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Sorption of steroidal hormones by electrodialysis membranes

Laura J. Banasiak

University of Wollongong, lbanasia@uow.edu.au

Andrea I. Schafer

University of Edinburgh

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

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¹ Present address: Faculty of Engineering, University of Wollongong, Wollongong NSW 2522,
Australia

* Corresponding author. Phone: +44 (0) 131 650 72090; Fax: +44 (0) 131 650 6781; Email: Andrea.Schaefer@ed.ac.uk

Abstract

The mechanisms of sorption of four steroidal hormones – estradiol, estrone, progesterone and testosterone – to electrodialysis (ED) membranes were investigated as a function of solution pH and presence of humic acid (HA). Hormone-membrane partition coefficients ($\log K_{\text{AEM/CEM}}$) determined through sorption isotherm experiments suggested that hormone sorption was due to hydrogen bonding and cation– π interactions between hormone and membrane functional groups. Progesterone sorption at pH 7 ($922 \mu\text{g}/\text{cm}^3$) during ED was greater than estrone sorption ($591 \mu\text{g}/\text{cm}^3$) due to its greater cation-exchange membrane (CEM) bonding affinity. Estrone sorption at pH 11 ($487 \mu\text{g}/\text{cm}^3$) was reduced due to estrone dissociation and electrostatic repulsion with

negatively charged CEMs. Permeation of estrone (30-100 ng/cm².h) through the anion-exchange membranes (AEMs) was observed. At pH 11, charge repulsion between estrone and HA coupled with AEM electrostatic attraction resulted in increased sorption. Partial membrane desorption was noted in isotherm (20-30%) and ED desorption (3.8%) experiments and was dependent on the initial mass sorbed, solution pH and resultant electrostatic interactions.

Keywords: Electrodialysis; Hormones; Adsorption; Ion exchange membranes; Organic matter.

1. Introduction

The presence of steroidal hormones at low concentrations (0.1-10 ng/L) in effluents from conventional wastewater treatment plants (WWTPs), receiving waterways and drinking water have received widespread attention [1-3]. The impact of hormones are prominent as they have higher endocrine disrupting potency than other endocrine disrupting chemicals (EDCs) [4]. Numerous studies have linked exposure to trace levels of EDCs to declining male sperm count and increases in occurrence of testicular, prostate, ovarian and breast cancer [5, 6]. EDCs also have potential to interfere with the endocrine system of fish, amphibians, birds, reptiles and mammals [7, 8].

Electrodialysis (ED) is a competing process to pressure driven membrane processes such as reverse osmosis (RO) for brackish water and water reuse applications. However, any contaminant that RO is designed to retain occurs in elevated concentrations in the concentrate making its discharge to the environment questionable. These concentrates contain salt, nutrients and inorganic and organic contaminants such heavy metals and steroidal hormones [9]. Currently there has been little research on the treatment of these concentrates [10], but the treatment of this waste stream will improve the health of receiving waters and reduce the risk of increased build up of contaminants if these wastes are recycled through wastewater treatment plants. While the treatment of steroidal hormones by membrane processes such as microfiltration (MF), nanofiltration (NF) and RO have been widely reported [11, 12], studies on the fate of hormones in ED are limited. Pronk *et*

49 *al.* [13] observed considerable sorption of 17 α -ethinylestradiol (75%) to membranes during batch
50 ED experiments for the treatment of urine. However, the mechanisms governing hormone sorption
51 by ion-exchange membranes are not understood.

52 The complexation of polar organic compounds with organic matter (OM) has previously been
53 reported [14]. Humic acid (HA), a component of OM, can cause serious fouling in ED due to its
54 negative charge and subsequent sorption by AEMs [15]. Previous studies have shown that hormone
55 sorption to membranes in other membrane processes are dependent on solution pH and properties of
56 the membrane, hormone and OM [16, 17]. The influence of OM on hormone sorption in ED is
57 unknown.

58 The purpose of this study was to elucidate the fate of steroidal hormones in ED and to
59 determine the influence of solution pH, OM and hormone type on these interactions. An
60 understanding of the partitioning of hormones between water and ion-exchange membranes ($\log$
61 $K_{AEM/CEM}$) is important for the prediction of their fate in ED. Therefore, differences in sorption of
62 the hormones estradiol, estrone, progesterone and testosterone to ion-exchange membranes were
63 investigated in sorption isotherm experiments. The behaviour of progesterone and estrone during
64 batch and continuous ED experiments were evaluated to identify differences in sorption between
65 undissociated (progesterone at pH 7 and 11, estrone at pH 7) and dissociated compounds (estrone
66 pH 11). ED experiments were conducted with and without HA.

