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Supplementary Material

Fate of steroid hormone micropollutant estradiol in a hybrid magnetic ion exchange resin–nanofiltration process

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1. Experimental error estimation of E2 concentration and mass loss

The error calculation was based on the uncertainties of several experimental parameters: a) temperature variation (ΔT), which was calculated as percentage error due to temperature change between 21 ºC and 23 ºC; b) pressure variation within the stirred cell during filtration (ΔP), which was related to the uncertainty of the values measured by the pressure sensor (variation between 9.4 and 9.7 bar); c) feed volume variation (ΔV) between 400 mL and 390 mL; d) permeability variation (ΔL_p) of the membrane coupons; e) sampling error (ΔC_{feed}), which was the error related to the preparation of E2 solution by dilution from the stock solution (variation of E2 concentration in the feed was between 95 ng/L and 105 ng/L E2); f) total pipetting error (ΔPip), which was related to the variation of volume in the pipettes. This error was measured by following the "Standard Operating Procedure for Manual Dispensing System" (Eppendorf AG). The errors of the different pipettes used for the experiments (dilution of feed and retentate samples, preparation of the E2 feed concentration) were as follows:

ΔPip (10 mL) = 1%

ΔPip (5 mL) = 3%,

ΔPip (1 mL) = 1%,

ΔPip (100 µL) = 4%

Pipettes with volume of 10, 5 and 1 mL were used for dilution of feed and retentate samples as well as preparation of samples for LSC analysis. The pipette with volume of 100 µL was used for the preparation of E2 feed solution from the stock solution. The total pipetting error was calculated with the propagation error as reported below (Eq. S1):

$$\Delta Pip_{(total)} = \sqrt{\Delta Pip\ (10\ mL)2 + \Delta Pip\ (5\ mL)2 + \Delta Pip\ (1\ mL)2 + \Delta Pip\ (100\ \mu L)2} \qquad \text{Eq. S1}$$

The system error (ΔS) was calculated using the propagation error (Eq. S2) and the experimental uncertainties:

$$\Delta S = \sqrt{(\Delta T2 + \Delta P2 + \Delta V2 + \Delta LP2 + 3 \cdot \Delta Pip\ (total)2 + \Delta Cfeed2)} \qquad \text{Eq. S2}$$

The experimental uncertainties were calculated as relative error using Eq. S3:

$$\Delta T, \Delta P, \Delta V,\ \Delta L_P, \Delta C_{feed} = \frac{\sigma}{\bar{x}} \qquad \text{Eq. S3}$$

where σ is the standard deviation and $\bar{x}$ is the average value. The standard deviation of ΔP and ΔT was calculated from the experimental measurements monitored with LabVIEW (e.g. pressure and temperature values measured by the sensors). The standard deviation of ΔV, ΔL_p and ΔC_{feed} was calculated from the experimental measurements of feed volume, permeability of the membrane coupons and E2 concentration in the feed solutions. The relative errors are reported in Table S1.

Table S1. Relative error calculation

Parameters	**ΔT (%)**	**ΔP (%)**	**ΔV (%)**	**ΔLp (%)**	**Δpip_{tot} (%)**	**ΔC_{feed} (%)**	**ΔS (%)**
(%)	4	1	1	11	5	5	14
σ	0.9	0.1	3.8	1	-	3.9	-
$\bar{x}$	22	9.6	396	9.4	-	99.8	-

2. Flux decline during filtration experiments in NF and hybrid MIEX-NF process

Flux decline during a filtration experiment is an indication of concentration polarization (reversible) and accumulation of organic or inorganic solutes on the membrane surface (which can cause irreversible fouling and scaling). Flux decline at the end of the experiment was calculated by normalizing the permeate flux (J_t) measured during filtration versus the initial pure water flux (J_{w0}) as reported in the previous study (Imbrogno et al., 2018). The normalized flux (J_t/J_{w0}) was relevant in this study to evaluate whether fouling occurred during filtration of feed solution containing E2, calcium and HA.

