A survey of endocrine disrupting chemicals in sewage and a preliminary treatment trial

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Abstract

This paper demonstrates that synthetic endocrine disrupting chemicals (EDCs) (e.g. bisphenol-A) and natural EDCs (e.g. estrone and 17β-estradiol) were found in the crude sewage from two sewage treatment works. Conventional biological processes can lower EDC concentrations to several hundred nanograms per litre. Because natural EDCs (e.g. estrone and 17β1-estradiol) have biological activity and an adverse impact on the environment at extremely low concentrations (several tens of nanograms per litre), and because the existing wastewater/sewage treatment processes are not adequate to reduce natural EDC concentrations lower than 100 ng L⁻¹, further treatment after conventional biological processes is required.

Preliminary trials with ferrate(VI) and electrochemical oxidation processes demonstrated that the former is more effective than the latter in reducing EDC concentrations, and that both the processes can effectively reduce EDCs to very low levels, ranging between 20 and 100 ng L⁻¹.

Keywords

Endocrine disrupting chemicals; sewage treatment; ferrate(VI); electrochemical oxidation

Introduction

Since the middle of last decade, a variety of adverse effects of endocrine disrupting chemicals (EDCs) on the endocrine systems of man and animals have been observed, which are of particular environmental concern (see, for example, Piva and Martini, 1998; Thorpe et al., 2001). These effects may be cumulative, possibly will only appear in subsequent generations, and the resulting effects may be irreversible, threatening sustainable development. Most EDCs are synthetic organic chemicals introduced to the environment by anthropogenic inputs (e.g. bisphenol-A) but they can also be naturally generated estrogenic hormones, e.g. estrone and 17β-estradiol, and therefore are ubiquitous in aquatic environments receiving sewage effluents.

The structures and physicochemical properties of EDCs influence their fate and behaviour. As shown in Figure 1, estrone (E1) and 17β-estradiol (E2) consist of three hexagonal rings (A, B, C) and one pentagonal ring (D); both E1 and E2 are characterised by their phenolic ring (A), and bisphenol A consists of two phenolic rings joined together by a bridging carbon atom, with OH groups in the para position. Both phenolic ring in E1 or E2 and OH groups in bisphenol A are crucial for high-affinity binding to the acceptor sites of the estrogen receptor, resulting in the disruption of endocrine systems. Considering the serious adverse impacts of EDCs on human health and the environment, the study of an efficient approach for removing such chemicals to minimise their entry into natural waters is urgently required.

This paper reports the findings of a preliminary survey to investigate whether the EDCs are present in the influent and effluent of selected sewage treatment works and to assess if the current treatment processes (e.g. trickling filter and the activated sludge process) could effectively remove EDCs. In addition, this paper reports the results of a
preliminary treatment trial, where ferrate(VI) oxidation and an electrochemical oxidation were used to degrade/remove EDCs. The results could provide useful information about potentially efficient approaches for removing EDCs and thus minimise their entry into natural waters.

**EDCs: survey and results**

The selected sewage samples were collected from different sampling points on three days at two sewage treatment works (STWs). They were delivered to the laboratory for analysis of EDCs using a solid-phase extraction (SPE) with GC/MS/MS and/or HPLC/FTMS analytical protocol. STW1 has primary sedimentation, two-stage trickling filters, and two stages of post sedimentation; whereas STW2 has primary sedimentation, an activated sludge process with the post-sedimentation, and sand filtration.

Synthetic EDCs (4-tert-octylphenol, 4-nonylphenol, bisphenol-A, 16α-hydroxyestrone) and natural EDCs (estrone and 17β-estradiol) were found in the crude sewage from the two STWs. For the samples from STW1, the concentrations of various synthetic EDCs were between 20 and 451 ng L$^{-1}$; the dominant EDC was bisphenol-A (378–451 ng L$^{-1}$), and the concentration of 17β-estradiol was higher than that of estrone. Bisphenol-A, estrone and 17β-estradiol were not significantly removed by primary sedimentation. However, all EDCs in the effluents after the second humus tank (after two-stage trickling filters) were significantly reduced: e.g. from 450 to less than 100 ng L$^{-1}$.

Concentrations of various EDCs in crude sewage at STW2 were higher than that at STW1. The dominant EDCs were bisphenol-A (549–890 ng L$^{-1}$) and 4-tert-octylphenol (546–611 ng L$^{-1}$). Concentrations of all EDCs in the effluents after the activated sludge process and sedimentation were greatly reduced from several hundred nanograms per litre to less than 100 ng L$^{-1}$. However, the sand filter did not help to remove the remaining EDCs.

