Use of Sorption Materials for Removing Cadmium from Water

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Abstract. Groundwater and surface water sometimes contain substances that do not occur frequently in such water. Such substances include some of the metals. Increased iron and manganese content is expected in groundwater; however, metals such as cadmium, nickel or arsenic in high quantities are not typical of this water. Still, there are sources where the occurrence of cadmium, arsenic and other metals is in concentrations exceeding the prescribed values for drinking water. Because of the toxicity of heavy metals, authors dealt with the possibilities of removing cadmium from water. There are many ways to remove heavy metals, however today iron hydroxide based granulated sorption materials are used due to their simplicity, efficiency and low economic demands. The laboratory experiments of the removal of cadmium from water were carried out at the Institute of Municipal Water Management, Faculty of Civil Engineering in Brno as part of a specific university research project. The aim of the experiment was to compare the ability of three sorption materials CFH 0818, Bayoxide E33 and GEH on the removal of cadmium from water. These materials were primarily designed to remove arsenic from water. Filtration columns filled with the mentioned sorbents were used for filtration. Drinking water was used as raw water during the measurement from the municipal water supply system in which increased cadmium concentration was achieved artificially by adding a chemical solution. During the experiment, the flow rate was set to reach the required retention time of 2.5, 5, 10 and 20 minutes taking into account the porosity of the media. The results of the laboratory measurement show that all three materials were able to reduce the concentration of cadmium deep below the limit laid down by Decree No. 252/2004 Coll. already at the shortest delay time. Contact filtration occurred unequivocally in all sorption materials during the removal of the cadmium.

1. Introduction
Cadmium is a chemical element belonging to the group of heavy metals. It is a white metal similar in its properties to zinc. The average concentration of cadmium in the Earth’s crust is about 0.15 – 0.2 mg/kg. Therefore it is in 67th place among the chemical elements of the Earth’s crust. It comes with zinc ores which are used to produce fraction distillation or electrolysis. During their process cadmium gets into waste water and the atmosphere. A significant anthropogenic source of cadmium is phosphate fertilisers and the application of sewage sludge in agriculture. A further source is waste water from electroforming and from the production of Ni-Cd batteries. Cadmium is part of some pigments and acts as a stabiliser of some thermoplastics such as PVC. During the burning of these plastics cadmium enters the atmosphere, just as during the burning of fossil fuels, diesel and heating oils. Due to atmospheric water from the contaminated atmosphere cadmium then gets into the subsoil [1].
2. Occurrence of cadmium in water

Cadmium occurs in water as a simple ion, hydro complexes, carbonate complexes or even sulphate complexes \([\text{CdSO}_4(\text{aq})]^0\). In sea water these can also be considered to be chloro complexes \([\text{CdCl}_2(\text{aq})]^0\). Complexes with humic substances above all occur from organic complexes. A simple cation \(\text{Cd}^{2+}\) together with \([\text{CdCO}_3(\text{aq})]^0\) and \([\text{Cd(OH)}_2(\text{aq})]^0\) are among the dominant forms of cadmium occurrence in water [1].

Solubility of cadmium in water is limited especially by the solubility of \(\text{CdCO}_3\) and \(\text{Cd(OH)}_2\). In anaerobic conditions \(\text{CdS}\), in the presence of sulphide sulphur, can also be separated from water. The concentration of dissolved cadmium in surface water can, up to a considerable extent, be affected by the processes of adsorption and desorption of cadmium in sediments whose sorption capacity depends on the contents of the humic substances. The value of the accumulation coefficient in the sediments ranges between \(10^3\) and \(10^4\). This is one of the causes of why real concentrations of cadmium in water are lower than the equilibrium concentration calculated from the products of solubility, even if side reactions affecting solubility are taken into account [2, 3].

The average cadmium concentration in drinking water of underground origin fluctuates around 0.95 µg/l and in drinking water from surface sources around 0.92 µg/l. Concentration of up to tens of mg/l can be found in acidic water in the vicinity of ore deposits. The contents of cadmium in mineral water ranges between 0.01 µg/l and 0.23 µg/l. In sea water the concentration is equal to about 0.1 µg/l [1].

In drinking water of the Czech Republic cadmium is limited by the threshold limit of 5 µg/l. The guideline value of WHO for cadmium in drinking water is 3 µg/l [4]. The general immission standard for permissible pollution of surface water is 0.7 µg/l. In water suitable for irrigation the highest permissible cadmium concentration is 10 µg/l, while concentrations above 20 µg/l in water used for these purposes can be considered unsuitable. The cadmium concentration limit in industrial waste water released into municipal sewerage is 0.1 mg/l. The permissible value in industrial waste water released into surface water for waste water from metalworking, enamelling, varnishing and electrical production is 0.2 mg/l [1].

