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Sorption of Pesticide Endosulfan by Electrodialysis Membranes

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Abstract

Endosulfan (ES) is a micropollutant found in reverse osmosis concentrates from water reuse applications. Electrodialysis (ED) can remove and recover charged solutes from such concentrates. While polar compounds cannot normally be removed, their fate in ED is important as they can contribute to membrane fouling/poisoning and be released during cleaning. High adsorption of ES to ED membranes was observed. Consequently, the influence of solution pH and presence of humic acid (HA) on sorption mechanisms of ES to ion-exchange membranes during batch sorption isotherm and ED experiments were investigated systematically. ES-membrane partition coefficients

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(log $K_{AEM/CEM}$) quantified through sorption isotherm experiments suggested that ES sorption was resultant of membrane catalysed ES degradation, hydrogen bonding and cation–π interactions between ES and membrane functional groups. ES sorption at pH 7 (550 μg/cm^3) was greater than sorption at pH 11 (306 μg/cm^3) due to alkaline hydrolysed ES and resultant decrease in bonding capacity with the membranes at high pH. The presence of HA reduced sorption at pH 7 (471 μg/cm^3) and 11 (307 μg/cm^3) due to HA competitive sorption. Partial membrane desorption was noted in isotherm (≤ 20%) desorption experiments and was dependent on the initial mass sorbed, solvent pH and resultant membrane interactions.

Keywords: Electrodialysis; Endosulfan; Adsorption; Ion exchange membranes; Organic matter; Pesticide.

1. Introduction

ES is a organochlorine insecticide that has been used extensively in agriculture for the control of insect pests of crops such as cotton, vegetables, fruit and tobacco [1]. ES movement via runoff and spray drift leads to contamination of aquatic environments [2]. Studies have shown that ES is toxic to fish and aquatic invertebrates [3], while potential human health impacts include cardiovascular, endocrine, gastrointestinal and respiratory toxicity [4]. The European Commission Directive on the Quality of Water Intended for Human Consumption sets a maximum admissible concentration of 0.1 μg/L per individual pesticide and 0.5 μg/L for the sum of pesticides in drinking water [5]. While ES concentrations in aquatic environments are generally low (< 1 μg/L) [2], in areas of application ES has been found in brackish groundwater at 4.2 μg/L [6] and up to 1700 μg/L in surface water [7]. Reverse osmosis (RO) concentrates from water reuse contain concentrated amounts of ES because ES is retained by RO.

ES is a mixture of two stereoisomers, α-endosulfan (α-ES) and β-endosulfan (β-ES) in the range of 64-70% and 29-32%, respectively [8] and may contain 2% endosulfan diol (ES diol) and 1% endosulfan ether (ES ether) [4]. The primary degradation product of concern is endosulfan sulfate

(ES sulfate), which is formed in the environment via microbial degradation of α- and β-ES [9]. ES can be hydrolysed to form less toxic ES diol [10].

The treatment of pesticides by membrane processes such as nanofiltration (NF) and RO has been widely reported [11-14]. Two mechanisms for pesticide adsorption to membranes have been suggested: hydrophobic interaction between pesticide and membrane surface [13] and hydrogen bonding between pesticide functional groups and membrane active layer [12]. ED is a viable technology for the desalination of brackish water [15], seawater [16] and solutions containing organics [17]. ED is more cost effective than RO in the salinity range of 1.5-5 g/L [18] and has the potential to treat the waste stream generated by pressure driven membrane processes, which are commonly used in desalination and water reuse applications. Such waste streams, or brines, contain salts, nutrients, organic matter (OM) and numerous micropollutants including pesticides, heavy metals, endocrine disrupting chemicals [19].

Mechanisms governing ES behaviour in ED and interaction with ion-exchange membranes have to date not been identified. Previous studies have suggested electrostatic and hydrophobic interactions between organic molecules and ion-exchange membranes [20]. Quantification of these mechanisms has to date not been possible. An understanding of ES partitioning between water and anion- (AEM) and cation- (CEM) exchange membranes is important for prediction of its fate in ED.

