Experimental evaluation of the effectiveness of the adsorbent Bayoxide E33 in removing micropollutants from water

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Abstract

Micropollutants in the environment are still a topical issue in the field of water management at present. Since micropollutants in water can be harmful not only to the environment but also to humans, new technologies are constantly being tested to eliminate them. Standard treatment technologies for removing micropollutants from water include adsorption, advanced oxidation processes and membrane processes. For the experimental determination of the efficiency of the adsorbent Bayoxide E33, selected micropollutants were removed by adsorption. Micro-pollution removal efficiency was compared in removing three micropollutants, namely a metal, pharmaceutical and pesticide. The removal of the metal through the Bayoxide E33 material was successful, while the pharmaceutical and pesticide were not removed because of the occurrence of slight desorption during removal.

Key words: adsorption, Bayoxide E33, micropollutants, sorption materials, water treatment

Highlights

- Micropollutants – new pollution in the environment (pharmaceuticals, pesticides, metals, etc.).
- Drinking water treatment – very important process in the world for quality water.
- Sorption material – Bayoxide E33 for metal removal tested for other micropollutants.
- Turbidity – Bayoxide E33 for metal removal tested for other micropollutants.

Graphical Abstract

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INTRODUCTION

Various harmful substances called pollutants have recently begun to be investigated in water. Since they are thus far present in small quantities, we call them micropollutants. In most cases, these pollutants are of an anthropogenic origin. Some of the best known micropollutants in drinking water sources are pesticides and their degradation products, pharmaceuticals and daily care products, polycyclic aromatic hydrocarbons, metals, microplastics and others.

The issue of micropollutants in water has already been dealt with by experts not only in our country, but also around the world. A significant amount of foreign substances are entering the environment, which can also affect other (non-target) agents, endanger human health or initiate the disturbance of terrestrial or aquatic ecosystems. They have been shown to occur in waste water, in drinking water sources; that is, in surface and groundwater, as well as in drinking water itself (Halešová & Seifertová 2015). A recent study looked at the occurrence of pesticides in the Moravian Karst PLA. The presence of pesticides has even been confirmed in this area as well. Using such studies, it is possible to monitor the transport of micropollutants into groundwater (Halešová & Bortiáková 2017).

Water technology processes for pharmaceutical removal include membrane processes, ozonization, activated carbon sorption and oxidation processes carried out using ultraviolet radiation, oxygen, ozone, hydrogen peroxide, or a combination of some of these. Membrane processes are very efficient but also costly. They are more often used to remove bacteria and desalinate seawater. Ozonization is also a more costly treatment process, therefore it is not much used to remove micropollutants. Advanced oxidation processes are evaluated positively for the removal of selected pharmaceuticals. Sorption on activated carbon is one of the least expensive ways of removing micropollutants from water (Silva et al. 2015). Since adsorption appears to be an efficient and economically advantageous technological process, it was selected as a treatment process for the experimental removal of micropollutants from water. An adsorption material that had not been tested for pesticide and pharmaceutical removal was selected for the experiment. Laboratory experiments for the removal of individual micropollutants from water were performed separately. At the end of the paper, an evaluation of the Bayoxide E33 material is performed in terms of removal efficiency.

SELECTION OF THE SORBENT AND MICROPOLLUTANT

Sorption material

Bayoxide E33 is a sorption crystalline medium based on iron oxides developed especially for the removal of arsenic and other metals from water. The advantages of the material include a long lifetime in continuous operation, low investment and operating costs and the long lifetime of a dry medium (Ilavský & Barloková 2008). The sorption material is capable of removing arsenic up to a value of 4 μg·l⁻¹. The sorbent is used in granular form; that is, Bayoxide E33 or in the form of Bayoxide E33P tablets (Severn Trent Services 2005). In Figure 1 below, Bayoxide E33 is shown at its original size and at 5,000x magnification.

The Bayoxide E33 sorption material was selected for experimental removal of micropollutants based on an already performed metal removal experiment. Metals were removed on a total of four materials – GEH, CFH 0818, CFH 12 and Bayoxide E33. At the beginning of the experiment, there was an increased concentration of iron, manganese and above all a high concentration of nickel in the model water. The resulting analysis showed that the best way to remove metals was the sorption material Bayoxide E33, with an efficiency of 99.72% (Biela Kučera & Pěkňý 2017). Another criterion for sorbent selection was that Bayoxide E33 had not yet been tested to remove pesticides and pharmaceuticals from water. Table 1 shows the technical and physical parameters of the selected adsorbent.
The presence of micropollutants in drinking water sources may be of natural origin, but also of anthropogenic origin. Three different types of micropollutants were selected for the experiment. Arsenic, which is one of the common metals occurring in the environment, was chosen as the metal to be removed. The pesticide chosen was Metazachlor ESA, mainly used for the protection of agricultural crops. The pharmaceutical removed was salicylic acid, which is contained in frequently used cosmetic products.

