Effect of pH and pressure on uranium removal from drinking water using NF/RO membranes

Effect of pH and pressure on uranium removal from drinking water using NF/RO membranes.

Helfrid M.A. Schulte-Herbrüggen[a*], Andrea J.C. Semião[a], Perrine Chaurand[b], Margaret C. Graham[c]

[a]School of Engineering, The University of Edinburgh, Edinburgh, UK

[b]Aix-Marseille Université, CEREGE, Aix en Provence, France

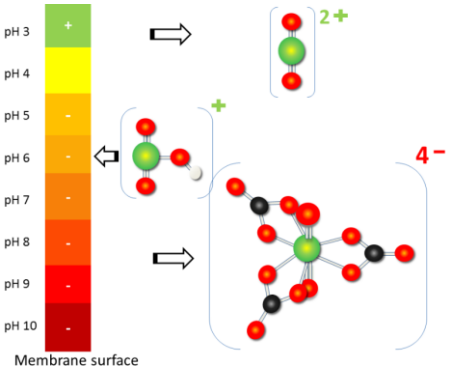
[c]School of GeoSciences, The University of Edinburgh, Edinburgh, UK

*_Current Address:_ KTH Royal Institute of Technology, Department for Sustainable Development, Environmental Science and Engineering (SEED), Teknikringen 76, SE-100 44 Stockholm, Sweden; _Tel:_ +46(0)761624665; _E-mail:_ hschulte@kth.se

17 ABSTRACT ART

18

19



Abstract. Groundwater is becoming an increasingly important drinking water source. However, the use of groundwater for potable purposes can lead to chronic human exposure to geogenic contaminants, *e.g.* uranium. Nanofiltration (NF) and reverse osmosis (RO) processes are used for drinking water purification, and it is important to understand how contaminants interact with membranes since accumulation of contaminants to the membrane surface can lead to fouling, performance decline and possible breakthrough of contaminants. During the current study laboratory experiments were conducted using NF (TFC-SR2) and RO (BW30) membranes to establish the behaviour of uranium across pH (3-10) and pressure (5-15 bar) ranges. The results showed that important determinants of uranium-membrane sorption interactions were (i) the uranium speciation (uranium species valence and size in relation to membrane surface charge and pore size) and (ii) concentration polarisation, depending on the pH values. The results show that it is important to monitor sorption of uranium to membranes, which is controlled by pH and concentration polarisation, and, if necessary, adjust those parameters controlling uranium sorption.

Key words: sorption, concentration polarisation, nanofiltration, reverse osmosis, speciation, uranium

Introduction. Groundwater is an increasingly important source of drinking water,[1] especially for developing nations in *e.g.* Africa[2] but also in European countries, where 20-100% of drinking water is sourced from groundwater.[3] As a consequence of hydrological and geochemical processes uranium is naturally present in groundwater at concentrations from below detection to hundreds of μg L^{-1}. [4–6] Indirect release of uranium into water may also occur through *e.g.* phosphate ore processing, phosphate fertilizer use, gold and tin-mining.[7–10] Uranium is above all chemically toxic, and although chronic exposure to uranium is not well understood,[11–14] studies have identified kidney, bone, liver, heart and brain as potential targets following exposure through ingestion of uranium-containing water.[11,15–18] The maximum acceptable concentrations (MAC) for uranium vary between public authorities, *e.g.* Canada uses an interim MAC of 20 μg L^{-1}, whilst the US has adopted the same limit as the WHO provisional drinking water limit of 30 μg L^{-1}.[19] However, concentrations as low as 2 μg/L may be hazardous for infants.[20] Membrane technology such as nanofiltration (NF) and reverse osmosis (RO) are frequently used for drinking water purification[21–24] since they efficiently remove a wide range of contaminants, including uranium.[25] Membrane technology is also being considered for application in remote sites due to the modular and flexible configuration and, if coupled with renewable energy, their independence from intermittent or absent energy supplies.[26–28] The performance of a membrane system using ultrafiltration, NF or RO membranes, coupled with a renewable energy supply was tested in the field. The results showed that although the system performed well in terms of producing permeate with low concentrations of most analytes *e.g.* Ca^{2+}, Mg^{2+}, Mn^{2+}, SO_4^{2-}, Na^+ and Cl^-, the behaviour of uranium in the system differed from that of most other inorganic species found in the water.

Moreover, uranium strongly interacted with the membranes.[29] It was deduced that this was largely due to the complex chemical behaviour of uranium, since its speciation varies widely depending on physico-chemical parameters such as available inorganic or organic ligands and pH of the water.[29–32] For instance, the presence of calcium affects uranium speciation and is likely to affect uranium interaction with the membranes.[29] A variety of processes can be responsible for the observed uranium uptake, including precipitation of uranium to the membrane, physi-sorption (such as hydrogen bonding or electrostatic attraction) or chemi-sorption resulting in bond formation between uranium and membrane functional groups. Before the exact mechanisms are determined, the more general terms "sorption" or "uranium-membrane interaction" will be used in this paper. To establish the processes involved in the interaction of uranium with the membrane, controlled laboratory experiments are needed, isolating one factor at a time: individual membranes, solution composition, pH and pressure ranges. The present study focused on uranium in the absence of other major ions, *e.g.* calcium, in order to determine the membrane interactions due to uranium alone. Although there have been studies investigating uranium retention using NF and RO[33–36] none have investigated the specific interactions between membranes and uranium during the water purification process. Therefore, the aims of this study were to determine (i) the effect of pH and speciation on uranium-membrane interactions by NF and RO membranes; (ii) the effect of membrane pore size and (iii) the effect of pressure on the uranium-membrane interactions.

Materials and Methods. The behaviour of uranium was investigated using an experimental feed solution containing 0.5 mg L^{-1} uranium (uranyl nitrate, TAAB, UK), background electrolyte and buffer (20 mM NaCl and 1 mM $NaHCO_3$, Fisher Scientific, UK). The uranium concentration chosen is comparable to concentrations found naturally.[4,29,37,38] MilliQ water was used to prepare all solutions (Elga Purelab Ultra, High Wycombe, UK). The pH of the experimental solution was adjusted (1 M HNO_3, VWR Aristar, or 1 M NaOH, Fisher Scientific) according to the conditions to be tested (described later), prior to adding the solution to the stainless steel cross-flow system (MMS, Switzerland). Two membranes with different molecular-weight cut-off (MWCO) values but of similar materials (polyamide active layer on a polysulphone support layer) were selected: TRC-SR2, a NF membrane (Koch Membrane systems, USA) and BW30, a RO membrane (Dow Filmtec). Cross-flow experiments were carried out with and without applied pressure to investigate the effects of pressure on uranium-membrane interactions. Two types of cross-flow experiments were conducted: 1) across the pH range 3-10 (in units of one, with one pH value per experiment) but with *no* applied pressure and 2) at two selected pH values (pH 6 and 8.5), across the pressure range 5-15 bar (in steps of 2.5 bar, one pressure and pH value per experiment).