Natural EDCs (e.g. estrone and 17β-estradiol) were present in the treated effluents at the two STWs, although their concentrations were very low (several tens of nanograms per litre) in the effluents of either the second humus tank at SWT1 or post-sedimentation tank at SWT2. This is consistent with previous studies (Desbrow et al., 1998; Ternes et al., 1999), where natural estrogenic hormones were demonstrated to be among the most potent of all EDCs and were stable enough to survive in conventional wastewater and sewage treatment processes. Compared with synthetic EDCs, which have environmental impacts at concentrations of tens and hundreds of micrograms per litre, natural estrogenic hormones are biologically active at extremely low concentrations: less than 10 ng L$^{-1}$. This makes them even more threatening and difficult to deal with. Further
treatment (after conventional biological sewage treatment processes) has to be applied to completely remove natural EDCs. A preliminary trial was thus conducted.

**Treatment trials**

Bisphenol-A, 17 β-estradiol and estrone were used as targeted EDCs for the treatment feasibility study. For electrochemical oxidation, the working electrodes were made from DSA (dimension stable anode, titanium coated with transition metal oxides), graphite felt and titanium, whereas the corresponding counter electrodes were titanium, graphite felt and stainless steel, respectively. The geometric area of all electrodes was 34 cm². A double junction Ag/AgCl electrode was used as a reference electrode. The electrode potential or current density was controlled by an Autolab PGSTAT30 with the General Purpose Electrochemical System (GPES) software. Test solutions containing one of three EDCs at concentrations of either 0.1 or 1 mg L⁻¹ were prepared by mixing given amounts of EDC with one of electrolytes, either 3 g L⁻¹ Na₂SO₄ solution (which made the pH of the final solution approximately 7), or 3 g L⁻¹ Na₂SO₄ plus 4 g L⁻¹ NaOH solution (which made the pH of the final solution approximately 13). The sewage samples from STW1 were taken for the treatment trials, which were either primary sedimentation effluent or effluent from the first humus tank. Before and after electrochemical treatment, the concentrations of EDCs in the test solutions and real sewage were analysed. For the treatment of sewage, total and soluble COD were also measured. The test solutions and sewage were also used to examine the treatment efficiency of ferrate(VI) oxidation, where a jar test procedure was used to perform the experiments, involving a fast mixing after dosing the ferrate(VI) at 400 rpm for 1 min, slow mixing at 35 rpm for 20 min, and sedimentation for 60 min. The solution/sewage pH was kept between 7 and 8, and ferrate(VI) doses between 10 and 20 mg L⁻¹ were applied. After sedimentation, the supernatant was withdrawn for analysis of EDC concentrations.

**Results of electrochemical oxidation**

Cyclic voltammetry tests of 17β-estradiol, bisphenol-A and estrone at different solution conditions (pH 7 and 13) showed that there were no oxidation current peaks: i.e. the oxidation charge during the sweep in the positive direction was approximately equal to the reduction charge during the reverse sweep in the negative direction. An example of the results can be seen in Figure 2, which shows the voltammograms of the DSA electrode in 1 mg L⁻¹ of 17β-estradiol solution (pH 7) and at different sweep rates ranging from 2 to 200 mV s⁻¹. No current peak for 17β-estradiol oxidation was found in the test. The current varied with time was integrated to obtain oxidation charge and reduction charge in one cycle (listed in Table 1), and the data suggested that when the sweep rate was greater than 50 mV s⁻¹, the oxidation charge in positive direction was approximately equal to the...

![Figure 2](https://iwaponline.com/wst/article-pdf/52/8/1/434319/1.pdf)
reduction charge in negative direction during a reverse sweep. This implies that the process was essentially a reversible electrochemical oxidation and the reduction happened at the electrode surface. However, when the sweep rate was decreased to 2 mV s\(^{-1}\), the oxidation charge was increased to 2.491 C, while the reduction charge was almost the same as that at the sweep rate of 50 mV s\(^{-1}\). This suggests that the electrode surface was saturated by the oxidation product at the sweep rate of 50 mV s\(^{-1}\). The further decrease of the sweep rate made the most oxidation product leave the electrode surface and would not be reduced during reverse sweep. Such an explanation was supported by the voltammograms obtained with and without stirring in the same electrolyte (Figure 3). Figure 3 shows that the stirring had very little influence on the oxidation and reduction process, and the electrochemical process was essentially controlled by charge transfer. However, the oxidation of 17\(\beta\)-estradiol might be controlled by mass transport because its concentration in the solution was very low.

