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Adsorption of estrone in microfiltration membrane filters

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ABSTRACT

Adsorption of estrone was identified in microfiltration membrane filters with 0.1–0.45 μm nominal pore sizes. This phenomenon is of concern as it may lead to distortion when such filters are used to process estrone solutions prior to chromatography analysis, such as in slurry-type photocataltytic degradation studies. The adsorption of estrone was comparatively assessed in a variety of membrane filters, and considerable adsorption was observed in nylon (NYL), polypropylene (PP), polytetrafluoroethylene (PTFE) and cellulose acetate (CA) filters. While estrone adsorption gradually approached equilibrium in most filters, it maintained at near 100% in NYL filters during most of the filtration process and remained substantial (42.2%) when the filter capacity was reached. This rather unusual phenomenon was investigated, and ascribed to the hydrogen bonding between estrone and NYL membranes as demonstrated by Fourier transform infrared spectroscopy. Further studies showed that estrone adsorption in NYL membranes could be substantially reduced by increasing the pH to facilitate the deprotonation of estrone molecules. Similar improvements were obtained in PP and PTFE filters by pre-dosing estrone solutions with anhydrous ethanol (1:1, vol:vol). The only filter that showed consistently low estrone adsorption (<2.3%) was the 0.45-μm glass microfibre (GMF) filter.

GMF and PTFE filters were further selected to process estrone solutions in a slurry-type photocatalytic degradation system using P25® TiO_2 photocatalysts. Both types of filters showed satisfactory performance in terms of estrone solute recovery, as verified by samples simultaneously processed by high-speed centrifuging. It is suggested that caution should be taken when using MF membrane filters to process estrone aqueous solutions. Although GMF and PTFE filters (with solvent pre-dosing) may be appropriate to use, verifications on solute recovery are highly recommended.

1. Introduction

Endocrine-disrupting chemicals (EDCs) can adversely affect reproductive behaviour of aquatic species and interfere with normal working of hormones that control reproduction and development in terrestrial animals. Reported adverse effects in animals include increased femininity in fish, declining fertility in alligators, and testicular weight reduction in Japanese quails [1]. Studies on human exposure suggested the link to decreasing male sperm counts and increasing risks of testicular, prostate, ovarian and breast cancer [2]. Estrone and 17β-estradiol are of particular concerns for their widely occurring nature and high estrogenic potencies [3]. Elevated levels of estrone and 17β-estradiol have been found in waterways downstream of many wastewater treatment facilities [4,5]. Their presence in waterways poses direct risks to aquatic species and indirect risks to human through food and drinking water exposure.

With its proven capability to mineralise persistent organic pollutants and unique potential to utilise solar radiation, photocatalytic degradation emerges as a promising approach for removing estrogens from contaminated water [6,7]. A typical slurry-type photocatalytic degradation system contains an aqueous solution with the co-presence of target compounds and dispersed photocatalyst particles. When exposed to UV, the photocatalysis process activates, generating highly reactive oxidants which can aggressively attack any organic compounds in contact. In these studies, reaction kinetics is the key to evaluate photocatalyst activity, photoreactor design and the overall degradation efficiency. The establishment of reaction kinetics relies on proper sampling and accurate analysis of residual compounds in the solution. Due to their low concentrations, quantification of estrogens and degradation residues generally involves chromatography analysis [6,7], which requires samples to be free of particulate matters to avoid column blockage and undue wear on mechanical parts. The benchmark photocatalyst P25® TiO_2 presents as micron-sized particles in aqueous solutions [8]. Removing such fine particles from water is a rather difficult task and generally requires high-speed centrifuging or microfiltration. Microfiltration offers many advantages over

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its counterpart, which include efficient sample processing, reliable particle removal, low costs and minimal energy consumption. The use of microfiltration membrane filters has been documented in a number of studies on estrogen sampling and removal, where membrane filters with different pore sizes (0.2–1.0 μm) and membrane materials are used, such as glass fibres [9,10], cellulose [11,12] and PTFE [13,14].

A fundamental issue still exists, which is the potential adsorption of estrogens in filter membranes during filtration. Any loss of estrogen analytes will affect the results from subsequent chromatography analysis, resulting in overestimated efficacy of the concerned photocatalytic degradation process. This issue, however, has not been adequately investigated and there is a lack of experimental data and evidences in literature. In this paper, we report our findings on the adsorption of estrone in microfiltration membrane filters. Estrone has been selected as the model analyte for its high estrogenic potency and persistence in the environment [15]. It is also the metabolite and breakdown product of 17β-estradiol, and has been found as more commonly present in the environment [5]. The extent of estrone adsorption was comparatively assessed in relation to the physicochemical properties of membranes and the interactions between membranes and estrone molecules. Fourier transform infrared spectroscopy (FT-IR) was used to examine the potential hydrogen bonding between estrone and NYL membranes. Adsorption mechanisms were proposed and effective mitigation methods were developed to minimise estrone adsorption in NYL, PP and PTFE membrane filters. The performance of GMF and PTFE filters was verified in a slurry-type photocatalytic degradation system using P25® TiO_2 photocatalysts.

2. Experimental

2.1. Preparation of estrone stock solution

Estrone solids (>99%, Sigma) were added in deionised water (18 MΩ, Milli-Q) and the mixture was continuously stirred (250 rpm) in dark at controlled temperature (15 ± 1.5 °C), in an attempt to prepare a 1.2 mg/l estrone solution. Samples were intermittently collected from the solution over a period of 14 days. All samples were centrifuged at 14,000 rpm for 20 min on a bench-top centrifuge (5417C, Eppendorf), and subsequently analysed by a High Performance Liquid Chromatography (HPLC, 1100 series, Agilent) equipped with a UV detector at 205 nm. In each analysis, a 50 μl injection was analysed by a C18 column (5 μm, 4.6 mm × 150 mm, Agilent). Methanol (>99.9%, Romil) and deionised water were mixed (60:40, vol:vol) and used as the mobile phase at a flow rate of 1.0 ml/min. As the prepared estrone solution was found to be over-saturated, a more diluted estrone solution (0.4 mg/l) was prepared under the same conditions. The solution was kept in dark under controlled temperatures (15 ± 1.5 °C) and used as the stock solution.