Filtration set-up and procedure. New rectangular membrane coupons (membrane area of 0.0046 m^2) were cut for each experiment from a membrane sheet. The coupons were washed and soaked in MilliQ water at 4°C overnight, washed again, before being mounted in the stainless steel cross-flow system, operated in total recirculation mode. Membranes were compacted using MilliQ water at 25 bar prior to

experiments and a solution sample was collected as a quality check. A detailed description of the experimental set-up is given in the supporting information (SI) and a schematic is published in Semião and Schäfer.[39] The system was drained and experimental solution added (feed volume of 2 L). The flow-rate was set to 0.6 L min^{-1} and, for *pressure experiments*, pressure was applied at this point. Temperature, pressure, feed flow, feed and permeate pH and conductivity were monitored throughout the experiments which lasted up to seven hours. Feed and permeate samples were regularly collected. The pH value of the feed solution was adjusted (1 M HNO_3, VWR Aristar, or 1 M NaOH) during experiments to maintain the pH value within ± 0.2. The pH value of permeate samples deviated from that of the feed with up to a value of ± 0.5.

The mass of uranium sorbed by the membrane (mg U m^{-2} of membrane) was simply calculated as the mass uptake of uranium by the membrane divided by the membrane area. To report the mass sorbed as percentage uptake, the uranium mass sorbed by the membrane was calculated in relation to the initial mass of uranium available in the feed (*i.e.* 1 mg U):

$$Uptake\,(\%) = \frac{V_{b0}C_{b0} - V_{bf}C_{bf} - \sum_{i=0}^{i=n} V_S C_{si}}{V_{b0}C_{b0}} \times 100 \qquad \text{Eq. 1}$$

where, V = volume (L), C = uranium concentration (mg L^{-1}), s = permeate or feed sample taken, b = bulk (or feed), f = final, 0 = initial and n indicates the number of samples collected during the experiment.

Following completion of each experiment and the removal of the membrane, the system was thoroughly washed using dilute HNO_3 (2%, v/v Analar, VWR) followed by consecutive washes with MilliQ water. For quality control purposes a sample was collected of the final system washes and analysed for uranium content (below detection in washes).

Chemical analysis and quality control. The uranium concentrations in the feed samples was determined by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES, Optima 5300 DV, Perkin Elmer, USA) whilst those in the permeate samples were determined by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS, Agilent 7500ce). Calibration standards were prepared using a uranium stock solution (1000 mg L^{-1} U, Merck) and dilute HNO_3 (2% v/v, Aristar, VWR International, UK). For both ICP-OES and ICP-MS analysis, check standards and blank samples (2% v/v HNO_3) were inserted after every 5-10 samples during the run. The accuracy of the calibration was asserted for both techniques by analyzing a standard reference solution (ICP Multi Element Standards Solution VI, Certipur). The average value obtained for the standard reference material during ICP-OES analysis was 0.978 ± 0.140 mg L^{-1} (expected: 1.0 ± 0.05 mg L^{-1}). The average value for the ICP-MS analysis was 0.979 ± 0.59 µg L^{-1} (expected: 1.0 ± 0.05 µg L^{-1}).

Micro-X-ray Fluorescence spectroscopy. The penetration of uranium into membranes was explored for selected experiments using micro-X-ray Fluorescence spectroscopy (μ-XRF, XGT-7000 microscope from Horiba Jobin Yvon). Cross-sections of the dry membranes were cut using scissors and placed between paperboard support for analysis in a line over multiple points (1000s/point) along the membrane cross-section with an incident X-ray beam size of 10 μm (Rh target, accelerating voltage of 50 kV, current 1 mA). More detailed information on this method is provided in the Supporting Information.

Speciation modeling. The modeling of the uranium and other ions present in the aqueous solution was carried out across the pH range 3-10 using visual Minteq 2.53 (KTH, Stockholm, Sweden), as described in Rossiter et al.[29]

Membrane characterization. NF and RO membranes have been shown by other studies to have different surface chemistries. The BW30 membrane consists of a fully aromatic polyamide active layer coated with an aliphatic layer rich in alcoholic groups, whilst other membranes have a fully or semi aromatic polyamide active layer with no coating.[40] As these different functional groups may affect membrane surface charge[41] and hence potentially, the interaction with different uranium species, the membrane zeta potential was measured in background electrolyte solution (1 mM $NaHCO_3$ and 20 mM NaCl) using an electro-kinetic analyzer (EKA, Anton Paar, Austria). MWCO and pore-size was determined experimentally using a range of neutral organic molecules (dioxane, dextrose (Fisher, UK), xylose (Acros Organics, UK) and polyethylene glycol of different molecular weight (400, 600 and 1000 g mol^{-}

182 [1], Fisher, UK)) at a concentration of 25 mg carbon L^{-1} applied to the same membrane
183 sample, following methods described in Hilal et al. and Nghiem et al.[42,43] For the
184 determination of pore radius, film theory was used[44] and a correlation was used to
185 estimate the mass transfer coefficient of UO_2^{2+}.[45,46] Organic carbon concentrations
186 were measured in non-purgeable organic carbon mode using a TOC Analyser
187 (Shimadzu TOC-VCPH, UK) with an ASI autosampler and high-sensitivity catalyst.
188 Salt flux was calculated using conductivity measurements. Average permeability and
189 standard deviation of the membrane coupons was calculated using the stabilized flux
190 measurements during compaction.
191
192 **Results and Discussion.**
193 **Membrane characterisation.** The zeta potential measurements showed that the net
194 charge of TFC-SR2 and BW30 were similar to each other and varied with pH: the
195 overall charge was positive at pH 3, the iso-electric points for TFC-SR2 and BW30
196 were at pH 4.25 and pH 4.19 (Table 1), respectively, after which the magnitude of the
197 negative charge increased with increasing pH value. The nominal MWCO (90%
198 retention), permeability measurements and pore radius calculation showed that TFC-
199 SR2 has a more open structure compared with BW30 (Table 1).
200
201 **Uranium sorption to NF and RO membrane across the pH range 3-10.** The
202 objective of these experiments was to determine the influence of pH on the extent of
203 uranium sorption by the membrane without the application of pressure. The results for
204 uranium sorption by the membrane are shown in Figure 1 together with the dominant
205 uranium species across the pH range. Sorption increased from < 5.5% at pH 3 for both

membranes, to a maximum of 31% for BW30 and 50% for TFC-SR2 at pH 6. Thereafter sorption decreased to < 10% at pH 10 for both membranes. Notably, the sorption was similar for both membranes at the pH extremes, whereas, although following the same pattern, the sorption was at least 20% lower for BW30 at peak sorption than for TFC-SR2.