When the positive potential limit was increased from 1.12 V to 2 V (Figure 4), the oxidation charge in a positive sweep was four times more than the reduction charge in a reversible negative sweep, even at a high sweep rate of 200 mV s\(^{-1}\), indicating that as the electrode potential became higher, the oxidation product left the electrode surface quicker and the process was less reversible. There was still no current peak for oxidation of 17\(\beta\)-estradiol. However, it did not mean that 17\(\beta\)-estradiol could not be oxidised. When the electrode potential was high enough (e.g. 2.00 V versus Ag/AgCl, or 2.20 versus SHE), the rate of oxidation is to be determined by mass transport and the relation between the mass transport and limiting current density can be expressed by Equation 1:

\[
i = n \times F \times k \times c
\]

where \(i\) is the limiting current density, \(n\) is the number of electrons involved in the reaction, \(F\) is Faraday constant, \(k\) stands for mass transport coefficient and \(c\) for concentration of electro-reactive species. The concentration of 17\(\beta\)-estradiol in the experiment was only 1 mg L\(^{-1}\), i.e. 3.67 \(\times\) 10\(^{-6}\) M. Assuming that two electrons are involved in the total charge transfer and that the mass transport coefficient for 17\(\beta\)-estradiol is 10\(^{-5}\) m\(^{-1}\), the

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**Table 1** Oxidation charge and reduction charge of DSA electrode in 1 mg L\(^{-1}\) 17\(\beta\)-estradiol solution (pH 7) at sweep at different sweep rates

<table>
<thead>
<tr>
<th>Charges</th>
<th>200 mV s(^{-1})</th>
<th>100 mV s(^{-1})</th>
<th>50 mV s(^{-1})</th>
<th>2 mV s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation/C</td>
<td>0.479</td>
<td>0.6516</td>
<td>0.8665</td>
<td>2.491</td>
</tr>
<tr>
<td>Reduction/C</td>
<td>-0.4566</td>
<td>-0.6050</td>
<td>-0.7151</td>
<td>-0.7106</td>
</tr>
</tbody>
</table>

**Figure 3** Cyclic voltammograms of DSA electrode in 1 mg L\(^{-1}\) 17\(\beta\)-estradiol and sodium sulphate electrolyte of pH 7 at a sweep rate 100 mV s\(^{-1}\)
mass transport limiting current density would be only 0.0071 A m$^{-2}$. Therefore, such a small current density occurred after large oxygen evolution was buried in the water oxidation process. It would be impossible to form a separate visible current peak. Nevertheless, under various study conditions, the removal efficiency of three targeted EDCs could approach 99.9%.

The effluent from the primary settling tank was further treated with electrochemical oxidation. For the use of DSA as an anode at a current density of 58.8 A m$^{-2}$, and with electrolysis for 3 hours, most EDCs were completely removed, except for 4-nonylphenol and 4-tert-octylphenol; and the solution COD concentrations did not change. However, UV-254 absorbance decreased by more than 50%, indicating that the aromatic structure of the EDCs was destroyed but perhaps transformed into some other compounds. Using graphite felt as an anode at a current density of 29.4 A m$^{-2}$ could reduce all EDCs in the settling tank effluent to very low levels; however, the absorption capacity of the graphite felt electrode should be taken into account when considering the general results.

The results of using DSA as an anode at current densities of 58.8 and 117.6 A m$^{-2}$ for treating the effluent from the first humus tank demonstrated that estrone and 17β-estradiol can be reduced to very low concentrations (20–100 ng L$^{-1}$), but total and soluble COD concentrations did not change greatly before and after treatment.

**Results of ferrate(VI) oxidation**

Ferrate (VI) ion has the molecular formula FeO$_4^{2-}$ and is a very strong oxidant. In acidic conditions, the redox potential of ferrate (VI) ions is greater than ozone (Jiang and Lloyd, 2002). Moreover, during oxidation, ferrate (VI) ions are reduced to Fe(III) ions or ferric hydroxide, which simultaneously generates a coagulant in a single dosing and mixing unit process. A trial using ferrate(VI) to treat EDCs was conducted. Test solutions and sewage and jar test procedures used for the study were as described previously. For treating test solutions, ferrate(VI) can effectively reduce three EDCs concentrations to low levels (tens of nanograms per litre) at doses ranging from 13 to 7 mg L$^{-1}$ as Fe, with the removal percentage being 99.99%. For treating sewage effluent from the first humus tank, ferrate(VI) also performed very well at relative low doses (1–5 mg L$^{-1}$ as Fe). As