The normalized flux (J_t/J_{w0}) as a function of pH in NF and hybrid MIEX-NF process and for both NF membranes (NF90 and NF270) is reported in Figure S1.

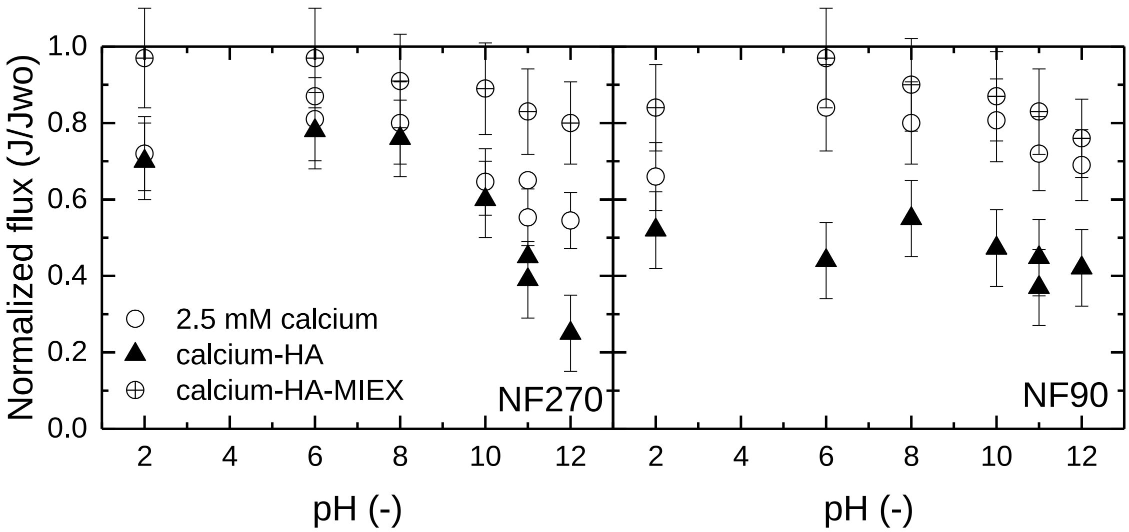


Figure S1. Normalized flux as a function of pH for NF90 and NF270 in NF and hybrid MIEX-NF process (10 mM NaCl, 1 mM $NaHCO_3$, 2.5 mM $CaCl_2$, 100 ng/L E2, 12.5 mgC/L HA, 10 mL/L MIEX, 9.6 bar, 400 rpm, 60% recovery)

Flux decline was higher at alkaline pH (pH>10) compared to acidic and neutral pH in individual NF due to Ca^{2+}-HA complex and bridging with the membrane as reported in previous studies (Ang et al., 2011, Chang et al., 2012). Flux decline was higher for NF90 compared to NF270 and presence of calcium and HA because of higher calcium rejection by NF90 (range 92-98%) compared to NF270 (range 65-75%) (Imbrogno et al., 2018).

MIEX addition reduced flux decline significantly (Imbrogno et al., 2018).

An osmotic pressure of 0.9 bar in the retentate side was estimated using the Van't Hoff equation (Robert H. Perry, 1999) and the salt rejection of NF90 (calcium 92-98%, NaCl 85%, carbonate 75-97%) and NF270 (calcium 65-75%, NaCl 40-60%, carbonate75-89%) (Imbrogno et al., 2018). The osmotic pressure caused a reduction of 10% of the applied pressure due to concentration of feed solutes in the stirred cell.

3. Conductivity and osmotic pressure of the feed solution at different pH

Conductivity of the feed solution at different pH was measured (Figure S2) in order to estimate the osmotic pressure (Π) by the total dissolved solids (TDS, mg/L) contribution due to pH adjustment as described before (Imbrogno et al. 2018). This was relevant to evaluate the loss of driving force in the filtration experiment. The volume of 1 M acid (HCl) and base (NaOH) added into the feed solution to adjust the pH is reported in Table S2. The HA stock solution (500 mg/L) that was used to prepare the feed solutions was strongly alkaline (pH 11). Hence, no pH adjustment was required to prepare the feed solution at pH 11.

