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Removal of Androgens and Estrogens from Water by Reactive Materials*

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Abstract

Nowadays, endocrine disruptor compounds in the water system have become a concern due to the risk of contamination to wild life and humans even at the nanogram level. Excess estrogens and androgens are a major contributor group of endocrine compounds. Statistical surveys have shown that dairy farms contribute to over 90% of the total estrogens in the UK and US. Reporter gene assays (RGAs) is being developed to assess the efficiency of reactive materials to remove target hormonal contaminants from dairy farm wastewater. This study demonstrates that 2 g of reactive materials (granular activated carbon (GAC), zero-valent iron (ZVI) and organoclay) efficiently removed over 50% of 17β-estradiol and 92% Testosterone over a 24 h period from 20 ml of HPLC grade water spiked at a concentration of 1000 ng l⁻¹. Therefore, these materials may be useful adsorbents for the advanced treatment of residual natural hormones in dairy farm wastewater.

Keywords: Dairy Farm Wastewater, Natural Hormones, Reactive Materials, Reporter Gene Assay

1. Introduction

Over the past twenty years, considerable scientific concerns and public debate have been expressed over the potential health risk posed by endocrine disrupting compounds (ECDs) which can alter the normal function of the endocrine system in wildlife and humans. Potential adverse effects of ECDs have concentrated mainly on reproductive and sexual development, immune function, the nervous system, thyroid function and hormone-related cancers. In addition, the concern of ECDs has been heightened by a number of human and experimental animal studies [1].

Drinking water is a potential source for human exposure to ECDs and is also a target for external measurements [1-3]. Surface waters destined for drinking water can be contaminated by a variety of natural steroid hormones (e.g. estrogens, androgens) as shown by surveys carried out on water samples taken near dairy farms [7,8].

Furthermore, similar concentrations of these hormones were found in fish within the same water system, providing further evidence of the potential for dairy farm wastewater in contaminating water systems [8].

In 2004, researchers began to study whether steroid hormones excreted by livestock in the UK are reaching streams and rivers where they could be feminising male fish. Related research in the US shows that intensive agriculture and aquaculture are sources of steroids capable of causing endocrine disruption in the aquatic environment [2].

A survey of dairy farm wastewater have demonstrated very high levels of estrogenic compounds compared to piggery or goat farm wastewater [9]. According to a Department for Environment, Food and Rural Affairs (DEFRA) survey of agricultural statistics on predicted estrogenic discharge from both the human and farm animal population in the UK, nearly half of the total UK estrogen discharges were attributed to dairy cattle, even though the population of cattle were only 1% of the total collective population of humans and farm animals [7].
The literature reports that 17α-estradiol, 17β-estradiol, estrone, testosterone (T) and androstenedione (ADT) are the potential contaminants detected in dairy farm waste water [1,10,13]. A summary of the levels and locations of these hormones detected in previous studies is presented in Table 1. These hormones have been selected as target compounds for the study of their efficient removal by reactive materials.

The best performers from selected reactive materials, which included granular activated carbon (GAC), zerovalent iron (ZVI) and organoclay, were determined using batch tests. ZVI has previously been used for groundwater remediation in permeable reactive barriers [10]. Granular activated carbon has been shown to have absorption capability for the removal of ECDs [3,11]. Previous studies have demonstrated that the removal efficiencies of GAC were greater than 90% for many ECDs [11]. Three types of ZVI (Connelly Iron, Gotthart Maier Iron, and Tübingen Iron) were used in the batch test. Although numerous studies have been carried-out on the treatment of organic and inorganic contaminants in water by ZVI [12,13], little research has been conducted on its remediation in permeable reactive barriers [10].

2. Materials and Methods

2.1. RGA Procedure

An estrogen (MMV-Luc) and androgen responsive cell line (TARM-Luc) were previously produced as described by Willemensen et al., 2004 [15]. For reporter gene assays, cells were seeded in a 96 well plate in 100 ml assay media (DMEM, 10% hormone depleted serum) and incubated overnight at 37℃. The next day, 100 ml assay media containing reconstituted samples was added to the cells and again incubated at 37℃ for 24 h or 48 h for the estrogen and the androgen assay respectively. The supernatant was then discarded and the cells washed with PBS prior to lysis and luciferase measurement on a luminometer.

RGA data was fitted with the sigmoidal dose-response curve equation to a four-parameter Hill plot, Y = Min Response + (Max response-Min response) / (1 + X/EC_{50})

Table 1. Hormonal contaminants detected in dairy farm wastewater.

<table>
<thead>
<tr>
<th>Group</th>
<th>Name</th>
<th>Detected concentration (ng L^{-1})</th>
<th>Sample location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estrogens</td>
<td>17α-estradiol</td>
<td>18.8–1028</td>
<td></td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>17β-estradiol</td>
<td>28.8–331</td>
<td></td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>Estrone</td>
<td>41–3123</td>
<td>New Zealand</td>
<td>[9]</td>
</tr>
<tr>
<td>Androgens</td>
<td>T</td>
<td>840± 75</td>
<td>Israel</td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td>ADT</td>
<td>650</td>
<td>US</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
the RGA.

3. Results and Discussion

RGAs have been successfully established with the ability to detect androgens and estrogens. A standard curve was also generated using increasing concentrations of T and the androgen responsive cell line TARM-Luc (Figure 1). The EC$_{50}$ obtained was 0.21 ng ml$^{-1}$. A standard curve was generated using increasing concentrations of 17β-estradiol and the estrogen responsive cell line MMV-Luc (Figure 2). The EC$_{50}$ obtained was 0.0012 ng ml$^{-1}$. These results correspond with the previously published data of Willemsen et al., 2004 [15]. The two assays provide highly sensitive tools for analysis of hormonal activity in the time-scale batch-test.

Figure 1. Androgen standard curve obtained using increasing concentrations of T, EC$_{50}$ = 0.21 ng ml$^{-1}$, incubation time 24 h. Error bars show ± standard deviation.

Figure 2. Estrogen standard curve obtained using increasing concentrations of 17β-estradiol, EC$_{50}$ = 0.0012 ng ml$^{-1}$, incubation time 24 h. Error bars show ± standard deviation.

Our preliminary data shows that all reactive materials removed over 92% of T and 50% of 17β-estradiol from spiked HPLC grade water (Figure 3). Tübingen Iron showed a higher capacity to remove both T (99.94%) and 17β-estradiol (79.40%), compared to the other reactive materials in this study.

To conclude, the previous studies confirm that dairy farm wastewater is a source of EDCs with androgenic and estrogenic activity, capable of contaminating surrounding surface and ground water. In order to reduce the potential environmental risk from dairy farm wastewater an efficient treatment system needs to be employed. The results from this study have confirmed that reactive materials can be used to remove this contaminating hormonal activity. Batch-testing is limited in its ability to select the best performing reactive materials as the dynamic flow condition in environments is more complicated than the rolling flow system used during batch-testing. Future studies could include investigations into how the reactive materials perform under various conditions including hydraulics and temperature. This could then influence the application of the reactive materials.

4. Acknowledgements

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5. References


[2] M. Burke, “UK to Tackle Endocrine Disrupters in Waste-