67

68 **2. Materials and Methods**

69 *2.1. Chemicals*

70 All chemicals used were of analytical grade. The background solution was comprised of 5 g/L
71 NaCl and 84 mg/L NaHCO₃ (Fisher Scientific, UK). NaOH and HCl used for pH adjustments (1
72 mol/L) and membrane desorption experiments (0.002 mol/L) and Na₂SO₄ (0.5 mol/L) used in the
73 electrode rinse were purchased from Fisher Scientific (UK). Radiolabeled [2,4,5,7-³H] 17 β -
74 estradiol, [2,4,5,7-³H] estrone, [2,4,5,7-³H] progesterone and [2,4,5,7-³H] testosterone (> 98.5%

75 purity; 37 MBq/mL) were purchased from GE Healthcare (UK). Non-labelled hormones ($\geq 98\%$
76 purity) were purchased from Sigma Aldrich (UK). Stock solutions of radiolabeled (100 $\mu\text{g/L}$) and
77 non-labelled (990 mg/L and 1000 mg/L) hormones were prepared in methanol (CH_3OH) (Fisher
78 Scientific, UK). Physicochemical properties of the hormones are outlined in Table 1.

79 The OM used was HA sodium salt (Sigma Aldrich, UK). While the concentration of OM in
80 treated wastewater and natural waters is highly variable (0.5-100 mg C/L) [18], 12.5 mg C/L was
81 used for experiments containing HA. The negatively charged HA (neutral-basic pH) includes
82 carboxylic, phenolic, alcohol/aldehyde acids and methoxyl functional groups [19].

83

84 [Table 1]

85

86 2.2. Sorption isotherm and desorption experiments

87 Radiolabeled (100 ng/L) and non-labelled hormones were added to 100 mL background
88 solutions (adjusted to pH 7) to make the following concentrations: 0.1, 0.5, 1, 10, 100 and 2500
89 $\mu\text{g/L}$. A 2 cm^2 segment of anion- (AEM) or cation-exchange membrane, the same type used in the
90 ED experiments (CEM) (3 replicates/membrane; thickness: AEM 0.14 mm, CEM 0.17 mm), was
91 added to each solution bottle and shaken in an incubator shaker (Certomat BS-1, Sartorius) at 200
92 RPM and 25°C for 100 hours. All membranes used in this study were equilibrated in 0.5 M NaCl
93 solution before each experiment. Samples (0.5 mL) were taken from each bottle before membrane
94 addition and periodically during each experiment for hormone analysis. Solutions without
95 membrane addition were shaken to determine possible hormone sorption to the glass bottles.
96 Hormone desorption from the membranes used in the 1 $\mu\text{g/L}$ isotherm experiments was determined
97 by AEM or CEM addition to 100 mL solutions of 0.002 mol/L NaOH and HCl and ultrapure water
98 (UW) shaken for 288 hours.

99

100 2.3. Electrodialysis system, membranes and protocol

ED experiments were carried out using a BEL-500 ED stack (Berghof, Germany) with six Neosepta AEMs and seven CEMs (supplied by Eurodia, Germany; manufactured by ASTOM Corporation, Japan) with an available membrane area of 58 cm² each. The membranes contain alkylammonium (AEM) and sulfonic acid (CEM) ion-exchange groups, attached to a polystyrene-divinylbenzene matrix (PS-DVB) on a polyvinyl chloride (PVC) gel supported by PVC cloth [20]. The thicknesses of the AEMs and CEMs were 0.14 and 0.17 mm, respectively. The volumes of the AEMs and CEMs were 4.9 and 6.9 cm³, respectively [21]. The distance between the membranes in the stack (i.e. membrane spacer distance) was 0.06 cm. The stack was connected to a DC power supply (Model GPR-1810HD, GW Instek, Taiwan) with an applied voltage of 10 V fixed for all ED experiments. The feed, diluate, concentrate and electrode rinse flow rate was 1.5 L/min (I/P Variable speed pump system, Masterflex, USA).

