Monitoring the effectiveness of selected sorption materials in removing diclofenac from water

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Abstract. One of the contemporary problems is the widespread use of medicaments, which leads to an increased occurrence of these substances in the environment. The efficiency of conventional treatment processes for removing drugs from water is in most cases very little, if not zero. Treatment processes for removal of drugs include adsorption on activated carbon, membrane processes, and advanced oxidation processes. Within a specific university research project, a laboratory test was performed at the Institute of Municipal Water Management of the Faculty of Civil Engineering, Brno University of Technology, to monitor the effectiveness of diclofenac removal by selected sorption materials. Diclofenac was chosen for this experiment as a representative of one of the most widespread groups of drugs - non-steroidal anti-inflammatory drugs. The removal of diclofenac from water was performed using columns filled with sorption materials Filtrasorb F100, GEH and Bayoxide E33. The aim of the test was to compare the selected sorption materials in terms of their effectiveness in removing diclofenac from water. From analyses of water taken at predetermined time intervals after filtration through said materials, it was found that the most suitable material for removing diclofenac from water is Filtrasorb F100.

1. Introduction

One of the contemporary problems is the widespread use, in many cases even overuse, of medicaments. Its consequence is an increased occurrence of these substances in the environment. Drugs used in human medicine enter sewage water mainly with urine and solid faeces. [1] Another way they can get into wastewater is through disposal of unused drugs. These are often flushed into the waste, or they are stored together with municipal waste in landfills, from where these substances then enter the groundwater as seepage. [2] The possible negative impact of drugs on the environment leads to monitoring these substances in the water environment.

With regard to the properties of the drugs, the probability that the drugs present in the raw water will be significantly removed using conventional treatment procedures (aeration, flocculation, filtration/sand filtration, disinfection) is very small. Treatment processes used to remove drugs from water include activated carbon adsorption, membrane processes, and advanced oxidation processes. [3]

Within a specific university research project, a laboratory test was performed at the Institute of Municipal Water Management of the Faculty of Civil Engineering, Brno University of Technology, to monitor the effectiveness of diclofenac removal by selected sorption materials. The aim of the test was to compare the selected materials in terms of their effectiveness in removing diclofenac from water. Diclofenac was chosen for the laboratory experiment as a representative of non-steroidal anti-inflammatory drugs, one of the most widely used groups of drugs. These drugs are also most prevalent in the environment. Drugs included in this group are used to relieve pain, mitigate the symptoms of inflammation as well as reduce higher body temperature. They are used mainly in various joint
inflammatory diseases connected with pain and reduced mobility, they are also used in various painful diseases of soft tissues (especially muscles). Worldwide, about 200 different anti-rheumatic drugs are used. They may differ in properties, but the basic principle of the mechanism of their action remains the same. They are often prescribed to treat rheumatoid arthritis, arthrosis, acute gout and other rheumatic diseases. However, these drugs do not cure the disease, they just reduce inflammation, thus eliminating pain and swelling. [4]

Diclofenac is used in acute or chronic inflammatory or degenerative diseases of joints and spine (e.g. rheumatoid arthritis or osteoarthritis). It mitigates the symptoms of extra-articular rheumatism, as well as postoperative and post-traumatic inflammation. It is also used for its analgesic and antipyretic effects. It is used for pain of various origins and locations (pain in the teeth, head, muscles, back, pain during menstruation, pain accompanying inflammatory diseases, pain caused by injury). It can also be used for pain accompanying the flu and cold, because besides having analgesic effects, it also reduces high temperature. [5]

As diclofenac is a major environmental micropollutant, the public awareness of it was raised in the 1990s. Current research confirms the negative effect of diclofenac on some aquatic animals. The effects of diclofenac have a negative impact on the function of some organs, such as the kidneys or gills of fish. [6]

The experiment was based on the principle of dynamic adsorption. During dynamic adsorption, the adsorbate solution flows in the column through a stationary layer of granular adsorbent. During flowing through the layer of adsorbent, the substance is adsorbed in the upper part of the column (water flows through the column from top to bottom) and in its other parts, pure liquid phase then flows. [7]

Adsorption is a phase transfer process that is widely used to remove substances from liquid phases (gases or liquids). It can also be observed as a natural process in various components of the environment. In water treatment, adsorption has proven to be an effective process during the removal of many dissolved substances. The molecules or ions are removed from the water solution by adsorption on solid surfaces. The substance that is adsorbed is called an adsorbate and the material on which the adsorption takes place is called an adsorbent. The opposite of adsorption is desorption. Desorption can be caused by the depleted capacity of the sorbent as well as by the different properties of the sorbed pollutants. [8]

2. Materials and methods

2.1. Sorption materials
Sorption materials Filtrasorb F100, Bayoxide E33 and GEH were chosen for experimental removal of diclofenac.