2.2. Estrone adsorption tests

All filters used in this study were donated by Whatman and Phenomenex (NZ). Filters were selected by their rated capacity, membrane pore size and chemical compatibility of membrane material. The characteristics of the selected filters are shown in Table 1. Each filter consists of a circular polypropylene housing and a microfiltration membrane inside as the filtration media. Most of the selected filers have a diameter of 13 or 15 mm with a rated capacity of 10 ml, except the GMF filters which were only available as 25 mm diameter ones. The 10 ml capacity was considered both sufficient and appropriate for typical sampling requirements in photocatalytic degradation studies. When available, filters with the same membrane material but different pore sizes were all included in our study. All selected filters have excellent resistance to organic substances, except that CA filters were specifically included for CA's good resistance to ethanol, dilute acid, alkali and phenolic solvents [16] and their reported uses in previous studies.

A new membrane filter was used in each adsorption test as recommended by the manufacturers. In the screen test, 1 ml of estrone stock solution was fed into each filter using a disposable syringe (Terumo). Permeates were collected in 2 ml amber glass vials (Agilent) and subsequently analysed by HPLC to measure the estrone concentrations. The rated hold-up volume was negligible (25 μl) for 13 and 15 mm diameter filters. For the 25 mm diameter GMF filter, 5 ml feed was used due to its relatively significant hold-up volume (1 ml). Adsorption equilibrium was further studied in the 0.45-μm NYL, PTFE, RC, CA, GMF filters and the 0.2-μm PP filter using a series of 1 ml feed solutions. In each test, a total of 10 ml estrone solution was fed into the filter, where 10 permeate samples, each of a volume of 1 ml, were collected and analysed by HPLC separately.

2.3. FT-IR analysis and mitigation methods

A NYL membrane was extracted from a fresh 0.45-μm NYL filter and cut into two pieces for further studies. Each piece was immersed in deionised water or estrone solution (0.4 mg/l) for 16 h, and subsequently characterised by Fourier transform infrared spectroscopy (FT-IR, Spectrum 100, Perkin-Elmer). The influence of pH increase on estrone adsorption was studied in 0.45-μm NYL filters. In each test, the pH of the feed solution was adjusted to 11.0 prior to filtration, by adding calculated amounts of concentrated NaOH solution (analytical, Scharlau Chemie) into 5 ml of estrone stock solution, and subsequently topping the volume to 10 ml with deionised water. The initial estrone concentration in the resultant solution was determined by HPLC prior to each adsorption test. A reference solution was also prepared by adding NaCl solids (analytical, Scharlau Chemie) into 5 ml estrone stock solution, and subsequently topping the volume to 10 ml with deionised water. In each test, a total of 10 ml estrone solution was fed into the filter, where 10 permeate samples, each of a volume of 1 ml, were separately collected and analysed by HPLC.

Table 1
Characteristics of selected membrane filters and screen test results using 0.4 mg/l estrone aqueous solution as feed solution.

Brand and model	Membrane material	Wettability	Diameter (mm)	Filtration area (cm^2)	Pore size (μm)	Estrone adsoprtion
Whatman puradisc	Nylon (NYL)	Hydrophilic	13	1.3	0.1	100.0%
Whatman puradisc	Nylon (NYL)	Hydrophilic	13	1.3	0.2	96.4%
Whatman puradisc	Nylon (NYL)	Hydrophilic	13	1.3	0.45	96.9%
Whatman puradisc	Polypropylene (PP)	Hydrophobic	13	1.3	0.2	96.3%
Whatman puradisc	Polytetrafluoroethylene (PTFE)	Hydrophobic	13	1.3	0.1	80.0%
Whatman puradisc	Polytetrafluoroethylene (PTFE)	Hydrophobic	13	1.3	0.45	41.7%
Whatman puradisc	Cellulose acetate (CA)	Hydrophilic	13	1.3	0.45	18.6%
Phenomenex phenex	Regenerated cellulose (RC)	Hydrophilic	15	1.8 (estimated)	0.45	8.1%
Whatman GD/X	Glass microfibres (GMF)	Hydrophilic	25	4.6	0.45	2.3%

The effect of organic solvent on estrone adsorption was studied in PTFE and PP filters. In each test, 5 ml of estrone stock solution was pre-dosed with anhydrous ethanol (analytical, ECP, New Zealand) at a mixing ratio of 1:1 (vol:vol). The solution was then transferred into a glass vial and mounted on a shaker (Innova 4000, New Brunswick Scientific). The glass vial was shaken at 150 rpm for 10 min to enhance mixing in the solution. The resultant solution was used as the feed solution in subsequent adsorption tests, where a series of 1 ml feed were fed into each filter and the permeate samples were separately collected and analysed by HPLC. The initial estrone concentration in the ethanol-dosed solution was determined by HPLC before the start of each adsorption test.

2.4. Photocatalytic degradation

The degradation of estrone was conducted in a slurry-type photocatalytic degradation system. Membrane filters were selected from above adsorption tests and used to process treated estrone solutions to verify their performance. Titanium dioxide particles (10 mg, Degussa P25®) were dispersed in 1000 ml estrone solution (0.4 mg/l) by stirring at 250 rpm. The slurry was continuously stirred in dark for 30 min for adsorption, before exposed to UV radiation for 40 min under an 18w UV lamp (365 nm, Osram). The distance from the lamp to the slurry surface was set as 14 cm. A solution sample (12 ml) was collected at each pre-determined time interval. Each sample was divided into three parts to undertake different pre-treatment prior to HPLC analysis, i.e. 2 ml was centrifuged at 14,000 rpm for 20 min, 5 ml was processed by a 0.45-μm GMF filter, and 5 ml was dosed with 5 ml anhydrous ethanol then processed by a 0.45-μm PTFE filter.

