Evaluation of the Use of Activated Carbon Powder for Removal of Emerging Micropollutants from Sewage Wastewater

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Abstract

In order to remove micropollutants from wastewater, it is necessary to adopt advanced treatment technologies, one of which is adsorption with activated carbon powder (ACP). This study evaluated the process of ACP adsorption to remove 18 emerging micropollutants from secondary wastewater effluent in the wastewater treatment plant in Büsnau, Stuttgart, Germany. Norit ACP was selected for this study. The contact time was 30 minutes. In this configuration, removal efficiency of pharmaceuticals was higher than 77% with 10 mg/L of ACP, and with 30 mg/L it was higher than 90%. For PCPs, removal efficiency with 10 mg/L of ACP varied from 50% for triethyl citrate and up to 88% for tonalide (AHTN), while 20 mg/L removed more than 83% of each PCP analyzed. For the FROPs, removal rates with 10 mg/L of ACP varied from 49% for N,N-Diethyl-meta-toluamide (TCEP) and 91% for tris-(1,3-dichloroisopropyl)-phosphate (TDCP), and 20 mg/L attained removal rates of 86% for TCEP and 99% for TDCP. Finally, MTBT and BT obtained removal levels equal to or higher than 60% with initial doses of 5 mg/L of ACP. It was confirmed that treatment with ACP is an efficient solution for the removal of examined emerging micropollutants.

Keywords

Emerging Micropollutants, Wastewater, Adsorption, Activated Carbon

1. Introduction

Emerging organic micropollutants are substances that are continually being introduced into the environment. Although they may have a harmful effect on human beings and the environment, micropollutants are still not included in national or international monitoring programs. Some sources of these substances are: pharmaceuticals, personal care products (PCPs), flame retardant and organophosphate plasticizers, among others [1, 2].

The primary route of these micropollutants into the environment is through domestic wastewater discharged as end wastewater from water treatment plants (WTPs), or even through discharge of raw wastewater. Various authors have reported the occurrence of different emerging micropollutants in the environment, including in rivers, lakes, seas, groundwater and aquatic organisms [3-9, 2], as well as reported occurrences of emerging micropollutants in water that is treated and distributed for human consumption [10, 11].

Emerging micropollutants have been found in different concentrations in different locations around the world. Pharmaceuticals stand out, with maximum concentrations of diclofenac of up to 28.4 µg/L in Canada, and up to 22 µg/L of carbamazepine in Germany, where synthetic fragrances such as galaxolide (HHCB) has a maximum value of up to 13.3 µg/L, and up to 6.8 µg/L of tonalide (AHTN). In the United States (USA), DEET insect repellants are reported to be 2.1 µg/L. TCPP flame retardant had maximum concentrations of 22 µg/L in Sweden, and in South Korea, TCEP had a maximum concentration of 2.6 µg/L. BT and MTBT had maximum concentrations of 22 µg/L in Sweden, and 6.2 µg/L in Spain.

Many of these emerging micropollutants are not removed, or are only partially removed, through conventional wastewater treatment processes. It was confirmed that in low concentrations of ng/L, endocrine disruptor compounds (for
example hormones) already cause feminization or masculinization of aquatic organisms [12, 8, 13, 14]. Cleuvers [15] demonstrated that toxicity can be enhanced in mixtures, as the toxicity of carbamazepine and clofibrate acid in *Daphnia* increased when both pharmaceuticals were mixed in the test. Toxicity is not the only worrying factor; there is also the possibility of conception from other emerging pollutants with special biological effects that are dangerous to the environment.

Different advanced wastewater treatment techniques are being studied for the satisfactory removal of these emerging contaminants, including ozonation, advanced oxidation processes (AOPs), filtration techniques with membranes and adsorption with activated carbon [1, 16, 17]. Among these techniques, those that use activated charcoal powder (ACP) are increasingly used due to their positive results [18, 19]. There are many studies in the literature about the removal of emerging micropollutants through the activated carbon process, either through the use of ACP or granular activated carbon (GAC), but there are few studies on the use of these technologies in matrices for wastewater treatment from Wastewater Treatment Plants (WWTPs). Activated carbon is mostly used in surface water matrices, waters treated for public supply and even pure waters with only solutes of interest [7, 20-25].

