Removal of bromates from water

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Abstract. Bromates are substances that are usually not present in drinking water. They are obtained by ozone disinfection in the presence of bromine ions in water, as an impurity of sodium hypochlorite, respectively. Because of their specific properties, bromates are classified as very dangerous substances, that can cause serious illnesses in humans. There are several technological processes that have been used to the removal of bromates from water at present. In this article, the removal of the bromates from water by the adsorption using various sorbent materials (activated carbon, zeolite, Klinopur-Mn, Bayoxide E33, GEH, Read-As and Activated alumina) are presented. The effectiveness of selected sorbent materials in the removal of bromates from drinking water moves in the interval from 10 to 40%. Based on laboratory results, the zeolite can be used to reduce the concentration of bromates in water.

1. Introduction

Bromates are substances that are usually not present in natural waters; they can be present in sea and mineral waters (up to 100 µg/L). Presence of bromates in drinking water is usually relating to water disinfection. The water source Dvorníky containing 1 to 40 µg/L of natural bromates is the exception. Bromates (BrO₃⁻) are formed as by-products of water disinfection by ozone in the presence of bromine ions (BrO⁻). Under certain conditions, bromates may be present in concentrated solutions of hypochlorite used for water disinfection (e.g. at the NaCl electrolysis containing bromine ions or at the solution ageing). Bromates are also formed by oxidation of natural bromine in the presence of oxidisers [1,2].

Pursuant to SR Government Regulation No. 354/2006 Coll. as amended, the limit value of bromates in drinking water in Slovakia is 0.01 mg/L; this value complies with the recommendations of the World Health Organization (WHO), and Council Directive 98/83/EC [3].

The formation of bromates during ozonisation consists of a complex multistage process including bromine ions, molecular ozone, hydroxide radicals, and the water quality as such. In the case of bromide oxidation, reactive bromine is formed to react with water with the formation of hypobromous acid (HBrO) and a bromine ion (BrO⁻). Formation of HBrO/BrO⁻ compounds depends primarily on the pH value of water. The higher pH of water, the more bromine ions (BrO⁻) formed, and vice versa, the lower pH of water, the more amount of hypobromous acid (HBrO) formed.

There are also other parameters except for the pH value that can affect the formation of bromates in drinking water such as concentration of bromine in water, the concentration of organic substances, ammonia, alkalinity, water temperature, ozone concentration and dose [4].

The level of concentration of bromates in water has been monitored in Canada and England in particular; in Slovakia, we do not have too many records of their presence in waters. The Canadians have been monitoring presence of bromine in water for many years. In 1993, there were 53 samples of
drinking water taken there and the presence of bromates in the range from 0.2 to 0.5 mg/L was detected in two of them. The concentration of bromates in water has been increasing continuously and, in accordance with the results of 2013 published, the average level of concentration of 0.62 mg/L was detected in 22 of 23 samples [4].

The presence of bromates was also detected in European waters, where the concentration approximately 2 μg/L was detected in two of 36 samples of raw water taken including rivers and groundwater [4]. In the public water-mains in the Czech Republic, the concentration of bromates around 2.7 μg/L was detected [2].

As for bottled water, the concentration of bromates in the range from 0.2 to 37.3 μg/L was detected with the average concentration of 3.72 μg/L for water that is not subject to ozonisation, and 18.14 μg/L for water subject to ozonisation [4].

Bromates substance is restricted for its negative impacts on the human health. The Environmental Protection Agency (EPA) considers bromates potential human carcinogen, but its effects were assessed on the laboratory animals only [5].

Toxic symptoms occurred due to bromine salts consumed include vomiting, abdominal pain, diarrhoea, various degrees of central nervous system depressions, pulmonary oedema, and haemolytic anaemia. Majority of these effects can be cured. Failure of kidneys and loss of hearing remain as lasting consequences at the use of potassium bromate [5].

In accordance with SR Government Regulation No. 354/2006 Coll., bromates belong among the indicators of the drinking water quality as a part of the complete water analysis [3]. Methods used for defining dissolved bromates shall meet the requirements of Council Directive 98/83/EC. Currently, we have seven methods approved by the Environmental Protection Agency - US EPA used for defining concentration of bromates in drinking water. All the methods are based on the principle of ion chromatography using various detection methods (such as conductivity detector, inductively coupled plasma and mass spectrophotometer, post-column reagent and UV/VIS spectrophotometer, suppressed conductivity detection, and so on). They differ from one another by the detection definition limit to be from 0.02 to 1.3 μg/L [4].