3. Results and discussion

3.1. Estrone solubility and stability

The solubility and stability of estrone in water was briefly investigated before the stock solution was prepared. A concentrated estrone aqueous solution was preferred to use in the adsorption tests as higher concentrations improve the accuracy of HPLC analysis and peak integrations. Meanwhile, it is also important not to have an oversaturated solution as undissolved estrone solids may enter the HPLC system and dissolve in the mobile phase which would distort the results. The fact that estrone solubility data in the literature is highly variable [17–19] necessitated an estrone solubility test under the specific conditions in our study. Our first attempt was to prepare a 1.2 mg/l estrone aqueous solution based on the results from a recent study on estrogen aqueous solubilities [17]. However, this solution was found to be oversaturated under these conditions, i.e. continuous stirring (250 rpm) in dark under controlled temperatures ($15 \pm 1.5\,^{\circ}C$). Furthermore, intermittent sampling results showed that estrone dissolved in the solution at a very slow rate, taking approximately 12 days before the estrone concentration reached a plateau at 0.61 mg/l. It was noted that this value was lower than most estrone solubility data published in literature. Based on this result, a 0.4 mg/l estrone solution was prepared and used as the estrone stock solution.

A prudent advice from a chemical supplier suggests that any storage of estrone aqueous solution for more than one day should not be recommended [20]. Therefore, the stability of estrone in the stock solution was examined by intermittent sampling and analysing through the entire period of study. The last solution sample was taken from the stock solution at the completion of this study, which was 35 days after the preparation of the stock solution. No other peaks could be seen in the HPLC spectrum of this sample. Peak integration results also verified that the estrone concentration still remained consistent after 35 days of storage. The results confirmed that estrone showed satisfactory stability and consistent solubility under the controlled conditions during the entire period of study.

3.2. Estrone adsorption in microfiltration membrane filters

3.2.1. Screen test

A screen test was conducted to identify the adsorption of estrone in all selected microfiltration membrane filters. The results are presented in Table 1. Several interesting facts are noted. Firstly, all filters showed considerable estrone adsorption, with the 0.45-μm GMF filter being the only exception which showed minimal adsorption (2.3%). Secondly, the extent of estrone adsorption in PTFE filters was sensitive to membrane pore sizes. The amount of estrone adsorption in the 0.1-μm PTFE filter was twice as much as that in the 0.45-μm one. Finally, and perhaps most remarkably, all NYL filters showed very high estrone adsorption (96.4–100%) which was largely unaffected by membrane pore sizes.

The considerable estrone adsorption observed in most filters was rather unexpected. Microfiltration processes are primarily based on the principle of size exclusion, and the extent of solids removal is largely dependent on membrane pore sizes. Substances larger than the nominal membrane pore size are generally fully removed, while smaller substances may be partially removed subject to the build-up of a 'refuse layer' on membranes. In this study, the size of estrone molecule is approximately 0.8 nm [21], far smaller than the membrane pore sizes (0.1–0.45 μm). There was no 'refuse layer' building on membranes as the estrone feed solutions did not contain any particulate matters. If size exclusion was mainly accounted for estrone adsorption in these filters, the only rational explanation is that estrone molecules existed as either undissolved solids or large hydro-complexes in the solution which might have steric hindrances comparable to membrane pore sizes. This assumption is not supported by the results in Table 1, which shows significantly different estrone adsorption results in filters with identical membrane pore sizes. This leads us to consider other possible mechanisms: (1) physical adsorption inside the membranes due to their highly porous structures; (2) charge interactions between estrone molecules and membranes; (3) estrone molecules bonding onto membranes by reacting with certain functional groups on membrane surfaces.

The second fact is related to PTFE membrane filters. PTFE is highly resistant to chemicals, and it was unlikely that estrone could react with PTFE membranes. Therefore, the higher estrone adsorption in the 0.1-μm PTFE filter was likely to be the result of enhanced physical adsorption and/or enhanced electrostatic interaction, as discussed above. By having a smaller pore size, the membrane surface area is likely to increase, which in turn provides more surface sites for estrone adsorption. Meanwhile, charge interaction might have also been enhanced. Porter and Porter [22] reported the adsorption of small cations on microfilters and ascribed the phenomenon to long-range electrostatic forces. The deprotonation of estrone molecules is governed by the disassociation of the phenolic hydroxyl group on the benzene ring. The acid dissociation constant (pK_a) of estrone is approximately 10.3 [17], indicating that estrone has slightly weaker acidity than phenol ($pK_a = 10$) [23]. The combined result of low aqueous solubility and high pK_a value is that most estrone molecules remained un-dissociated hence neutrally charged in the solution, while only a limited number of estrone molecules deprotonated and existed as negatively charged anions. As a result, the influence of charge interaction was minimal and unlikely to be the primary cause of the significant estrone adsorption.