The removal efficiency of the emerging micropollutants through ACP treatment is directly related to the following factors: concentration of organic material present in the wastewater, type and amount of activated carbon, contact time, molecular structure and properties of the contaminants and the configuration adopted for adsorption treatment [17-20]. Other benefits from the use of ACP in wastewater treatment include further reduction of the organic load, removal of phosphorous [18, 19] and reduction of total estrogenic activity from wastewater at levels higher than 99% [26].

2. Objectives

This study aimed to evaluate the removal efficiency of 18 different types of emerging micropollutants found in the secondary wastewater effluent from the Büsnau WWTP, located in Stuttgart, Germany, through treatment with ACP. The substances studied included the pharmaceuticals carbamazepine, diclofenac, lidocaine and mirtazapine, the personal care products (PCPs) HHCB, HHCB-lactone, AHTN, triethyl citrate, BHA, BHT, benzophenone and DEET, and the flame retardants and organophosphate plasticizers (FROPs) TCEP, TCPP, TDCP and TiBP, and other MTBT and BT compounds.

3. Methods

This experimental study was developed in a laboratory. The study consisted of determination and analysis of the occurrence of emerging micropollutants in the secondary wastewater effluent from samples collected in the Büsnau WWTP; selection of emerging micropollutants and types of activated carbon to be evaluated; and experiments for the removal of the selected contaminants from the secondary wastewater effluent from the WWTP with ACP.

3.1. Büsnau Wastewater Treatment Plant (Büsnau WWTP)

The Büsnau WWTP is a tertiary treatment system to remove nitrogen and phosphorous, with a treatment capacity of 30 L/s. This WWTP receives a load equivalent to 10,000 residents, with removal efficiency of COD from the WWTP higher than 95%. The system is operated by the University of Stuttgart, and performs treatment of part of the wastewater generated in the suburbs of Stuttgart, including Lauchhau in the north zone of Vaihingen, and the University of Stuttgart region, also in the Pfaffenwald region of Vaihingen. The WWTP is also used as the experimental plant for different research and studies in the field of wastewater treatment by the Institute for Sanitation Engineering, Water Quality and Solid Waste Management (ISWA) of the University of Stuttgart.

3.2. Selection of ACP Type and Emerging Micropollutants

This study used NORIT® SAE SUPER activated carbon by Cabot, because previous evaluation (not addressed in this article) showed that this brand had the best results for micropollutant removal.

Table 1 lists the primary characteristics of the selected activated carbon.

Table 2 shows the micropollutants analyzed in this study and some of their properties. The compounds are divided into pharmaceuticals, personal care products, flame retardant and organophosphate plasticizers, and others (MTBT and BT).
Table 1. Characteristics of activated carbon powder used and its primary properties

<table>
<thead>
<tr>
<th>Characteristics/ properties</th>
<th>NORIT SAE SUPER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brand name</td>
<td>Norit</td>
</tr>
<tr>
<td>Adsorption in methylene blue (g/100g)</td>
<td>28</td>
</tr>
<tr>
<td>BET Surface Area (m²/g)</td>
<td>1150</td>
</tr>
<tr>
<td>Mean particle diameter (µm)</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 2. Emerging micropollutants evaluated and their primary physicochemical properties

<table>
<thead>
<tr>
<th>Substances</th>
<th>CAS Nº</th>
<th>Molecular Formula</th>
<th>Molar Mass (g/mol)</th>
<th>Log KOW</th>
<th>Water solubility at 25°C (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceuticals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>298-46-4</td>
<td>C₁₅H₁₂N₂O₂</td>
<td>236.28</td>
<td>2.45</td>
<td>112</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>15307-86-5</td>
<td>C₁₄H₁₅ClNO₂</td>
<td>296.16</td>
<td>4.51</td>
<td>2.37</td>
</tr>
<tr>
<td>Lidocaine</td>
<td>137-58-6</td>
<td>C₁₄H₂₂N₂O₂</td>
<td>234.4</td>
<td>2.44</td>
<td>4.100</td>
</tr>
<tr>
<td>Mirtazapine</td>
<td>85650-52-8</td>
<td>C₁₇H₁₉N₃</td>
<td>265.35</td>
<td>3.1</td>
<td>9.800</td>
</tr>
</tbody>
</table>

