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## 2 Trace Contaminant Removal using Hybrid Membrane Processes in Water Recycling

A. I. Schäfer and T.D. Waite

### 2.1. INTRODUCTION

Water recycling plays an essential role in integrated water management, especially in an arid country like Australia but also worldwide [1]. Water recycling, however, has suffered extensive constraints due to "toilet to tap" media campaigns and "yuck factor" attitudes in the community. The support of the community for water recycling projects generally decreases as the personal contact with the recycled water increases [2]. Some of the very valid concerns of the community stem from uncertainties involved in water recycling, such as the issue of persistent organic pollutants (POPs) potentially present in recycled waters or the ever growing group of endocrine disrupting chemicals have been of particular concern to sections of the community.

Endocrine disrupters have the potential to interfere with our normal growth, development and reproduction. Modulation of that system could cause severe adverse health effects. Industrial chemicals, consumer chemicals and chemicals in the environment can be endocrine disrupters that mimic, enhance or inhibit the action of hormones [3, 4]. Sewage disposal to water sources may be a major exposure pathway for pharmaceuticals, synthetic and natural hormones, industrial chemicals to humans and wildlife, directly and via the food chain. This concerns disposal of treated effluents and applications of recycled water.

This paper aims to address some of the uncertainties and risks involved in recycling technology and aims to stress caution and the need for well designed recycling projects. This risk expands to water treatment in situations where contaminated waters are treated.

#### 2.1.1 Selection of High Priority Trace Contaminants

The list of trace contaminants or endocrine disrupters stemming from human activity found in wastewaters is long [5-15] and the problem has been apparent since the 1970s [16].

It was chosen to select the most relevant compounds for research activities based on four criteria- abundance in waters and wastewaters, high persistence in the environment, high potency as endocrine disrupters and analysis to below ng/L levels is feasible.

Compounds that suit those criteria best are natural and synthetic estrogens excreted by men and women in urine and faeces and with increased levels during pregnancy and hormone replacement therapy. Those compounds are excreted in conjugated form and are reactivated during biological treatment [17, 18]. While those compounds have an average persistence, synthetic hormones and chemicals have a much higher persistence, but lower potency. Natural hormones can be expected to be present in all municipal wastewaters and hence have a global relevance.

#### 2.1.2 Removal of Trace Contaminants in Treatment

Conventional wastewater treatment is not an effective barrier to trace contaminants. While removal rates published in the literature vary greatly, this appears to depend on local conditions and the nature of the contaminant [19-22].

The main characteristics which determine the fate of such contaminants in the water cycle is their ability to interact with particulates. These particulates can be naturally occurring (clays, sediments, colloids coated with natural organics, microorganisms) or added during treatment (activated sludge, powdered activated carbon, ion exchange resin, coagulants). The transition of trace contaminants to the solid phase will greatly enhance chances of removal. In contrast, the interaction of trace contaminants with dissolved organics can increase their mobility in the environment and through treatment [23].

The fate of natural and synthetic estrogens in wastewater treatment plants is uncertain. It is estimated that less than 10% of the compounds are removed via biodegradation, the majority of the compounds remain in the water phase while a considerable amount is adsorbed to the sludge [24].

The results reported here represent a component of a multi-faceted investigation into the mechanisms of removal of natural and synthetic estrogens in water and wastewater treatment. This involves adsorption to common particulates and membrane processes. An understanding of those mechanisms is essential to predict the likelihood of removal and the reliability of treatment.

### 2.2. MATERIALS & METHODS

#### 2.2.1 Chemicals and Analysis

All chemicals were of analytical grade. Radiolabelled estrone-2,4,6,7-<sup>3</sup>H(N) and estradiol-2,4,6,7-<sup>3</sup>H(N) were purchased from Sigma Aldrich (Saint Louis, Missouri, USA). The background electrolyte consisted of 1 mM NaHCO<sub>3</sub>, and 20 mM NaCl unless otherwise stated.

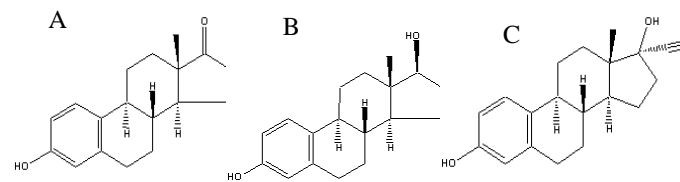


Figure 1 Structure of the contaminants of concern A: Estrone, B: 17β estradiol and C: 17α ethinylestradiol.