Strong interactions between OM and pesticides have been reported with pesticide sorption to OM influencing transport and fate of these compounds in other processes [21-22]. Agbekodo *et al.* [21] studied atrazine and simazine removal by NF in the presence and absence of OM. Removal increased from 50% to 90-100% with OM. The principle mechanisms for removal in the presence of OM were pesticide-OM complexation, membrane electrostatic repulsion and adsorption. In ED, OM deposits on membranes leading to fouling [23]. However, Park *et al.* [24] found that a small fraction of OM may permeate AEMs. The influence of OM on ES membrane sorption during ED is unknown.

The objectives of this study were to investigate 1) the interaction mechanisms between ES and ion-exchange membranes, 2) the influence of solution pH and OM on this interaction and 3) the fate

of ES during ED. Membrane-water partition coefficients (log $K_{AEM/CEM}$) for ES were determined in sorption isotherm experiments to elucidate the mechanisms governing membrane sorption. The influence of solution pH on ES membrane sorption during batch and continuous ED experiments was evaluated to identify differences in sorption between undissociated (pH 7) and degraded (pH 11) ES. Sorption isotherm and ED experiments were conducted with and without the presence of an OM. Results from this study were compared to membrane sorption of the steroidal hormone estrone during ED, due to similar sorption behaviour, whereby electrostatic interactions along with sorption and diffusion mechanisms were found to play an important role.

2. Materials and Methods

2.1 Chemicals

All chemicals used were analytical grade. NaOH and HCl used for pH adjustments (1 mol/L) and membrane desorption experiments (0.002 mol/L) and Na_2SO_4 (0.5 mol/L) used in the electrode rinse solution, were purchased from Fisher Scientific (UK). All experiments were conducted in a background solution of 5 g/L NaCl and 84 mg/L $NaHCO_3$ (Fisher Scientific, UK). Radiolabeled [2,3-^{14}C] ES (> 95% purity; 18.5 MBq solid form) was purchased from the Institute of Isotopes Co., Ltd. (Hungary). Radiolabeled [2,4,5,7-^{3}H] estrone (> 98.5% purity; 37 MBq/mL) (3.55 TBq/mmol) was purchased from GE Healthcare (UK). Non-labelled ES compounds (≥ 99% purity) and estrone (≥ 98% purity) were purchased from Sigma Aldrich (UK). Stock solutions of radiolabeled (100 μg/L) and non-labelled (990 mg/L and 1000 mg/L) ES compounds and estrone were prepared in methanol (CH_3OH) (Fisher Scientific, UK). Dichloromethane (CH_2Cl_2), used in the liquid-liquid extraction of unlabeled ES compounds was obtained from Acros Organics (Belgium) while trifluralin (75 mg/L) was used as an internal standard (Riedel-de Häen, Germany). Physicochemical properties of the ES isomers, degradation products and the hormone estrone are outlined in Table 1.

The OM selected for use was humic acid sodium salt (HA) (Sigma Aldrich, UK). Although OM concentration in natural waters is variable (0.5-100 mg C/L) [25], a concentration of 12.5 mg C/L

was used for experiments containing HA. The major functional groups of the negatively charged (neutral-basic pH) HA include carboxylic, phenolic and alcohol/aldehyde acids, and methoxyl [26].

[Table 1]

2.2 Sorption isotherm and desorption experiments

Radiolabeled (100 ng/L) and non-labelled ES (70:30 α-ES:β-ES mix) was added to 100 mL background solution (adjusted to pH 7) to make up concentrations of 1, 2, 10, 100 and 2500 μg/L. A 2 cm^2 segment of AEM or CEM (3 replicates/membrane) was added to each solution bottle and shaken in an incubator shaker (Certomat BS-1, Sartorius) at 200 RPM and 25°C for 100 hours. A sample (1 mL) was taken from each bottle prior to membrane addition and periodically during each experiment for ES analysis (total 11 samples per bottle). Solutions without membrane addition were included to determine possible ES sorption to the glass bottles. For experiments undertaken in the presence of HA the bottles were shaken for 24 hours prior to membrane addition to allow for ES-HA equilibrium. Samples (3.5 mL) from each bottle were taken prior to membrane addition and periodically during each ES-HA experiment for HA analysis. ES desorption from membranes used in the 1 μg/L isotherm experiment was measured in 100 mL solutions of 0.002 mol/L NaOH/HCl/ultrapure water shaken for 170 hours.

