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Roles of membrane and organic fouling layers on the removal of endocrine disrupting chemicals in microfiltration

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ABSTRACT

To understand the adsorption behavior of endocrine disrupting chemicals (EDCs) is important for enhancing the treatment performance and preventing potential secondary pollution caused by EDCs desorption in a microfiltration system. The dynamic adsorption of four representative EDCs, namely estriol (E3), 17β-estradiol (E2), 17α-ethynylestradiol (EE2), and 4-nonylphenol (4-NP) in a microfiltration system was investigated using the Thomas' model. The product of the equilibrium constant and the total adsorption capacity of the membrane, *Ka*, for E3, E2, EE2, and 4-NP were 4.91, 9.78, 15.6, and 826, respectively, strongly correlating with the compound octanol–water partition coefficient (K_{OW}). Adsorption appeared to be enhanced when organic fouling formed on the surface of membrane, indicating the role of an additional adsorption column for EDCs acted by a fouling layer in microfiltration. Results of a comparison between the *Ka* values for clean membrane and fouled membrane illustrated that the significant contribution made by fouling layers may be attributed to the foulant layer's hydrophobicity (in the case of calcium humate layer) and thickness (in the case of calcium alginate layer). This study provided a novel perspective to quantitatively analyze the dynamic adsorption behavior of trace pollutants in membrane process.

Introduction

Endocrine disrupting chemicals (EDCs) can interfere with the hormone system and adversely affect the reproductive behavior of aquatic and terrestrial animals (Bhandari et al., 2015; Han et al., 2010). Moreover, human exposure to EDCs at trace concentration level is potentially linked to obesity, decreasing of male sperm counts, and increasing risks of cancer (Kabir et al., 2015). With the rapid development of modern analytical techniques, the presence of EDCs in urban water cycles has been widely detected (Kolpin et al., 2002; Nakada et al., 2006; Sun et al., 2014; Writer et al., 2011; Wu et al., 2017; Xue et al., 2010; Zhang et al., 2016). Hence, increasing efforts have been made to understand the behavior of EDCs in waterways, especially in various water and wastewater treatment processes, in order to effectively minimize the health risk with regard to this special group of emerging pollutants.

Microfiltration has been widely applied in water treatment and wastewater reclamation since 1990s. Hence, its ability to remove trace pollutants is attracting increasing concerns (Han

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et al., 2010, 2013; Prasertkulsak et al., 2016; Silva et al., 2012; Zhu and Li, 2013). Adsorption and desorption are the primary mechanisms that dominate the fate of trace pollutants such as neutral EDCs in membrane processes. This is particularly evident in the case of microfiltration, where size exclusion is invalid due to the small molecular weight of EDCs. Although porous membrane processes are usually not considered to be effective barriers for EDCs, the repeated adsorption and desorption of EDCs on membrane materials due to backwash and cleaning processes may lead to a special scenario for the discharge of EDCs from membrane treatment systems. Several researchers have focused on describing the adsorption capabilities of EDCs using the partition coefficients in either a static circumstance (by simply exposing the contaminated solution to membrane material) or a dynamic circumstance (by filtering the contaminated solution through membrane material) (Chang et al., 2003; Dong et al., 2010; Han et al., 2010, 2013; Schäfer et al., 2011). Nevertheless, few have attempted to delineate the process from the perspective of adsorption thermodynamics, which has the potential to provide more insight into the dynamic properties of EDC adsorption and desorption. The presence of organic matter in surface water and wastewater is one of the principle causes of fouling in membrane treatment processes. Accompanied by the formation of membrane fouling, the fate of trace organic contaminants may alter due to the additional adsorption sites provided by the fouling layers (Jermann et al., 2009). To our best knowledge, a modeling interpretation and a comparison of the roles played by membranes and organic fouling layers in terms of the removal of EDC by microfiltration have not been performed in previous studies.

The objectives of this study were to quantitatively determine the adsorption capabilities of representative EDCs in a microfiltration system with the contribution of synthetic organic fouling layers. The predominant mechanisms for EDC removal by the organic fouling layers were interpreted by comparing the adsorption capacities of clean membranes and fouled membranes. Unlike in previous studies, the adsorption kinetics of selected EDCs during the membrane filtration process were described using the Thomas' model, which was specifically applied to simulate the dynamic adsorption on an adsorption column.

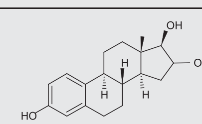
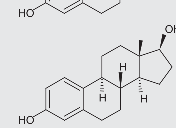
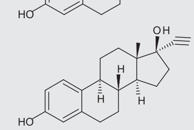
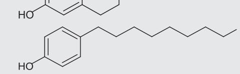
1. Materials and methods

1.1. *Target EDCs and chemicals*

The four EDCs selected for membrane adsorption tests included two natural hormones (estriol [E3] and 17β-estradiol [E2]), one synthetic hormone (17α-ethinylestradiol [EE2]), and one industrial product (4-nonylphenol [4-NP]) with endocrine disrupting activity, whereas E3 and EE2 were used for the adsorption experiment for gel-membrane assemblage. Their physicochemical characteristics are summarized in Table 1. The presence of these EDCs in both natural water matrices and municipal secondary effluents has been widely reported in the literature (Sun et al., 2014; Xue et al., 2010). Stock solutions were separately prepared for each EDC by dissolving the corresponding compound into methanol at 1 g/L and stocked at −20°C. Each EDC stock solution was diluted to 100 μg/L using a salt solution composed of 20 mmol/L NaCl and 2 mmol/L $NaHCO_3$ for adsorption experiments.

Two model organic foulants, sodium alginate (NaAlg) and sodium humate (NaHA), which were provided by Sigma-Aldrich, USA, were used to form the synthetic fouling layers on the microfiltration membranes. Each model compound was dissolved in a salt solution composed of 16 mmol/L NaCl and 2 mmol/L $NaHCO_3$ at 1 g/L, and the mixture was well stirred overnight prior to further experimentation. The concentration of the model foulant was higher than that in practical wastewater in order to shorten the duration of fouling layer formation in the subsequent experiment. The 2 mmol/L $CaCl_2$ was then added into the solution to enhance the growth of calcium alginate (CaAlg) or humic acid calcium (CaHA) colloid, followed by gently blending for another 24 hr. To remove the undissolved particles, CaHA solutions were pre-filtered using 0.45 μm nylon filters prior to the gel layer formation tests. The CaAlg colloid possessed an average particle diameter

Table 1 – Physicochemical properties of target EDCs (Ahel and Giger, 1993; Xue et al., 2010; Yamamoto et al., 2003).

EDCs	Molecular formula	Molecular weight (g/mol)	Solubility in water (mg/L)	$LogK_{OW}$	Molecular structure
Estriol (E3)	$C_{18}H_{24}O_3$	288.4	30.2	2.45	
17Beta-estradiol (E2)	$C_{18}H_{24}O_2$	272.4	3.85	4.01	
17Alpha-ethinylestradiol (EE2)	$C_{20}H_{24}O_2$	296.4	19.1	3.67, 4.15	
4-Nonylphenol (4-NP)	$C_{15}H_{24}O$	220.4	1.66	5.76, 4.48	

EDCs: endocrine disrupting chemicals.

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