| Personal care products |        |                   |                    |         |                                 |
| HHCB                 | 1222-05-5 | C₁₈H₂₆O₂     | 258.41             | 5.9     | 1.75                            |
| HHCB-Lactone         | 256393-37-0 | C₁₈H₂₆O₂   | 272.38             | 4.71    | 8.2                             |
| AHTN                 | 21145-77-7 | C₁₈H₂₆O₂     | 258.41             | 5.7     | 1.25                            |
| DEET                 | 134-62-3  | C₁₈H₂₆NO     | 191.28             | 2.18    | 912                             |
| BHA                  | 25013-16-5 | C₁₈H₂₆O₄   | 360.4              | 3.5     | 213                             |
| BHT                  | 128-37-0  | C₁₈H₂₆O₂     | 220.36             | 5.1     | 0.6                             |
| Benzophenone         | 119-61-9  | C₁₈H₂₆O₂     | 182.22             | 3.18    | 137                             |
| Triethyl citrate     | 77-93-0  | C₁₈H₂₆O₂     | 276.29             | 0.33    | 65.000                          |

| Flame retardant and organophosphate plasticizers |        |                   |                    |         |                                 |
| TCEP                | 115-96-8  | C₁₂H₂₂Cl₃O₅P  | 285.49             | 1.44    | 7.000                           |
| TCP                 | 13674-84-5 | C₁₈H₃₈Cl₃O₅P | 327.57             | 2.59    | 1.200                           |
| TDCPP               | 13674-87-8 | C₁₈H₃₈Cl₃O₅P | 430.91             | 3.65    | 7                               |
| TiBP                | 126-71-6  | C₁₈H₃₈O₅P    | 266.32             | 3.60    | 16.2                            |

| Other compounds     |        |                   |                    |         |                                 |
| MTBT                | 615-22-5  | C₈H₇N₅S₂     | 181.28             | 3.15    | 125                             |
| BT                  | 95-16-9   | C₈H₇N₅S     | 135.19             | 2.01    | 4.300                           |

Source: Adapted from Syracuse Research Corporation, (2011) and Dagenais et al., 2009 [27].

Figure 1. Removal rates of micropollutants through treatment with different amounts of Norit activated carbon powder (ACP), with a contact time of 30 minutes.
3.3. ACP Treatment and Quantification of Micropollutants

The amounts of 5, 10, 20 and 40 mg/L of the selected ACP were used to evaluate the removal efficiency of the emerging micropollutants. Up to 20 mg/L of ACP is considered to be economically viable [25, 18, 19], and 40 mg/L of ACP was adopted to permit extrapolations from the results of removal of the emerging contaminants.

The contact time adopted was 30 minutes. This amount of time was considered ideal through a previous evaluation (not treated in this article), and that, according to Metzger and Kapp [18] and Zwickenpflug et al. [19], is the time limit for this type of study. The wastewater from the secondary decanter of the Büsnau WWTP was used as the matrix for the treatment. The sample was stored in a dark, acclimatized room at a temperature of 4º C, to avoid microbiological activity, and thus variation in the concentration of the micropollutants to be analyzed.

The application of the different amount of ACP was done in a one-liter sample of wastewater, through suspension solution in deionized water, to avoid possible losses of carbon. In order to promote the reaction during the contact time, devices for magnetic agitation were used, and separation of the carbon from the wastewater samples was done through the process of filtration under pressure, with an approximate pressure of 3 bar. The filtering material used was cellulose nitrate filters with a pore size of 0.45 µm. After treatments with ACP, the samples underwent liquid phase extraction with dichloromethane, and quantification by gas chromatography-mass spectrometry (GC/MS).

4. Results

Figure 1 shows the results of removal by ACP treatment for the 18 emerging micropollutants evaluated in this study, at 5, 10 and 20 mg/L of Norit Carbon, with a treatment time of 30 minutes.