2.3 Electrodialysis system, membranes and protocol

A BEL-500 stack (Berghof, Germany) with six Neosepta AMX-SB AEMs and seven CMX-SB CEMs (supplied by Eurodia, Germany; manufactured by ASTOM Corporation, Japan) with an available membrane area of 58 cm^2 each was used in the ED experiments. The positively charged AEMs (basic) and negatively charged CEMs (acidic) used in the sorption isotherm and ED experiments contain alkylammonium and sulfonic acid ion-exchange groups, respectively, attached to the aromatic rings of a polystyrene-divinylbenzene (PS-DVB) matrix on a microporous polyvinyl chloride (PVC) gel supported by plasticized PVC cloth [27]. The thicknesses of the membranes were

0.14 and 0.17 mm for the AEM and CEM, respectively. The volumes of the membranes used during ED experiments were 4.9 cm^3 and 6.9 cm^3 for the 58 cm^2 AEM and CEM, respectively [28]. The stack was connected to a DC electric potential (GW Instek DC Power supply Model GPR-1810HD, Taiwan) through TiO_2-coated titanium electrodes. Flow rates in all compartments (diluate, concentrate and electrode rinse) were 1.5 L/min (Masterflex I/P Variable speed pump system, US). Continuous (diluate and concentrate recirculated to one feed container) and batch (separate diluate and concentrate containers) experiments were undertaken.

An applied voltage of 10 V was fixed for all ED experiments. Preliminary batch ED experiments (4L each, separate diluate and concentrate) with 100 μg/L (non-labelled) α-ES and ES sulfate were undertaken to establish the behaviour of these compounds during ED at pH 3 and 7. Feed solutions (2500 μg/L ES, 4L total) for subsequent continuous ED experiments were prepared in background solution. The ES concentration used in the ED experiments was much greater than the concentration usually found in natural waters due to the high sorption capacity of the membranes. To determine the influence of solution pH on ES sorption during continuous ED experiments, the feed pH was maintained constant by the addition of 1 mol/L HCl and/or NaOH. A new set of membranes was used in each continuous ED experiment to avoid interference from ES sorbed in previous experiments. Sorption within the diluate and concentrate was evaluated in batch experiments undertaken after the completed continuous experiments (continuous solution separated into diluate and concentrate). A mixed ES and estrone (2500 μg/L each) continuous experiment was undertaken to evaluate competitive sorption between compounds exhibiting similar behaviour. Samples were collected at the beginning of each ED experiment and periodically for ES and/or estrone (1 mL) and UV-Vis absorbance (3 mL) analysis.

2.4 Analytical methods

Radiolabeled ES and estrone were analysed using a Beckman Coulter scintillation counter (LS 6500). Samples (1 mL) were mixed with 7 mL Ultima Gold® scintillation cocktail (Perkin Elmer, UK) and measured in triplicate. ES and estrone concentration was ascertained from a linear

regression performed on calibration standards (ES: 0.1, 1, 2 and 5 μg/L; Estrone: 0.01, 0.1, 1, 10, 100 and 1000 ng/L). Gas Chromatography-Electron Capture Detection (GC-ECD) (Autosystem XL chromatograph with an electron-capture detector, Perkin Elmer, UK) was used for the determination of unlabeled α-ES, ES sulfate and ES diol within samples (100 mL) taken during preliminary ED experiments. Liquid-liquid extraction was undertaken with dichloromethane (50 mL) and the internal standard trifluralin (5 μL).

The pH, electrical conductivity and temperature of samples periodically taken from the feed, diluate and concentrate during ED experiments were measured using a pH/Conductivity meter (Multiline P4 pH electrode, WTW, Germany). UV-Visible Spectrometry (Varian Cary 100 Scan, UK) was used to determine the absorbance of HA (wavelength of 254 nm) in experimental samples.

