Research Advancements in Ozone Treatment for Estrogenic Activities in Hospital Wastewater

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ABSTRACT: Hospital wastewater (HWW) is a source of estrogen activity compounds in the environmental water system. Once released into water bodies, these compounds disrupt the aquatic ecological balance and even affect human health. On the basis of domestic and foreign literature, the potential chemicals and their properties, such as construction features and toxicological effects, in HWW were summarized and discussed. The advantages of ozone in removing target substances were also summarized.

INTRODUCTION

Hospital wastewater (HWW) can lead to pollution as well as acute and chronic infections because of its complex composition once discharged. HWW contains a large quantity of pharmaceuticals, abstergents, organics, hormones, and hormone-like substances, and most of them are considered to have endocrine-disrupting effects [1,2]. The potential chemicals with estrogenic activities are common in HWW and should be a cause for concern. Research has extensively explored natural and synthetic estrogens as well as pharmaceutical compounds. These compounds harm the endocrine system and disrupt reproductive functions even at nd/L levels [3]. Most of these compounds have been investigated in drinking water, municipal sewage, and resurgent water. In addition, these compounds are relatively stable and are not always removed effectively in sewage treatment plants, thus making HWW a steady pollution source affecting natural water bodies [4]. Once discharged into the aquatic environment, the potential chemicals destabilize the aquatic ecosystem balance and even pose a threat to humans. Because estrogen is not easy to degrade in waste water and it infiltrates into the soil pollution of groundwater, soil and rivers. Lead to fish from a male to a female and human estrogen too much and other hazards. Thus, controlling and removing these contaminants are important and urgent undertakings.

Ozone disinfection is considered an efficient and optimal disinfection method that is only slightly affected by wastewater ammonia concentrations and does not cause secondary pollution [5]. Ozone is a highly selective oxidant that has been increasingly used to remove endocrine-disrupting compounds (EDCs) in wastewater treatment. At the same time, ozone not only remove estrogen, but also improve the biodegradability, decolorization, disinfection and so on.

This work aims to discuss the potential chemicals in HWW and the potency of ozone in removing EDCs. The potential chemicals are discussed in terms of variety, content, and character. The advantages and impact factors of ozone disinfection are described in detail.

POTENTIAL CHEMICALS IN HWW

HWW is an important source of estrogenic/antiestrogenic activity compounds in natural water bodies. Because many drugs contain estrogen substances, such as Nilestriel Tablets, estradiol, estradiol valerate, estradiol benzoate and so on. Potential chemicals can be released into wastewater through human excretion, consumed pharmaceuticals, abstergents used, and medical devices utilized [6–8]. Estrone (E1), estradiol (E2), and estriol (E3) are excreted in urine and feces as conjugated estrogens, which could be restored into parent chemicals via microbial actions [9,10]. Di-(2-ethylhexyl) phthalate (DEHP) injected into humans via mainline is quickly excreted before changing into mono-(2-ethylhexyl) phthalate or secondary metabolites after the use of medical devices [11]. Most of
these potential chemicals are detected in HWW in the range of ng/L to µg/L, and some of them show no significant difference to the chemicals found in municipal wastewater [12]. The potential chemicals and relevant concentrations in HWW are presented in Table 1. E2 and 17α-ethinylestradiol (EE2) are regarded as major substances that contribute to water estrogenic activity; EE2 plays a main role because E2 could change into E1 during bio-treatment [13]. After consumption, most of these chemicals are excreted as mixture metabolites and parent chemicals or other conjugates. Moreover, some of these metabolites and conjugates may reactivate and change back to parent chemicals under hydrolysis [14].

The research on diethylstilbestrol (DES) and other compounds is lacking despite the need to consider their potential hazards. DEHP is a plasticizer that is commonly used in polyvinyl chloride products to improve their flexibility [6]. DES is a synthetic estrogen that is routinely used to prevent spontaneous abortion [15]. Nonylphenol (NP) is widely used as a surfactant in laundry and cleaning practices and is a steady metabolite of nonylphenol ethoxylates in a natural environment [7].

**TOXICOLOGICAL EFFECTS AND DAMAGES OF POTENTIAL CHEMICALS**

Estrogen is the most diverse environmental hormone that can impede the development of the male reproductive system and induce breast hyperplasia [24]. The concentration of potential chemicals may be related to hospital scale, that is, large hospitals equate to high concentrations of potential chemicals [25]. Although traditional wastewater treatment technologies could remove these potential chemicals to some extent, the remaining compounds are harmful to aquatic organisms and even to humans who experience a prolonged exposure at low concentrations [26]. The toxicological effects and damages of potential chemicals are listed in Table 1. As shown in the table, these compounds manifest carcinogenic–mutagenic–teratogenic properties. Therefore, the removal of these compounds to reduce the negative effects of HWW is an urgent problem that requires an immediate resolution.

