REMOVAL OF EMERGING POLLUTANTS THROUGH WASTEWATER DISINFECTION

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EXTENDED ABSTRACT

Emerging contaminants is a rather diverse and heterogeneous group of chemicals consisting of pharmaceuticals and personal care products, steroids and hormones, drugs, fragrances, surfactants, flame retardants, perfluorinated compounds, complexing agents, etc. Among these, endocrine disrupting chemicals (EDCs), pharmaceuticals (Phs) and benzotriazoles (BTs) are compounds which present significant scientific interest due to their toxicological and chemical characteristics and their persistent detection in the aquatic environment. Wastewater treatment plants are a well known source and one of the most significant pathways for the transfer of such chemicals to the environment. It is well evidenced that most of these chemicals are only partially removed through biological treatment and therefore being detected in secondary effluents. Disinfection is most often the last stage of treatment before wastewater being disposed to the aquatic environment. The primary goal of disinfection is to reduce the pathogenic content of wastewater and its effectiveness on the removal of such chemicals is not well studied.

The objectives of this study were to assess the effectiveness of chlorination and UV disinfection to remove selected EDCs, Phs and BTs from secondary treated wastewater and to further investigate the role of crucial operating parameters such as chlorination contact time and UV dose, wastewater pH and total suspended solids content on process performance. Several chlorination batch tests have been performed with secondary treated wastewater samples, which were spiked with the target compounds and chlorine. A collimated UV source consisting of one low pressure lamp, was employed to assess dose response curves for each sample tested. UV dose (Ct) was calculated as the product of the UV intensity and the contact time. For the determination of the target compounds, wastewater samples before and after disinfection were analyzed. According to the results chlorination leads to an appreciable removal of EDCs and Phs even at the first minutes of chlorination. In contrast, the removal of BTs even at high chlorine doses of 245 mgCl2/Lt x min were very low. Regarding the effect of pH on chlorination efficiency, it seems that the removal of EDCs and Phs increases at pH values around 7. On the other hand, BTs removal is not significantly affected by the pH and TSS content of wastewater during chlorination. Furthermore UV disinfection at UV doses in the order of 40-150 mWs/cm² is not effective to remove Phs. From the target compounds tested, only ketoprofen and diclofenac exhibited appreciable removal only at higher UV doses.

KEYWORDS: Benzotriazoles, Chlorination, Disinfection, Emerging contaminants, Endocrine disrupting chemicals, Pharmaceuticals, UV disinfection.
1. INTRODUCTION

Emerging contaminants is a rather diverse and heterogeneous group of chemicals consisting of pharmaceuticals and personal care products, steroids and hormones, drugs, fragrances, surfactants, flame retardants, perfluorinated compounds, complexing agents, etc. Among these, endocrine disrupting chemicals (EDCs), pharmaceuticals (Phs) and benzo-triazoles (BTs) are compounds which present significant scientific interest due to their toxicological and chemical characteristics and their persistent detection in the aquatic environment. Several studies reported the frequent detection of these compounds into the aquatic environment in wastewater, surface waters, ground waters and in some cases in the drinking water (Pojana et al., 2011; Jonkers et al., 2012; Martinez Bueno et al. 2012). In the environment, emerging contaminants (ECs) are substances released from domestic, industrial, and agricultural sources (Yan et al., 2010). Wastewater treatment plants (WWTPs) are a well known source and one of the most significant pathways for their transfer to the environment (Tan et al., 2007; Stasinakis et al., 2008; Samaras et al., 2009). Beside the fact that these compounds are detected in low concentrations (ng/l) (Ratola et al., 2012), some of them present significant scientific interest due to their toxicological and chemical characteristics. In a recent study published in Science, Schwarzenbach et al. (2006) reported that one of the challenges that Environment Technology has to face in the future is the optimization of wastewater treatment processes, in order to achieve efficient removal of micropollutants. Under this frame, during the last years several scientific papers have been published, studying the removal of specific micropollutants in specific stages of wastewater treatment (Andersen et al. 2003; Joss et al. 2006; Radjenovic et al. 2009; Santos et al. 2009; Gros et al. 2010; Behera et al. 2011). The results which have been published for specific micropollutants categories and specific treatment processes indicate that partial or full removal of synthetic organic compounds can be achieved (Miege et al. 2009; Kasprzyk-Hordern et al. 2009; Onesios et al. 2009; Santos et al. 2009). In cases where synthetic organic compounds are not sufficiently degraded by biological processes during wastewater treatment, either because of a high persistence to biodegradation or limited biological activity during treatment, as can be found in cold areas, improvement at the wastewater treatment plants by addition of further treatment technology such as chemical oxidation seems to be a reasonable solution (Hey et al. 2011; Hey et al. 2012).