The results attained for 5 mg/L of ACP removed more than 25% of all of the micropollutants evaluated, and about 70% for lidocaine and MTBT, and 10 mg/L of ACP had removal rates that varied from 49.3% to 92% for the compounds TCEP and MTBT, respectively. For 20 mg/L, the removal rates were higher than 80% for all of the substances.

5. Discussion

In this study, the removal rates for pharmaceuticals with 10 mg/L of ACP had results higher than 77%, similar to the results found by Metzger and Kapp [18], who had an average removal rate of 80% for the 67 pharmaceuticals they evaluated. However, the authors reused the ACP in the biological treatment phase, which increases the efficiency of removal of the treatment, as verified by Zwickenpflug et al. [19], who attained an increase of about 20% to 40% in the removal of the pharmaceuticals and other micropollutants with this practice. The removal rate of carbamazepine attained in this study was 77.7%, and 87.4% for diclofenac; at the same amount and without recycling the ACP, Zwickenpflug et al. [19] found removal rates of 77% and 68% for these pharmaceuticals, respectively. Yet at the same amount with reuse of the ACP carried over from the biological treatment, the removal rates attained by the authors were 96% for carbamazepine and 86% for diclofenac.

In this study, the removal rates attained for both carbamazepine and diclofenac were about 96% at 20 mg/L of ACP. Metzger and Kapp [18] attained similar results for 20 mg/L of ACP reusing the carbon carried over from the biological treatment, with removal higher than 95% for diclofenac and close to 100% for carbamazepine.

Considerable results were obtained in the removal of PCPs, even at 5 mg/L of ACP, varying from 27% for triethyl citrate to 63% for HHCB-Lactone, and 10 mg/L of ACP attained removal rates from 50% to 88%, respectively. Removal rates were higher than 83% for all of the PCPs, reaching 97% for HHCB-Lactone, with 20 mg/L. At 5 mg/L, the removal rates for TCEP and MTBT varied from 28 to 73%, respectively, while at 10 mg/L, the removal efficiency for TCEP reached 49%, and 92% for MTBT. At 20 mg/L, the compound that had the lowest removal rate was BT at 80%, while TCEP had a result of 86%. For this amount, the compounds that attained the best removal results were MTBT and TDCPP, with values higher than 98%.

Some substances which previously had insignificant removal rates through the ozonation process, including chlorinated organophosphate flame retardant TCEP, TCP and TDCPP [13], as well as partial removals of around 60%, such as HHCB-Lactone, AHTN, DEET and TiBP [13,28,29], attained removal rates higher than 80% with 20 mg/L of ACP.

6. Conclusions

The results from this study show that adsorption with ACP is an efficient process to remove emerging micropollutants, even with amounts considered to be economically viable, up to 20 mg/L.

In addition to the efficiencies found in this experiment, a possible removal efficiency gain by about 20 to 40% through the reuse of the ACP in the biological treatment, as reported by different authors. However, this practice is not appropriate in cases where the sludge from the wastewater is recycled for agricultural purposes. The use of the loaded ACP in the biological treatment would make use in agriculture unviable, and it should be properly disposed of separately from the wastewater sludge, which can be reused for agricultural purposes.

It was verified that ACP treatment promotes the removal
of emerging micropollutants that remain through processes currently used in WWTPs, and may bring other benefits such as the reduction of the COD in the effluent, the elimination of phosphorous, reduction of toxicity and estrogenicity of the wastewater, and could contribute to wastewater sanitation.

The treatment process with ACP was shown to be capable of efficiently removing the majority of emerging micropollutants found in the wastewaters from WWTPs. Additionally, the results for ozone treatment of recalcitrant compounds such as TCEP, TCPP and TDCPP had removal rates higher than 85%.

For continuity of this study, experiments with ACP treatment on a pilot scale is recommended, in order to certify the efficiency of removal of these contaminants, and establish operation criteria that better meet the needs of the Büsnau WWTP such as: the ideal amount of ACP, contact time and length of time of the ACP during treatment, and sizing criteria.

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