**EFFICIENCY OF EDC REMOVAL VIA OZONE**

Some advanced oxidation processes have been used to improve the removal efficiency of potential chemicals. Ozone disinfection has been increasingly used in wastewater treatment, thus improving technologies and reducing costs. Ozone disinfection is regarded as one of the most efficient methods of sterilization, given its minimal dependency on ammonia nitrogen content and in some extent negligible secondary pollution, in addition a relatively stable and staggering efficiency of approximately 600–3000 times of chlorine disinfection. Ozone reacts with hydroxyl ions to form OH radicals (·OH), which can rapidly react with many dissolved organic compounds [27]. Most potential chemicals show double bond and phenolic hydroxyl structures. Ozone can quickly react with double bonds, non-protonated amines, activated aromatic systems, and phenolic hydroxyls [28]. Many studies have demonstrated the superiority of ozone in removing EDCs. Xu et al. determined that approximately 90% of bisphenol A (1.0 mg/L) in raw water can be removed after treatment with ozone (2.0 mg/L) for 30 min [29]. Liu et al. reported that more than 90% of E1, E2, EE2, DES, and 4-n-NP can be removed with ozone (63.6 µg/L) in a static test [30]. Broséus et al. achieved more than 80% removal rate for caffeine, pharmaceuticals, and EDCs with the use of ozone (2 mg·min/L) to treat wastewater [27]. However, HWW is rarely involved in previous research on EDC removal via ozone because most of

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration [ng/L]</th>
<th>Detrimental Effects</th>
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</thead>
<tbody>
<tr>
<td>E3</td>
<td>17±15/6.4–385.5/17–1,000 [1,7,16,17]</td>
<td>Fetus, immune system, and reproductive effects [20]</td>
</tr>
<tr>
<td>EE2</td>
<td>nd–432/5–400 [1,18]</td>
<td>Fetus, immune system, and reproductive effects [20]</td>
</tr>
<tr>
<td>DEHP</td>
<td>nc</td>
<td>Cancer, fetus, reproductive, and liver effects [21]</td>
</tr>
<tr>
<td>DES</td>
<td>nc</td>
<td>Cancer, immune system, and reproductive effects [15, 22]</td>
</tr>
<tr>
<td>NP</td>
<td>nc</td>
<td>Cancer, development, and reproductive effects [23]</td>
</tr>
</tbody>
</table>

*Average concentration; nd: below detectable limit; nc: uncertain.*
these studies focused on drinking water and resurgent water.

The oxidation of potential chemicals in wastewater mainly occurs via ozone, ·OH, or a combination thereof, but may affect water qualities (e.g., temperature and alkalinity) during ozonation. The ozone concentration and oxidation rate of organic compounds are affected by water temperature [30]. Alkalinity and pH can change the ratio of ozone and ·OH by directly affecting the decomposition rate of ozone [31]. Bicarbonate can hamper ozonation by reacting with ·OH to form carbonate ions [32]. In general, the ratio of ozone and ·OH is the most important factor in ozonation. Furthermore, the results of previous studies have shown that bromates/iodates could be produced during the ozonation of wastewater containing bromide/iodide [33]. Therefore, water qualities must be considered to ensure the efficient removal of potential chemicals via ozone. In addition, the ozone oxidation mechanism must be investigated to develop and present a specific plan to reduce the negative effects of HWW.

**CONCLUSION AND OUTLOOK**

HWW is an important source of estrogenic activity compounds in natural water systems. The chemicals that remain in discharged water in the range of ng/L to µg/L are attributed to the low removal efficiency of traditional wastewater treatment processes. These residual chemicals may pose a threat to aquatic organisms and even to humans who experience prolonged exposure at low concentrations. In particular, these chemicals manifest carcinogenic–mutagenic–teratogenic properties, thus their detrimental effects. Therefore, these compounds should be removed to reduce the negative effects of HWW.

Ozone is considered to be an efficient disinfectant and is increasingly used in wastewater treatment. The application of ozone to remove EDCs from HWW is rarely investigated despite its proven superiority. Ozoneation is affected by water qualities, and the quality of HWW is different from that of resurgent water and drinking water. Therefore, the ozone oxidation mechanism for removing estrogenic activity compounds must be investigated, and a specific plan must be developed to reduce the negative effects of HWW. Overall, this issue is of significance.

**ACKNOWLEDGMENT**

This study was supported by the Guangxi Scientific Experiment Center of Mining, Metallurgy and Environment (No. KH2012ZD004), by the Guangxi Talent Highland for Hazardous Waste Disposal Industrialization, and by the Colleges and Universities in Guangxi Province Science and Technology Research Project (No. 2013ZD032).

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