The objectives of this study were to assess the effectiveness of chlorination and UV disinfection to remove selected EDCs, Phs and BTs from secondary treated wastewater and to further investigate the role of crucial operating parameters such as chlorination contact time, UV dose, wastewater pH and total suspended solids content on process performance.

2. MATERIALS AND METHODS

2.1 Chlorination batch experiments

Chlorination batch experiments were performed in 4 l reactors. All batch experiments were performed with secondary treated wastewater samples spiked with the target compounds (presented in Table 1) at a concentration of 960 ng/l. Chlorine was added to the samples as liquid chlorine in the form of NaOCl and the initial chlorine dose in all experiments was equal to 15 mgCl₂/l. In order to test the effectiveness of chlorination, the chlorinated wastewater samples were collected at several contact times (2.5, 6, 15 and 40 min). After sampling and before analyses, residual chlorine was inactivated through sodium sulphite addition and accordingly was analyzed to confirm zero residual chlorine values.
Also, batch experiments were performed in order to investigate the behaviour of the aforementioned compounds at different pH values (6, 7.5 and 10). Based on the experimental protocol, the initial chlorine dose was 15 mg/l and the chlorinated wastewater samples were collected at a specific contact time (11 min). pH adjustment was done through addition of H₂SO₄ (1 N) to achieve a pH value of 6 and NaOH (1 N) to achieve a pH value of 10. The measured pH never varied by more than 0.2 units during the course of the experiments. After sampling and before analyses, residual chlorine was inactivated through sodium sulphite addition and accordingly was analyzed to confirm zero residual chlorine values.

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Short name</th>
<th>Group of compounds</th>
<th>Molecular type</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonylphenol</td>
<td>NP</td>
<td>EDCs</td>
<td>C₁₅H₂₄O</td>
<td></td>
</tr>
<tr>
<td>Nonylphenol monoethoxylate</td>
<td>NP1EO</td>
<td>EDCs</td>
<td>C₁₇H₃₀O₂</td>
<td></td>
</tr>
<tr>
<td>Nonylphenol diethoxylate</td>
<td>NP2EO</td>
<td>EDCs</td>
<td>C₁₉H₃₂O₃</td>
<td></td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>BPA</td>
<td>EDCs</td>
<td>C₁₅H₁₆O₂</td>
<td></td>
</tr>
<tr>
<td>Triclosan</td>
<td>TCS</td>
<td>EDCs</td>
<td>C₁₂H₇Cl₃O₂</td>
<td></td>
</tr>
<tr>
<td>Naproxen</td>
<td>NPX</td>
<td>Phs</td>
<td>C₁₄H₁₄O₃</td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>IBF</td>
<td>Phs</td>
<td>C₁₃H₁₆O₂</td>
<td></td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>KFN</td>
<td>Phs</td>
<td>C₁₆H₁₄O₃</td>
<td></td>
</tr>
<tr>
<td>Diclofenac</td>
<td>DFC</td>
<td>Phs</td>
<td>C₁₄H₁₀Cl₂NO₂Na</td>
<td></td>
</tr>
<tr>
<td>1H-benzotriazole</td>
<td>1H-BTR</td>
<td>BTs</td>
<td>C₆H₅N₃</td>
<td></td>
</tr>
<tr>
<td>1-hydroxy-benzotriazole</td>
<td>1-OH-BTR</td>
<td>BTs</td>
<td>C₆H₇N₂O</td>
<td></td>
</tr>
<tr>
<td>benzothiazole</td>
<td>BTH</td>
<td>BTs</td>
<td>C₇H₈NS</td>
<td></td>
</tr>
<tr>
<td>2-hydroxybenzothiazole</td>
<td>2-OH-BTH</td>
<td>BTs</td>
<td>C₇H₇NSO</td>
<td></td>
</tr>
<tr>
<td>Tolyltriazole</td>
<td>TTRI</td>
<td>BTs</td>
<td>C₈H₈NS</td>
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<tr>
<td>Me-S-Benzothiazole</td>
<td>Me-S-BTH</td>
<td>BTs</td>
<td>C₈H₇NO₂S₂</td>
<td></td>
</tr>
</tbody>
</table>