Continuous (diluate and concentrate recirculated to one feed container) and batch (separate diluate and concentrate containers) experiments were undertaken. Feed solutions (2500 µg/L progesterone or estrone, 4L total) for continuous ED experiments were prepared in the background solution. The hormone concentration used in the ED experiments was greater than the concentration found in natural waters due to the high sorption capacity of the membranes. To determine the influence of solution pH on hormone sorption during continuous ED experiments, the feed pH was maintained constant by the addition of 1 mol/L HCl and/or NaOH. Before the continuous experiments with HA were performed, the feed was stirred for 24 hours to allow for hormone-HA equilibrium. Sorption within the diluate and concentrate was evaluated in batch experiments undertaken after the completed continuous experiments (continuous solution separated into diluate and concentrate). Due to estrone dissociation at pH 11, extended batch ED experiments (estrone concentration 2500 µg/L) were carried out to evaluate possible estrone breakthrough. Desorption of estrone in ED was evaluated, whereby the diluate and concentrate was filled with background electrolyte solution (adjusted to pH 7) and the system was rerun in batch desalination mode.

126 Samples were collected at the beginning of each ED experiment and periodically for hormone (0.5
127 mL) and UV-Vis absorbance (3 mL) analysis.

128

129 2.4. Analytical methods

130 Hormone samples (0.5 mL) were mixed with 3.5 mL Ultima Gold® LLT (Perkin Elmer, UK)
131 and analysed using a scintillation counter (LS 6500, Beckman Coulter, USA). Hormone
132 concentration was ascertained from a linear regression performed on calibration standards (0.01,
133 0.1, 1, 10, 100 and 1000 ng/L). The pH, electrical conductivity and temperature of samples
134 periodically taken from the feed, diluate and concentrate during ED experiments were measured
135 (Multiline P4 pH electrode, WTW, Germany). The conductivity of the feed (continuous
136 experiments) and the initial diluate and concentrate conductivity (batch experiments) was on
137 average 15.5 mS/cm. UV-Visible Spectrometry (Varian Cary 100 Scan, UK) was used to determine
138 the absorbance of HA (wavelength of 254 nm) in samples.

139

140 3. Results and Discussion

141 3.1. Hormone sorption in batch sorption isotherm tests

142 Hormone concentration decreased significantly in the isotherm experiments indicating
143 membrane sorption with two sorption processes: (1) Initial surface sorption and (2) diffusion
144 limited sorption within the membrane (Figure S1). The amount of hormone sorbed ($\log C_{AEM/CEM}$)
145 increased as the solution phase concentration ($\log C_w^t$) increased ($R > 0.99$) (Figure 1). Isotherm
146 deviation from linearity at 2500 µg/L indicates that membrane sites were beginning to be saturated.
147 The hormone-membrane partition coefficients ($\log K_{AEM/CEM}$, calculated for equilibrium at 100
148 hours) are given in Table 2.

149 Photodegradation and biotransformation of hormones from aqueous samples have been
150 reported [22]. Control sorption experiments using covered solutions and biocide addition (0.5 %
151 sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$)) were carried out to measure hormone sorption to and/or

152 volatilisation from the sample bottles. There was no significant difference between the control (e.g.
153 Estradiol, Covered: AEM 155.2 ± 3.8 ng/cm³, CEM 85.5 ± 2.7 ng/cm³; Biocide: AEM 153.4 ± 3.7
154 ng/cm³, CEM 80.0 ± 3.7 ng/cm³) and experiments without degradation prevention (AEM $159.0 \pm$
155 2.8 ng/cm³; CEM 84.9 ± 1.2 ng/cm³). Sorption to glassware was minimal with the bulk lost within
156 48 hours (% of initial hormone mass, Estradiol: $3.2 \pm 1.1\%$, Estrone: $2.7 \pm 0.9\%$, Progesterone: 3.4
157 $\pm 2.3\%$, Testosterone: $3.9 \pm 1.2\%$). Log $K_{AEM/CEM}$ values were adjusted accordingly to account for
158 this loss.