#### 2.2.2 Adsorbents

Adsorbents and other compounds that interact with pollutants used in this study were natural organic matter and IHSS FA and HA as previously characterised [25]. Cellulose with an average particle size of 20 μm, kaolin and bentonite, and FeCl<sub>3</sub> were purchased (Sigma Aldrich (Saint Louis, Missouri, USA)). Monodispersed spherical hematite particles with an average diameter of 75 nm were synthesized [25] and activated sludge taken from Brendale sewage treatment plant (Pine Rivers Shire, QLD, Australia). Magnetic ion exchange resin MIEX<sup>®</sup> was supplied by Orica Watercare (Melbourne, Australia) and powdered activated carbon type NORIT SAM 52 purchased from Norit (The Netherlands). The PAC had an average diameter of 20 μm and a surface area of 72.5 m<sup>2</sup>/g.

#### 2.2.3 Membranes & Filtration Protocols

Membrane filtration was performed in stirred cell experiments as described elsewhere [25]. Ultrafiltration (UF) and microfiltration (MF) flat sheet membranes were supplied by Millipore (Australia). UF submerged modules were supplied by Zenon Environmental (Burlington, Canada) and MF submerged membranes by Memcor (Windsor, Australia). Nanofiltration (NF) and reverse osmosis membranes (RO) were supplied by Koch Membrane Systems (San Diego, USA) and Trisep Corporation (Goleta, USA).

### 2.3. RESULTS & DISCUSSION

#### 2.3.1 Trace Contaminants - Natural Particle Interactions

The interactions of estrogens with natural particles was studied at particle concentrations to be expected in the environment, or in the case of activated sludge, during treatment. A summary of results is presented in Table 2.1.

Table 2.1 Interactions of Estrone with naturally occurring particulates (pH 7-8, 100 ng/L estrone, 1mM NaHCO<sub>3</sub>, 24h of adsorption)

Particle	Average Particle Diameter [μm]	Particle Concentration [g/L]	Estrone Adsorption [%]	Estrone Adsorption [ng/g*]
Hematite	0.075	6.3 · 10 <sup>-3</sup>	0.74	150.64
Kaolin	0.1-4	0.1	8.87	140.46
Bentonite	0.1-10	0.1	13.53	175.84
Cellulose	20	0.1	8.35	113.96
Activated Sludge	100	5.4	22.38	6.15

\* dry weight

When organic matter is added to the particle system, the adsorption of estrone increases considerably (see Figure 2) for all organics used (HA, FA and NOM) and over the pH 3-12 range. The largest increase of adsorption was provoked by HA at pH 3, hence the most aromatic, least soluble compound at conditions where the organics have the lowest charge. The increase due to the presence of natural organics can be explained with a modification of the colloid surface the interaction of estrone with the natural organics which adsorb on the hematite. Due to the high octanol-water partitioning coefficient the contaminants interact strongly with the natural organics.

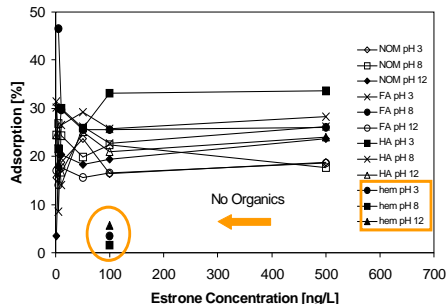


Figure 2 Impact of organic matter on adsorption of estrone by hematite

The implication of this is that trace pollutants in water and wastewater treatment systems are likely to be found associated with colloids as in natural systems most colloids have an organic coating. Further this effect can be taken advantage of to promote the removal of trace contaminants in water and wastewater treatment with the addition of adsorbents.

### 2.3.2 Removal of Trace Contaminants by Particle Addition

The addition of adsorbents is of advantage for the removal of trace contaminants, especially when membrane processes are used which do not retain trace contaminants. The objective of this study was a comparative investigation of common adsorbents used in the water and wastewater treatment industry, hence powdered activated carbon (PAC), ferric chloride coagulant (FeCl<sub>3</sub>) and Magnetic Ion Exchange Resin (MIEX) were used.

Figure 3 shows the impact of pH and ferric chloride dosage on estrone removal in jar test experiments. The removal of such compounds is minimal during coagulation. This was expected as coagulation tends to favour the removal of large and hydrophobic compounds. Adsorption to the iron hydroxide precipitates is very low. This interaction and removal may change in the presence of natural organics and such experiments are yet to be conducted.