Filtrasorb F100 is made from selected types of black coal by steam activation in compliance with relevant quality standards. In addition to the actual capture of mechanical impurities, the sorption and chemisorption properties of the specific surface are used in activated carbon. GAC is thus able to capture substances dissolved in water, especially those of an organic nature. The use of this material is one of the few options for removing petroleum substances and organic toxic compounds from water. Another exceptional feature is its ability to capture toxic heavy metals such as mercury, cadmium and lead. [9]

Activated carbon is resistant to wear associated with repeated washing and hydraulic transport. Another of its advantages is the possibility of reactivation for repeated use. [10]

Bayoxide E33 is a dry crystalline granular sorbent based on iron hydroxide. It was developed by Severn Trent in collaboration with Bayer AG. It is produced by LANXESS Deutschland GmbH, Leverkusen in Germany. The material has been designed to remove arsenic, its advantage is that together with both forms of arsenic (AsIII and AsV) it also removes iron and manganese. [11] It is also very effective in removing other heavy metals, such as copper, lead, antimony and others. [12]

GEH sorption material is based on granular iron hydroxide. This material is suitable for economical and efficient removal of arsenic and antimony from water. It was developed at the University of Berlin at the Department of Water Quality Control. It is produced by the German company GEH-Wasserchemie GmbH. The GEH treatment technology is based on the adsorption of the contaminant on granular ferric hydroxide (GEH sorbent) stored in a reactor through which the treated water flows. The adsorption capacity of the material depends on the operating conditions. [13]
The following table 1 contains overview of the sorption material properties.

<table>
<thead>
<tr>
<th>Parameter/Unit</th>
<th>Filtrasorb F100</th>
<th>Bayoxide E33</th>
<th>GEH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size/mm</td>
<td>0.8–1.0</td>
<td>0.5–2.0</td>
<td>0.2–2.0</td>
</tr>
<tr>
<td>Volume density/g·cm⁻³</td>
<td>0.58</td>
<td>0.4–0.6</td>
<td>1.25</td>
</tr>
<tr>
<td>Specific adsorption surface/m²·g⁻¹</td>
<td>900</td>
<td>120–200</td>
<td>250-300</td>
</tr>
<tr>
<td>Colour</td>
<td>black</td>
<td>amber</td>
<td>dark brown to black</td>
</tr>
</tbody>
</table>

2.2. The course of the experiment

The experiment was performed in three columns with an inner diameter of 4.4 cm. A drainage layer was created at the bottom of these columns that served to prevent leakage of sorption materials during filtration. The lowest part of the drainage layer was formed by stones with a size of 1 to 2 cm, above this layer, there was a layer of glass beads with a diameter of 4 mm. The upper part of the drainage layer was formed by glass beads with the size of 2 mm. The sorption materials were then poured over the drainage layer. The height of this last layer was chosen based on the manufacturer's recommendation, when the largest bulk height required for Filtrasorb F100 was at least 0.75 m. For the purposes of comparison, the same height was chosen for the other two materials. After pouring the required height of sorption materials and attaching the columns, it was necessary to rinse the materials before performing the experiment. The washing was carried out in a bottom-up direction until clear drinking water began to flow out of the column. The washing water was drained into the sewage system. The washing and filtration scheme is evident from the figure 1.

It was also necessary to prepare model water. It consisted of water from the water supply network, where the drug to be removed - diclofenac - was added. Diclofenac was prepared at the Institute of Chemistry and Technology of Environmental Protection, Faculty of Chemistry, Brno University of Technology. It was prepared in such a way that after mixing with 30 liters of water from the supply network, the concentration of drug in the water was about 1 µg·L⁻¹. After adding diclofenac to a 30-litre barrel filled with water, it was necessary to mix the substances thoroughly in order to disperse the drug throughout the model water volume. Afterwards, the water was left to stand in the barrel for half an hour in order to stabilize the diclofenac concentration.