3. Health risk of cadmium

Cadmium is one of the few elements whose effect on the health condition of human organism is clearly negative. This fact seems to be curious because in chemical terms it is very similar to zinc which, on the contrary, is an integral part of food and plays an important role in the correct development and health condition of the human organism. However, the mutual chemical similarity of these elements causes problems because cadmium can easily enter various enzymatic reactions in place of zinc and the subsequent biochemical processes do not take place or take place in a different way. An example is the blocking of the insulin cycle which can cause serious health complications. Cadmium typically accumulates in the prostate in men where there is normally high zinc content and here this accumulated cadmium can cause very extensive prostate cancer subsequently metastasizing throughout the body [5].

A further cadmium risk factor is the fact that this involves an extraordinarily cumulative poison. The received cadmium is secreted from the organism very slowly and with difficulty, most of it is concentrated above all in the kidneys and to a smaller extent in the liver. It was shown that cadmium can remain in the kidneys for decades. So it is the kidneys that are most at risk of chronic cadmium poisoning. The main medical signs of long-term (chronic) cadmium poisoning, apart from kidney and liver damage, is also osteoporosis – a common condition of loss of bone tissue and anaemia, while there is increased risk of heart and vascular disease [6]. A higher content of cadmium has an effect on the calcium metabolism and causes its increased secretion from the organism with subsequent bone fragility. It has also been shown that cadmium is carcinogenic and its high content in the organism increases the risk of cancer. By the IARC cadmium has classified as a human carcinogen, group I [7]. A single high dose of cadmium causes abdominal pain, diarrhoea and vomiting. Cadmium also poses a risk to the functionality and quality of sperm [5].
Cadmium enters the organism in two ways – in food and by breathing. A particular food risk factor is giblets (liver, kidneys) or fish which have been contaminated by cadmium during their growth. Agricultural crops cultivated in cadmium contaminated soil can also pose a risk [5].

4. Experimental removal of cadmium from water

There are many ways to remove heavy metals from water, however today iron hydroxide based granulated sorption materials are used due to their simplicity, efficiency and low economic demands. These are sorbents which were produced above all to reduce the concentration of arsenic, of which the most well-known are CFH, Bayoxide E33 and GEH.

CFH is material for the removal of arsenic, selenium, phosphorus, silver, nickel, lead, molybdenum, silicon, vanadium, copper and further metals by adsorption from water. The advantage of the material is its easy application and simple water pre-treatment. The manufacturer is launching two materials – CFH 12 and CFH 0818, which differ above all in granularity (see table 1) [8]. Both granulated materials are strikingly similar in their colour of brown to red-brown. The manufacturer is the Finnish company Kemira, and the distributor in this country is Kemwater ProChemie s.r.o.

| Table 1. Granularity of filtration materials Kemira CFH [9] |
|-----------------|-----------------|
|                 | CFH 12          | CFH 0818        |
| Dispersion [mm] | Abundance [%]   | Dispersion [mm] | Abundance [%] |
| 2.0 – 0.85      | 92.7            | 2.0 – 0.5        | 97.6          |
| < 0.85          | 5.9             | < 0.5            | 2.4           |
| > 2.0           | 1.4             | > 2.0            | 0.0           |

Bayoxide is a dry crystalline granular sorbent based on iron oxide. It was developed by Severn Trent in cooperation with Bayer AG and produced by LANXESS Deutschland GmbH, Leverkusen in Germany. It is produced in two versions i.e. Bayoxide E33 and Bayoxide E33P. The difference is that Bayoxide E33 is granulated whereas Bayoxide E33P is produced in tablets [10]. The material was primarily designed for removing arsenic, but it was shown that it is effective for removing other metals too [11].

The sorption material GEH (Granulated Eisen Hydroxide) was developed at the Department of Water Quality Control of Berlin University in order to remove arsenic and antimony from water. It is produced by the German company GEH-Wasserchemie GmbH. The treatment technology consists of the contaminant adsorption to granulated 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. It is imported into the Czech Republic by Inform-Consult Aqua s.r.o, Příbram [10, 12].

The aim of the experiment was to compare the ability of three sorption materials CFH 0818, Bayoxide E33 and GEH on the removal of cadmium from water. Filtration columns filled with the mentioned sorbents were used for filtration. Drinking water was used as raw water during the measurement from the municipal water supply system in which increased cadmium concentration was achieved artificially by adding a chemical solution.