Arsenic is found in nature mainly in the form of sulphides, accompanying most sulphide ores, and is a part of various rocks and soils. It can get into groundwater and surface waters by erosion. The concentration of arsenic in groundwater and surface water is up to $10^{3} \mu g\cdot l^{-1}$. About 20% of groundwater sources contain arsenic at concentrations of $100 \mu g\cdot l^{-1}$ to $250 \mu g\cdot l^{-1}$. Arsenic is strongly absorbed on suspended solids and sediments containing hydrated ferric oxide and alumina and clay particles. It is then remotely transported by surface water with these particles. The anthropogenic source of arsenic is the combustion of fossil fuels, the metallurgical and ore industry, tanneries and the application of some pesticides. A significant amount of arsenic is contained in extracts from power fly ash. Arsenic is highly toxic and the long-term ingestion of water with low concentrations of arsenic causes chronic diseases. In some countries, arsenic is the most important toxic metal found in groundwater and drinking water. Cases of chronic arsenic poisoning have been observed for example, in India, Taiwan and Bangladesh. In the Czech Republic, the highest limit value for arsenic in drinking water is $10 \mu g\cdot l^{-1}$ (Pitter 2015).

Metazachlor ESA is a metabolite of the pesticide Metazachlor, which belongs to the group of herbicides. This pesticide is used to eliminate a wide range of unwanted weeds in the cultivation of crops, ornamental trees and shrubs. It can reach groundwater through the application of the pesticide to crops. Metazachlor can reach the surface water by flushing the farmland to which the pesticide has been applied. Metazachlor is approved for use in almost all European Union countries (FOOTPRINT 2007). A metabolite is considered significant or ‘relevant’ if there is reason to assume that its natural properties are comparable to those of the parent substance in terms of its effect on the biological target, or pose a higher risk to organisms than the parent substance or comparable or if it has certain

**Selected micropolultants**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO$_3$ content</td>
<td>$&gt;$70</td>
<td>%</td>
</tr>
<tr>
<td>Specific adsorption surface</td>
<td>120–200</td>
<td>m$^2$·g$^{-1}$</td>
</tr>
<tr>
<td>Porosity</td>
<td>85</td>
<td>%</td>
</tr>
<tr>
<td>Grading analysis</td>
<td>$&lt;$0.5 mm</td>
<td>max. 20</td>
</tr>
<tr>
<td></td>
<td>$&gt;$2.0 mm</td>
<td>max. 5</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.4–0.6</td>
<td>kg·cm$^{-3}$</td>
</tr>
<tr>
<td>Working pH</td>
<td>5.5–8.5</td>
<td>–</td>
</tr>
<tr>
<td>Minimum bulk height</td>
<td>0.8</td>
<td>m</td>
</tr>
</tbody>
</table>

Table 1 | The technical and physical parameters of the sorbent Bayoxide E33 (Severn Trent Services 2005)
toxicological properties considered unacceptable. The methodology of the European Commission Guidance document on the assessment of the relevance of metabolites in the groundwater of substances regulated under Council Directive 91/414/EEC is used to assess the relevance of metabolites of pesticides. According to the methodology, the recommended limit value of the metabolite in drinking water is $5 \mu g \cdot l^{-1}$, provided that the value of the parent substance Metazachlor is lower than $0.1 \mu g \cdot l^{-1}$ (SZÚ 2014). The occurrence of pesticides in water was monitored in the framework of research into the occurrence of pesticides in soil, groundwater, surface water and drinking water. The presence of the pesticide Metazachlor ESA was confirmed in soil, groundwater and surface water in concentrations of up to $10 \mu g \cdot l^{-1}$ (Halešová & Bortňáková 2017).