The results of these experiments confirm the observations by Rossiter et al.[29] that there is a strong interaction between uranium and NF/RO membranes, especially at pH values 5-7. The speciation modelling showed that the dominant uranium species vary greatly with pH and the valence of the uranium species also changed from being positive at acidic pH (pH 3-6), to either neutral or carrying single negative charge under near-neutral conditions to highly negative at alkaline pH (pH 8-10). Since the overall membrane charge also varies with pH, going from weakly positive (pH 2-4) to highly negative at pH values above pH 5, charge interactions are likely to play an important role in uranium sorption. Electrostatic repulsion can explain the low interaction between uranium and the membranes at pH 3-4 and pH 8-10, where uranium species and membrane carry the same charge. Electrostatic attraction is a likely contributor to the greater sorption of uranium to the membrane at pH 5 and 6, which was 49% for the TFC-SR2 and varied from 25 to 31% for the BW30 membrane. Charge interactions between uranium species and NF/RO membranes hence govern uranium sorption to the membranes.

The uranium species also vary in molecular weight (Table 2), and hence size exclusion might contribute to the difference in sorption for both membranes studied.

At pH 5-6, where high uranium sorption takes place, the MW of the main uranium species (UO_2OH^+, UO_2^{2+} and UO_2CO_3, Figure 1) is considerably lower (270-330 g mol^{-1}) than the MWCO of the TFC-SR2 membrane (MWCO: 486 g mol^{-1}). The size difference between the membrane MWCO and the uranium species, allied to charge attraction between the negatively charged membrane and the positively charged or neutral uranium species, suggests ease in penetrating the TFC-SR2 membrane[47] in the absence of pressure and with access to the active and support layers for sorption. Charge attraction will also occur between the uranium species and the BW30 membrane, as both TFC-SR2 and BW30 membranes have similar negative surface charge.[48] However, the BW30 membrane has a MWCO of 88 g mol^{-1}, hence based on size exclusion, a much lower uranium penetration into the membrane active layer and support layer would be expected. In fact, the sorption by TFC-SR2 reached equilibrium more slowly (generally 30-60 minutes longer) than for BW30, which would be consistent with slower diffusion of uranium, followed by sorption into the porous active and support layer structure. The higher sorption onto the TFC-SR2 membrane as opposed to the BW30 membrane could hence be caused by a higher surface area available for the uranium species to sorb onto the membrane.

To provide further evidence for the penetration of uranium into the TFC-SR2 membrane, μ-XRF analysis was performed on four selected membrane samples after experiments at pH 6 and pH 8.5 for both BW30 and TFC-SR2. These pH values were selected in order to investigate a point of high sorption of uranium at pH 6 and one of lower uranium sorption at pH 8.5. The μ-XRF analysis showed significant differences with regards to uranium distribution for both membranes studied (Figure 2). As the spatial resolution of this method is relatively low (the incident X-ray beam size is 10

μm and penetrates through the sample so the lateral resolution is very low *i.e.* mm range), the exact location of uranium cannot be conclusively determined, *i.e.* whether uranium is present in the active layer, support layer or both, since the NF/RO membrane active layers have a thickness of around 200 nm.[49] Neither the thickness of the active layer nor that of the membrane can be accurately determined with this method as the method picks up the sulfur signal of the polysulphone support layer but not the signal corresponding to the polyester support layer. However, the sulfur signals indicate the presence of the polysulfone support layer, whereas the calcium signals indicate the *approximate* boundaries of the membrane since the calcium signals originate from the mounting material (see Supporting Information). The XRF analysis presented in Figure 2 a confirms that uranium entered into the more open membrane structure of the TFC-SR2 at pH 6, as the uranium peak for this membrane overlapped with the sulfur peak. In contrast, no uranium could be detected for the BW30 membrane (Figure 2 c), showing low or no penetration into this membrane. Size exclusion hence plays an important role in uranium sorption. At pH 8.5, albeit lower compared to pH 6 due to charge repulsion, uranium penetration and internal sorption occurred for the TFC-SR2 membrane (Figure 1 and Figure 2 b). This occurred independently of conditions of charge repulsion between the negatively charged membrane and the negatively charged uranium species, showing the effect of membrane pore size and hence size exclusion in uranium penetration and sorption into the membrane structure. Uranium sorption onto the more opened TFC-SR2 membrane is hence not only governed by charge interactions but also by access to internal surface area governed by membrane pore size. In contrast, no uranium could be detected for the BW30 membrane for pH 8.5, as can be seen in Figure 2 d, showing

that any sorption observed in Figure 1 by this membrane was not likely to occur deep inside the membrane structure but mainly on the surface: uranium sorption for the dense RO membrane is hence governed by charge interactions. The lower penetration into BW30 compared to TFC-SR2 hence indicates that membrane pore size acts as a limiting factor to sorption of uranium by the membranes. Pore size has similarly been determined as an important factor in membrane sorption of hormones.[50]

Uranium sorption by membrane at pressures 5-15 bar. The previous section demonstrated the higher penetration of uranium species into the membrane of greater porosity (TFC-SR2), across the pH range and irrespective of uranium species present. The objective of these experiments was to investigate the effect of pressure on the uranium sorption to the membranes. Pressure is likely to enhance the permeation of solutes inside the membrane and hence facilitate access to the internal membrane surface area, where sorption may occur. It may also lead to a higher concentration of uranium at the membrane surface (through concentration polarisation) and, as a consequence, precipitation might occur. To investigate this, a pressure range of 5-15 bar was selected based on the typical range for spiral wound membranes (3-20 bar)[51] and manufacturer recommendations.[52,53] Again, pH values 6 and 8.5 were selected.