3. Results and discussion

3.1 Preliminary electrodialysis experiments

In the early stages of this research, significant difficulties were encountered with the ES mass balance. Preliminary ED experiments showed a decrease in α-ES and ES sulfate within the diluate and concentrate (Figure 1). The concentration of α-ES within the diluate and concentrate (91.4% and 88.6% initial mass lost, respectively) decreased more than that of ES sulfate (80.6% (diluate) and 79.1% (concentrate)) at pH 3. The same trend was observed at pH 7. This observation led to thorough investigations of (a) losses to equipment, (b) volatilisation, and (c) degradation in an attempt to recover the ES.

[Figure 1]

Losses to equipment (a) are material dependent. Polystyrene sample containers were reported to sorb ES strongly, compared with glass [29] and stainless steel. In consequence, all process stream lines were converted from plastic to stainless steel where possible (small sections of silicon tubing were required for the peristaltic pump). ED experiments with α-ES and ES sulfate were repeated

with results showing a similar trend shown in Figure 1 indicating that losses to equipment were not significant.

Volatilisation (b) of ES from aqueous media in laboratory experiments has been attributed to its low water solubility and high volatility [29]. Control sorption experiments were undertaken to measure ES sorption to and/or volatilisation from 100 mL glass sample bottles. A loss of up to 20% was noted with the bulk lost in the beginning of the experiment. Log $K_{AEM/CEM}$ values determined in the sorption isotherm experiments were adjusted accordingly to account for this loss due to volatilisation. Diluate and concentrate containers were subsequently closed to prevent volatilisation during the experiments.

Heterogeneous electrochemical degradation (c) of organic compounds may occur on membranes and electrodes [30]. To establish if this is the case, diluate and concentrate were analysed for the presence of the degradation product ES diol (Figure 1A and C). ES diol was not detected in the initial diluate and concentrate samples at pH 3. However, a slight increase to 10.1 and 9.5 µg occurred during the experiment, respectively. While this indicates that such degradation occurs, it cannot account for the observed losses.

In consequence, the only other possible mechanism for ES losses is sorption to the membrane polymers. Sorption isotherm experiments were undertaken to quantify such ES sorption to the ion-exchange membranes.

3.2 Endosulfan sorption is batch sorption isotherm tests

ES concentration decreased significantly in the isotherm experiments indicating important membrane sorption. Two sorption processes are suggested; (1) Initial rapid surface sorption and (2) sorption in the internal surface of the membrane, which is slow and diffusion limited (Figure A1). Diffusion of ES within the membrane pores, of which ED membranes have an approximate radius of 3 nm [31], is possible along with sorption to the PVC support. The amount of ES sorbed (log $C_{AEM/CEM}$) increased as solution phase concentration ($\log C_w^t$) increased ($r^2 > 0.99$) (Figure 2). The isotherm linearity at low concentration (0.1-100 µg/L) suggests that partitioning into the membranes

was the dominant mechanism and that adsorption sites within the membranes were far from being saturated [32]. The deviation of the isotherms from linearity at 2500 μg/L indicates sites beginning to be saturated. As constant mass sorbed was not reached, 100 hours was arbitrarily chosen for the determination of the ES-membrane partition coefficients. There was no significant difference in AEM sorption with and without HA, and the slight decrease in CEM sorption in the presence of HA is within experimental error. In the absence of HA the determined membrane partition coefficients (log $K_{AEM/CEM}$) were 0.46 ± 0.10 L/m^3 and 0.14 ± 0.05 L/cm^3 for the AEM and CEM, respectively. In the presence of HA, log $K_{AEM/CEM}$ values were 0.42 ± 0.07 L/cm^3 and 0.01 ± 0.002 L/cm^3, respectively.