A pump suction hose terminated with a suction basket was inserted into the model water barrel. The water was then pumped from the barrel through a flow meter to the individual columns. The volumetric feed flow rate during the experiment was 25 L·h⁻¹. Filtered water samples were then taken from the bottom outlets of the columns into the labelled plastic containers with a volume of 0.5 l. Samples were taken at 1, 2, 4 and 6 minutes from the time the water began to flow out of the column. During the experiment, measurement of pH, temperature and turbidity was performed directly in the laboratory. A Voltcraft PHT-01 ATC pH meter was used to measure pH. The temperature was measured using a Voltcraft digital needle thermometer ranging from -50 to +150 °C. Turbidity measurements were performed with a portable Hach 2100Q IS turbidimeter, which was calibrated using a set of attached standards before starting the measurement. After the end of the experiment, the samples were taken to the Institute of Chemistry and Technology of Environmental Protection, Faculty of Chemistry, Brno University of Technology, where diclofenac concentrations were determined.

2.3. Analytical methods

Concentration of the samples was performed by SPE (solid phase extraction) and then, the concentrated samples were evaluated by liquid chromatography with mass detection (HPLC/MS). An ion trap was used as a mass detector. The analytes were evaluated using internal standards that are added to the sample before the SPE. Diclofenac concentrations were determined with a measurement uncertainty of ± 35%. The LOD (limit of detection) value of diclofenac was 0.006 µg·L⁻¹. The actual concentration of diclofenac in model water was also checked by these methods, its value was 1.2852 µg·L⁻¹.
Figure 1. Filtration equipment scheme.

3. Results and discussion
The following table 2 shows the values of diclofenac concentrations in individual samples determined at the Faculty of Chemistry. The values of diclofenac concentrations are then plotted in a graph, which allows a clear comparison of the efficiency of the filter materials used.

<table>
<thead>
<tr>
<th>t [min]</th>
<th>Filtrasorb F100 $c_{\text{diclofenac}}$ [$\mu$g·L$^{-1}$]</th>
<th>Bayoxide E33 $c_{\text{diclofenac}}$ [$\mu$g·L$^{-1}$]</th>
<th>GEH $c_{\text{diclofenac}}$ [$\mu$g·L$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.2852</td>
<td>1.2852</td>
<td>1.2852</td>
</tr>
<tr>
<td>1</td>
<td>0.0988</td>
<td>0.6491</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td>2</td>
<td>&lt; LOD</td>
<td>0.8542</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td>4</td>
<td>0.1205</td>
<td>0.9311</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td>6</td>
<td>&lt; LOD</td>
<td>0.9730</td>
<td>&lt; LOD</td>
</tr>
</tbody>
</table>

With a focus on the main monitored value, i.e. the concentration of diclofenac, the best results in its reduction were achieved by the material GEH (see Fig. 2), which removed the drug below the limit of detection (LOD) after 1 minute and the concentration remained below this value throughout the rest of the measurement. With Filtrasorb F100, the concentration of diclofenac fluctuates over time, but is still at very low values, at 2 and 6 minutes even below the limit of detection. The worst results in drug removal were achieved by Bayoxide E33, which partially removed diclofenac after a minute, but increasing concentrations were found in other times. There was a supersaturation of the material, which gradually stopped removing diclofenac.
Figure 2. Course of diclofenac concentrations during the experiment.

The following table 3 shows the pH, temperature and turbidity values measured in the laboratory during the experiment.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.52</td>
<td>16.2</td>
<td>1.70</td>
<td>7.52</td>
<td>16.2</td>
<td>1.70</td>
<td>7.52</td>
<td>16.2</td>
<td>1.70</td>
</tr>
<tr>
<td>1</td>
<td>7.50</td>
<td>20.3</td>
<td>0.67</td>
<td>7.64</td>
<td>22.5</td>
<td>0.43</td>
<td>5.99</td>
<td>22.9</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>7.61</td>
<td>17.8</td>
<td>0.58</td>
<td>7.59</td>
<td>20.7</td>
<td>0.37</td>
<td>5.91</td>
<td>21.3</td>
<td>0.19</td>
</tr>
<tr>
<td>4</td>
<td>7.72</td>
<td>16.7</td>
<td>0.63</td>
<td>7.62</td>
<td>18.1</td>
<td>0.41</td>
<td>5.95</td>
<td>19.2</td>
<td>0.24</td>
</tr>
<tr>
<td>6</td>
<td>7.74</td>
<td>16.4</td>
<td>0.56</td>
<td>7.76</td>
<td>17.6</td>
<td>0.48</td>
<td>5.93</td>
<td>18.7</td>
<td>0.28</td>
</tr>
</tbody>
</table>