159

160

161 [Figure 1]

162

163 [Table 2]

164

165 3.2. Hormone sorption mechanisms

166 Pronk *et al.* [13] postulated that hormone sorption to ion-exchange membranes was related to
167 hydrophobicity. Poor correlation between the log K_{ow} (Table 1) and log $K_{AEM/CEM}$ values (Figure S3,
168 SI) suggests other mechanisms contribute to sorption at neutral pH. Since the hormones are
169 undissociated at pH 7 (pH of isotherm experiments) electrostatic interactions are not possible.
170 Previous studies have suggested hydrogen bonding as the mechanism for the adsorption of
171 hormones to membranes [12, 23]. The possible hydrogen bonding formations between the
172 hormones that exhibited strongest AEM (estrone) and CEM (progesterone) sorption are illustrated
173 in Figure 2. Hormones can be hydrogen-donors (contain phenolic OH groups) or hydrogen-
174 acceptors (contain C=O groups). The AEM functional group (N(CH₃)₃) can bond with molecules
175 containing hydrogen-donor and acceptor groups [24] and presents more opportunities for bonding
176 than the CEM, thus accounting for the higher log K_{AEM} values. Since the AEM functional group is
177 dissociated and may be strongly hydrated, another interaction mechanism namely cation- π

178 interactions are proposed for the interaction between the AEM and the hormones. Cation- π
179 interactions, which are comparable in strength to hydrogen bonding, are prominent in a wide range
180 of chemical and biological systems and should be considered as an important and general non-
181 covalent binding force [25]. The interaction of RNH_3^+ with double bonds is thought as a form of X-
182 $\text{H}\cdots\pi$ hydrogen bonds. Because many different forces contribute to molecular binding (e.g. donor-
183 acceptor, cation- π , hydrophobic, ion pair and ion-dipole interactions, dispersion and van der Waals
184 forces), it is often difficult to define the contribution from a specific interaction. However, cation- π
185 interactions between the hormone functional groups and the AEM functional group and PS-DVB
186 membrane matrix can further explain the higher hormone sorption to the AEMs. Estrone and
187 estradiol sorption to the AEM would be facilitated through hydrogen bonding between the AEM
188 $\text{N}(\text{CH}_3)_3$ hydrogen-donor group and the C-17 $\text{C}=\text{O}$ and C-17 OH groups, respectively, coupled with
189 minor contribution from the predominantly hydrogen-donor C-3 OH group [26]. The higher log
190 K_{AEM} for estrone ($0.53 \pm 0.13 \text{ L/cm}^3$) compared to estradiol ($0.39 \pm 0.10 \text{ L/cm}^3$) suggests the
191 bonding strength of C-17 OH in estradiol is lower compared to C-17 $\text{C}=\text{O}$ in estrone. Testosterone
192 exhibited the lowest sorption by AEM due to the poor hydrogen accepting ability of its C-17 OH
193 group [26].

194

195 [Figure 2]

196

197 Studies on the determination of steroids using molecularly imprinted polymers (MIPs) found
198 that the C-17 OH group is more important for interactions compared to the C-3 OH group due to
199 steric constraints between the MIPs and C-3 OH groups [27]. Hormone sorption to ion-exchange
200 membranes would be influenced by hormone structure and the space available for interaction. The
201 lower log K_{AEM} of progesterone can be attributed to the steric constraints around the C-20 $\text{C}=\text{O}$
202 group available for approaching the AEM compared to the C-3 $\text{C}=\text{O}$ group [28]. Although estrone
203 and progesterone both contain C-17,20 $\text{C}=\text{O}$ groups, studies have demonstrated that the C-3 $\text{C}=\text{O}$

moiety in progesterone is a triple hydrogen acceptor (i.e. can accept hydrogens directed from 3 positions) and provides for more space for approaching the CEM hydrogen-bond donors [28, 29]; thus explaining the greater $\log K_{CEM}$ for progesterone ($0.22 \pm 0.13 \text{ L/cm}^3$) than estrone ($\log K_{CEM} 0.04 \pm 0.01 \text{ L/cm}^3$), testosterone ($\log K_{CEM} -0.16 \pm 0.05 \text{ L/cm}^3$) and estradiol ($\log K_{CEM} -0.24 \pm 0.05 \text{ L/cm}^3$). These results suggest that the C-17 OH group in estradiol and testosterone is not as strong as the C-20 and C-17 C=O group in progesterone and estrone, respectively. This is substantiated by Gancia *et al.* [30] who quantitatively estimated the hydrogen bonding strengths of hydrogen donor ($\log K_\alpha$, C=O) and acceptor ($\log K_\beta$, OH) functional groups in a range of chemical structures. It was found that the hydrogen bonding strength of the C-17,20 C=O group ($\log K_\beta 1.52\text{-}1.61$) was greater than the C-17 OH group ($\log K_\alpha 0.91$), thus explaining the higher $\log K_{AEM}$ for estrone ($\log K_\beta 1.61$) compared to estradiol ($\log K_\beta 1.36$).