When defining bromates, one can also use isotachophoresis or a combination of capillary isotachophoresis and capillary zone electrophoresis Coulometry and spectrophotometric methods are using reactions of bromates with bromides in a strongly acidic environment with the formation of bromine; methyl orange or fuchsin is used as a colour indicator. These are less selective (detection limit of 1 to 5 μg/L) [6].

An important factor for reducing concentration of a bromate is knowing basic characteristics of a water source such as water temperature, pH, content of bromine ions, water chemistry and its changes during seasons, ozone dose, and so on.

Currently, we have several technological methods for providing bromates removal from drinking water: coagulation, UV radiation, membrane processes, ion exchangers and adsorption [7, 8]. Reduced generation of bromates can also be achieved by controlling the pH value, by adding ammonia or H₂O₂ [4].

Adsorption processes are usually used for the water treatment, and they ensure removal of undesired substances causing water colouring, changed taste and odour properties, substances formed at the water disinfection, for removal of various inorganic and organic substances.

There are several types of sorption materials classified into groups upon the purpose of removing substances from water. In the water management, removal of undesired substances from drinking water is most frequently performed using sorption (filtration) materials such as granulated active coal, zeolite (clinoptilolite), Activated alumina, Bayoxide E33, Kemira CFH 12 and CFH 18, and materials with layers of MnO₂, TiO₂, CeO₂ on their surfaces.

2. Material and methods
Compared to the limit value (according to SR Government Regulation No. 354/2006 Coll.), some natural sources of drinking water can contain higher concentrations of bromates. In the territory of
Slovakia, there is a water source Dvorníky with the concentration of bromates oscillating from 0.001 to 0.04 mg/L. Due to this reason, the experimental part was focused on removing bromates from water with using selected sorption materials.

The chemical analysis of raw water is stated in table 1. Regarding low concentration of bromates as well as for increasing the accuracy of measurements, standard sodium bromate (NaBrO₃) has been added into raw water samples from Dvorníky with consequent increase of the concentration of bromates in model water up to the value of 91.3 μg/L.

Table 1. Chemical analysis of groundwater from the water source Dvorníky (2 March 2017).

| Parameter | Unit | Value | Parameter | Unit | Value |
|-----------|------|-------|-----------|------|-------|
| pH        |      | 7.39  | Ca²⁺      | mg/L | 102   |
| conductivity | mS/m | 65    | Mg²⁺      | mg/L | 25.84 |
| TDS (105°C) | mg/L | 570   | Ca + Mg   | mmol/L | 3.60 |
| alkalinity | mmol/L | 5.71 | Cl⁻       | mg/L | 24.35 |
| acidity   | mmol/L | 0.55 | NO₃⁻      | mg/L | 29.21 |
| COD-Mn    | mg/L | 0.68 | SO₄²⁻     | mg/L | 98.46 |
| Fe total  | mg/L | 0.02 | F⁻        | mg/L | 0.26  |
| Mn        | mg/L | 0.024 | PO₄³⁻    | mg/L | 0.63  |

The following sorption materials were used there:
- GEH (0.6 – 1.6 mm), (ferric hydroxide, GEH Wasserchemie, Germany);
- Bayoxide E33 (0.5 – 2.0 mm), (ferric oxide, Severn Trend, England);
- Klinopur Mn (0.6 – 1.6 mm), (zeolite with a layer of MnO₂ on the surface, Zeocem, a.s.);
- Read – As (0.3 – 1.0 mm), (ceric oxide, Nihon Kaisui Co Ltd, Japan);
- Activated alumina (1.5 – 2.5 mm), (aluminium oxide, China);
- GAU - Filtrasorb F 400 (0.42 – 1.68 mm), (Chemivron Carbon, Belgium);
- Natural zeolite (0.5 – 1.5 mm), Zeocem, a.s. Bystré.

The experiment was performed by means of a static test in the laboratory. 2.0 g of the sorbent was added into 200 ml of model water with pH of 7.38. The samples were mixed continuously, and 100 ml of water was taken off after one hour, four hours, and eight hours. In order to stabilize bromates, we have added EDA – ethylenediamine (0.1 ml into 100 ml of the sample).

The concentration of bromates was defined using the device EcaFlow 150 GLP made by ISTRAN s.r.o. Slovakia, which works on the basis of flow-through coulometry and in-electrode coulometric titrations. Using this method, bromates in the acidic environment are reduced to bromine.

The area of the signal – chronopotentiogram – recognized is directly proportional to the concentration of bromates in water. In order to remove distorting impacts of chlorites and other oxidation reagents, Fe²⁺ is added to the sample [9].