The high estrone adsorption observed in NYL membrane filters is particularly interesting. Unlike PTFE filters, the estrone adsorp-

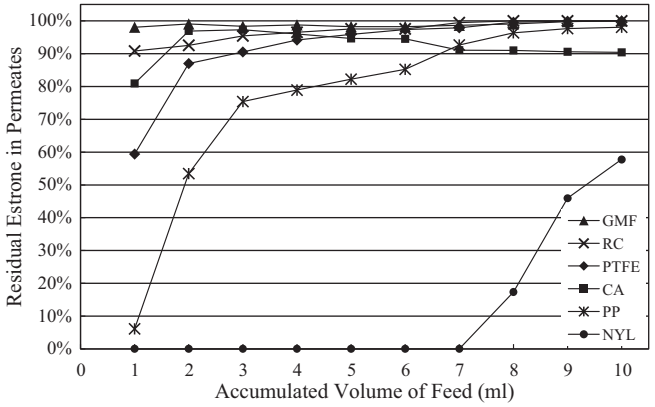

Fig. 1. Estrone adsorption in 0.45-μm GMF, RC, PTFE, CA, NYL filters and 0.2-μm PP filter using 0.4 mg/l estrone aqueous solution as feed solution.

tion in NYL filters showed little dependence on membrane pore sizes. This indicates that the aforementioned enhancement of physical adsorption in smaller-pore membranes was almost completely masked by a much stronger interaction between estrone and NYL membranes. As discussed above, the effect of charge interaction was expected to be minimal due to the limited deprotonation of estrone molecules. Furthermore, NYL membranes are negatively charged under neutral/alkaline conditions [15], which would impose repulsive forces on negatively charged anions. The only rational explanation left is that some strong bonding was formed between estrone molecules and NYL membranes during the filtration process. This will be further discussed in the following sections.

3.2.2. Adsorption equilibrium study

The adsorption equilibrium of estrone was studied in selected filters and a characteristic V_{eq} value was determined for each filter. The concept of V_{eq} is introduced as an approximate yet convenient method to mitigate the effect of estrone adsorption in filters. For each filter, V_{eq} equals to the minimum amount of feed solution required to achieve estrone adsorption equilibrium inside the filter. If V_{eq} is relatively small, it may still be practical to use this filter to process estrone solution by sacrificing the initial output of permeates. Using this method, one would be able to easily establish the amount of sample required and when a valid permeate can be collected with no considerable loss of estrone solute inside the filter. Fig. 1 shows the comparative results of estrone adsorption in filters, where concentrations of residual estrone in permeates were normalised against the initial estrone concentration in the feed solution (expressed as percentages), and plotted versus the accumulated volume of estrone feed solution. Breakthrough points can be seen in PP, PTFE and RC filters as a series of feed solutions passed through. Gradual decrease of estrone adsorption was observed on continued filtration in these filters, which suggests that physical adsorption should be the primary cause of estrone adsorption. As more feed solution passed through, adsorption sites on membrane surfaces were gradually occupied by estrone molecules, and adsorption equilibrium was eventually reached due to site saturation. No further net adsorption occurred after this point. V_{eq} values were derived from Fig. 1 as 8 ml, 7 ml and 6 ml for PP, PTFE and RC filters, respectively.

While this is a useful method, we do not recommend any direct uses of the V_{eq} values obtained in this study due to the inevitable measurement errors and the fact that they were derived from tests on particular filters under specific conditions. It should also be noted that these values are high comparing to the rated filter capacity (10 ml) [24,25], which in some cases may not be feasible to be extracted from a photocatalytic degradation system without interfering the process. In such cases, GMF filter may be the only viable option if microfiltration membrane filters are to be used for sample pre-filtration. The 0.45-μm GMF filter, which has a coarse glass fibre layer and a glass microfibre (GMF) layer made from borosilicate glass [24], showed less than 2% estrone adsorption during the adsorption equilibrium test (Fig. 1).

The results in Fig. 1 indicated that any direct use of NYL membrane filters for estrone aqueous solutions is clearly improper. Complete adsorption of estrone was observed in the 0.45-μm NYL filter for the initial 7 ml of feed. Although estrone adsorption started decreasing as the filtration progressed further, it remained prohibitively high (42.2%) at the end of the filtration course when the filter capacity (10 ml) was reached. This provides further support for our assumption that the high estrone adsorption in NYL filters was caused by chemical bonding between estrone molecules and NYL membranes.

3.2.3. Hydrogen bonding between estrone and NYL membrane

The molecular structures of estrone and the material of NYL membranes (Nylon 6,6) are shown in Fig. 2(a) and (b), respectively. Each estrone molecule contains a phenolic hydroxyl group which was considered as an ideal proton donor for hydrogen bonding [23]. Nghiem et al. [21] also proposed that estrone may act as either a proton donor or acceptor as both the hydroxyl group and carbonyl group may participate in hydrogen bonding. Although generally weaker than shared covalent bonds, hydrogen bonding is substantially stronger than van der Waals forces in physical adsorption [26]. In our case, the formation of hydrogen bonding between estrone and NYL membranes would provide a boost to estrone adsorption.

Possible mechanisms of hydrogen bonding between estrone and the membrane material (Nylon 6,6) are illustrated in Fig. 2(c) and (d). Briefly mentioned in previous studies [1,21,23], the hydrogen bonding between estrone and NYL has not been experimentally verified in literature. In this study, FT-IR was used to investigate the possible interactions between estrone and NYL membranes that occurred during the filtration process. Fig. 3(a) and (b) shows the FT-IR spectra of NYL membranes after 16 h of continuous immersion in estrone stock solution (0.4 mg/l) and deionised water, respectively. Peaks of water have been removed in each spectrum by producing a difference spectrum based on the FT-IR spectrum of water. The subtle differences in Fig. 3(a) and (b) necessitated the production of a difference spectrum (Fig. 3(c)). The attainment of Fig. 3(c) was a delicate task which itself warrants some explanation

Table 2
Peaks and assignments of NYL membrane (Nylon 6,6) associated with intermolecular hydrogen bonding and changes of peak strength after 16 h of immersion in 0.4 mg/l estrone aqueous solution.

