during treatment and in receiving environments is the subject of much study and several recent reviews (e.g. García-Galán et al., 2012; Zhang and Li, 2011; Watkinson et al., 2009). Conventional wastewater treatment plants were not designed to target trace contaminants, but instead are focused on removal of bulk constituents, such as solids and oxygen-demanding organic materials. Advanced treatment techniques such as membrane bioreactors, activated carbon and advanced oxidation are effective for removal of some PPCPs, but efficacy varies and in some cases, more toxic by-products may be formed (García-Galán et al., 2012a, 2012b; Zhang and Li, 2011; Watkinson et al., 2009; Snyder et al.,

Abbreviations: CMC, = critical micelle concentration; CTAB =, cetyltrimethylammonium bromide; DOM, = dissolved organic matter; MEUF, = micellar enhanced ultrafiltration; PPCPs, = pharmaceuticals and personal care products; R, = rejection coefficient; SG =, sulfaguanidine; ST, = sulfathiazole; SMR, = sulfamerazine; UF, = ultrafiltration.

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2006). The processes involved in removal and by-product formation are poorly understood for many PPCPs; improved methods for removal of contaminants are thus still sought.

Membrane filtration processes have become common elements of drinking water and wastewater treatment and can be very useful in trace contaminant removal (Monteiro and Boxall, 2010; Snyder et al., 2006). Nanofiltration and reverse osmosis processes will remove many PPCPs, but require high pressures and therefore have relatively high energy requirements, as well as often requiring the inclusion of upstream pretreatment to reduce problems due to membrane fouling. Microfiltration (MF) and UF membranes, on the other hand, are characterized by larger pore sizes and lower pressures, but therefore do not target small, dissolved molecules. One remedy is to increase the effective size of lower molecular weight material by binding it to a larger entity; this approach forms the basis of micellar enhanced ultrafiltration, MEUF (Dunn et al., 1985).

The MEUF technique employs a surfactant in solution at concentrations higher than its critical micelle concentration (CMC), at which point surfactant aggregates, or micelles, form. Contaminants may be solubilized by micelles in various ways: the interior, low polarity region of the micelle can solubilize more hydrophobic molecules, while in the case of an ionic surfactant, the outer charged layer will also interact strongly with oppositely charged ions or molecules with strong dipoles (Dunn et al., 1985). Micellar solubilization is also commonly employed in remediation technologies for groundwater and soils contaminated with organic substances, such as soil washing (Paria, 2008). In MEUF, micelle-bound contaminants have a higher effective size and are thus rejected by the UF membrane (Dunn et al., 1985); the technique has been shown to be effective in the removal of metals, nutrients, and such organic pollutants as phenols, dyes and naphthenic acids (e.g. Deriszadeh et al., 2010; Baek and Yang, 2004; Dunn et al., 1985).

The effectiveness of contaminant uptake by surfactant micelles is affected by a number of parameters, including micelle composition and surfactant charge, as well as the nature of the contaminant. Cationic surfactants possess positively charged head-groups that are partially neutralized by anions (such as Br^-, Cl^-), whereas anionic surfactants possess negatively charged head groups that are partially neutralized by cations (such as Na^+ or K^+). Cationic surfactants have been identified as particularly suitable for MEUF due to their relatively large micelle sizes, low CMC values and high solubilization potential for many typical organic solutes (Dunn et al., 1985). In this study, we selected cetyltrimethylammonium bromide (CTAB), a well-characterized cationic surfactant commonly used in a variety of commercial products and industrial processes.

In evaluating the potential utility of MEUF processes in removing trace contaminants during wastewater treatment, however, it is important to recognize that the target molecules will interact with other constituents of the wastewater, as well. Dissolved organics may directly interfere with some physicochemical treatment processes, competing for adsorption sites or increasing chemical demand. Environmental solids and bulk organic material could also adsorb trace contaminants, which may help or hinder their removal, depending on the treatment process (Tchobanoglous et al., 2003). The potential for adsorption of sulfonamides to environmental solids is debatable: Zhang and Li (2011) reported that sulfonamides have been commonly shown to have low adsorption potential to sludge, while others (e.g. Kümmerer, 2009; Thiele-Bruhn et al., 2004; Tolls, 2001) have reported the sorption of sulfonamides to soils to be significant, although affected by the composition and structure of soil colloids. Bialk-Bielinska et al. (2012) demonstrated that the environmental mobility and bioavailability of a number of sulfonamide antibiotics are strongly impacted by the organic content of soils or sediments. Consequently, to evaluate the individual effects of such bulk wastewater components on the removal of sulfonamide antibiotics during UF and MEUF treatment, we produced a synthetic wastewater containing commercially available aquatic organic material and well-characterized solids.

In the present study we used stirred cell UF to explore the interactions between sulfonamide antibiotics and CTAB and evaluated the effects of synthetic wastewater containing additional solids and dissolved organic matter (DOM) on contaminant removal by UF and MEUF. The results were validated by comparison with UF and MEUF of spiked samples of real secondary effluent, providing the first report of MEUF for antibiotic removal from wastewater effluents. The results reported herein provide a "proof-of-concept" for the feasibility of removing antibiotics by MEUF, while also providing greater insight into the physicochemical factors influencing the removal of contaminants from wastewater streams during MEUF, as well as during conventional wastewater treatment.

2. Materials and methods

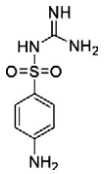
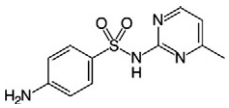
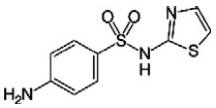
2.1. Materials

The cationic surfactant, CTAB (Sigma Aldrich, Oakville, Ontario), was used for all MEUF experiments. The three sulfonamides (all from Sigma Aldrich, Oakville, Ontario, Canada) selected for this study were sulfaguanidine (SG), sulfathiazole (ST) and sulfamerazine (SMR); some relevant physicochemical characteristics are listed in Table 1.

Test solutions consisted of a mixture of SG, ST and SMR, each at a concentration of 500 ppb (μg L^{-1}) in MilliQ water. While higher than typically observed in environmental samples, this elevated concentration was used to facilitate accurate measurement in permeate and retentate solutions while providing insight into the processes operating at lower concentrations.

Surrogate materials were selected to simulate the effects of solids and DOM on the MEUF process in municipal or industrial wastewaters. For the examination of the effects of DOM on the MEUF process, Nordic aquatic natural organic matter was purchased from the International Humic Substances Society (Georgia). Solids were added in the form of sediment collected from Lake Erie site 303 (Bartlett et al., 2012). Prior to use, the sediment was dried and homogenized by hand.

Table 1
Sulfonamides used in this study; relevant physicochemical characteristics from ChemIDPlus Advanced database, United States National Library of Medicine.

Sulfonamide	Sulfaguanidine (SG)	Sulfamerazine (SMR)	Sulfathiazole (ST)
Structure			
Molar mass (g mol^{-1})	214.24	264.30	255.32
log K_{OW}	−1.22	0.14	0.05
pK_{a2}	11.2	6.8/7.00	7.2