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# Rejection and adsorption behaviour of phytoestrogens by nanofiltration and reverse osmosis membranes

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ABSTRACT

This study investigated the rejection and adsorption behaviour of two phytoestrogens, genistein and formononetin, by a NF270 nanofiltration (NF) membrane and an ESPA2 reverse osmosis (RO) membrane. Filtration experiments were conducted using a cross-flow membrane system at three different feed solution pH values of 4, 7 and 11. Mass balance calculations indicated that adsorption of both phytoestrogens to the membranes occurred under all pH conditions. The rejection efficiency of the phytoestrogens by the ESPA2 membrane was considerably higher than for the NF270 membrane under all conditions. For the NF270 membrane, at pH 4 and 7, the rejection of phytoestrogens decreased dramatically over the first 4 h of operation and was relatively stable during the later stages of filtration, suggesting that size exclusion, adsorption and convection were the main rejection mechanisms for these compounds. By contrast, at pH 11, there was only a slight reduction in the rejection of these compounds with time and that electrostatic repulsion became the overriding rejection mechanism. Conversely, the phytoestrogen rejection by the ESPA2 membrane was relatively stable at all pH conditions, which could be attributed to size exclusion being the dominating rejection mechanism.

*Keywords:* Phytoestrogens; Nanofiltration; Reverse osmosis; Adsorption; Rejection mechanisms

## 1. Introduction

Phytoestrogens are naturally occurring plant compounds that have estrogenic like properties. They can be found in soy and other legumes and a range of vegetables and fruits [1]. The discharge of phytoestrogens from municipal wastewaters, surface waters and food production plants are regarded as the main sources in the natural aqueous environment [2]. The presence of phytoestrogens in the effluent of wastewater treatment plants (WWTPs), receiving waters and some treated drinking waters has received much attention and concern. These phytoestrogens were released from WWTPs at concentrations ranging from 3 to 1,700 ng/L [3]. Lundgren and Novak [4] found that the concentration of phytoes-

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trogens in industrial effluent can be much higher (up to 250 μg/L). Genistein, formononetin, biochanin A, daidzein and coumestrol are the most commonly identified phytoestrogens in the aquatic environment, and they have been found in rivers in Australia, Germany and Italy ranging from 1 to 10 ng/L [2,5]. Daidzein and genistein have been detected in river water in Japan at 43 μg/L and 143 μg/L, respectively [6]. The higher concentration of certain phytoestrogens found in Japanese river water was found to be directly related to widely consumed foods with a high amount of soy and other legumes. In the aquatic environment, phytoestrogens are essentially endocrine disrupting chemicals [7]. Exposure of fish to phytoestrogens has been shown to induce vitellogenesis and feminization and produce changes in gonadal development of males [8]. Therefore, there is a significant need for advanced treatment technologies to prevent phytoestrogens from entering the aquatic environment and particularly prior to potable water recycling.

The rejection of organic solutes by nanofiltration (NF)/reverse osmosis (RO) membranes can be governed by a range of physicochemical processes including size exclusion, adsorption, diffusion and electrostatic interaction. These mechanisms can be influenced by several things, including the properties of the compounds, characteristics of the membrane, operating conditions and the feed water composition [9,10]. Nghiem et al. [11] showed that the initial removal of hydrophobic compounds was governed by adsorption and that subsequently when adsorption had reached equilibrium, size exclusion became the predominant rejection mechanism. Nghiem et al. [11] also observed that the steady state rejection of some hydrophobic compounds was lower than what might be expected based solely on size exclusion considerations. In a later study, Braeken et al. [12] reported a decrease in rejection with increasing hydrophobicity due to the adsorption of the organic compounds onto the NF/RO membranes during filtration.

Despite a large volume of research on the rejection of many trace organic compounds by NF/RO membranes, to date, there have only been a few studies on the rejection of phytoestrogens by NF/RO membranes. Dudziak and Bodzek [13] demonstrated that there was a strong correlation between rejection of phytoestrogens (daidzein, coumestrol, genistein and biochanin A) and their molecular mass. Their findings also showed that an increase in the rejection of most phytoestrogens after membrane fouling or scaling was observed for both NF and RO. In an another study, Dudziak and Bodzek [14] suggested that the rejection of phytoestrogens by loose NF membranes may be mainly governed by their physicochemical properties such as hydrophobicity, molecular weight and Stokes radius. For RO membranes, the rejection efficiency could also be significantly influenced by the dipole moment of the solute. However, in these studies, the concentrations of phytoestrogens in the feed solution were significantly higher than environmentally relevant values. Thus, the adsorption of phytoestrogens and its effects on their rejection were not investigated.