Peak (cm^{-1})	Peak assignment	Peak weakening (cm^{-1})	Peak strengthening (cm^{-1})	Shift (cm^{-1})
3300	Hydrogen-bonded N–H stretch	3295	3312	17
1745[a]	Free C=O stretching	n.a.	n.a.	n.a.
1630	Amide I band, contributed by hydrogen bonded C=O stretching (major), C–N stretching and C–C–N deformation vibrations	1620	1635	15
1535	Amide II band, contributed by N–H in-plane bending (major), C–H stretching and C–C stretching vibrations	1536	1520	16

[a] Very weak.

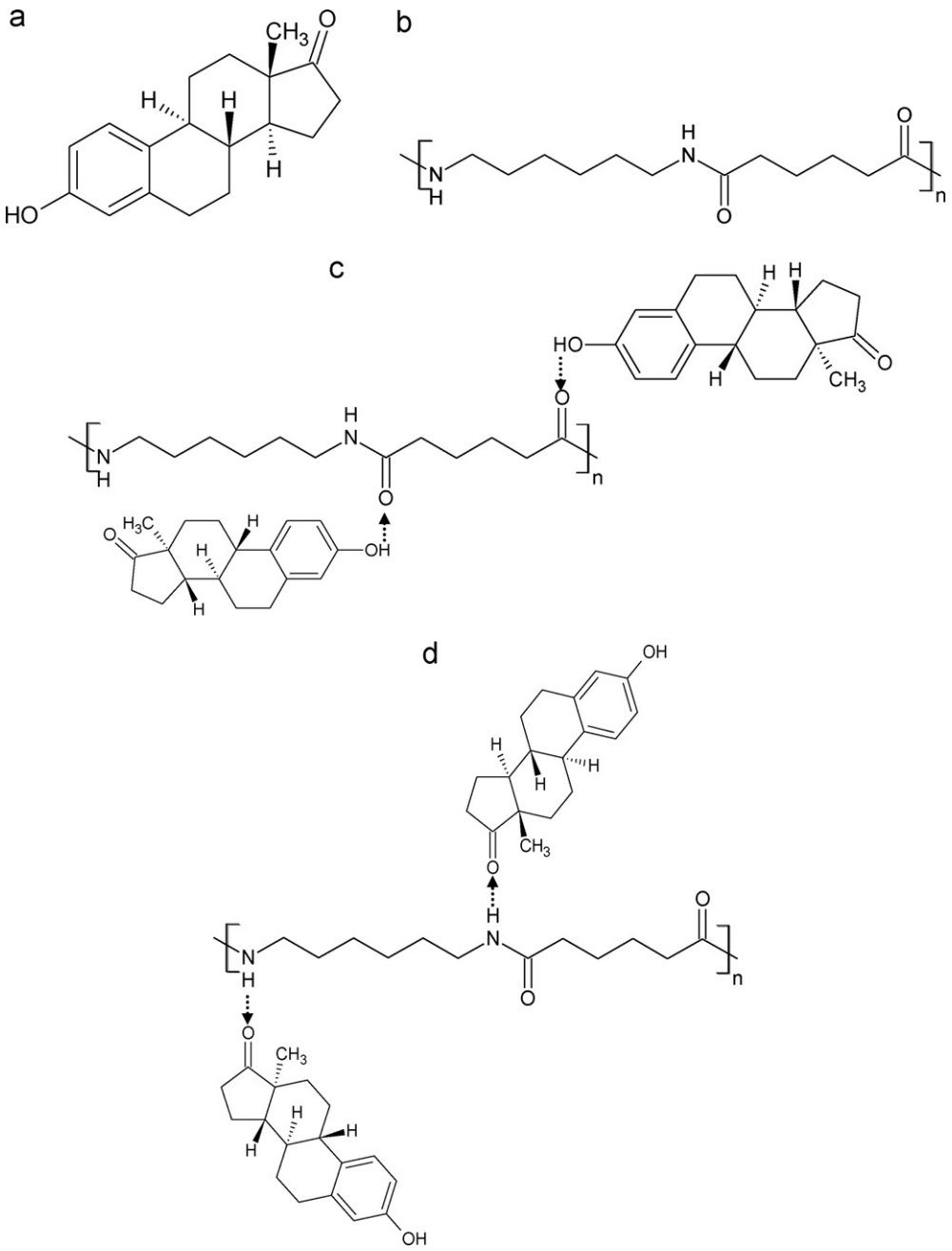

Fig. 2. Molecular structures of (a) estrone and (b) NYL membrane (Nylon 6,6), and (c and d) hydrogen bonding between estrone and NYL membrane.

here. The first step was to manually plot the source data of Fig. 3(a) and (b), then align their base lines and normalise the peaks in the two spectra, giving the difference spectrum. A 15 times magnification was then applied to the vertical axis to enlarge the peaks. The obtained spectrum is shown in Fig. 3(c).

Table 2 shows the characteristic peaks associated with intermolecular hydrogen bonding in NYL and their assignments [27,28]. As shown in Fig. 3(c), subtle yet evident changes of peak strength can be seen at the characteristic peaks of the NYL membrane after estrone adsorption. Details of these shifts are also shown in Table 2. The strengthening of the N–H stretching peak at 3312 cm^{-1} and simultaneous weakening at 3295 cm^{-1} suggest that a small portion of hydrogen-bonded N–H groups transformed into higher energy states after estrone adsorption. These N–H groups were still hydrogen bonded, as indicated by their frequency (3312 cm^{-1}) that is still substantially lower than the frequency of free N–H groups (3400 cm^{-1}). Therefore, this positive shift (17 cm^{-1}) is likely to be the result of the breakage of intermolecular hydrogen bonding in NYL and simultaneous formation of new hydrogen bonding with C=O groups on estrone molecules. The newly formed hydrogen bonds are of higher energy states due to the greater mobility of estrone molecules and hence the less restricted stretching of N–H groups. This is reinforced by the observation at the Amide II band where the peak corresponding to N–H in-plane bending strengthened at lower frequencies [28,29]. A similar result is observed at the Amide I band (hydrogen bonded C=O), which shifted to a higher frequency due to the increased double bond character of the C=O moiety after forming hydrogen bonding with the OH group on estrone molecules [27,28]. These results support the view from a previous study [3,21] that estrone could form hydrogen bonding with polyamide membrane by acting as both a donor and acceptor of proton.