Batch experiments at three different total suspended solids (TSS) concentrations (0, 10 and 70 mg/l) were also performed in order to estimate the effect of TSS on chlorination performance regarding the removal of target compounds. The initial chlorine dose in all experiments was equal to 15 mgCl₂/l and the chlorinated wastewater samples were collected at a specific contact time (30 min). After sampling and before analyses, residual chlorine was inactivated through sodium sulphite addition and accordingly was analyzed to confirm zero residual chlorine values. All experiments were carried out in triplicates.

2.2 UV batch experiments

Several UV batch experiments were performed in triplicates in 3 l reactors. All batch experiments were performed in secondary treated wastewater samples spiked with the target compounds (NP, NP1EO, NP2EO, TCS, BPA, DCF, NPX, KFN, IBF, Benzothiazole, 1-OH-Benzotriazole) at a concentration of 960 ng/l. A collimated UV source consisting of one low pressure lamp, was employed to assess dose response curves for each sample tested. The intensity of UV radiation was measured using an IL 1700 radiometer with an SED 240 detector. Average UV intensity was calculated using Beer’s Law taking into account the reduction of UV light through the depth of the sample. In order to test the effectiveness of UV radiation, the radiated wastewater samples were collected and analyzed at several contact times (15, 31 and 225 min).
Batch experiments at three different TSS concentrations (0, 6 and 60mg/l) were also performed in order to estimate the effect of TSS on UV radiation efficiency. The radiated wastewater samples were collected at a specific contact time (35min). All experiments were carried out in triplicates.

2.3 Analytical Methods

For the determination of the EDCs and PhCs, wastewater samples before and after chlorination and UV disinfection were analyzed using a chromatographic method developed by Samaras et al., (2011). Samples were filtered, acidified to pH 2.5, and extracted using C18 SPE cartridges. The eluates of the extraction were evaporated to dryness, and the dried residues were subjected to derivatization reaction using BSTFA (1% TMCS) and pyridine. For the qualitative and quantitative analyses, an Agilent Gas Chromatograph 7890A connected to an Agilent 5975C Mass Selective Detector (MSD) was used. For the determination of BTrs and BThzs an analytical method developed by Asimakopoulos et al. (2012) was used. The analysis of BTrs and BTs was performed using a Thermo ultra high performance liquid chromatography (UHPLC) Accela system (pump and autosampler) interfaced with a Thermo TSQ Quantum Access triple quadrupole mass spectrometer (Thermo, San Jose, CA, USA). Wastewater characteristics (pH, COD, TSS, turbidity) were determined according to Standard Methods (APHA, 1992).

3. RESULTS

3.1 Chlorination experiments

3.1.1 Effect of contact time
The effect of chlorination on the removal of target compounds was evaluated for several contact times between 2.5 – 40 min. According to the results a satisfactory removal of the selected EDCs and Phs was recorded through chlorination, whereas this was not the case for most of the BTs. Only 1-OH-BTR and BTH exhibit a moderate removal of 73% and 36% respectively, whereas removal efficiencies for the other compounds of this group were minimal (less than 5%). The results, which are referred on EDCs and Phs, are in good agreement with the results reported by other research studies (Ying et al.,2002(a); Ying et al.,2002(b); Pinkston & Sedlak,2004; Boyd et al.,2005; Rule et al.,2005; Quintana et al.,2010; Korshin et al.,2006; Ratola et al.,2012). Figure 1 presents the chlorination removal efficiencies for the target compounds. As shown, an abrupt removal of the compounds is taking place in the first minutes of reaction and then the removal rate is decreasing until the end of the experiments. Therefore it seems that oxidation of the target compounds through chlorination is almost instant and 2-3 minutes are enough to gain the most out of the process.