[Figure 2]

3.3 Endosulfan sorption mechanisms

Pronk *et al*. [33] studied the sorption of the hormone 17α-ethinylestradiol (75% initial mass sorbed) to ion-exchange membranes during batch ED experiments for the treatment of urine and postulated that sorption was due to hydrophobicity. However, a study by Banasiak [34] suggested that trace organic sorption (of steroidal hormones) to ion-exchange membranes was influenced by mechanisms other than hydrophobic interactions. The possible interactions between ES and the AEM and CEM functional groups are illustrated in Figure 3. Previous studies have demonstrated that trace organics primarily interact with membranes through hydrogen bonding [35-36]. The AEM functional group is capable of forming hydrogen bonds with molecules containing hydrogen-donor and acceptor groups [37] and presents more opportunities for bonding; thus accounting for greater ES sorption affinity compared to the CEM. AEM sorption of ES would be facilitated through bonding between the S-1 (S=O, C-7) and C-10 (C-O) hydrogen-acceptor groups and the AEM CH_3 hydrogen-donor group, while bonding between ES diol and the AEM would be between the C-7 and C-10 OH groups. However, the AEM quaternary ammonium group is dissociated and the cation may be strongly hydrated. Therefore, a novel interaction mechanism not previously considered is

proposed which is cation–π interactions [38]. The fixed positive charges of the AEM have high potential to attract the negative electron imbalance of the ring structure. The interaction of the non-metallic cation RNH_3^+ with double bonds can be thought of as a form of X-H···π hydrogen bonds. It is difficult to define the contribution to bonding from a specific interaction due to the fact that many different forces (e.g. donor-acceptor, cation–π, hydrophobic interactions, dispersion and van der Waals forces) contribute to molecular binding. However, the occurrence of cation–π interactions could further explain the higher sorption of ES to the AEM membranes. Bonding between ES and the CEM would be facilitated between the ES S-1 S=O group and the CEM OH group. In aqueous solutions, ES diol is the most common degradation product and can be reduced on a charged surface. It is postulated that ES is hydrolysed to ES diol on contact with the strongly basic AEM. Detection of ES diol (but not individual identification) in the form of ES was possible because of the utilisation and position of the ^{14}C label on ES. Bonding between ES diol and the CEM functional group would be facilitated through the ES diol OH bipolar groups.

[Figure 3]

Nerin *et al*. [39] studied ES sorption on low-density polyethylene (LDPE) films used as agricultural soil covers. A comparison between ES sorbed per unit area (ng/cm^2) showed greater sorption to the polystyrene based membranes (7 days: AEM 17.0 μg/cm^2; CEM 10.1 μg/cm^2) compared to LDPE (7 days: α-ES 0.3 ng/cm^2, β-ES 1.3 ng/cm^2). Considering one polymer repeating unit, the AEM (9 hydrogen-donors) presents more opportunities for bonding than LDPE (4 hydrogen-donors); thus demonstrating the influence of polymer type on sorption.

3.4 Endosulfan sorption in Electrodialysis

ED experiments were undertaken to elucidate the mechanisms of ES membrane sorption during ED. Sorption kinetics during continuous ED experiments exhibited immediate rapid sorption within 15 minutes followed by a steady increase to 550 μg/cm^3 at 4 hours (57.0% initial mass) (Figure 4).

Constant ES mass sorbed was not reached at pH 7 and 11 (306 μg/cm^3, 33.6%) with the kinetics indicating membrane diffusion. After the feed solution was separated, sorption continued within the diluate and concentrate at pH 7; indicating sorption to both the AEMs and CEMs. This confirms the results by Pronk *et al*. [33] whereby neutral compounds were assumed to sorb to both AEMs and CEMs. Above pH 10, ES degradation results from cleavage of the cyclic sulfite group [10] leading to the formation of ES diol. This process is accelerated by NaOH addition. The reduced sorption of ES diol at pH 11 can be predominantly attributed to the reduced bonding capability between ES diol and the membranes compared to ES.