The resulting membrane sorption of uranium as a function of pressure is presented in Figure 3. The sorption varied significantly between membrane types and also between pH values and thus uranium species present. For TFC-SR2 at pH 6, a constant sorption of 50 ± 5% of uranium (equivalent to a range of 109-125 mg U m^{-2} of the membrane surface) was observed across the pressure range (5-12.5 bar) (Figure 3a);

only at 15 bar was there a significant increase in uranium sorption to 69%. The sorption for the same membrane but at pH 8.5 was different: sorption *increased with pressure*, from < 20% at 5 bar up to 61% at 12.5 and 15 bar (Figure 3b). Conversely, for BW30 the sorption of uranium by the membrane remained unaffected by pressure at both pH 6 and pH 8.5 (Figure 3c and d). The results show that irrespectively of pressure and pH, uranium sorption is higher in TRC-SR2 than in BW30. TFC-SR2 also gave lower retention for uranium, across the pressure range of 5-15 bar: 90% ± 6% at pH 6, 94% ± 5% at pH 8.5 while for BW30 uranium retention was 99.7% ± 0.3% for both pH values and across the entire pressure range. The results are consistent with the larger pore size of TFC-SR2 compared to BW30 which is related with permeability. The permeability of the two membranes were compared using the pure water flux before and after completed experiments, and the permeate flux during experiments (Figure 4). Pure water flux for BW30 was approximately half of that for TFC-SR2 at the same pressure, reflecting the difference in permeability between the two membranes. As expected, BW30 experienced a flux decline during the uranium experiments, consistent with effects of concentration polarisation and osmotic pressure difference between the feed and permeate side.[54] Once the pure water flux was again measured after the uranium experiments, it was restored to its original value. By contrast, the flux of TFC-SR2 unexpectedly increased with the addition of experimental solution (and also with addition of salt solution not containing uranium; results not included) and remained high even when the experimental solution was drained and pure water was filtered. Although unusual, a similar effect has been reported by several studies.[55–57] Nilsson et al. linked the flux increase to pore expansion caused by salt ions reducing the strength of the membrane cross-links.[57]

Such pore expansion within the TFC-SR2 membrane would further enhance the penetration of uranium into the membrane.

Furthermore, concentration polarisation, which increases with increasing permeability, is likely to affect the filtration, leading to an accumulation of solutes and consequently higher concentration adjacent to the membrane surface. Taking concentration polarisation into account, the solute concentration at the membrane surface was calculated using Equation 2,[44]

$$\frac{Cm - Cp}{Cb - Cp} = \exp\left(\frac{Jv}{k}\right) \qquad \text{Eq. 2}$$

where Cm = concentration at membrane surface (mg L^{-1}), Cp = concentration in permeate (mg L^{-1}), Cb = concentration in bulk solution (mg L^{-1}), Jv = permeate flux (m s^{-1}) and k = the mass transfer coefficient (m s^{-1}). Whereas Cp, Cb and Jv are determined experimentally, k had to be calculated using correlations relevant to the experimental conditions (slit channel and laminar flow). For the experimental conditions of the system used, the Sherwood number can be related to the Reynolds and Schmidt number[58] as described in Equation 3:

$$Sh = 1.85 \times \mathrm{Re}^{0.33}\, Sc^{0.33} (d_h / L)^{0.33} \qquad \text{Eq. 3}$$

where Re = the Reynolds number, Sc = the Schmidt number, dh = channel hydraulic diameter, L = the length of the membrane cell. The Reynolds, Schmidt and Sherwood number were calculated as described in Semião et al.[37]

The extent of concentration polarisation experienced by a membrane can be reported as the concentration polarisation modulus, giving the ratio of initial concentration at the membrane surface (Cm) to that in the bulk solution (Cb) at the start of the experiment. The concentration polarisation modulus for each pressure experiment are displayed together with the uranium uptake in Figure 3. During filtration with BW30, uranium uptake (around 30 and 20% for pH 6 and 8.5, respectively) for both pH values remained unaffected by pressure and concentration polarisation (Figure 3c and d). Due to its high permeability the TFC-SR2 membrane was more affected than BW30 by concentration polarisation. There were some important differences between the results for TFC-SR2 at the two pH values. At pH 8.5, uranium sorption to the membrane clearly followed the polarisation modulus trend. This trend was similar to a previous study with hormones and a NF270 membrane, where higher polarisation modulus resulted in higher concentration at the membrane surface translating into a higher adsorption.[37] In contrast, at pH 6 the uranium uptake to the TFC-SR2 membrane remained constant despite pressure and concentration polarisation increase, with the exception of the highest pressure point. It appears that concentration polarisation does not affect the interaction between the uranium species and membrane at pH 6, suggesting that variations in uranium concentration only have a small effect on the amount of uranium sorbed by the membranes. To confirm this, an adsorption isotherm for uranium at pH 6 was plotted (Figure S2). Using linear fit of

372 the sorption isotherm, the uranium sorption, based on the concentration at the
373 membrane surface Cm of 0.62-1.03 mg L^{-1} for pressures 5 to 15, was estimated to
374 around 107-123 mg U m^{-2} of membrane surface, i.e. a sorption of 50% to 57% based
375 on mass balance, showing that pressure and hence concentration polarisation had an
376 insignificant effect on uranium sorption at pH 6. Precipitation as an uptake
377 mechanism could be excluded, as even at high concentration polarisation the uranium
378 concentration at the membrane surface was calculated to be a maximum of 1.03 mg L^{-1}
379 and still remained below maximum solubility of uranium, thus confirming sorption
380 to be the main mechanism governing uranium-membrane interactions.
381
382 This study confirmed that the uranium-membrane interactions were highly speciation
383 and pH dependent, with affinity determined by the charge of both membrane and
384 uranium species (*e.g.* UO_2OH^+ or $UO_2(CO_3)_3^{4-}$) as well as species size relative to
385 membrane pore size. Pore size and subsequent permeability of the membranes
386 governed uranium sorption, where TFC-SR2 was subject to higher uranium sorption
387 than BW30 under all experimental conditions. Concentration polarisation affected
388 only one of the uranium species, $UO_2(CO_3)_3^{4-}$, a species which generally tends to
389 display low sorption and high mobility,[59,60] but its sorption to TFC-SR2 increased
390 with increasing pressure. UO_2OH^+, whose sorption to TFC-SR2 was initially higher,
391 remained largely unaffected by concentration polarisation. This study has provided a
392 first insight into the nature of the interactions of uranium with NF and RO membranes
393 and the clear effects of pH and charge interactions, membrane pore size and
394 concentration polarisation on uranium sorption. Uranium sorption might be further
395 affected by the presence of different functional groups on the membrane active layer.