3.1.2 Effect of pH
The effect of chlorination on the removal of target compounds was evaluated at three different pH values (6, 7.5 and 10) at a specific contact time of 11min. Based on the experimental results, it was shown that the removal of the target compounds is favoured at pH values around 7 for most of the target compounds. Indicative results for a representative compound from each target group are presented in Figure 2. As shown, chlorination efficiency seem to be decreased for pH values above 8. Especially, for Phs the corresponding removal efficiencies keenly decreased when pH values risen from 6 to 10 considering the contact time of 11 min. This is in good agreement with the findings of other studies (Rule et al. 2005; Li & Zhang 2012).
Figure 1 Effect of chlorination on (a) EDCs, (b) Phs and (c) BTs.

Figure 2 Effect of pH values on (a) BPA, (b) DFC and (c) 1-OH-BTR removal during chlorination.
3.1.3 Effect of TSS concentration
The effect of chlorination on the removal of EDCs, Phs and BTs was evaluated for three different TSS concentrations (0, 10 and 70 mg/l) at a specific contact time of 30min. Suspended solids contain organic substances that could compete with the target compounds for chlorine. However based on the experimental results it can be stated that the effect of TSS content of wastewater on the removal of the target compounds during chlorination is minimal. Figure 3 presents indicative results for BPA, DFC and BTH.

![Figure 3](image)

**Figure 3** Effect of TSS concentration on (a) BPA, (b) DFC and (c) BTH removal during chlorination

3.2 UV experiments
The effect of UV radiation on the removal of target compounds was evaluated for three different doses (Ct) 70 - 150 - 1000 mW×sec/cm² (C represents intensity and t contact time). According to the results, UV disinfection is not effective to remove most of the compounds even at such high Ct values (1000 mW×sec/cm²). From the target compounds only KFN exhibits a high removal of 95% at Ct values between 70 – 150 mW×sec/cm², whereas almost complete DFC removal can be achieved only for the high UV dose of 1000 mW×sec/cm² (Figure 4). The results, which are referred on EDCs and Phs, are in good agreement with the results reported by others (Gagnon et al.,2008; Baeza & Knappe,2011; Fang et al.,2009; Kim et al.,2009; Pereira et al.,2007).

![Figure 4](image)

**Figure 4** Effect of UV radiation on (a) EDCs and (b) Phs
4. CONCLUSIONS

Several batch experiments were performed in order to assess the effectiveness of chlorination and UV radiation to remove selected EDCs, Phs and BTs from secondary treated wastewater. According to the results chlorination leads to an appreciable removal of EDCs and Phs during the first minutes of the process. More specifically it can be stated that a contact time to the order of 2-5 minutes seemed to be enough to achieve high removal of TCS, BPA, NPX and DFC to the order of 92%, 85%, 85% and 65% respectively. However, this was not the case for BTs for which removal efficiencies were low even at high contact time (40min). It is also concluded that chlorination removal of the target compounds increases at pH values around 7 and decreases dramatically when pH values increased at pH values around 10. This might be attributed to the fact that OCl\(^-\) (which is the dominant chlorine species at high pH values) is a weaker oxidant than HOCl (which is the dominant chlorine species at lower pH values). Finally it is anticipated that UV disinfection is not effective to remove most of the compounds even at high doses (1000 mW·sec/cm\(^2\)). From the target compounds tested, only KFN exhibited appreciable removal at UV doses 70–150 mW*sec/cm\(^2\) (94-96%) as this compound is one of the most photodegradable pharmaceuticals.

ACKNOWLEDGMENTS

This project was implemented under the Operational Program «Education and Lifelong Learning» and funded by the European Union (European Social Fund) and National Resources – THALIS

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