The aim of the present study was to evaluate rejection and adsorption behaviour of phytoestrogens by NF/RO membranes at different pH values. Experiments were conducted using a laboratory-scale cross-flow NF/RO membrane filtration cell with genistein and formononetin as the analytes under investigation. These compounds are representatives of one of the main classes of phytoestrogens, namely isoflavones. On the basis of these results, effects of the solution pH on the adsorption and rejection of these phytoestrogens were delineated, and relevant mechanisms were discussed and elucidated.

## 2. Materials and methods

### 2.1. NF and RO membranes

A loose NF membrane (NF270, Dow-Filmtec, Minneapolis, MN) and an RO membrane (ESPA2, Hydranautics, Oceanside, CA) were used in this study. Their properties differ significantly from each other (Table 1). The permeability of the NF270 membrane is substantially higher than that of the ESPA2 membrane. The average pore diameter of the NF270 membrane is 0.84 nm [11], while the ESPA2 is assumed to be a dense membrane, with no effective pore diameter. This difference in pore size is also reflected in a significant difference in their salt rejections. Both membranes are relatively hydrophilic as exhibited by their low contact angles and at pH 4 and above, and these membranes are negatively charged [15,16].

### 2.2. Phytoestrogens and analytical chemicals

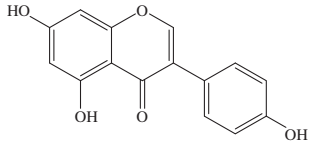
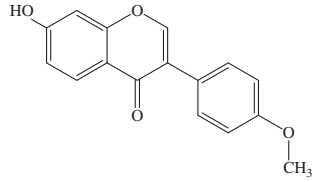
Analytical grade genistein and formononetin were purchased from Sigma-Aldrich (Sydney, Australia) and used as model phytoestrogens. Stock solutions (100 μg/mL) of each compound were prepared in pure methanol and stored at −18°C in the dark. They have similar molecular weights and molecular dimensions (Table 2). Their molecular weights are considerably larger than the MWCO of the ESPA2 membrane but are comparable with that of the NF270 membrane.

Table 1
Properties of the NF270 and ESPA2 membranes used for the experiment

| Membrane | Average pore diameter (nm)[a] | Contact angle (°)[b] | NaCl rejection (%)[c] | MWCO (g/mol)[c] | Permeability (L/bar m$^2$ h)[d] | Operation pH range[d] |
|---|---|---|---|---|---|---|
| NF270 | 0.84 | 51.4 | 45.0 | 200 | 10.85 | 2–11 |
| ESPA2 | Not available | 69.0 | 96.5 | ~100 | 3.68 | 1–12 |

[a]Nghiem et al. [11].
[b]Norberg et al. [17].
[c]Alturki et al. [18].
[d]Based on the technical data sheets of the manufacturers.

Table 2
Physicochemical properties of genistein and formononetin

| Compound | | Genistein | Formononetin |
|---|---|---|---|
| Molecular formula | | $C_{15}H_{10}O_5$ | $C_{16}H_{12}O_4$ |
| Molecular structure | |  |  |
| Molecular weight (MW) (g/mol) | | 270.24 | 268.26 |
| Log $K_{ow}$[a] | | 3.114 | 2.860 |
| p$K_a$[a] | | 6.51 | 6.99 |
| log $D$[b] | pH 4 | 3.11 | 2.86 |
| | pH 7 | 2.34 | 2.55 |
| | pH 11 | −1.38 | −1.15 |
| Molecular dimension (nm)[c] | Length | 1.033 | 1.015 |
| | Height | 0.706 | 0.760 |
| | Width | 0.354 | 0.412 |

[a]Scifinder scholar.
[b]Calculated by the equation: $\log D_{(pH)} = \log K_{ow} - \log(1 + 10^{(pH-pK_a)})$.
[c]Calculated using Molecular Modeling Pro$^{TM}$ Plus software.