396 Tang et al,[61] for example, showed that some RO membranes possess a surface layer
397 coating rich in -COH groups in addition to the aromatic or semi-aromatic polyamide
398 active layer. Hence, future work focused on a more in-depth analysis to determine the
399 chemical nature and spatial distribution of the uranium sorption to the membranes, as
400 well as the effect of hardness on the removal of uranium by NF and RO membranes is
401 needed.
402
403 The results are of significance in the wider membrane application context since it
404 illustrates the importance of taking sorption of contaminants into account. The
405 retention *observed* in experimental and applied water treatment settings may not be
406 the actual or real retention, and the long-term consequences of sorption to the
407 membranes remains unknown. One possible consequence is the risk of uranium de-
408 sorption from the membrane into the permeate line during operation, especially at
409 acidic pH values, which could pose a health risk to water consumers. There is great
410 variability in membrane life-time and performance from location to location and
411 contaminant sorption (not necessarily picked up since it may not cause obvious
412 fouling and consequent flux decline) may be one of the determining factors.
413
414
415
416

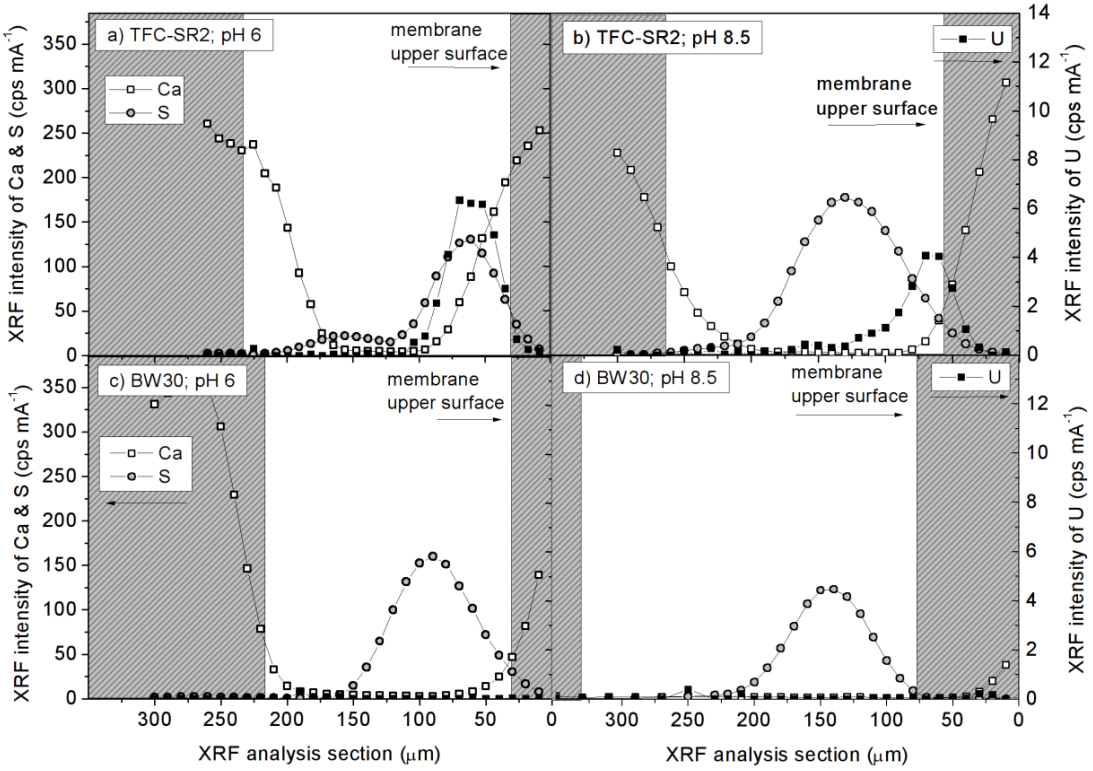
417 FIGURES

418

419

420 Figure 1. Uranium speciation (lines) and uranium uptake or sorption (columns)
421 by membranes TFC-SR2 and BW30 across the pH range 3-10. Experimental
422 solution: 0.5 mg L^{-1} uranium, 20 mM NaCl and 1 mM $NaHCO_3$. Experimental
423 conditions: flow-rate = 0.6 L min^{-1}, temperature = 24°C, no applied pressure.
424 The variation in uptake was within ± 4% for repeated experiments for TFC-
425 SR2 and ± 1% for BW30.

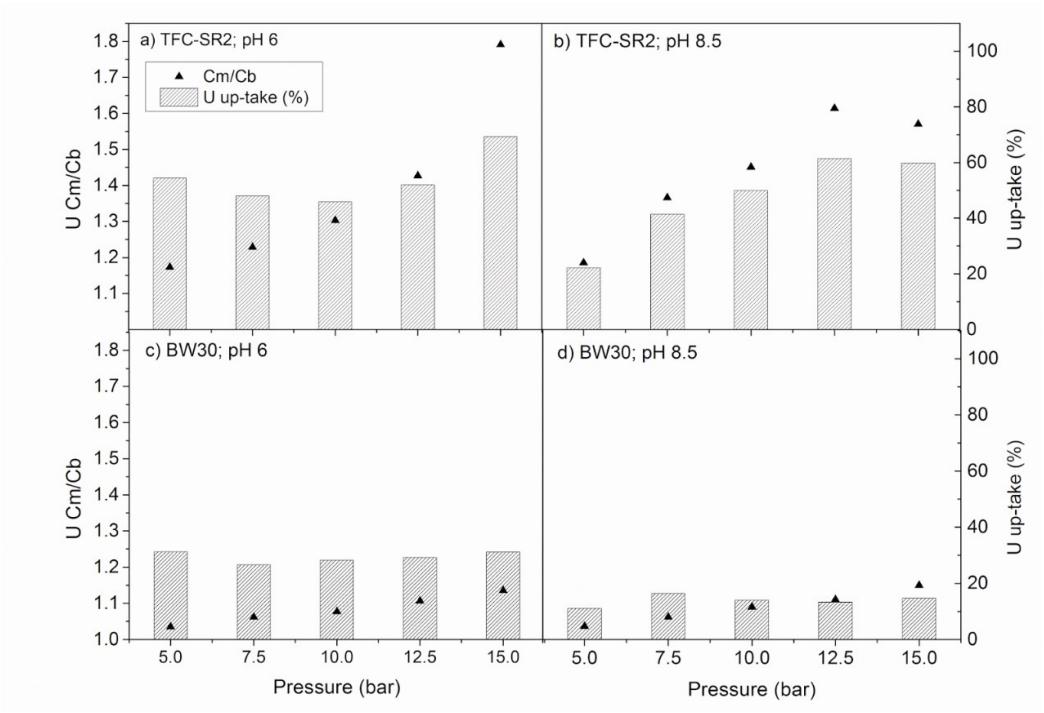
426



427

428 Figure 2. Cross-sections of TFC-SR2 and BW30 showing the elemental
429 distribution of U, S and Ca for experiments performed without pressure for
430 TFC-SR2 at pH 6 (a) and pH 8.5 (b) and BW30 at pH 6 (c) and pH 8.5 (d)
431 determined by μ-XRF. The *approximate* top and bottom edge of the
432 membrane is indicated by the shaded area based on the detection of the
433 calcium mounting material. Note the different intensity scales for Ca and S
434 compared to U.

