



Removal of adsorbing estrogenic micropollutants by nanofiltration membranes. Part A—Experimental evidence

Andrea J.C. Semião ^{*,1}, Andrea I. Schäfer

School of Engineering, The University of Edinburgh, Edinburgh, EH9 3JL, United Kingdom

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ABSTRACT

Nanofiltration membranes should be effective in removing hormones based on hormone molecular size. However, the occurrence of adsorption onto the membranes results in a lower performance than would be expected by size exclusion. It is hence important to understand the retention mechanisms involved in the removal of adsorbing trace contaminants.

The focus of this study was to elucidate how estrone and estradiol adsorption and retention are affected by intrinsic membrane characteristics such as different polymeric materials and membrane pore radius.

Polyamide raw material and polyamide active layer of TFC NF membranes were found to adsorb much higher amounts of hormones than any of the other membrane materials that constitute the membranes, *i.e.*, polysulfone and polyester. These results show that the bulk of the adsorption occurs in the active layer. The adsorption isotherm onto the different raw polymeric materials was found to be of the Freundlich type, and interactions between hormones and the different polymers can be explained by H-bonding and weak π - π interactions, amongst other interactions, and not hydrophobic interactions.

Adsorption and retention were further found to be affected by the membrane active layer pore size, hence the steric exclusion capacity of the membrane, which dictates how much hormone partitions into the membrane pores. An increase of pore radius from 0.32 nm to 0.52 nm increased the amount of hormone that partitions into the membrane pores, thus affecting adsorption, which increased from 0.17 ng cm⁻² to 1.10 ng cm⁻². Retention, on the other hand, decreased from 88% to 34%.

Finally, hormones were shown to penetrate and adsorb inside the active layer at pH 7, whilst at pH 11, adsorption was confined to the membrane surface due to electrostatic repulsion. The membrane internal surface area of the active layer played a role in adsorption. At neutral pH, the more internal surface area the membrane had, the more adsorption took place. There is therefore a combination of partitioning effect and internal surface area access playing a role in hormone adsorption and retention by NF membranes.

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1. Introduction

Trace organics, including hormones, pesticides and personal care products are discharged into surface waters from the ng L⁻¹ up to the µg L⁻¹ concentration [1]. Since they pose an environmental risk to organisms and in consequence, possibly to human health, [2], they should be removed from natural and potable water sources.

Nanofiltration (NF) is a possible application for water treatment. Removal of adsorbing trace organics by NF membranes is however not well understood. It has been well established that

adsorbing trace contaminants have a lower retention than would be expected by size exclusion [3]. This is thought to be caused by the partitioning of trace organics onto the polyamide active layer [4]. No link has however yet been established between adsorption of trace contaminants and the membrane characteristics (*e.g.*, pore size, solute-membrane affinity). The parameters affecting adsorption and transport of trace contaminants by NF membranes need therefore to be elucidated.

Understanding transport of adsorbing compounds through NF membranes in filtration mode requires the knowledge of the mechanisms and physical parameters governing the process. It was previously found that the concentration at the membrane surface governs hormone adsorption onto NF membranes [5]. The membrane was, however, treated as a black box and no membrane characteristics were included in the study. Determining such mechanisms and physical parameters as far as membrane

^{*} Corresponding author. Tel.: +353 17161974, +353894125869.

E-mail address: Andrea.Correia-Semiao@ucd.ie (A.J.C. Semião).

¹ Presently at University College Dublin, School of Chemical and Bioprocess Engineering, Belfield Campus, Dublin, Ireland.

characteristics are concerned (e.g., pore radius, membrane materials) is therefore a necessary next step.

Adsorption of trace contaminants onto different types of polymeric membranes has been extensively reported in the literature [6]. Polyamide based membranes, for example, have been shown to adsorb more trace contaminants than cellulose acetate ones [7]. Other polymeric materials such as polypropylene and polyimide have shown to adsorb trace contaminants [8,9]. The adsorption of trace contaminants onto NF polymeric membranes have been proposed to be either caused by charge interactions [10], hydrophobic interactions [11] or hydrogen-bonding interactions [12]. Other mechanisms such as dipole–dipole, induced dipole–dipole interactions might also affect the interaction between the contaminant and the membrane [6]. However, for the particular case of hormones, when comparing the amount adsorbed with their chemical properties for the NF270 [6], electrostatic repulsion, hydrophobicity and dipole moment do not explain the differences in sorption obtained for the several hormones.

Thin film composite (TFC) NF and RO membranes are made of three different polymeric layers and to understand and model the removal of adsorbing trace contaminants it is necessary to determine in which layer(s) adsorption occurs onto.