Their p$K_a$ values fall within the pH range of environmental water. It should be noted that at pHs above the p$K_a$, both genistein and formononetin will increasingly dissociate into an ionic form. Therefore, at pH 4, both compounds are uncharged and exist in a neutral form. When the experiments were performed at pH 7 and 11, they were negatively charged. In addition, it is noteworthy that with increasing solution pH, the hydrophilicity of the compounds increases (as indicated by decreasing log $D$ values).

Analytical grade NaCl, $Na_2CO_3$, $NaHCO_3$, $CaCl_2$, $NaH_2PO_4$, NaOH, HCl, $CH_3COOH$ and $CH_3COONa$ were obtained from Sigma-Aldrich (Castle Hill, Australia) and were used as background electrolytes, buffer solutions and for pH adjustment. HPLC-grade acetonitrile (ACN) and methanol were from Crown Scientific (Sydney, Australia). Formic acid (FA) was purchased from Sigma-Aldrich (Sydney, Australia). Milli-Q water (Millipore, Billerica, MA, USA) was used for the preparation of the feed solution.

### 2.3. Cross-flow NF/RO membrane filtration system

A laboratory-scale cross-flow NF/RO system (Fig. 1) was used. This consisted of a rectangular stainless steel membrane cell with an effective surface area of 40 cm$^2$ (4 cm × 10 cm) and a channel height of 2 mm. It was fed by a stainless steel reservoir of 10 L and a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN) capable of providing a maximum pressure of 6,800 kPa. The temperature of the feed solution was controlled by a chiller/heater (Neslab

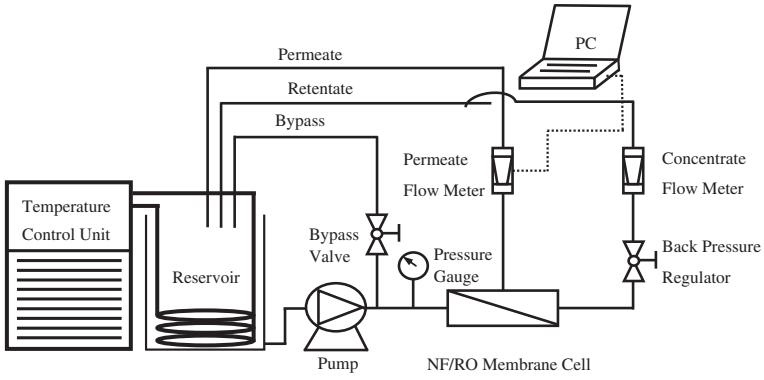



Fig. 1. Schematic diagram of the cross flow NF/RO filtration system.

RTE 7, Thermo Scientific Inc., Waltham, MA, USA) equipped with a stainless steel heat exchanger coil which was submerged directly into the feed reservoir. A digital flow meter (Optiflow 1000, Agilent Technologies, Palo Alto, CA) connected to a PC was utilized to measure permeate flow, and the cross flow was monitored using a rotameter.

### 2.4. Experimental protocol

Prior to each experiment, the membrane samples were gently washed with copious amounts of Milli-Q water to remove any preservatives. They were then compacted using Milli-Q water at 1,000 or 1,800 kPa for the NF270 and the ESPA2 membrane, respectively, for at least 1 h until a stable permeate flux had been obtained. A new membrane sample was used for each experiment. The background electrolytes and buffers were then introduced to the feed reservoir to obtain the desired ionic composition. For experiments at pH 4, the feed solution contained 1 mM of $CaCl_2$, 9 mM of $CH_3COOH$ and 2 mM of $CH_3COONa$. For experiments at pH 7, the feed solution contained 10 mM of NaCl, 1 mM of $CaCl_2$ and 1 mM of $NaH_2PO_4$. For experiments at pH 11, the feed contained 0.2 mM of NaCl, 0.3 mM of $NaHCO_3$ and 4.5 mM of $Na_2CO_3$. These feed solutions were employed as representative model electrolytes simulating environmental waters to maintain a constant pH and did not form any precipitates for the duration of the experiment. Moreover, all these feed solutions had the same ionic strength in order to avoid any influence of ionic strength on the rejection and adsorption of the target compounds. Genistein and formononetin were introduced to the feed reservoir to obtain a concentration of 50 μg/L of each phytoestrogen. During the experiment, the cross-flow velocity, feed reservoir temperature and permeate flux were kept constant at 31 cm/s for the NF270 and 42 cm/s in the case of the ESPA2, 20 ± 0.1°C and 42 $L/m^2$ h, respectively. The permeate and retentate flows were recirculated to the feed reservoir and a small volume of 1 M of NaOH or 1 M of HCl was added to the feed solution every hour to maintain the pH at the desired set point. Approximately, 1 mL of feed and permeate samples were taken at specified time intervals for analysis by liquid chromatography–mass spectrometry (LCMS).