435

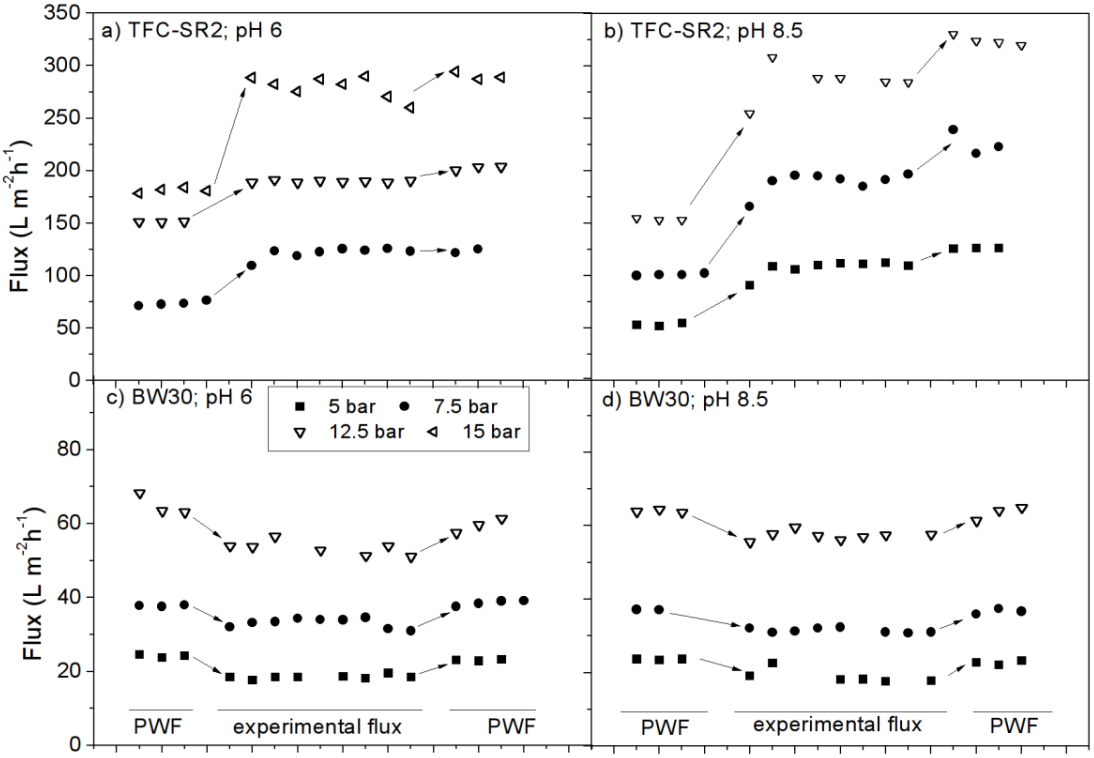


436

437 Figure 3. The percentage uptake (sorption) of uranium (columns) during the
438 experiments is shown on the right y-axis, while the calculated polarisation
439 modulus (Cm/Cb) for uranium is indicated by points and displayed on the left
440 y-axis. Repeatability of U uptake for selected experiments was within ± 4% for
441 TFC-SR2 and ± 1% for BW30.

442

443


a) TFC-SR2; pH 6
b) TFC-SR2; pH 8.5
c) BW30; pH 6
d) BW30; pH 8.5
5 bar
7.5 bar
12.5 bar
15 bar
Flux (L m-2h-1)
PWF
experimental flux
PWF

444

Figure 4. Pure water flux (PWF) before and after selected pressure experiments, and permeate flux during pressure experiments (5-15 bar) for TFC-SR2 and BW30 at pH 6 and 8.5. Permeability variability for TFC-SR2 was ± 13% and BW30 was ± 3% based on pure water flux experiments. Variability of permeate flux during experiments was within ± 10% for TFC-SR2 and ± 2% for the BW30. Please note different flux scales for TFC-SR2 and BW30.

TABLES

Table 1. Membrane characteristics

Parameter	**TFC-SR2**	**BW30**
Iso-electric point/pH	4.25	4.19
Nominal MWCO/g mol^{-1}	486[a]	88
Pore radius/nm	0.52 ± 0.03	0.32 ± 0.01[b,43]
Permeability/L m^{-2} h^{-1} bar^{-1}	10.97 ± 1.51	4.84 ± 0.15

[a]Absolute MWCO (100% retention) for TFC-SR2 was determined as 1033 g mol^{-1}.

[b]Note that RO membranes are considered to have dense, non-porous structures and so "pore-radius" for BW30 was determined only as a comparison with the more open structure of TFC-SR2.

Table 2. Main uranium species present for pH range 3-10[a]

pH value	**Uranium species**	**Molecular weight (g mol^{-1})**
3-4	UO_2^{2+}	270
5-6	UO_2OH^+	287

6-7	UO_2CO_3	330
7	$(UO_2)_2CO_3(OH)_3^-$	651
8	$UO_2(CO_3)_2^{2-}$	390
8-10	$UO_2(CO_3)_3^{4-}$	450

[a]Note that each pH value may contain a mixture of several species.

ASSOCIATED CONTENT

Supporting information. Details of experimental set-up and filtration procedure, ICP-OES, ICP-MS and XRF analysis, salt retention and isotherm experiment. This material is available free of charge via the internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Tel +46 (0)87906291

E-mail: hschulte@kth.se

Present Addresses

*Department for Sustainable Development, Environmental Science and Engineering (SEED), KTH Royal Institute of Technology, Teknikringen 76 1 tr, SE-100 44 Stockholm, Sweden.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

ESRC-EPSRC PhD scholarship, FFWG for additional living allowance and EPSRC Doctoral Prize Fellowship for H. Schulte-Herbrüggen.

ACKNOWLDEGMENT

Acknowledgements. The authors are grateful to the following organisations and individuals: The School of Engineering (University of Edinburgh, UoE) for funding cross-flow equipment, Koch Membrane Systems and Filmtec Corporation for NF and RO membrane sheets, Dr Annalisa De-Munari (UoE), Dr Alexander Bismarck and Dr Kingsley Ho (Imperial College, UK) for zeta potential measurements, Steven Gourlay (UoE) for cross-flow system design, Dr Alan Simm (UoE) for LabVIEW set up, Dr Lorna Eades (UoE) for assistance with ICP-MS analysis. Prof Andrea Schäfer (UoE) is thanked for facilitating the work and Prof Viatcheslav Freger (Technion, Israel) and the anonymous reviewers are thanked for constructive suggestions to improve the work.

References.

(1) Wada, Y.; van Beek, L. P. H.; van Kempen, C. M.; Reckman, J. W. T. M.; Vasak, S.; Bierkens, M. F. P. Global depletion of groundwater resources. *Geophys. Res. Lett.* **2010**, *37* (20), L20402.

(2) MacDonald, A. M.; Bonsor, H. C.; Dochartaigh, B. É. Ó.; Taylor, R. G. Quantitative maps of groundwater resources in Africa. *Environ. Res. Lett.* **2012**, *7* (2), 24009.