![Figure 4](https://iwaponline.com/wst/article-pdf/52/8/1/434319/1.pdf)

**Table 2** Analysis of treated sewage samples with ferrate(VI)$^+$ (ng/L)

<table>
<thead>
<tr>
<th>Samples</th>
<th>4-tert-Octylphenol</th>
<th>4-Nonylphenol</th>
<th>Bisphenol-A</th>
<th>Estrone</th>
<th>17β-estradiol</th>
<th>16α-hydroxyestrone</th>
</tr>
</thead>
<tbody>
<tr>
<td>TW1 supernatant</td>
<td>188.5</td>
<td>39.90</td>
<td>1209</td>
<td>30.10</td>
<td>52.54</td>
<td>63.7</td>
</tr>
<tr>
<td>After filtration</td>
<td>51.60</td>
<td>47.01</td>
<td>199.67</td>
<td>26.25</td>
<td>104.2</td>
<td>**</td>
</tr>
</tbody>
</table>

$^*$The original sewage taken from the effluent of the first humus tank in STW1

$^{**}$Lower than detection limits
shown in Table 2, all EDCs presenting in the first humus effluent were reduced to a low level, especially bisphenol-A, which was reduced substantially from 1.2 μg L\(^{-1}\) to 46 ng L\(^{-1}\). In outline, the optimum ferrate(VI) dose required to achieve the maximum EDC removal (>99.99%) was 0.10 mg EDC: 1 mg ferrate (as Fe) for treating test solutions, and 0.06 mg EDC: 1 mg ferrate (as Fe) for treating primary sedimentation effluents.

Table 3 shows the changes in COD and UV254 absorbance in treating sewage effluent. Ferrate(VI) can effectively remove approximately 31% soluble COD, 57% UV-absorbance, and 40% of total COD, demonstrating that the ferrate(VI) oxidation can mineralise the part of EDCs and other remaining organic contaminants. Comparing with electrochemical oxidation, which cannot reduce COD after treatment, ferrate(VI) should possess greater oxidation potential than the electrochemical oxidation process to degrade the EDCs.

Concluding remarks
This work demonstrated that synthetic EDCs (e.g. bisphenol-A) and natural EDCs (e.g. estrone and 17β-estradiol) were found in the crude sewage from two STWs. Primary sedimentation in the processes does not remove EDCs significantly, but two-stage trickling filters and activated sludge with post-sedimentation can lower EDC concentrations to between several tens and hundreds of nanograms per litre.

Because natural EDCs, e.g. estrone and 17β-estradiol, are most potent and have biological activity and an adverse impact on the environment at extremely low concentrations (several tens of nanograms per litre), further treatment after conventional biological sewage treatment processes is required.

Preliminary trials in treating either EDC test solutions (with starting concentrations of 1 mg L\(^{-1}\) or 0.1 mg L\(^{-1}\)) or sewages demonstrated that ferrate(VI) is more effective than electrochemical oxidation in reducing EDC concentrations, and both processes can effectively reduce EDCs to very low levels, ranging between 20 and 100 ng L\(^{-1}\). Since the starting concentrations of three targeted EDCs in test solutions were relatively high, the two natural EDC concentrations in the treated waters were still higher than 10 ng L\(^{-1}\). A fundamental study on EDC degradation with either ferrate, electrochemical oxidation or other oxidation technologies should be conducted in treating natural EDCs at lower starting concentrations (e.g. <10 μg L\(^{-1}\)), which will provide more useful information for the determination and selection of potential technologies for the effective degradation of EDCs.

Acknowledgements
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Table 3 Analysis of treated sewage samples with ferrate (VI)*

<table>
<thead>
<tr>
<th>Samples</th>
<th>pH</th>
<th>COD total (mg L(^{-1}))</th>
<th>tCOD(_{\text{soluble}}) (mg L(^{-1}))</th>
<th>tUV254-abs. (cm (^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TW1</td>
<td>7.8</td>
<td>89.0</td>
<td>67</td>
<td>0.17</td>
</tr>
<tr>
<td>Supernatant</td>
<td>5.5</td>
<td>53</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>After filtration (0.45 μl)</td>
<td>5.5</td>
<td>–</td>
<td>46.1</td>
<td>0.073</td>
</tr>
<tr>
<td>Percentage removal</td>
<td>40.4</td>
<td>31.2</td>
<td>57.1</td>
<td></td>
</tr>
</tbody>
</table>

*The original sewage taken from the effluent of the first humus tank in STW1
†The samples were filtered by 0.45 μ filter before analysis
References