3. Results and discussion

The efficiency of removal of bromates from water using sorption materials was observed at pH of 7.38, input concentration of bromates of 91.3 μg/L, and the contact of water with the sorbent after one hour, four hours, and eight hours. Results of the static test were always obtained from two parallel sample measurements. At every set of analyses, the accuracy of measurements was checked by a reference material with the concentration of 100 μg/L and 75 μg/L of bromates (BrO₃⁻). Results are listed in table 2.
Table 2. Values measured at the experiment (pH = 7.38).

| No. | Material                        | 0 hour | 1 hour | 4 hour | 8 hour |
|-----|---------------------------------|--------|--------|--------|--------|
| 1   | Zeolite - SK (0.5 – 1.5 mm)     | 91.3   | 65.8   | 57.5   | 55.2   |
| 2   | Filtrasorb F400 (0.42 - 1.68 mm)| 91.3   | 84.6   | 77.1   | 72.0   |
| 3   | Act. Alumina (1.5 - 2.5mm)      | 91.3   | 85.5   | 80.3   | 76.4   |
| 4   | Read - As (0.3 - 1.0 mm)        | 91.3   | 80.2   | 70.5   | 63.6   |
| 5   | Klinopur Mn (0.6 - 1.6 mm)      | 91.3   | 87.2   | 85.8   | 85.2   |
| 6   | GEH (0.6 - 1.6 mm)              | 91.3   | 79.0   | 72.5   | 66.0   |
| 7   | Bayoxide E33 (0.5 - 2.0 mm)     | 91.3   | 82.3   | 78.8   | 76.1   |

Based on the defined values, the efficiency of bromates removal - $\eta$ [%] (equation (2)) and immediate adsorption capacity of selected sorption materials – $a_t$ [mg.g$^{-1}$] (equation (1)) were calculated:

$$a_t = \frac{(c_0 - c_m)V}{m} \text{[mg/g]}$$  \hspace{1cm} (1)

$$\eta = \frac{(c_0 - c_m)100}{c_0} \text{[%]}$$  \hspace{1cm} (2)

where $a_t$ is the immediate adsorption capacity in µg.g$^{-1}$, $\eta$ is the adsorption efficiency [%], $c_0$ is the concentration of bromates before the adsorption, 91.3 µg/L, $c_m$ is the concentration of bromates after the adsorption at the time $t$ [µg/L], $V$ is the volume of water solution of 0.2 L, $m$ is the weight of sorption material, 2.0 g.

Results of the adsorption efficiency (in %) and calculated values of the adsorption capacity for particular sorption materials at the concentration of bromates of 91.3 µg/L and pH of 7.38 are shown in figure 1.

![Figure 1](image-url)  
**Figure 1.** Course of the adsorption efficiency of bromates removal from water (left) and adsorption capacity of bromates removal from water (right).

Based on the given results we can state that, at pH of 7.38 and at the initial concentration of bromates before the adsorption (91.3 µg/L), none of the materials used was able to reduce the concentration of bromates under the limit value defined by GR No. 354/2006 Coll. (10.0 µg/L). Zeolite (clinoptilolite) was proven the most efficient sorption material able to remove 27.93% of bromates.
from the model water after the first hour and 39.54% of the same after eight hours. The adsorption capacity of zeolite was changing upon the duration of the contact and oscillated from 2.55 μg.g⁻¹ after the first hour up to 3.61 μg.g⁻¹ after eight hours. The efficiency of other sorption materials was relatively low, it did not exceed 30.0% after eight hours. In the literature, it is frequently recommended to use GAU for bromates removal, but not every active coal is suitable. In some works, the efficiency of 50-80% is stated, some of them refer to the GAU material specification, some of them even state that GAU is inefficient for bromates [8].

4. Conclusion
The experiment monitored the efficiency of selected sorption (filtration) materials at the removal of bromates from the model sample under laboratory conditions, and the resulting concentration of bromates was 91.3 μg/L. Based on the static tests, the adsorption efficiency of particular materials observed was compared, and their adsorption capacity was calculated.

Based on the results, the possibility of using zeolite from Nižný Hrabovec at the removal of bromates from water comes into account, and this can be caused by sorption, but also by the ion exchange capacity of zeolite. In the case of granulated active coal Filtrasorb F400, the efficiency of bromates removal after the contact with water lasting for eight hours was only 20.2% of the total amount of bromates in water. From among the rest of the materials observed, a good sorption efficiency is shown by GEH and Read-As (30% after eight hours of the contact with water).

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