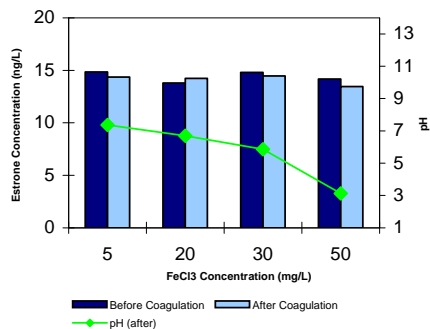


Figure 3 Removal of estrone with ferric chloride

With powdered activated carbon this is different. At relatively low concentrations of 5-10 mg/L PAC a substantial removal of estrone can be achieved as shown in Figure 4. Effects of competition are visible where adsorption in a 'clean'

buffer solution is much higher than in surface water or secondary effluent. In surface water and effluent other organics compete for adsorption. This competition could be due to the blockage of pores and restriction of diffusion of trace contaminants to the adsorbent surface or due to the competition for adsorption sites. At higher dosages there is a large excess of adsorbent and hence the difference in matrix diminishes.

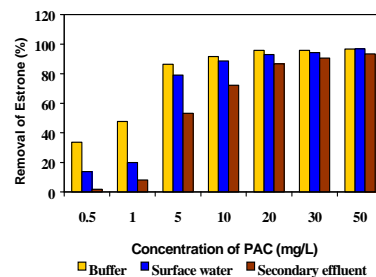


Figure 4 Removal of estrone with powdered activated carbon

Magnetic ion exchange resin (MIEX®) has been developed for water treatment applications for enhanced natural organics removal [26, 27]. The resin preferentially adsorbs small and charged compounds from natural organics mixtures [28]. In Figure 5 a light micrograph shows particles in the order of 10-100 µm and an electron micrograph a MIEX® particle with several small fractions broken off from particles. In higher resolution electronmicrographs the particles show a composition of the particles of very dense fibres, presumably magnetic iron compounds which give the resin its magnetic characteristics which lead to rapid aggregation if magnetised.

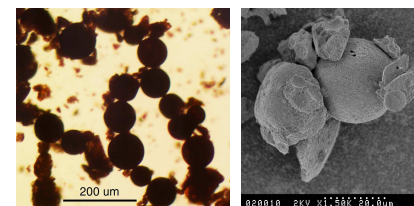


Figure 5 Light and electron micrograph of MIEX®

While the compounds studied are uncharged at neutral conditions, polar or hydrogen bonding interactions are responsible for a removal of up to 45% of the estrone which corresponds to an adsorption of 80-100 ng/g (Figure 6). This increases with pH- when the molecules are dissociated at a pH above 10.4, the removal increases drastically to about 70%. This strong pH dependence can be explained with an additional ion exchange mechanism when the molecules are dissociated and carry a negative charge. Given the nature of those contaminants, the removal of small polar compounds is somewhat surprising. The interactions are attributed to hydrogen bonding or hydrophobic interactions.

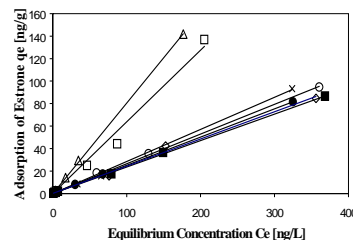


Figure 6 Removal of estrone with magnetic ion exchange resin (MIEX®)

There are a number of consequences from the above results. Both FeCl<sub>3</sub> and MIEX® are not very suited to remove the majority of the trace contaminant. PAC is better suited and appears to be the preferential choice PAC is added in a sufficiently high dosage.

However, both MIEX® and PAC are both commonly used in water treatment. It is very likely that those particles will accumulate contaminants and to date very little is understood about the behaviour of such contaminants during regeneration and changes in feed water characteristics.

### 2.3.3 Removal of Trace Contaminants by Membranes

While MF and UF are not expected to remove such small and polar compounds, a similar removal was observed initially for all processes. Removal was high at low and neutral pH, while it decreased substantially at a pH larger than 10.5. This could be attributed to adsorption effects, assumedly hydrogen bonding and hydrophobic sorption. This is shown for submerged MF (Memcor) and UF (Zenon) membranes in Figure 7. Those experiments were performed by adsorption tests of estrone on the membrane material without filtration. The adsorption of contaminants on hydrophobic membranes is higher than on hydrophilic materials.