Each filtration column consisted of a glass tube with an inner diameter of 4.4 cm. A plastic elbow with a regulating valve was mounted on the bottom of the glass tube. To prevent the fine particles of the filtration material from escaping during filtration, at the bottom of the tube a drainage layer was formed of 4 mm glass balls and on top of this another layer of 2 mm balls. A filtration mass to a height of 0.55 to 0.7 m was placed above the drainage layer (see table 2). A plastic stopper with a regulating valve...
sealed the top of the tube. The complete filtration equipment consisted of 30 litre vessels with model water, a pump, pipe, flow meter, three filtration columns and several filtrate vessels.

Table 2. Column properties

| Sorption material | Material porosity n [%] | Material height h [m] | Total volume Vc [m³] | Water volume Vv [m³] |
|-------------------|--------------------------|-----------------------|----------------------|----------------------|
| CFH 0818          | 76                       | 0.58                  | 0.00088              | 0.00067              |
| Bayoxide E33      | 85                       | 0.70                  | 0.00106              | 0.00090              |
| GEH               | 75                       | 0.55                  | 0.00084              | 0.00063              |

Before the actual experiment the filters were washed. During the washing, the optimal rate of flow was selected so that the filtration material gets into the suspension, but it does not get washed out into the sewerage and is decreased. The ideal washing rate was about 20 l/h. The washing lasted for so long until clear water flowed from the filter.

During the filtration the flows through the column changed according to the required delay time of 2.5 min, 5 min, 10 and 20 minutes. Besides the cadmium concentration in water, the water temperature and pH was also monitored. A digital pH meter was used for pH measurement which can also determine the liquid temperature. Cadmium concentrations were determined in accredited laboratories of the National Institute of Public Health in Brno.

5. Results and discussions

The analysis of the raw water including the turbidity, which was low (1.35 ZF), is stated in table 3. The results of the water analysis after filtration through individual sorption materials are shown in table 4.

Table 3. Raw water analysis

| Time | pH   | Temperature | Turbidity | Cd concentration |
|------|------|-------------|-----------|------------------|
| t [min] | T [°C] | c Cd [μg/l] | ZF | c Cd [μg/l] |
| 0    | 7.56 | 14.8            | 1.35    | 12.6             |

Table 4. Analysis after filtration through sorption materials CFH 0818, Bayoxide E33 and GEH

| t [min] | CFH 0818 | Bayoxide E33 | GEH |
|--------|---------|--------------|-----|
| pH     | T [°C]  | c Cd [μg/l]  | pH | T [°C]  | c Cd [μg/l]  | pH | T [°C]  | c Cd [μg/l]  |
| 2.5    | 7.76    | 19.1         | <0.2| 7.72   | 17.3         | <0.2| 7.61   | 20.2         | <0.2 |
| 5      | 7.79    | 17.0         | <0.2| 7.72   | 15.9         | <0.2| 7.63   | 19.8         | <0.2 |
| 10     | 7.82    | 15.6         | <0.2| 7.73   | 15.9         | <0.2| 7.63   | 18.1         | <0.2 |
| 20     | 7.88    | 16.0         | <0.2| 7.76   | 16.7         | <0.2| 7.65   | 18.1         | <0.2 |

It is clear from the results that all three materials are excellent for the removal of cadmium and achieve similar filtration outputs (see figure 1). Already at the shortest delay time of 2.5 minutes, cadmium concentration in the treated water was deep below the limit of the highest threshold limit according to Decree No. 252/2004 Coll. (HTL for cadmium 5 μg/l). Other delay time no longer had a more significant effect on the fall in the concentration of this substance in treated water. Contact filtration clearly occurred in all sorption materials during the removal of cadmium.

Maximum possible cadmium values (<0.2 μg/l) were measured on laboratory instruments and the actual values are below the limit of detection. The pH values and temperature was monitored as well as
the removal of cadmium. The water pH value with the delay time rises negligibly in all the columns. The water temperature during the experiment was higher than the raw water temperature which was affected by the temperature in the laboratory. However, the temperature change had no effect on the experiment.

Figure 1. Course of the removal of cadmium from water

6. Conclusions
The laboratory experiments of the removal of cadmium from water were carried out at the Institute of Municipal Water Management, Faculty of Civil Engineering in Brno as part of a specific university research project. It was shown by measurement that there is a very reliable and effective method for reducing the concentration of cadmium in water using sorption materials based on iron hydroxide. For the purpose of the experiment three filtration materials were tested – CFH 0818, Bayoxide E33 and GEH. The results of the laboratory measurement show that all three materials were able to reduce the concentration of cadmium deep below the limit laid down by Decree No. 252/2004 Coll. already at the shortest delay time. Contact filtration occurred unequivocally in all sorption materials during the removal of the cadmium.

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