Several authors have carried out static adsorption experiments with membrane coupons of the polysulfone (PSu) support with and without the polyamide (PA) active layer. Williams et al. [13] and Steinle-Darling et al. [14] obtained much higher adsorption of phenolic compounds and perfluorochemicals, respectively, onto PA+PSu compared to just PSu. McCallum et al. [15] results showed that hormone adsorption onto PA+PSu was slightly higher than PSu only. Polyester (PET), the third material of TFC membranes, was shown not to adsorb any hormones. These results give a good indication of the affinity of the contaminant with the different materials. However, it is difficult to determine the affinity of the contaminant for each material independently. The affinity with PA is carried out in the presence of PSu since these two layers are not possible to separate and competition between the two layers might occur. A systematic study for the separate polymers is therefore necessary to properly establish the differences in affinity between the hormone and the polymeric materials.

The effect of pore radius on trace contaminant adsorption and retention by NF membranes is important since it allows determining if steric exclusion (*i.e.*, solute to pore radius ratio) needs to be taken into account when modelling adsorption onto NF membranes. In general, retention increases with increase of compound molecular weight [16] showing a size exclusion mechanism. Nghiem et al. [17] however, showed that adsorbing hormones have a lower retention than would be expected if only steric interactions were considered. Furthermore, hormone adsorption was found to be higher for two NF membranes compared to an RO membrane, suggesting a pore radius effect in hormone adsorption and retention by polymeric membranes [12].

Several studies [18,19] have suggested the occurrence of internal adsorption of trace contaminants on the NF active layer. Kimura et al. [20] obtained lower contaminant extraction in static mode from membranes saturated under pressure (40–60%) compared to membranes saturated under static conditions (100%). McCallum et al. [15] on the other hand obtained 100% extraction efficiency when carrying out the desorption under pressure of a pre-saturated membrane. All these studies indicate that membrane adsorption occurs inside the active layer. If this is the case, then pore radius could not be the only parameter affecting adsorption and retention of trace contaminants by NF membranes: internal surface area may play an important role as well.

In consequence, a systematic study to determine the contribution of internal surface area is required.

In our previous review [6] preliminary experiments indicated an effect of pore radius and internal surface area on the adsorption of hormones in NF membranes and showed there was a difference between the hormone adsorption onto one weight of the different raw polymers. A more in depth study on the effect of these different parameters in adsorption of trace contaminants in NF membranes was however needed.

In the present study the relevant membrane characteristics needed to understand and model transport of adsorbing hormones through NF membranes were systematically determined, extending the preliminary work showed in the review by Schäfer et al. [6]. Understanding how these parameters, such as pore radius and internal surface area, affect adsorption and retention of hormones by NF membranes is a first step as it allows deciding which approach is the most appropriate to model transport of adsorbing hormones through NF membranes.

The affinity of the hormones onto the different raw materials that constitute TFC membranes was established, as well as the isotherm and its parameters. The adsorption of hormones onto the polyamide and polysulfone layers of the NF 270 membrane was further quantified. Several TFC NF membranes were then characterised in terms of pore radius and active layer thickness to porosity ratio. This allowed to study the effect that pore radius has in hormone adsorption and retention. Moreover, the effect of the active layer internal surface area in hormone adsorption was considered in this study. Finally, the occurrence of internal sorption on the active layer was showed by carrying out desorption experiments of pre-saturated membranes under pressure.

2. Materials and methods

2.1. Filtration set-up

A stainless steel cross-flow system (Fig. 1) used for the filtration experiments, has been described elsewhere [6]. The system is connected to a flat sheet membrane cell (MMS,

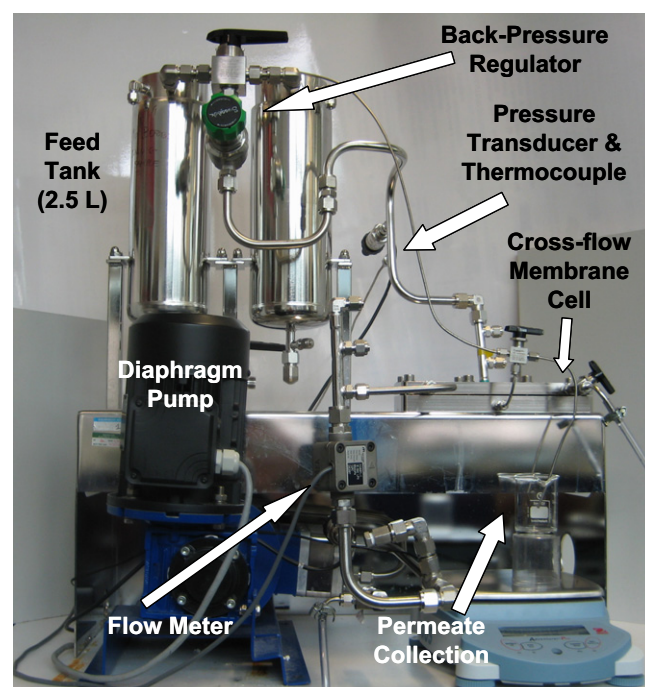


Fig. 1. Cross-flow filtration set-up.

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