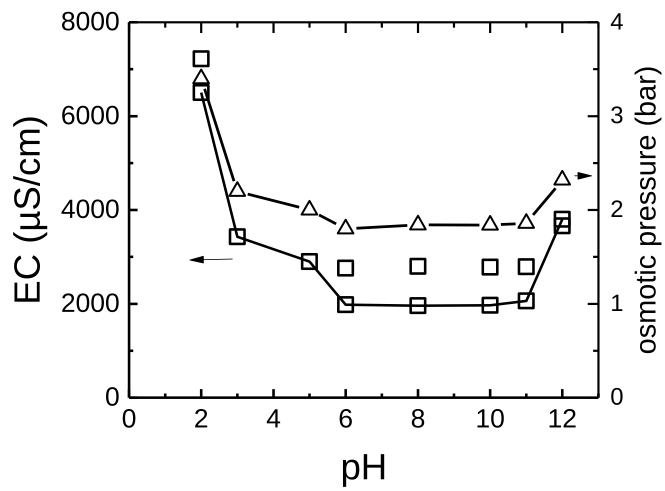


Figure S2. Conductivity of the feed solution as a function of pH. 10 mM NaCl, 1 mM $NaHCO_3$, 2.5 mM $CaCl_2$, 100 ng/L E2, 12.5 mgC/L HA

Conductivity (EC) and osmotic pressure of the feed solution in the range of pH 6 to 11 were relatively constant at values about 2000 µS/cm and 2 bar, respectively. At extreme pH values (2 and 12) both conductivity and osmotic pressure of the feed solutions increased. This was correlated with higher volume of acid (HCl) and base (NaOH) that was added to adjust pH of the feed solution as reported in Table S2. The highest loss of driving force at the beginning of the filtration was 37% and 24% at pH 2 and 12, respectively, due to pH adjustment and, as a consequence, significantly higher osmotic pressure.

Table S2. Volume of acid (HCl 1M) and base (NaOH 1M) added to the feed solutions to adjust the pH (feed solutions containing HA were prepared from HA stock solution at pH 11).

pH	HCl (mL)	NaOH (mL)
2	5.3	-
3	4.8	-

5	3.4	-
6	0.9	-
8	0.6	-
10	0.4	-
11	-	-
12	-	2.8

4. Pure water flux reduction in NF and hybrid MIEX-NF process

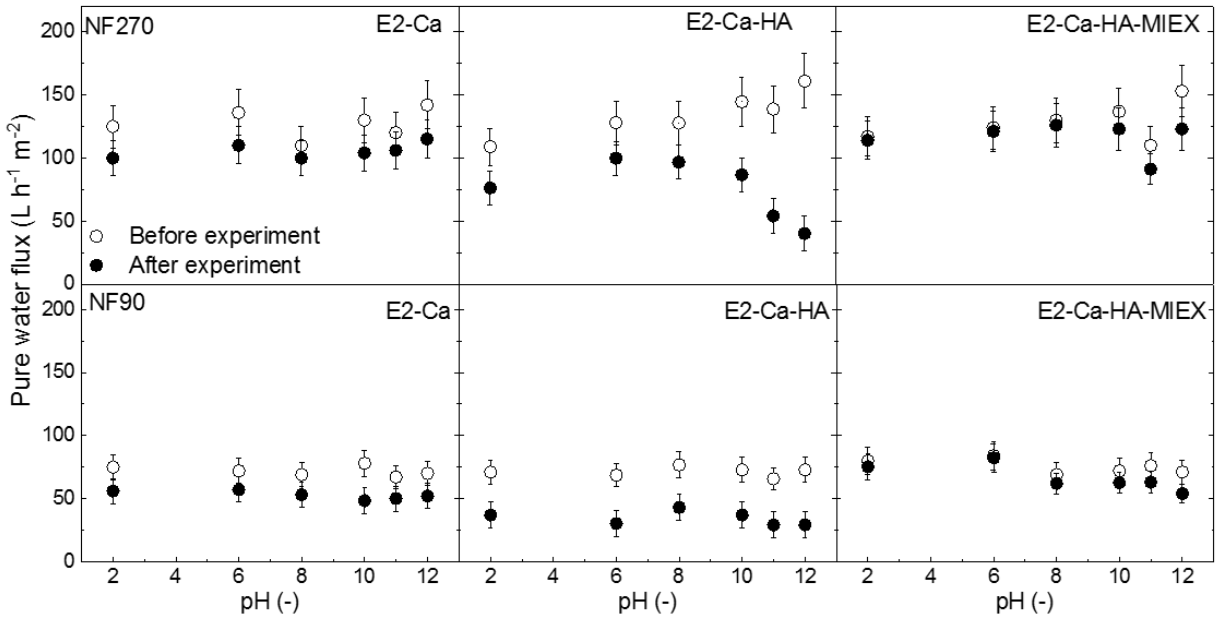
Pure water flux was measured before and after the filtration experiments in order to evaluate whether fouling was reversible or irreversible and the efficiency of MIEX to reduce it. The pure water flux measured for both membranes and as a function of pH is reported in Figure S3. Three conclusions can be drawn:

1) No water flux reduction was observed in presence of calcium and there was no evidence of calcite deposition at pH>10. This result confirmed the negligible impact of calcium on E2-membrane interaction and transport through NF.

2) Significant flux reduction was measured for both NF270 and NF90 in presence of calcium and HA especially at pH≥10 (about 60%). This was consistent with the lower E2 mass partitioned with HA at pH 10 compared to pH 6.

3) No flux reduction was observed in hybrid MIEX-NF for both membranes and at all pH conditions. This was related to HA-MIEX interaction as discussed in more detail in our previous study (Imbrogno et al., 2018). This result highlighted that both HA-MIEX and E2-MIEX interaction took place in the hybrid MIEX-NF process."

Figure S3. Pure water flux before and after the filtration experiment as a function of pH for NF90 and NF270. (10 mM NaCl, 1 mM $NaHCO_3$, 2.5 mM $CaCl_2$, 12.5 mgC/L HA, 10 mL/ MIEX, 100 ng/L E2, 9.6 bar, 400 rpm, 60% recovery)



5. Calibration of estradiol and interference of humic acid and calcium with LCS analysis

The calibration of estradiol was performed in a concentration range of 1 to 100 ng/L (1, 10, 50, 100 ng/L). The relation between estradiol concentration and radioactivity (Bq/mL) was linear as shown in Figure S4. No significant quenching was observed when feed and retentate samples were diluted 10 times (that is for E2 concentration below 20 ng/L).

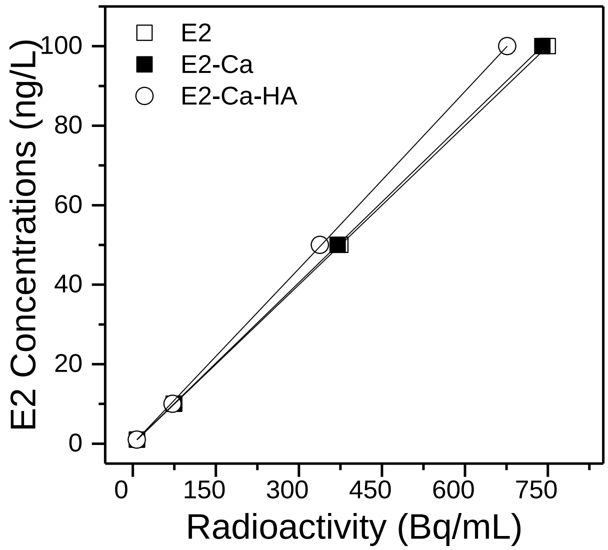


Figure S4. Calibration of estradiol concentration and quenching by humic acid and calcium. (1 mM $NaHCO_3$, 10 mM NaCl. 12.5 mgC/L HA, 2.5 mM $CaCl_2$, 23 ºC)

References

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