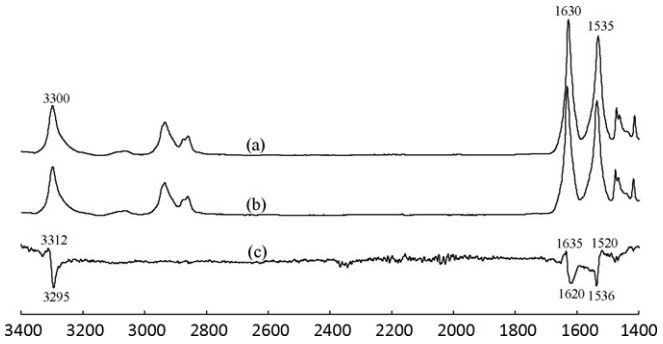

Fig. 3. FT-IR spectra of NYL membranes (a) immersed in deionised water (16 h), (b) immersed in estrone aqueous solution (0.4 mg/l, 16 h), and (c) difference spectrum.

3.3. Mitigation methods

3.3.1. Effect of pH

Highly alkaline environment may adversely interfere the hydrogen bonding between estrone and NYL by facilitating the deprotonation of estrone molecules. Deprotonated estrone molecules lose the protons on phenolic hydroxyl groups hence become unable to participate in hydrogen bonding with carbonyl groups on NYL. Schäfer et al. [15] presented a graph of the speciation of estrone as a function of pH. At pH 11, estrone predominantly (~75%) exists as negative anions in aqueous solution, with the balance remaining undissociated.

The results of estrone adsorption at pH 11 in the 0.45-μm NYL filter was shown in Fig. 4(a). Higher pH levels were desirable but not used because NYL membranes would become unstable. The effect of ionic strength was excluded by using a neutral estrone solution with identical ionic strength as the reference. As shown in Fig. 4(a), the high pH in estrone feed solutions caused a significant decrease of estrone adsorption in the NYL filter. Estrone adsorption dropped to negligible levels (<1.5%) after 5 ml feed passed through. The significant decrease of estrone adsorption under the high pH level proves that deprotonation of estrone molecules could negatively affect their ability to form hydrogen bonding with NYL membranes, which also provides further support to the hydrogen bonding mechanism. While estrone molecules may still act as a proton acceptor and form hydrogen bonding with N–H groups on NYL membranes (Fig. 2(d)), this effect is likely to be restricted by the greater repulsive forces from the more negatively charged NYL membranes at the high pH level.

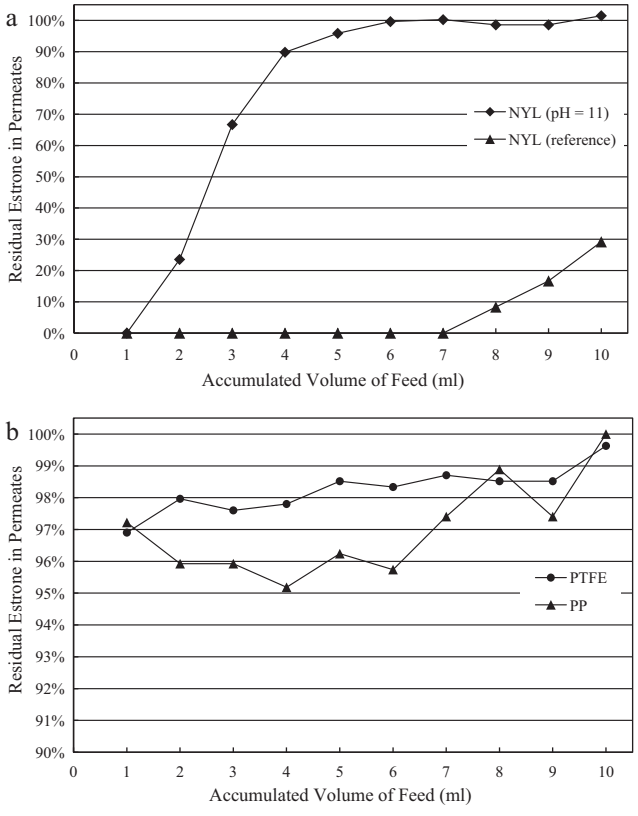

Fig. 4. Estrone adsorption in (a) 0.45-μm NYL filter with pH-adjusted feed solution (pH 11.0; 0.2 mg/l estrone aqueous solution), and (b) PTFE and PP filters with pre-dosed feed solution (anhydrous ethanol:deionised water = 1:1, vol/vol; 0.2 mg/l estrone solution).

3.3.2. Effect of organic solvent

Estrone has a high octanol–water partitioning coefficient ($\log P_{o/w}$) of 3.1 [30], implying its strong tendency to adsorb onto lipophilic materials and dissolve in organic solvents. Cartinella et al. [3] reported that the presence of organic matters could reduce the retention of estrone in membranes as the hydrophobic estrone molecules may interact with organic matters hence become no longer available for adsorption on membranes. It is therefore expected that the presence of organic solvents would facilitate the hydrophobic partitioning of estrone in the solution phase with a simultaneous reduction of adsorption onto filter membranes.