The rejection ($R$) was defined as:

$$R = 100 \times \left(1 - \frac{C_p}{C_f}\right) \quad (1)$$

where $C_f$ and $C_p$ were the feed and the permeate concentrations, respectively.

The adsorption ($A$) of phytoestrogens to the membrane was determined by a mass balance,

$$A = 100 \times \left(\frac{1}{n} \times \sum_{i-1}^{n} \frac{C_0 - C_i}{C_0}\right) \quad (2)$$

where $C_0$ is the initial phytoestrogens concentration of the feed solution, $C_i$ is the phytoestrogens concentration of the sample $i$ collected from the feed reservoir, and $n$ is the number of samples collected.

### 2.5. Analytical methods

The concentration of genistein and formononetin in the feed and permeate samples were determined using a Shimadzu LCMS-2020 system (Japan) and a direct injection method. This system comprised of an autosampler (SIL-20A HT), pump (LC-20AD × 2 units), column oven (CTO-20A) equipped with a C18 column (Kinetex 2.6 μm XB-C18 100 A (100 × 3.0 mm)), detector (SPD-M20A), MS detector (LCMS-2020), and a computer with LabSolutions chromatographic software. The detection wavelength was 254 nm. A

binary solvent system was used with 0.1% FA in Milli-Q water as solvent A and ACN as solvent B. The flow rate of the mobile phase was 0.5 mL/min and a sample injection volume of 20 μL was used. The column temperature was set at 30˚C. Analyte detection was performed by a mass spectrometer using negative electrospray ionization mode. High-purity nitrogen was used as both the nebulizing and drying gas. Interface parameters for the LC/MS system were as follows: interface temperature: 350˚C, desolvation line temperature: 250˚C heat block temperature: 200˚C, and the nebulizing gas flow and drying gas flow rate were 1.5 and 5 L/min, respectively. This method was adapted from previous reports [5]. Calibration standards (0, 5, 10, 25, 50 and 100 μg/L) were prepared and analysed in background buffer solutions at each appropriate pH value. The calibration yielded a linear curve with a coefficient of determination ($R^2$) greater than 0.99.

A Metrohm 744 pH Meter (Metrohm AG, Herisau, Switzerland) was calibrated before each experiment and utilized to measure the feed solution pH during the experiment.

## 3. Results and discussion

### 3.1. Adsorption behaviour of phytoestrogens

Under all experimental pH conditions for both the NF270 and ESPA2 membranes, both genistein and formononetin significantly adsorbed onto the membranes during 24 h of filtration, which was evident from the considerable decrease in their feed concentrations with time (Figs. 2 and 3) and confirmed by a mass balance analysis (Table 3).

These results can be explained through key factors that can impact the adsorption capacity, including hydrogen bonding interaction between the phytoestrogens and the membranes, the pore size of the NF270 membrane and surface roughness of the ESPA2 membrane. As shown in Table 2, both genistein and formononetin have certain functional groups (such as –OH and C=O) which facilitate the formation of hydrogen bonding between them and the membrane surface, resulting in their strong adsorption onto both membranes. This is consistent with the investigations of Nghiem et al. [19], who also reported that hydrogen bonding interactions played an important role in the adsorption of oestrone onto TFC-S and X-20 membranes. In addition, phytoestrogen adsorption was also related to the NF270 pore size. The average pore diameter of this membrane is markedly larger than the molecular width and height of the phytoestrogens, and results in greater compound adsorption within the membrane pore structure. It has already been reported in the literature that membranes with larger pore sizes allow organic compounds to access their internal adsorption sites, support layer and pore in addition to their surface, whereas access to these internal sites might be limited with tighter membranes [20]. It is also important to note that the ESPA2 membrane exhibited considerable surface roughness [16]. This may be a significant factor in the high level of adsorption of phytoestrogens onto this membrane, due to the larger surface area, leading to greater opportunity for molecular contact and interaction [21]. Adsorption behaviour will of course have a major influence on the rejection efficiency as is discussed in the next section.