(3) Estrela, T.; Marcuello, C.; Iglesias, A. *Water resources problems in Southern Europe*; 1996.
(4) Nriagu, J.; Nam, D.-H.; Ayanwola, T. A.; Dinh, H.; Erdenechimeg, E.; Ochir, C.; Bolormaa, T.-A. High levels of uranium in groundwater of Ulaanbaatar, Mongolia. *Sci. Total Environ.* **2012**, *414*, 722–726.
(5) Norrström, A. C.; Löv, Å. Uranium theoretical speciation for drinking water from private drilled wells in Sweden – Implications for choice of removal method. *Appl. Geochem.* **2014**, *51*, 148–154.
(6) Vesterbacka, P. Natural radioactivity in drinking water in private wells in Finland. *Radiat. Prot. Dosimetry* **2004**, *113* (2), 223–232.
(7) Winde, F.; Jacobus van der Walt, I. The significance of groundwater–stream interactions and fluctuating stream chemistry on waterborne uranium contamination of streams—a case study from a gold mining site in South Africa. *J. Hydrol.* **2004**, *287* (1–4), 178–196.
(8) Arogunjo, A. M.; Höllriegl, V.; Giussani, A.; Leopold, K.; Gerstmann, U.; Veronese, I.; Oeh, U. Uranium and thorium in soils, mineral sands, water and food samples in a tin mining area in Nigeria with elevated activity. *J. Environ. Radioact.* **2009**, *100* (3), 232–240.
(9) Vandenhove, H.; Sweeck, L.; Mallants, D.; Vanmarcke, H.; Aitkulov, A.; Sadyrov, O.; Savosin, M.; Tolongutov, B.; Mirzachev, M.; Clerc, J. J.; et al. Assessment of radiation exposure in the uranium mining and milling area of Mailuu Suu, Kyrgyzstan. *J. Environ. Radioact.* **2006**, *88* (2), 118–139.
(10) H. Vandenhove. European sites contaminated by residues from the ore-extracting and -processing industries. *Int. Congr. Ser.* **2002**, *1225*, 307–325.
(11) Craft, E. S.; Abu-Qare, A. W.; Flaherty, M. M.; Garofolo, M. C.; Rincavage, H. L.; Abou-Donia, M. B. Depleted and natural uranium: chemistry and toxicological effects. *J. Toxicol. Environ. Health Part B* **2004**, *7* (4), 297–317.
(12) Kurttio, P.; Harmoinen, A.; Saha, H.; Salonen, L.; Karpas, Z.; Komulainen, H.; Auvinen, A. Kidney Toxicity of Ingested Uranium From Drinking Water. *Am. J. Kidney Dis.* **2006**, *47* (6), 972–982.
(13) Prat, O.; Vercouter, T.; Ansoborlo, E.; Fichet, P.; Perret, P.; Kurttio, P.; Salonen, L. Uranium speciation in drinking water from drilled wells in southern Finland and its potential links to health effects. *Environ. Sci. Technol.* **2009**, *43* (10), 3941–3946.
(14) Vicente-Vicente, L.; Quiros, Y.; Perez-Barriocanal, F.; Lopez-Novoa, J. M.; Lopez-Hernandez, F. J.; Morales, A. I. Nephrotoxicity of Uranium: Pathophysiological, Diagnostic and Therapeutic Perspectives. *Toxicol. Sci.* **2010**, *118* (2), 324–347.
(15) Miller, A. C.; Brooks, K.; Smith, J.; Page, N. Effect of the militarily-relevant heavy metals, depleted uranium and heavy metal tungsten-alloy on gene expression in human liver carcinoma cells (HepG2). *Mol. Cell. Biochem.* **2004**, *255* (1–2), 247–256.
(16) Hogan, A.; Vandam, R.; Markich, S.; Camilleri, C. Chronic toxicity of uranium to a tropical green alga (sp.) in natural waters and the influence of dissolved organic carbon. *Aquat. Toxicol.* **2005**, *75* (4), 343–353.
(17) Kurttio, P.; Auvinen, A.; Salonen, L.; Saha, H.; Pekkanen, J.; Mäkeläinen, I.; Väisänen, S. B.; Penttilä, I. M.; Komulainen, H. Renal effects of uranium in drinking water. *Environ. Health Perspect.* **2002**, *110* (4), 337.

(18) Kurttio, P.; Komulainen, H.; Leino, A.; Salonen, L.; Auvinen, A.; Saha, H. Bone as a Possible Target of Chemical Toxicity of Natural Uranium in Drinking Water. *Environ. Health Perspect.* **2004**, *113* (1), 68–72.
(19) World Health Organization. *Guidelines for drinking-water quality.*; World Health Organization: Geneva, 2011.
(20) Birke, M.; Rauch, U.; Lorenz, H.; Kringel, R. Distribution of uranium in German bottled and tap water. *J. Geochem. Explor.* **2010**, *107* (3), 272–282.
(21) Cyna, B.; Chagneau, G.; Bablon, G.; Tanghe, N. Two years of nanofiltration at the Méry-sur-Oise plant, France. *Desalination* **2002**, *147* (1–3), 69–75.
(22) Service, R. F. Desalination Freshens Up. *Science* **2006**, *313* (5790), 1088–1090.
(23) Al-Amoudi, A.; Lovitt, R. W. Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency. *J. Membr. Sci.* **2007**, *303* (1–2), 4–28.
(24) Van der Bruggen, B.; Vandecasteele, C. Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry. *Environ. Pollut.* **2003**, *122* (3), 435–445.
(25) Annanmäki, M.; STUK Radiation and Nuclear Safety Authority. *Treatment techniques for removing natural radionuclides from drinking water. Final report of the TENAWA project*; 2000.
(26) Thomson, M.; Infield, D. A photovoltaic-powered seawater reverse-osmosis system without batteries. *Desalination* **2003**, *153* (1–3), 1–8.
(27) Coffey, M. Renewable energy: Filtration and the green energy revolution. *Filtr. Sep.* **2008**, *45* (5), 24–27.
(28) De Munari, A.; Schäfer, A. I. Membrane plants for drinking water provision in remote scottish communities: performance, costs and lessons learnt. In *Membranes in Drinking and Industrial Water*; Trondheim, Norway, 2010.
(29) Rossiter, H. M. A.; Graham, M. C.; Schäfer, A. I. Impact of speciation on behaviour of uranium in a solar powered membrane system for treatment of brackish groundwater. *Sep. Purif. Technol.* **2010**, *71* (1), 89–96.
(30) Kantar, C. Heterogeneous processes affecting metal ion transport in the presence of organic ligands: Reactive transport modeling. *Earth-Sci. Rev.* **2007**, *81* (3–4), 175–198.
(31) Semião, A. J. C.; Rossiter, H. M. A.; Schäfer, A. I. Impact of organic matter and speciation on the behaviour of uranium in submerged ultrafiltration. *J. Membr. Sci.* **2010**, *348* (1–2), 174–180.
(32) Langmuir, D. *Aqueous Environmental Geochemistry*; Prentice-Hall, Inc.: Upper Saddle River, New Jersey, 1997.
(33) Huikuri, P.; Salonen, L.; Raff, O. Removal of natural radionuclides from drinking water by point of entry reverse osmosis. *Desalination* **1998**, *119* (1), 235–239.
(34) Raff, O.; Wilken, R.-D. Removal of dissolved uranium by nanofiltration. *Desalination* **1999**, *122* (2), 147–150.
(35) Favre-Reguillon, A.; Lebuzit, G.; Foos, J.; Guy, A.; Draye, M.; Lemaire, M. Selective Concentration of Uranium from Seawater by Nanofiltration. *Ind. Eng. Chem. Res.* **2003**, *42* (23), 5900–5904.
(36) Favre-Réguillon, A.; Lebuzit, G.; Murat, D.; Foos, J.; Mansour, C.; Draye, M. Selective removal of dissolved uranium in drinking water by nanofiltration. *Water Res.* **2008**, *42* (4–5), 1160–1166.