215

216 3.3. Hormone sorption in Electrodialysis

217 3.3.1. Effect of solution pH

ED experiments were carried out to elucidate the mechanisms of hormone sorption in ED. The mass of progesterone and estrone sorbed per unit volume of membrane within the ED stack ($\mu\text{g/cm}^3$) during continuous ED experiments is shown in Figure 3. Progesterone sorbed more than estrone at pH 7 as a result of the greater sorption of progesterone to the CEMs and the larger volume of CEMs within the ED stack compared to the AEMs. The mass of progesterone sorbed at pH 7 ($922 \pm 28 \mu\text{g/cm}^3$) was similar to the mass sorbed at pH 11 ($874 \pm 26 \mu\text{g/cm}^3$) due to progesterone being undissociated under both pH conditions. While sorption kinetics (Figure S2) demonstrated rapid sorption within 4 hours, constant hormone mass sorbed was not reached indicating membrane diffusion. After the feed solution was separated into diluate and concentrate, progesterone sorption to the membranes continued within the diluate and concentrate (Figure 4). Pronk *et al.* [13] assumed that neutral compounds sorb to both AEMs and CEMs, which is confirmed by these results.

[Figure 3]

The mass of estrone sorbed at pH 11 ($487 \pm 24 \mu\text{g}/\text{cm}^3$) was less than the mass sorbed at pH 7 ($591 \pm 30 \mu\text{g}/\text{cm}^3$) due to estrone dissociation (pK_a 10.4; Table 1). At pH 7, estrone sorption would occur on both the AEMs and CEMs facing the diluate and concentrate. This continues at pH 11 for the neutral fraction, while dissociated estrone no longer sorbs to the negatively charged CEMs due to electrostatic repulsion. At pH 11 estrone sorption within the diluate ($116.4 \pm 5.9 \mu\text{g}/\text{cm}^3$) was greater than within the concentrate ($19.8 \pm 1.0 \mu\text{g}/\text{cm}^3$, Figure 4), indicating preferential transport towards the positively charged AEMs facing the diluate. Therefore, AEM penetration by dissociated estrone is possible at pH 11.

[Figure 4]

While estrone flux was low ($30\text{-}100 \text{ ng}/\text{cm}^2\text{h}$), breakthrough into the concentrate was noted after 10 hours of extended batch ED experiments (Figure 5a), confirming estrone diffusion through the AEM pores, of which ED membranes have an approximate radius of 3 nm [31], to the concentrate. The low flux also indicates that after estrone molecules penetrate the AEM they find more binding sites within the membrane to interact with. These results correlate with the slow diffusion kinetics demonstrated in Figure S2 and are in accordance with literature [13], where permeation of dissociated organic contaminants increased with membrane sorption. Therefore, it is postulated that estrone permeation is dependent on sorption to the membrane surface, diffusion through the AEM, desorption and diffusion from opposing membrane boundary layer. The significant decrease in estrone concentration in the diluate at 10.5, 12 and 13.5 hours is postulated to be due to the reduction in the concentration of competitive ions within the diluate (i.e. after the

diluate has been desalinated) and thus, enhanced transport of negatively charged estrone into the concentrate.

[Figure 5]

3.3.2. Effect of organic matter

Solute-solute interactions, such as hormone and OM complexation, have implications on hormone removal during wastewater treatment [17]. The mass of progesterone sorbed decreased in the presence of HA (pH 7: $758 \pm 23 \mu\text{g}/\text{cm}^3$, pH 11: $739 \pm 22 \mu\text{g}/\text{cm}^3$; Figure 3). The same trend was noted with estrone at pH 7 ($535 \pm 16 \mu\text{g}/\text{cm}^3$), while at pH 11 estrone sorption was slightly higher with HA ($508 \pm 15 \mu\text{g}/\text{cm}^3$). Neale *et al.* [32] reported high partitioning of hormones to HA ($\log K_{OM}$: Progesterone: pH 7 $4.59 \pm 0.25 \text{ L}/\text{kg}$, pH 10 $4.48 \pm 0.24 \text{ L}/\text{kg}$; Estrone: pH 7 $4.82 \pm 0.26 \text{ L}/\text{kg}$). This was attributed to interaction between the C-17 and C-20 C=O hydrogen-acceptor groups of estrone and progesterone, respectively, and the OH hydrogen-donor groups of HA. As ionic strength has implications for OM charge and conformation, as well as charge and solubility of trace organics, partitioning of progesterone and estrone to HA within the ED feed solutions would be reduced at a higher ionic strength due to negative charge shielding [33]. However, studies on the influence of ionic strength on the partitioning of trace organics to OM present conflicting results with some reporting no significant difference with increasing ionic strength [34] and others reporting a slight decrease in partitioning [32, 35].