For the NF270 membrane, phytoestrogen concentrations in the permeate increased dramatically over the first 4 h of filtration at both pH 4 and 7. However, these values then decreased gradually for genistein or were relatively stable in the case of formononetin in the later stages of filtration. In particular, the permeate concentrations of genistein were nearly equal to the feed concentrations after more than 4 h of filtration, showing that all the genistein molecules can be adsorbed on or into this membrane after sufficient filtration. These observations can be attributed to the dominance of convection of these compounds through the NF270 membrane, due to their molecular width and height values being smaller than the average pore diameter of the membrane. This behaviour is in agreement with previous studies by Bellona et al. [9] and Kim et al. [10], who also demonstrated that convection is the overriding mechanism involved in the transport of most hydrophobic and hydrophilic compounds across the loose NF membrane. By contrast, in the current work, due to electrostatic repulsion between the negatively charged phytoestrogens and the negatively charged NF270 membrane (as reflected by its negative zeta potential value (approximately −26 mV at pH 11) [15]), there were only slight increases in the permeate concentrations of these compounds for the duration of the experiment at pH 11.

However, for the ESPA2 membrane, there was no significant difference in permeate concentrations of phytoestrogens at all pH conditions employed. Because of the very small pore size of the ESPA2 membrane, permeate concentrations of these compounds only slightly rose after more than 4 h of filtration at pH 4 and 7. At pH 11, the increased negative charge of both the phytoestrogens and the ESPA2 membrane (as indicated by its negative zeta potential value (approximately −22 mV at pH 11) [16]), in addition to the small pore size of the membrane, were directly responsible for the constant

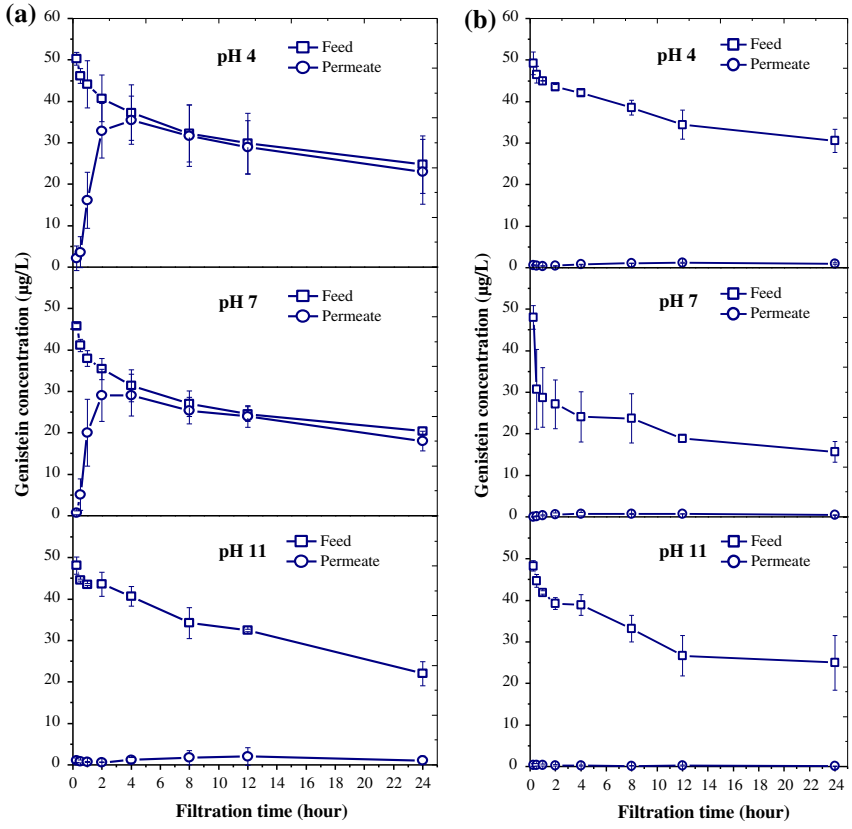



Fig. 2. Permeate and feed concentrations of genistein as a function of filtration time for the (a) NF270 membrane and (b) ESPA2 membrane at pH 4, pH 7 and 11. The error bars present standard deviation of data obtained from two independent experiments.