(37) Orloff, K. G.; Mistry, K.; Charp, P.; Metcalf, S.; Marino, R.; Shelly, T.; Melaro, E.; Donohoe, A. M.; Jones, R. L. Human exposure to uranium in groundwater. *Environ. Res.* **2004**, *94* (3), 319–326.
(38) Seldén, A. I.; Lundholm, C.; Edlund, B.; Högdahl, C.; Ek, B.-M.; Bergström, B. E.; Ohlson, C.-G. Nephrotoxicity of uranium in drinking water from private drilled wells. *Environ. Res.* **2009**, *109* (4), 486–494.
(39) Semião, A. J. C.; Schäfer, A. I. Estrogenic micropollutant adsorption dynamics onto nanofiltration membranes. *J. Membr. Sci.* **2011**, *381* (1–2), 132–141.
(40) Tang, C. Y.; Kwon, Y.-N.; Leckie, J. O. Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes: I. FTIR and XPS characterization of polyamide and coating layer chemistry. *Desalination* **2009**, *242* (1–3), 149–167.
(41) Tang, C.; Kwon, Y.; Leckie, J. Probing the nano- and micro-scales of reverse osmosis membranes—A comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements. *J. Membr. Sci.* **2007**, *287* (1), 146–156.
(42) Hilal, N.; Al-Abri, M.; Al-Hinai, H. Characterization and retention of UF membranes using PEG, HS and polyelectrolytes. *Desalination* **2007**, *206* (1–3), 568–578.
(43) Nghiem, L. D.; Schäfer, A. I.; Elimelech, M. Removal of Natural Hormones by Nanofiltration Membranes: Measurement, Modeling, and Mechanisms. *Environ. Sci. Technol.* **2004**, *38* (6), 1888–1896.
(44) Sutzkover, I.; Hasson, D.; Semiat, R. Simple technique for measuring the concentration polarization level in a reverse osmosis system. *Desalination* **2000**, *131* (1), 117–127.
(45) Gekas, V.; Hallström, B. Mass transfer in the membrane concentration polarization layer under turbulent cross flow: I. Critical literature review and adaptation of existing sherwood correlations to membrane operations. *J. Membr. Sci.* **1987**, *30* (2), 153–170.
(46) van den Berg, G. B.; Rácz, I. G.; Smolders, C. A. Mass transfer coefficients in cross-flow ultrafiltration. *J. Membr. Sci.* **1989**, *47* (1–2), 25–51.
(47) Borrini, J.; Bernier, G.; Pellet-Rostaing, S.; Favre-Reguillon, A.; Lemaire, M. Separation of lanthanides(III) by inorganic nanofiltration membranes using a water soluble complexing agent. *J. Membr. Sci.* **2010**, *348* (1–2), 41–46.
(48) Negaresh, E.; Antony, A.; Bassandeh, M.; Richardson, D. E.; Leslie, G. Selective separation of contaminants from paper mill effluent using nanofiltration. *Chem. Eng. Res. Des.* **2012**, *90* (4), 576–583.
(49) Freger, V. Swelling and Morphology of the Skin Layer of Polyamide Composite Membranes: An Atomic Force Microscopy Study. *Environ. Sci. Technol.* **2004**, *38* (11), 3168–3175.
(50) Semião, A. J. C.; Schäfer, A. I. Removal of adsorbing estrogenic micropollutants by nanofiltration membranes. Part A—Experimental evidence. *J. Membr. Sci.* **2013**, *431*, 244–256.
(51) Thorsen, T.; Fløgstad, H. *Nanofiltration in drinking water treatment*; Literature review D5. 3. 4B; Techneau, 2006.
(52) Dow Filmtec. Dow Filmtec Membranes.
(53) Koch Membrane Systems. Fluid Systems TFC-SR2 2.5" Element.

(54) Sablani, S.; Goosen, M.; Al-Belushi, R.; Wilf, M. Concentration polarization in ultrafiltration and reverse osmosis: a critical review. *Desalination* **2001**, *141* (3), 269–289.
(55) Wang, Y.; Shu, L.; Jegatheesan, V.; Gao, B. Removal and adsorption of diuron through nanofiltration membrane: The effects of ionic environment and operating pressures. *Sep. Purif. Technol.* **2010**, *74* (2), 236–241.
(56) De Munari, A.; Schäfer, A. I. Impact of speciation on removal of manganese and organic matter by nanofiltration. *J. Water Supply Res. Technol.* **2010**, *59* (2–3), 152.
(57) Nilsson, M.; Trägårdh, G.; Östergren, K. The influence of sodium chloride on mass transfer in a polyamide nanofiltration membrane at elevated temperatures. *J. Membr. Sci.* **2006**, *280* (1–2), 928–936.
(58) Schock, G.; Miquel, A. Mass transfer and pressure loss in spiral wound modules. *Desalination* **1987**, *64*, 339–352.
(59) Wazne, M.; Meng, X.; Korfiatis, G. P.; Christodoulatos, C. Carbonate effects on hexavalent uranium removal from water by nanocrystalline titanium dioxide. *J. Hazard. Mater.* **2006**, *136* (1), 47–52.
(60) Maher, K.; Bargar, J. R.; Brown, G. E. Environmental Speciation of Actinides. *Inorg. Chem.* **2013**, *52* (7), 3510–3532.
(61) Tang, C. Y.; Kwon, Y.-N.; Leckie, J. O. Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes. *Desalination* **2009**, *242* (1–3), 168–182.