The mass of hormone predicted to partition to HA as a percentage of the initial hormone feed mass was significant (Progesterone: pH 7 48.6%, pH 11 37.7%; Estrone: pH 7 82.6%). Experimental hormone sorption by the membrane L_{FD} (Progesterone: pH 7 84.6%, pH 11 82.0%; Estrone: pH 7 63.2) was greater than the predicted sorption PL_{FD} (Progesterone: pH 7 7.1%, pH 11 4.1%; Estrone: pH 7 8.4%), indicating the negligible contribution of solute-solute interactions to the membrane sorption. However, HA deposits on ion-exchange membranes can cause increases in

281 electrical resistance of the membranes and would reduce the area available for progesterone and
282 estrone sorption to the membrane surface. Thus, the decrease in progesterone sorption in the
283 presence of HA at pH 7 and pH 11 and estrone at pH 7 (Figure 3) is contributed to the deposition of
284 uncomplexed HA on the AEMs (HA sorption in hormone ED experiment: Progesterone: pH 7
285 19.7%, pH 11 15.2%; Estrone: pH 7 17.8%, pH 11 16.0%). At pH 11, charge repulsion between
286 dissociated estrone and HA coupled with electrostatic attraction between estrone and the AEMs
287 resulted in the increase in membrane sorption in the presence of HA.

288

289 Despite the high sorption of progesterone and estrone to the membranes, desalination was
290 achieved (Figure 6). The lower stack current from approximately 0.5 hours in the experiments
291 without HA is due to enhanced desalination and a subsequent lower conductivity. Also, while HA
292 deposited on the membranes, a decrease in current across the stack was not enhanced in the
293 presence of HA indicating that the membranes were not significantly fouled with deposited HA.
294 The increases in electrical resistance during batch experiments (Without HA: Progesterone 4.4-62.5
295 Ω , Estrone 4.5-71.4 Ω ; With HA: Progesterone 5.4-33.3 Ω , Estrone, 6.3-32.3 Ω) were due to the
296 depletion of ions within the diluate, of which this depletion was enhanced without the presence of
297 HA.

298

299 [Figure 6]

300

301 3.4. Desorption of hormones

302 Changes in solution chemistry influence the sorption process and can potentially release
303 hormones back into solution, particularly during backwashing and cleaning of membranes [11].
304 Analyses were carried out to determine whether hormones could be desorbed from the membranes
305 used in the sorption isotherm experiments. Partial desorption (20-30% initial mass sorbed) occurred
306 in the presence of HCl, NaOH and UW. Desorption from the CEMs, on average, was similar (HCl:

19.2 ± 5.1%; NaOH: 18.8 ± 8.3%; UW: 18.7 ± 0.8%) while it varied for the AEMs (HCl: 13.3 ± 4.5%; NaOH: 18.3 ± 12.6%; UW: 11.8 ± 3.8%). These results imply that waste attained from membrane cleaning processes may contain potentially high concentrations of trace organics. Membrane desorption was not only dependent on the initial mass sorbed but also on solvent pH and electrostatic interactions between the hormones and membranes. More estradiol (25.8 ± 0.3%) and estrone (24.7 ± 0.2%) was desorbed from the CEM with NaOH (pH ~10.8) compared to progesterone and testosterone, due to estradiol and estrone dissociation and subsequent electrostatic repulsion with the negatively charged CEM. Desorption of estrone from membranes used during continuous and batch ED experiments was investigated to determine if hormone desorption was facilitated by applied voltage and desalination. After 2 hours, 18.7 µg/cm³ of estrone was desorbed (3.8% of initial mass sorbed), indicating that desorption of estrone during desalination (at pH 7) is limited. However, the possibility that trace organics can desorb into the diluate exists.