[Figure 4]

At pH 7, when HA is > 99% dissociated, hydrogen bonding between the ES S=O and C-O groups and HA OH groups would occur. In the presence of HA ES sorption at pH 7 decreased by 79 μg/cm^3 (471 μg/cm^3, Figure 4) due to electrostatic repulsion between negatively charged ES-HA complexes and the CEMs. ES sorption at pH 11 was similar in the presence of HA (307 μg/cm^3). Hengpraprom *et al*. [40] found that ES diol sorption to HA-mineral complexes was less than α-ES due to its high water solubility. The complexation of ES diol and HA would not be as strong at pH 11 as undissociated ES diol contains 2 hydrogen acceptors compared to 3 hydrogen acceptors of ES (Table 1). Therefore, the minimal difference in sorption at pH 11 in the absence and presence of HA is due to reduction in ES diol-HA complexation coupled with the low mass of HA sorbed at pH 11 (0.52 mgC, 1.0% initial mass HA).

3.5 Desorption of endosulfan

Changes in solution chemistry can influence organic sorption and potentially release the organic back into solution. This has potentially serious membrane performance, health and environmental implications. Chang *et al*. [41] raised the issue of estrone desorption during backwashing and membrane cleaning of microfiltration (MF) membranes. Analyses were carried out to determine

whether ES could be desorbed from the membranes used in the sorption isotherm experiments. Partial desorption in the presence of HCl, NaOH (used in practical applications to clean membranes) and ultrapure water (UW) was noted with rapid desorption occurring within 24 hours (Figure A2). CEM desorption (HCl: 24.3% (% initial mass sorbed); NaOH: 27.9%; UW: 15.1%) was greater than AEM desorption (HCl: 12.4%; NaOH: 3.1%; UW: 8.3%) due to the greater mass of ES sorbed to the AEMs. More ES was desorbed from the CEM with NaOH (pH ~ 11) possibly due to ES degradation. Membrane desorption of ES is thus not only dependent on the initial mass sorbed but also on solvent pH. In practical applications, cleaning is usually performed with the ED membranes in situ, at relatively high flow velocity and under alkaline conditions. It is possible that trace organics such as ES can desorb into the diluate during reversal or cleaning. The significant desorption observed in this study further implies that wastewater obtained from the cleaning process of ED membranes used to treat water containing pesticides could contain potentially high concentrations of such contaminants. While the US EPA recommends less than 74 μg/L ES in waterways, exposure to just 1.3 μg/L is toxic to fish [3]. Exposure for short periods can cause adverse nervous system, stomach, blood, liver and kidney effects and death. Further treatment of the diluate, concentrate and cleaning solutions need to be considered when trace organics are amongst the target contaminants. These results are important as the risks associated with the disposal of ED membrane cleaning solutions have been not yet been addressed.

3.6 Comparison with hormone sorption

To gain insight into the general applicability of observations to other trace organics, the sorption of ES during ED was compared to that of estrone (E1). Estrone is a natural estrogen that is dissociated and negatively charged above pH 10.4 [42]. Estrone was selected due to its presence in effluents from conventional wastewater treatment plants [43] and its high sorption affinity for the ion-exchange membranes [34]. A dual compound ED experiment with both ES and estrone was undertaken at pH 7 and 11. Preferential sorption of ES was observed (Figure 5). Sorption ES and estrone was reduced at pH 11 possibly because of competitive sorption between the

degraded/dissociated ES and estrone and the ion-exchange membranes. It is interesting to note that ES sorption was greater in the dual compound experiment (pH 7: 596 ± 17.9 μg/cm^3; pH 11: 414 ± 12.4 μg/cm^3) than in the single compound experiment (pH 7: 550 ± 16.5 μg/cm^3; pH 11: 306 ± 9.2 μg/cm^3). A similar trend was noted for estrone at pH 11 (Single: 257 ± 4.9 μg/cm^3; Dual: 278 ± 5.6 μg/cm^3). However, the mass of estrone sorbed in the single compound experiment (pH 7: 380 μg/cm^3) was similar to the mass sorbed in the dual compound experiment (pH 7: 381 μg/cm^3). While further work is required to fully understand this competitive behaviour, results indicate that the sorption capacity of ED membrane is very high. In consequence saturation with ES and estrone was not reached at conditions that reflect the upper end of environmental concentrations.