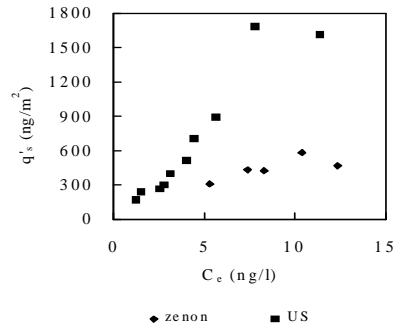


Figure 7 The Adsorption of estrone on submerged MF and UF membranes

Adsorption also dominates removal for some NF membranes. Some membranes remove estrone by size exclusion, others by adsorption. Figure 8 shows typical relationships between retention or permeate concentration and pH. As indicated previously the estrone molecule dissociates at pH 10.4 which leads to a drastic drop in retention. This behaviour shows that the retention occurs due to polymer-contaminant interactions as opposed to size exclusion. When the molecules take a negative charge at high pH, a repulsion between the negatively charged membrane and the organic anions causes reduced adsorption and facilitated transport through the membranes. For some very tight membranes (Figure 9) there is no effect of pH on retention which indicates that the 'pores' are smaller than the contaminants and the membrane is an effective barrier independent on solution chemistry.

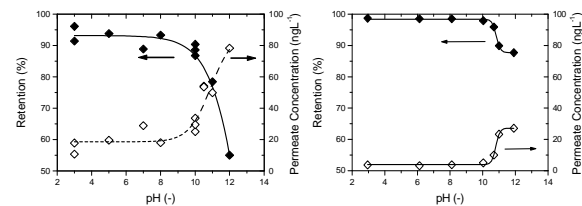


Figure 8 Retention and permeate concentration of NF (left, TFC-SR1) and RO (right, TFC-S) membranes

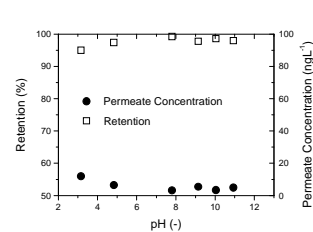


Figure 9 Retention and permeate concentration of X-20 membrane

The adsorption as a function of pH for the tighter membranes is illustrated in Figure 10. Results reflect the shape of the retention curves in Figure 8 and Figure 9. While the materials are different (polyamide on polysulfon support (TFC-S) and polyamide-urea composite (X-20) it appears that much of the adsorption of the TFC-S membrane is due to adsorption on the polysulfon support layer which offers a vast surface area. With the retention on the membrane surface of the X-20 membrane, the support is not available for adsorption and hence observed values are significantly smaller.

Those adsorption effects will only be operative during initial stages of filtration, but can cause the accumulation of a significant amount of trace contaminants and retention depends on the solution chemistry.

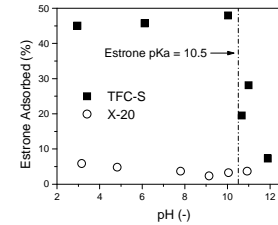


Figure 10 Adsorption for the TFC-S membrane and X-20 membrane as a function of pH

It is important to understand such retention and adsorption effects prior to membrane selection if the membrane is expected to act as a reliable barrier to contaminants. Such adsorption effects are also very important for the understanding of fate of pollutants in treatment systems and the possible desorption of contaminants during feed quality changes or cleaning operations.

## 2.4. CONCLUSIONS

While a broad range of results is presented in this paper, there is a common theme to the observations made regarding the interactions of trace contaminants, in this case a natural hormone estrone, and the materials used in treatment.

Powdered activated carbon clearly outperforms FeCl<sub>3</sub> and MIEX® in the removal of estrogens. Contaminants partition onto all particulates investigated in this study and interact with natural organics. Those findings are an essential contribution to the understanding of fate of contaminants in treatment systems as well as in the environment.

In membrane filtration, the retention mechanisms of some membranes are dominated by adsorptive effects while other membranes are capable of removing such small, polar compounds due to size exclusion. Adsorption decreases as the charge of the contaminants and the particle or membrane surface increases. During neutral charge conditions the adsorption of trace contaminants is maximised and this manifests itself with high intrinsic retention values. This retention, in the case of NF membranes, later shows a breakthrough behaviour (results not shown), unless the pore size of the membranes exhibits clear size exclusion phenomena. This was the case with tight RO membranes.

In water recycling, where a multiple barrier approach may be required to ascertain low risk for water users, treatment is likely to be beyond economic feasibility and the product water achieved using such technology would approach ultrapure water. It is hence essential to plan water recycling with an integrated water cycle approach and determine the most sustainable water usage.

In the light of such results and a heated public debate it appears unreasonable to assume that direct reuse of water for personal consumption is a sensible solution. However, if the discharge of moderately treated wastewater persists one needs to realise that the global water cycle is closed and contaminants will reach our drinking water sources. It is essential that further developments optimise the reduced use of synthetic chemicals, effective removal as well as destruction of the removed contaminants.

## 2.5. ACKNOWLEDGEMENTS

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