Salicylic acid is a colorless organic acid of great importance in the field of dermatology. It is a medicine obtained from the bark of white willow. It has anti-inflammatory effects and therefore it is classified in the group of non-steroidal anti-inflammatory drugs. Anti-inflammatory drugs alone do not cure anything but only suppress the unpleasant manifestations of various diseases (Šíblová 2017). It was known as far back as the 18th century that the extract of the bark of white willow reduces fever and in 1870 the substance called salicylic acid was discovered in it. Previously, salicylic acid was not an ideal drug because it was administered in the form of a bitter solution that induced vomiting and irritated the stomach walls. Therefore, acetylsalicylic acid was produced by synthesis of an acetylated derivative in 1899. This acid has good analgesic and anti-inflammatory effects such as salicylic acid, but its use is safer and more pleasant. Acetylsalicylic acid has become a major component of aspirin (Iversen 2006). Because pharmaceuticals are present in very low concentrations in water, limit values for them do not yet exist. As part of the primary pharmaceutical monitoring in the Czech Republic, tap water samples were taken from the end consumers of drinking water. It was found that there are increased concentrations of some pharmaceuticals in concentrations up to $0.08 \mu g \cdot l^{-1}$ in drinking water. The highest concentration was confirmed for salicylic acid (Halešová 2017).

**MATERIALS AND METHODS**

**Adsorption and desorption**

Adsorption is a phase transfer process that is widely used in practice to remove substances from liquid phases (gases or liquids). This can also be seen as a natural process in various environmental components. The most general definition describes adsorption as enrichment of liquid phase chemical substances on the surface of a liquid or solid. Since adsorption is a surface process, surface area is a key quality parameter for adsorbents. The proposed adsorbents are typically highly porous materials with surface areas ranging between $10^2$ to $10^3$ m$^2$·g$^{-1}$. The substance to be adsorbed is called the adsorbate and the substance on which adsorption takes place is called an adsorbent. The desorption can be caused by the exhausted capacity of the sorbent and also by the different properties of the sorbed pollutants. Since desorption is the opposite process of adsorption, all conditions that lead to a decrease in adsorption increase the amount of adsorbate that can be desorbed. The adsorbate that is desorbed is an aqueous solution that can affect properties such as concentration, temperature and pH as compared to the original adsorbate, in the case of an experiment with the model water (Worch 2012).

**The process of removing micropollutants from water**

For the removal of metal and pharmaceuticals, model water was prepared in the laboratory of the Institute of Water Management of the Faculty of Civil Engineering of the Brno University of Technology by adding a micro-pollutant to the drinking water. Raw water for pesticide removal was taken from the Svratka River in Brno. The method of removing all three micropollutants was the same, using a column packed with Bayoxide E33 sorption material for filtration (see Figure 2).
Prior to filtration, the sorption material was wetted and backwashed until clear water emerged from the column. The washing water was drained into the sewer. The filling height was 0.7 m, which kept the minimum height as recommended by the manufacturer. The flow rate of model (raw) water through the column ranged from 10 to 30 l·hr⁻¹. The filter assembly consisted of a 30 liter model or raw water barrel, a pump, flowmeter, piping with stop valves, and containers for filtered water.

A water sample was taken from the barrel before filtration began. During filtration, water was passed through a flowmeter with a throttle nozzle to control the flow of water. Next, the water was filtered through a sorption material on which adsorption took place. Individual samples were taken at different time intervals after 30 seconds, 1, 2 and 4 minutes. After sampling, water temperature, pH and turbidity were measured. Due to the complex analysis of the samples, the resulting concentrations of micropollutants in the water samples were determined by an accredited laboratory.

**Measurement of temperature, pH and turbidity**

In a laboratory experiment, pH measurement was performed using a pH meter with the ADWA AD14 thermometer, a high quality microprocessor-controlled portable pH meter with built-in temperature measurement by automatic temperature compensation (ADWA Instruments). Water reaction is a dimensionless indicator, which is also influenced by the water temperature. At water temperatures above 25 °C, the pH is less than 7, and at temperatures below 25 °C, higher. Temperature is also an important indicator of drinking water. It significantly influences chemical and biochemical reactivity even in a relatively narrow temperature range, from 0 °C to about 30 °C (Pitter 2015).

Turbidity was determined using a HACH 2100Q IS turbidimeter. Turbidity is a measure of the total energy that dissipates on all sides of the beam (HACH) when the light beam passes through the dispersion layer of unit thickness. Turbidity is one of the organoleptic indicators of drinking water and describes the clarity of water, which is an essential requirement for quality drinking water. Water turbidity is caused by inorganic or organic substances that may be of natural or anthropogenic origin (Pitter 2015).