permeate concentrations throughout the experiment. This observation has been widely reported in the literature for other trace organic compounds such as trichloroacetic acid and triclosan for reverse osmosis RO-XLE and BW-30 membranes, respectively [22,23].

### 3.2. Rejection behaviour of phytoestrogens

The rejection behaviour of the phytoestrogens over 24 h of filtration using the NF270 and ESPA2 membranes under the three different pH conditions (pH 4, 7 and 11) is shown in Fig. 4.

For the NF270 membrane, the rejection efficiency of genistein and formononetin changed significantly with time at pH 4 and 7. In general, their rejection was initially higher than 95% (pH 4) and 98% (pH 7) which was then followed by a sharp reduction until a stable rejection was attained after approximately 4 h of filtration. This may be explained by considering the major rejection mechanisms for these compounds, namely size exclusion, adsorption and convection. Both genistein and formononetin have molecular width and height values smaller than the pore size of NF270 membrane, thus after adsorption onto the membrane, their transport across the membrane should be due to the convection through the membrane pores. Consequently, the lower rejections at later stages of filtration can be easily understood by the fact that genistein and formononetin molecules can readily transport across the pores with larger sizes than their diameters. These results are also very similar to that observed previously [24], where the rejection of oestrone by a number of commercial NF membranes appeared to decline exponentially over time to a constant value. Conversely, rejection values for these compounds were very high and only decreased slightly over 24 h of filtration at pH 11 (from 98 to 95% and 95 to 89% for genistein and formononetin, respectively). The increased negative charge of both the membrane and the compounds is directly responsible for the improved rejection through electrostatic repulsion at this basic pH. Yangali-Quintanilla et al. [25] also reported similar rejection efficiencies and mechanisms for negatively charged

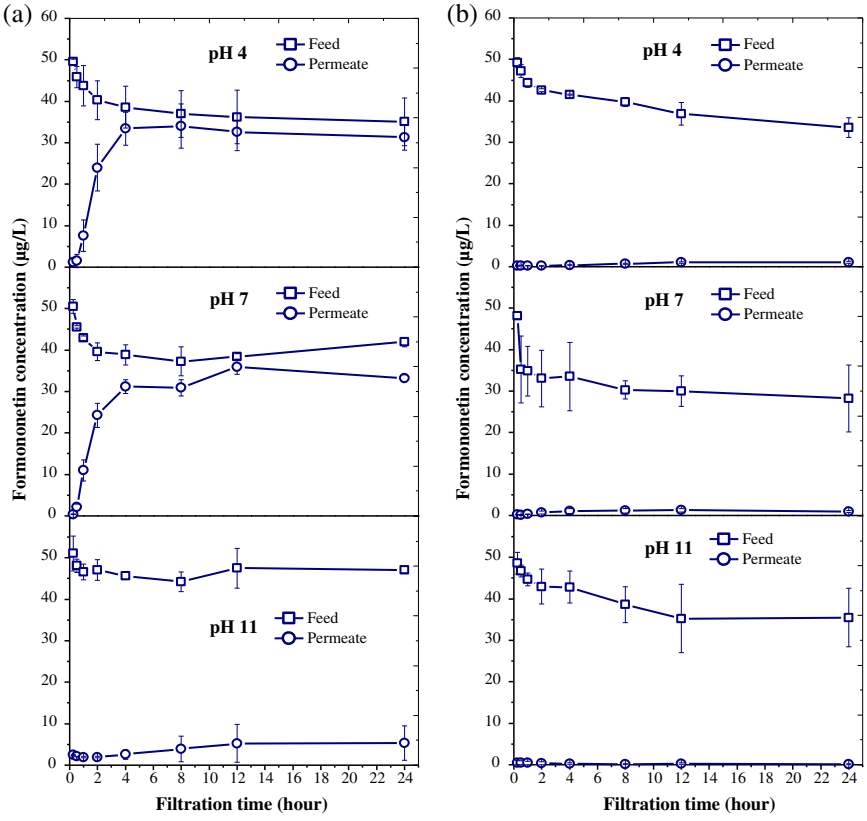



Fig. 3. Permeate and feed concentrations of formononetin as a function of filtration time for the (a) NF270 membrane and (b) ESPA2 membrane at pH 4, 7 and 11. The error bars present standard deviation of data obtained from two independent experiments.