The pH profile is similar for Filtrasorb F100 and Bayoxide E33, with a slight increase from 7.52 before filtration to values close to 7.75. The pH profile of the GEH material, on the contrary, is significantly different, after only 1 minute the pH drops sharply below 6.0 and throughout the whole experiment, it stays within the range of 5.91-5.99. These values are outside the pH limit for drinking water, which is 6.5-9.5.

If we focus on turbidity, already in the model water before filtration, its value meets the limit of 5 NTU, specifically, the value of 1.7 NTU was measured. This value was significantly reduced after filtration through all materials. In the case of Filtrasorb F100, the values of turbidity were all around 0.6 NTU, in the case of Bayoxide it was around 0.4 NTU and GEH reduced the turbidity to values close to 0.2 NTU.

The effectiveness of each material in removing diclofenac from water was calculated using the following formula:
\[ \eta = \frac{C_{RW} - C_F}{C_{RW}} \times 100 \]  

where \( \eta \) …pollution removal efficiency [%],  
\( C_{RW} \) …raw water pollution concentration [\( \mu g \cdot L^{-1} \)],  
\( C_F \) …pollution concentration after adsorption [\( \mu g \cdot L^{-1} \)].

**Table 4.** Effectiveness of sorption materials in removing diclofenac.

<table>
<thead>
<tr>
<th>t [min]</th>
<th>( \eta ) (Filtrasorb F100) [%]</th>
<th>( \eta ) (Bayoxide E33) [%]</th>
<th>( \eta ) (GEH) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92.31</td>
<td>49.50</td>
<td>&gt; 99.53</td>
</tr>
<tr>
<td>2</td>
<td>&gt; 99.53</td>
<td>33.53</td>
<td>&gt; 99.53</td>
</tr>
<tr>
<td>4</td>
<td>90.63</td>
<td>27.55</td>
<td>&gt; 99.53</td>
</tr>
<tr>
<td>6</td>
<td>&gt; 99.53</td>
<td>24.29</td>
<td>&gt; 99.53</td>
</tr>
</tbody>
</table>

**Figure 3.** Effectiveness of diclofenac removal from model water.

The graph shows that the highest effectiveness of diclofenac removal was achieved by the sorption material GEH, the drug concentration was below the limit of detection at all observed times. Very similar results were achieved by Filtrasorb F100 with more than 90% diclofenac removal effectiveness throughout the measurement. The drug removal effectiveness of Bayoxide E33 was significantly lower from the first minute and it further decreased. Based on this experiment, only Filtrasorb F100 can be considered a suitable sorption material for drug removal. Although GEH was most effective in removing diclofenac, it lowered the pH of the water below the drinking water limit during filtration and therefore it does not appear to be a suitable drug removal material. Bayoxide E33, which is normally very effective in removing metals from water, has not been successful in removing diclofenac.
4. Conclusions
The highest effectiveness of diclofenac removal was achieved in the performed experiment by the GEH material, which removed diclofenac below the detection limit at all monitored times. Filtrasorb F100 achieved very similar results, with more than 90% diclofenac removal effectiveness throughout the measurement. The removal effectiveness of Bayoxide E33 proved to be significantly lower, with a decreasing tendency. Based on this experiment, only Filtrasorb F100 can be considered a suitable sorption material for drug removal. Although GEH was the most effective in drug removal, it reduced the pH of water below the drinking limit during the experiment, so it does not appear to be the best option for drug removal. Bayoxide E33, which is normally very effective in removing metals from water, proved unsuitable for removing the selected drug, the material was most likely supersaturated and gradually stopped removing diclofenac.

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