[Figure 5]

4. Conclusions

The quantification of partition coefficients indicated strong sorption of ES to the ion-exchange membranes. While challenges remain to elucidate the contribution of specific interaction mechanisms to this sorption, it was postulated for those to occur predominantly due to hydrogen and cation–π interactions between ES and membrane functional groups. Alkaline hydrolysis of ES to ES diol influenced sorption whereby lower hydrogen bonding capacity between ES diol and the membranes reduced sorption at pH 11. The influence of solute-solute interactions between ES and HA on sorption during ED were minimal. The ED sorption behaviour of estrone (dissociated at pH 11) was similar to that of ES. Estimations based on ES sorption in the small-scale ED system used in this study, show that ES sorption in an industrial sized system would be significant. For example, in a commercially available ED stack with a membrane area of 370 m^2, approximately 17 kg of ES could potentially be sorbed. An accidental release to the environment or a water supply would have serious health implications, while this illustrates the potential of ED to concentrate and potentially remove a significant amount of such micropollutants via unconventional ED-sorption.

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Appendices

For further information on the calculation ES sorption to each membrane and the water-membrane partition coefficients along with sorption/desorption kinetics during batch isotherm and ED experiments and details of steroidal hormone sorption, refer to Appendix A.

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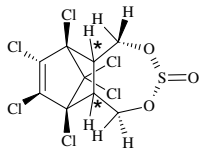
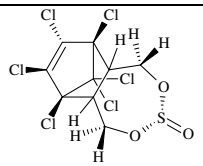
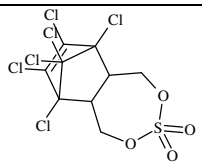
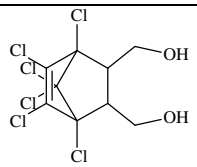
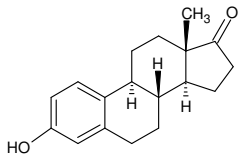
Table Captions

Table 1. Physicochemical characteristics of endosulfan compounds and the hormone estrone.

Table 1

Property	Endosulfan				Estrone
	α	**β**	**Sulfate**	**Diol**	
Formula	$C_9H_6Cl_6O_3S$	$C_9H_6Cl_6O_3S$	$C_9H_6Cl_6O_4S$	$C_9H_8Cl_6O_2$	$C_{18}H_{22}Cl_2$
Molecular Weight (g/mol)	406.93	406.93	422.9	360.88	270.4
Solubility in water (mg/L 20°C) [44-45]	0.51	0.45	0.48	300	1.3-30 (25°C)
pK_a [42, 46]	-	-	-	14.62-15.22	10.34
Log K_{ow} [47] [a]	3.83 (3.50)	3.83 (3.50)	3.66 (3.64)	(3.68)	3.13 (3.43)
Hydrogen acceptors	3	3	4	2 (bipolar)	2
Hydrogen donors	0	0	0	2 (bipolar)	1
Structure [b]					

[a] Values inside parentheses are estimated using KowWin Log P software [48]; [b] Asterix on α–ES indicates location of ^{14}C radiolabel.

Figure Captions

Figure 1. Concentration (μg/L) of α-ES, ES sulfate and ES diol within the concentrate (A, B) and diluate (C, D) at pH 3 and pH 7 (Average initial concentration of α-ES and ES sulfate were 92.4 and 92.0 μg/L, respectively).

Figure 2. ES sorption isotherms for the ion exchange membranes (A) CEMs and (B) AEMs with and without HA (± S.D. given to indicate standard deviation associated with data; time used to determine log $K_{AEM/CEM}$: 100 h).

Figure 3. Schematic of possible interactions between ES molecules and the CEM and AEM functional groups (Functional groups attached to polystyrene-divinylbenzene (PS-DVB) copolymer matrix).

Figure 4. Sorption (μg/cm^3) of ES to ion-exchange membranes during ED experiments (Average initial mass of ES 11176 ± 317 μg).

Figure 5. Sorption (μg/cm^3) of ES and estrone during mixed ED experiments (Initial mass of ES and estrone in solution were 889 ± 13 μg/cm^3 and 904 ± 37 μg/cm^3, respectively).