Table 3
Adsorption of genistein and formononetin to the NF270 and ESPA2 membranes

| Compound | Membrane | Adsorption (%) | | |
|---|---|---|---|---|
| | | pH 4 | pH 7 | pH 11 |
| Genistein | NF270 | 27.7 ± 9.4 | 32.0 ± 3.9 | 22.5 ± 0.1 |
| | ESPA2 | 18.5 ± 1.6 | 49.7 ± 10.8 | 26.1 ± 6.7 |
| Formononetin | NF270 | 20.3 ± 9.0 | 19.5 ± 0.5 | 8.9 ± 5.8 |
| | ESPA2 | 17.1 ± 0.8 | 33.1 ± 13.8 | 15.9 ± 4.6 |

pharmaceutically active compounds (e.g. ibuprofen, sulfamethoxazole and naproxen) using NF90 and NF200 membranes.

For the ESPA2 membrane, the rejection efficiency of the two compounds was extremely high at all pH conditions employed. At pH 4 and 7, rejection values were up to 96% over the 24 h period with only slight decreases after more than 4 h of filtration. This can be attributed to the very small pore size of the ESPA2 membrane. Because this membrane contains very narrow pores, phytoestrogens do not significantly penetrate into the membrane pores, resulting in adsorption occurring mainly at the membrane surface. Consequently, the diffusion of these compounds across the membrane is very limited, leading to high rejection efficiencies as observed. The combined effect of size exclusion and charge repulsion resulted in nearly complete rejection of these compounds for the duration of the experiment at pH 11. This rejection trend also agrees with the observations made by Bellona et al. [26], who found that the excellent rejections (> 95%) of hydrophilic compounds, including tris(1-chloro-2-pro-

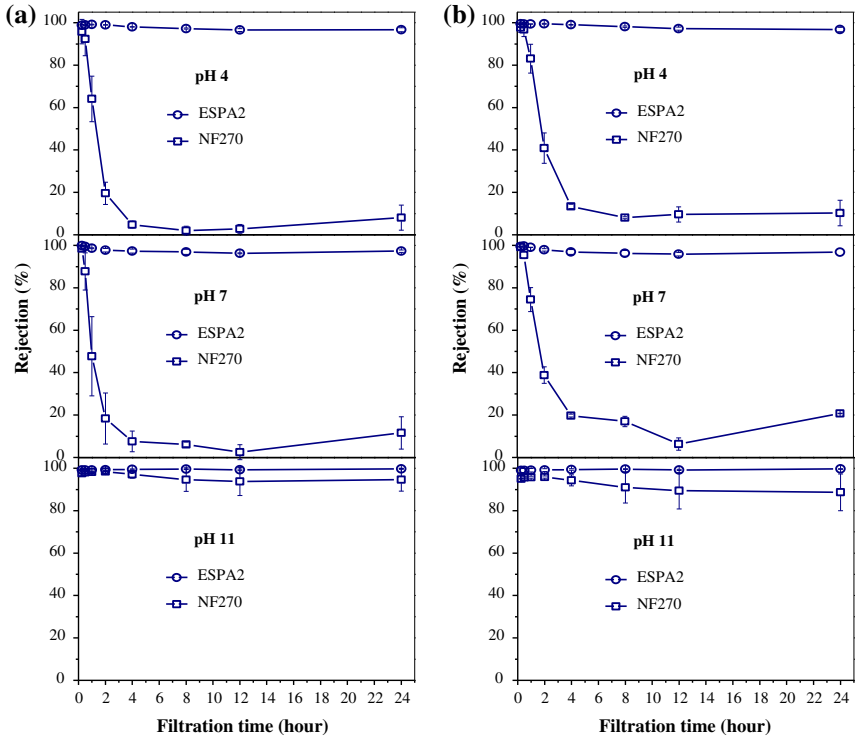



Fig. 4. Rejection efficiency of (a) genistein and (b) formononetin by the NF270 and ESPA2 membranes as a function of time.