4. Conclusions

The quantification of partition coefficients indicated strong sorption of steroidal hormones to the ion-exchange membranes and was postulated to be due to hydrogen bonding interactions and cation- π interactions between the hormone and membrane functional groups. Membrane sorption was dependent on hormone type, the position and strength of bonding of the hormone functional groups as well as the membrane bonding capacity. Electrostatic repulsion between dissociated estrone (which behaves similar to a charged organic acid) at alkaline pH and negatively charged CEMs reduces membrane sorption during ED. Adsorption/partitioning and diffusion mechanisms played a role in trace organic sorption with breakthrough of estrone noted after membrane saturation occurred. The permeation of trace organics is a possible environmental and health risk where removal is essential. The decrease in progesterone sorption in the presence of HA (pH 7 and 11) and estrone at pH 7 was attributed to uncomplexed HA sorption reducing the area available for hormone sorption to the membrane surface.

333 .

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340

341 **Supplementary Information Available**

342 For further information on the calculation of hormone sorption to the membranes, the water-
343 membrane partition coefficients, hormone-HA complexation and sorption/desorption kinetics
344 during isotherm and ED experiments, refer to Supplementary Information.

345

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443 **List of Tables**

444

445 Table 1. Physicochemical characteristics of the hormones studied.

446

447 Table 2. Membrane-water partition coefficients ($\text{Log } K_{AEM/CEM}$, L/cm^3) for the steroidal hormones.

Table 1

Property	[2,4,5,7- ³ H] 17 β -estradiol	[2,4,5,7- ³ H] Estrone	[2,4,5,7- ³ H] Progesterone	[2,4,5,7- ³ H] Testosterone
Formula	C ₁₈ H ₂₄ O ₂	C ₁₈ H ₂₂ O ₂	C ₂₁ H ₃₀ O ₂	C ₁₉ H ₂₈ O ₂
Molecular Weight (g/mol)	272.4	270.4	314.5	288.4
Solubility in water (mg/L 25°C) [36]	13	30	8.81	30
pK _a [37]	10.23	10.34	n/a	n/a
Log K _{ow} [38]	4.01	3.13	3.87	3.32
Hydrogen acceptors [39]	2	1	0	1
Hydrogen donors [39]	2	2	2	2
Structure ^a

^a Asterisk on hormone structure indicates location of tritium (³H) radiolabel.

Table 2

	$\text{Log } K_{AEM} (\text{L/cm}^3)^a$	$\text{Log } K_{CEM} (\text{L/cm}^3)^a$
Estradiol	0.39 (± 0.10)	-0.24 (± 0.05)
Estrone	0.53 (± 0.13)	0.04 (± 0.01)
Progesterone	0.37 (± 0.14)	0.22 (± 0.13)
Testosterone	-0.18 (± 0.03)	-0.16 (± 0.05)

^a $\pm$ indicates 95% confidence interval (C.I.)

List of Figures

Figure 1. Hormone-membrane sorption isotherms (AEM and CEM) for (A) estradiol, (B) estrone, (C) progesterone and (D) testosterone (1mM NaHCO₃, 85.5 mM NaCl, 0.1-2500 µg/L hormone, pH 7; sorption equilibrium 100 h).

Figure 2. Schematic of possible hydrogen bonding between the hormone molecules (A) estrone and (B) progesterone and the AEM and CEM functional groups at neutral pH.

Figure 3. Comparison between the mass of progesterone and estrone sorbed to the membranes (C_{stack} , µg/cm³) during ED experiments in the presence and absence of HA (1 mM NaHCO₃, 85.5 mM NaCl, 2500 µg/L hormone, pH 7-11, 10 V).

Figure 4. Concentration (µg/L) of estrone and progesterone in the diluate and concentrate at pH 7 and 11 in batch ED experiments (1 mM NaHCO₃, 85.5 mM NaCl, 10 V; diluate and concentrate feed solution sourced from continuous ED experiments; initial concentration: estrone pH 7 790 µg/L, pH 11 1055 µg/L, progesterone pH 7 374 µg/L, pH 11 466 µg/L).

Figure 5. (A) Concentration of estrone (µg/L) within the diluate and concentrate, (B) Stack electric current (A) and (C) Conductivity (mS/cm) during continued ED experiments; (1 mM NaHCO₃, 85.5 mM NaCl, pH 11, 10 V; 2500 µg/L estrone; step function indicates repetition of batch ED experiments).

Figure 6. (A, B) Conductivity (mS/cm) and (C, D) stack electric current (A) during batch ED experiments in the presence and absence of HA (1 mM NaHCO₃, 85.5 mM NaCl, 2500 µg/L hormone, pH 7, 10 V).