In this study, filters with hydrophobic membranes have shown overall high estrone adsorption (Fig. 1 and Table 1). It should be mentioned that the manufacturers recommend hydrophobic membrane filters to be rendered hydrophilic by first contacting with compatible organic solvents prior to filtering aqueous solutions [24,25]. This approach is useful for qualitative analysis, but it is problematic for our application as the uncertain amount of residual solvents in membranes may introduce random dilution to permeates. Many estrone degradation studies rely on accurate analysis of residual estrone levels in treated water to evaluate photocatalyst activity and degradation efficiency, optimise reactor design and reaction conditions. Therefore, a refined approach was adopted in this study by pre-dosing controlled amounts of compatible organic solvent (anhydrous ethanol) in estrone feed solutions. A calibration factor was determined to account for the volumetric change of the feed solution after mixing with solvent. Fig. 4(b) shows that this method is highly effective for the 0.45-μm PTFE filter, where estrone adsorption was maintained at minimal levels (<3.1%) through the filtration process. The decrease was also significant but to a lesser extent in PP filter, where estrone adsorption was below 4.8% through the filtration process.

3.4. Photocatalytic degradation

A slurry-type photocatalytic degradation experiment was conducted as an example of estrone degradation studies which involve particle removal from treated solutions prior to chromatography analysis. The 0.45-μm GMF and PTFE filters were selected to process treated estrone solutions sampled from the system. The 0.45-μm PTFE filter was specifically selected for its low costs and excellent chemical resistance which makes it suitable in a wide range of applications. When PTFE filters were used, estrone solution samples were pre-dosed with anhydrous ethanol (1:1; vol:vol) to eliminate the effect of estrone adsorption. High-speed centrifuging (14,000 rpm, 20 min) was used to provide a benchmark to evaluate the performance of GMF and PTFE filters.

Fig. 5 shows that both GMF and PTFE filters showed satisfactory performance in terms of estrone solute recovery, as compared to the results from samples processed by high-speed centrifuging. Variations in the results were generally less than 2.2% for GMF fil-

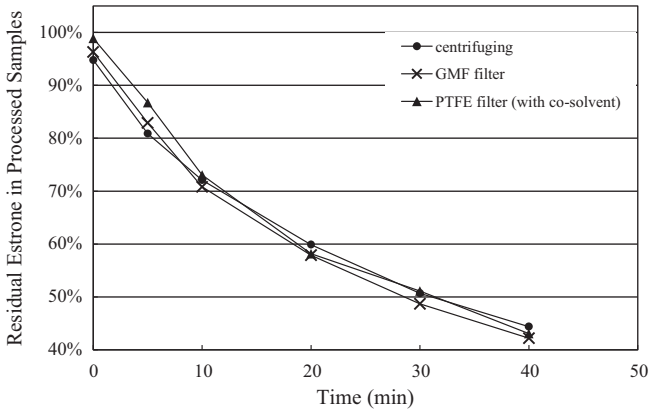

Fig. 5. Estrone concentrations in the solution after photocatalytic degradation (10 mg/l TiO_2; initial estrone concentration: 0.4 mg/l; 30 min pre-adsorption in dark), with samples separately processed by microfiltration or centrifuging.

ters and 1.7% for PTFE filters, except in the first two samples where samples processed by PTFE filters showed slightly higher estrone concentrations than those processed by GMF filters or centrifuging. This may be attributed to the desorption of estrone absorbed on photocatalyst particles due to the presence of organic solvent (ethanol) in the solution. By releasing the adsorbed estrone on photocatalyst particles into the solution, the results obtained with PTFE filters can actually exclude this surface adsorption effect and provide more accurate information on the photocatalytic degradation process.

While this study is aimed for photocatalytic degradation studies, the concept and methodology described is also applicable in other studies where membrane filters are used to perform microfiltration fro estrone solutions prior to quantitative analysis. Behaviours of other estrogens in membrane filters can also be investigated using similar approaches. Despite this potential issue, microfiltration by membrane filters remains a superior alternative to high-speed centrifuging for its efficient processing, reliable performance, low costs and minimal energy consumption.

4. Conclusions

Adsorption of estrone was found in microfiltration membrane filters during the filtration of estrone aqueous solutions (0.4 mg/l). The extent of estrone adsorption was highly dependent on the membrane material and to a lesser extent, the membrane pore size. Considerable adsorption of estrone was observed in NYL, PP, PTFE and CA membrane filters. Comparative testing results showed that estrone suffered the most severe adsorption in NYL membranes, in which estrone had near 100% adsorption in the initial 7 ml permeate and reduced to 42.2% when the filter capacity (10 ml) was reached. The only filter that showed consistently low estrone adsorption (<2.3%) was the 0.45-μm GMF filter.

FT-IR results showed that the significant estrone adsorption in NYL membranes was caused by the formation of hydrogen bonding between estrone molecules and the characteristic amide groups in NYL. This is also supported by the fact that estrone adsorption in NYL filters was substantially reduced by increasing the pH to 11.0 to facilitate the deprotonation of estrone molecules. It was also found that estrone adsorption in PTFE and PP filters could be reduced to minimal or negligible levels by pre-dosing estrone solutions with anhydrous ethanol (1:1, vol:vol).

The performance of GMF and PTFE filters was verified in a slurry-type photocatalytic degradation system using the benchmark P25® TiO_2 photocatalyst. Residual estrone levels in permeates from both filters were found to be highly consistent to the results of samples processed by high-speed centrifuging (14,000 rpm, 20 min). Despite the satisfactory performance of GMF and PTFE filters, it is suggested that caution should be taken when using membranes to process estrone solutions, and verifications on solute recovery should be conducted in advance for individual studies.