**Determination of removal efficiency**

The removal efficiency of micropollutants from water was determined according to the formula (Biela & Šopíková 2017):

$$\eta = \frac{C_{RW} - C_F}{C_{RW}} \times 100\%$$  \hspace{1cm} (1)

where \( \eta \) …… removal efficiency [%]
$C_{RW}$... micropollutant concentration in raw water [$\mu g\cdot l^{-1}$]  
$C_F$...... concentration of micropollutants after filtration [$\mu g\cdot l^{-1}$]

**RESULTS AND DISCUSSION**

Resulting values of the samples taken

The results of the measured values and the determination of the removal efficiency of the individual micropollutants through the Bayoxide E33 sorption material are shown in the following tables.

The removal of arsenic through the Bayoxide E33 sorption material was excellent. After just half a minute of filtration, the initial metal concentration in the model water of 62.3 $\mu g\cdot l^{-1}$ was almost removed. In the second minute of removal, the arsenic was completely removed from the water. This sorption material also handled well with turbidity removal, which was reduced to 0.84 ZF after four minutes. The model water temperature was lower than the water temperature in the individual samples. This was caused by the sampling of model water immediately after its preparation. The pH value increased slightly during the removal process, ranging from 7.53 to 7.77. Table 2 shows the results of arsenic removal.

**Table 2** | Results of arsenic removal

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>7.53</td>
<td>15.60</td>
<td>11.40</td>
<td>62.3</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>7.77</td>
<td>18.20</td>
<td>1.37</td>
<td>1.2</td>
<td>98.07</td>
</tr>
<tr>
<td>1</td>
<td>7.74</td>
<td>18.00</td>
<td>1.03</td>
<td>1</td>
<td>98.39</td>
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<tr>
<td>2</td>
<td>7.68</td>
<td>17.90</td>
<td>0.97</td>
<td>&lt;1</td>
<td>100.00</td>
</tr>
<tr>
<td>4</td>
<td>7.64</td>
<td>17.90</td>
<td>0.84</td>
<td>&lt;1</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The removal of Metazachlor ESA metabolite was not successful. After 30 seconds of removal, the initial concentration of 0.13 $\mu g\cdot l^{-1}$ was decreased, but over the next few minutes the concentration returned to its original value. The Bayoxide E33 sorption material was supersaturated and the pesticide was no longer removed. This is called desorption, which is the opposite of adsorption. The turbidity was reduced to the value 3.52 ZF during filtration. The temperature of the water gradually increased to 22.70 °C. The pH was highest in the raw water, dropped in the second minute and then increased slightly. Table 3 shows the ESA Metazachlor removal results.

**Table 3** | ESA Metazachlor removal results

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.32</td>
<td>20.70</td>
<td>7.38</td>
<td>0.13</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5</td>
<td>7.25</td>
<td>21.80</td>
<td>6.40</td>
<td>0.05</td>
<td>65.41</td>
</tr>
<tr>
<td>1</td>
<td>7.28</td>
<td>22.10</td>
<td>4.66</td>
<td>0.09</td>
<td>35.34</td>
</tr>
<tr>
<td>2</td>
<td>7.29</td>
<td>22.50</td>
<td>4.65</td>
<td>0.11</td>
<td>15.04</td>
</tr>
<tr>
<td>4</td>
<td>7.29</td>
<td>22.70</td>
<td>3.52</td>
<td>0.13</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The removal of salicylic acid via Bayoxide E33 was similar to that of pesticide removal. After 30 seconds of removal, the pharmaceutical concentration was reduced, but higher concentrations were measured from one minute. This means that desorption occurred again from one minute of removal.
Turbidity was reduced to 0.42 ZF. The model water temperature was 20.9 °C and decreased to 17.40 °C during the removal process. The pH in the model water was measured at 7.59 and decreased during removal as the temperature dropped. Table 4 shows the results of salicylic acid removal.