pyl)phosphate, tris(2-chloroethyl)phosphate, tris(1,3-dichloro-2-propyl)phosphate, carbamazepine and primidone were likely the result of their relatively large size, with size exclusion being the main rejection mechanism during the full-scale testing and monitoring using ESPA2 membrane. Ng and Elimelech [27] concluded the same from their study. The results here thus suggest that rejection efficiency of phytoestrogens over the 24 h of filtration for the ESPA2 membrane was not significantly affected by the pH of the feed solution and that size exclusion was the major rejection mechanism at play for these compounds.

Findings in this study also show clearly that the rejection efficiency of genistein and formononetin by the ESPA2 membrane is considerably higher than for the NF270 membrane at all pH conditions employed. This is not surprising due to the NF270 membrane having larger pore size than the ESPA2 membrane, as discussed above. When comparing the rejection efficiency for other NF/RO membranes, it has been found that the rejection of phytoestrogens, namely daidzein, coumestrol, genistein and biochanin A by an RO (DS-3-SE) membrane was very high (from 75 to 97%), whereas a loose NF (GE) membrane exhibited lower rejection efficiencies (from 61 to 63%) for these compounds [14]. Similarly, as an example, Dolar et al. [28] demonstrated that RO membranes (LFC-1 and XLE) showed a high level of rejection (>95%) for all the examined trace organic compounds (trimethoprim, dexamethasone, febantel, ciprofloxacin and sulfamethoxazole), while lower rejection (in the range of 15–82%) for these compounds occurred with a range of NF membranes (NF270, NF and HL).

It may therefore be concluded that filtration time considerably affected the rejection efficiency of phytoestrogens by the NF270 membrane, but it did not significantly impact on the rejection of these compounds for the ESPA2 membrane. It is also worth noting that rejection behaviour of genistein and formononetin are quite similar at all experimental pH conditions for the two membranes, due to the similar properties of the compounds.

## 4. Conclusions

Significant adsorption of genistein and formononetin to NF270 and ESPA2 membranes at pH 4, 7 and 11 occurred over 24 h of filtration. This was influenced by the hydrogen-bonding interaction between the phytoestrogens and the membranes, and the pore size

of NF270 and surface roughness of ESPA2. The rejection of phytoestrogens by the ESPA2 membrane was significantly higher than that by the NF270 membrane at all pH conditions. For the NF270 membrane, the rejection efficiency of genistein and formononetin was initially higher than 95% (pH 4) and 98% (pH 7) which was then followed by a sharp decrease until stable rejection was attained after approximately 4 h of filtration, while these corresponding values were consistently very high for the entire filtration time at pH 11. These results suggested that size exclusion, adsorption and convection were the major rejection mechanisms for these compounds at pH 4 and 7 for the NF membrane. By contrast, rejection of these compounds at pH 11 might be mainly attributed to electrostatic repulsion. On the other hand, for the ESPA2 membrane, filtration time did not significantly impact on the rejection of phytoestrogens at all experimental pH conditions trailed. A near complete rejection of these compounds was observed during 24 h of filtration at pH 11. At the pH 4 and 7, these corresponding values were up to 96% over the 24 h period. These data clearly demonstrated that phytoestrogens rejection by the ESPA2 membrane could be attributed to size exclusion considerations. In general, there was no marked difference in both the adsorption and rejection behaviour of these phytoestrogens, owing to their similar physicochemical properties. When comparing among other classes of common trace organic contaminants, which have been investigated by several other researchers, similar trends were observed compared with this study.

Findings in this research provide new understanding of phytoestrogens removal in advanced treatment processes using NF/RO membranes. Tight RO membranes show an excellent and stable rejection of phytoestrogens under different pH conditions. Rejection of these compounds by loose NF membranes dropped significantly and was very low after an initial filtration period at acidic and neutral pH values. However, for loose NF membranes, the rejection efficiency can be enhanced and was relatively stable under strong basic pH conditions.

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