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References

[1] L.D. Nghiem, A.I. Schäfer, Adsorption and transport of trace contaminant estrone in NF/RO membranes, Environ. Eng. Sci. 19 (2002) 441–451.
[2] G.M. Solomon, T. Schettler, Environment and health: 6. Endocrine disruption and potential human health implications, Can. Med. Assoc. J. 163 (2000) 1471–1476.
[3] J.L. Cartinella, T.Y. Cath, M.T. Flynn, G.C. Miller, K.W. Hunter, A.E. Childress, Removal of natural steroid hormones from wastewater using membrane contactor processes, Environ. Sci. Technol. 40 (2006) 7381–7386.
[4] A.C. Johnson, H.R. Aerni, A. Gerritsen, M. Gibert, W. Giger, K. Hylland, M. Jurgens, T. Nakari, A. Pickering, M.J.F. Suter, A. Svenson, F.E. Wettstein, Comparing steroid estrogen, and nonylphenol content across a range of European sewage plants with different treatment and management practices, Water Res. 39 (2005) 47–58.
[5] A.K Sarmah, G.L. Northcott, F. D.L. Leusch, L.A. Tremblay, A survey of endocrine disrupting chemicals (EDCs) in municipal sewage and animal waste effluents in the Waikato region of New Zealand, Sci. Total Environ. 355 (2006) 135–144.
[6] Y. Zhang, J.L. Zhou, B. Ning, Photodegradation of estrone and 17 beta-estradiol in water, Water Res. 41 (2007) 19–26.
[7] J.X. Mai, W.L. Sun, L. Xiong, Y. Liu, J.R. Ni, Titanium dioxide mediated photocatalytic degradation of 17 beta-estradiol in aqueous solution, Chemosphere 73 (2008) 600–606.
[8] W. Qiu, Y. Zheng, A comprehensive assessment of supported titania photocatalysts in a fluidized bed photoreactor: photocatalytic activity and adherence stability, Appl. Catal. B: Environ. 71 (2007) 151–162.
[9] Y.P. Zhang, J.L. Zhou, Occurrence and removal of endocrine disrupting chemicals in wastewater, Chemosphere 73 (2008) 848–853.
[10] T. Hashimoto, T. Murakami, Removal and degradation characteristics of natural and synthetic estrogens by activated sludge in batch experiments, Water Res. 43 (2009) 573–582.
[11] L. Viglino, K. Aboulfadl, M. Prevost, S. Sauve, Analysis of natural and synthetic estrogenic endocrine disruptors in environmental waters using online preconcentration coupled with LC-APPI-MS/MS, Talanta 76 (2008) 1088–1096.
[12] R.L. Gomes, M.D. Scrimshaw, J.N. Lester, Fate of conjugated natural and synthetic steroid estrogens in crude sewage and activated sludge batch studies, Environ. Sci. Technol. 43 (2009) 3612–3618.
[13] K. Yamada, M. Terasaki, M. Makino, A novel estrogenic compound transformed from fenthion under UV-A irradiation, J. Hazard. Mater. 176 (2010) 685–691.
[14] Y. Morishima, Y. Hirata, K. Jinno, C. Fujimoto, Solid-phase extraction device coupled to a microcolumn liquid chromatograph with a UV detector for determining estrogens in water samples, J. Liq. Chromatogr. Relat. Technol. 28 (2005) 3217–3228.
[15] A.I. Schäfer, L.D. Nghiem, T.D. Waite, Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis, Environ. Sci. Technol. 37 (2003) 182–188.
[16] H.P. Chin, Cellulose Acetate Electrophoresis – Techniques and Applications, Ann Arbor-Humphrey Science Publishers, Michigan, 1970.
[17] A. Shareef, M.J. Angove, J.D. Wells, B.B. Johnson, Aqueous solubilities of estrone, 17 beta-estradiol, 17 alpha-ethynylestradiol, and bisphenol A, J. Chem. Eng. Data 51 (2006) 879–881.
[18] A.R. Hurwitz, S.T. Liu, Determination of aqueous solubility and pK_a values of estrogens, J. Pharm. Sci. 66 (1977) 624–627.
[19] P. Kabasaka, E. Britt, M.D. Yudis, Solubility of some steroids in water, J. Pharm. Sci. 55 (1966) 642.
[20] Cayman Chemical Co., Product Information, Estrone (Catalogue No. 10006485), 2005.
[21] L.D. Nghiem, A.I. Schäfer, T.D. Waite, Adsorptive interactions between membranes and trace contaminants, Desalination 147 (2002) 269–274.
[22] J.J. Porter, R.S. Porter, Filtration studies of selected anionic dyes using asymmetric titanium dioxide membranes on porous stainless-steel tubes, J. Membr. Sci. 101 (1995) 67–81.
[23] W. Vermerris, R. Nicholson, Chemical properties of phenolic compounds, in: Phenolic Compound Biochemistry, Springer Science + Business Media B.V., 2008, pp. 38–41.

[24] Whatman Inc., Whatman Syringe Filter Collection, Document No. 51706 (US) S9036-833 (EU), 2007.
[25] Phenomenex Inc., Phenex Syringe Filters: Performance And Protection, 2008.
[26] S.W. Kuo, Hydrogen-bonding in polymer blends, J. Polym. Res. 15 (2008) 459–486.
[27] D.J. Skrovanek, S.E. Howe, P.C. Painter, M.M. Coleman, Hydrogen bonding in polymers: infrared temperature studies of an amorphous polyamide, Macromolecules 18 (1985) 1676–1683.
[28] Y.N. Kwon, J.O. Leckie, Hypochlorite degradation of crosslinked polyamide membranes – II. Changes in hydrogen bonding behavior and performance, J. Membr. Sci. 282 (2006) 456–464.
[29] G. Socrates, Infrared Characteristic Group Frequencies, 2nd ed., John Wiley & Sons, New York, 1994.
[30] P.H. Howard, W.M. Meylan, Handbook of Physical Properties of Organic Chemicals, CRC Press Inc., New York, 1997.