### Table 4 | Results of salicylic acid removal

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.59</td>
<td>20.90</td>
<td>1.16</td>
<td>659.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5</td>
<td>7.45</td>
<td>20.60</td>
<td>0.93</td>
<td>117.00</td>
<td>82.25</td>
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<tr>
<td>1</td>
<td>7.43</td>
<td>20.70</td>
<td>0.68</td>
<td>233.00</td>
<td>64.64</td>
</tr>
<tr>
<td>2</td>
<td>7.41</td>
<td>18.70</td>
<td>0.48</td>
<td>450.00</td>
<td>31.71</td>
</tr>
<tr>
<td>4</td>
<td>7.38</td>
<td>17.40</td>
<td>0.42</td>
<td>494.00</td>
<td>25.04</td>
</tr>
</tbody>
</table>

### Evaluation of adsorption column design parameters

The optimal course of adsorption depends on several parameters such as filtration rate, empty bed of material volume, the volume of flowing model water and the empty bed contact time of the adsorbent (EBCT). In order to evaluate these parameters, the condition must be:

\[ \frac{C}{C_0} \leq 0, 1 \]  

where \( C \) …… output concentration of the micropollutant in the model water [μg·l⁻¹]  
\( C_0 \) …… input concentration of the micropollutant in the filtered water [μg·l⁻¹]

This condition was only met for the removal of the metal from the water, since desorption occurred during the removal of the pesticide and the pharmaceutical. Therefore, the design parameters are evaluated only for the removal of arsenic from water. The calculated adsorption conditions are provided in Table 5.

### Table 5 | Fulfillment of the adsorption process

<table>
<thead>
<tr>
<th>Micropollutant/concentration</th>
<th>C [μg·l⁻¹]</th>
<th>C₀ [μg·l⁻¹]</th>
<th>C/C₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.9</td>
<td>62.3</td>
<td>0.01</td>
</tr>
<tr>
<td>Metazachlor ESA</td>
<td>0.134</td>
<td>0.133</td>
<td>1.01</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>494</td>
<td>659</td>
<td>0.75</td>
</tr>
</tbody>
</table>

The volume flow rate \( (Q_t) \), bed volume \( (BV) \) and the empty bed contact time \( (EBCT) \) according to the formulas were determined to evaluate the adsorption process. Table 6 shows the determined adsorption parameters (Worch 2012; Ünlü et al. 2015):

\[ Q_t = v_f \cdot A_r \]  

\[ BV = \frac{VF}{VR} = \frac{Q_t}{VR} \]  

\[ EBCT = \frac{h}{v_f} = \frac{VR}{Q_t} \]

where \( A_r \) …. bed area [m²]
Evaluation of the experiment

The aim of the experiment was to determine and compare the effectiveness of Bayoxide E33 in removing micropollutants from water. The material was 100% effective in removing arsenic from water. This sorption material is directly developed to remove arsenic and other metals from water. According to the experiment carried out, Bayoxide E33 was confirmed as a suitable sorbent for the removal of arsenic from water. When removing the pesticide and pharmaceutical from water, this sorption material did not prove to be suitable due to the desorption that occurred during filtration through the material.

In the experiment, turbidity values in individual samples were also measured. The values were measured because turbidity is one of the basic organoleptic properties of water and its limit value is given in the Decree of the Ministry of Health of the Czech Republic No. 252/2004 Coll. laying down hygiene requirements for drinking and hot water and the frequency and scope of controls on drinking water. The turbidity limit in this Decree is in NTU. From the results of the performed experiment it can be seen that the sorption material Bayoxide E33 reduced turbidity in all cases to values that meet the given decree.

CONCLUSION

The determined removal efficiency of micropollutants from water using Bayoxide E33 sorption material is shown in Figure 5. In terms of efficiency, the material Bayoxide E35 is best for removing metals from water, but also for removing turbidity. According to the experiment carried out, it does not seem suitable for the removal of pesticides and pharmaceuticals. In the case of the pharmaceutical, its non-removal could be due to the relatively low specific surface area of the material and the high initial pharmaceutical concentration.
The evaluation of the design parameters of adsorption was performed solely for removing metals from water. This was because desorption occurred when removing the pesticide and pharmaceutical from the water, and thus the condition of optimal adsorption was not met. This condition for the pesticide and pharmaceutical was probably not met because of the low specific surface area of the material. The delay contact time was calculated to be 2.129 minutes, corresponding to the course of the experiment. The arsenic concentration was removed from the water within 2 min. The evaluation of the design parameters of the adsorption column shows that the time periods in which the samples were taken were determined appropriately.

ACKNOWLEDGEMENTS

The paper was elaborated within the framework of the grant project of specific university research at VUT in Brno called ‘Removal of micropollutants from drinking water sources by adsorption’ (FAST-S-18-5115) and ‘Current problems of municipal water management’ (FAST-J-20-6431).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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