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Research on Fluoride Removal from Membranes Rejected Water

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Abstract. The excess of fluoride in water intended for human consumption can cause some problems in health of consumers from concentrations over than 1.5 mg/L. A detailed study has been carried out for the removal of fluoride from concentrated rejected water overcoming the drawback of membrane processes by using sorption techniques. Opoka mineral which is a natural sorbent and polonite have been chosen and valorized in this present work as fluoride sorbents for rejected water by membranes of the water treatment plant. These sorbents have been selected in order to reduce the treatment cost and to meet the standards of rejected water especially in term of fluoride. Opoka sorbent and polonite have shown effective results for fluoride removal from rejected water with efficiency over than 77%. In order to understand the sorption phenomenon and to validate the results with sorbents, we have applied experimental data on Freundlich Isotherm and SEM microscopic technique.

Keywords: fluoride removal, membrane rejected water, opoka, polonite.

Conference topic: Water engineering.

Introduction

The occurrence of groundwater with high fluoride concentrations is usually a case of natural process which is in general depending on the composition of the rocks and the occurrence of fluoride-containing minerals (Fawell *et al.* 2006). Fluoride can be dissolve in groundwater naturally when conditions favor the dissolution of some fluoride compounds (Mohapatra *et al.* 2009).

Groundwater contaminated by high concentrations of fluoride is obtained in numbers countries around the world, usually in India, China and USA (Azbar, Turkman 2000; Ayoob, Gupta 2006; Msonda *et al.* 2007; Rao 2009; Vithanage, Bhattacharya 2015). In the western part of Lithuania, the concentration of natural fluoride in water is high and varies from 1.5 to 5 ppm (Petersen *et al.* 2000). In the region of Kretinga (Baltic region) groundwater contains many excessive ions, especially fluoride with approximately 4 $mg \cdot L^{-1}$ of concentration. A detailed description on the highest concentrations of fluoride reported in groundwater of some regions around the world based on literature (Ayoob, Gupta 2006; Vithanage, Bhattacharya 2015). According to WHO recommendations (Fawell *et al.* 2006), the optimal fluoride level in drinking water is 1.5 mg/L, the same concentration is required by European Directive and local Lithuanian Hygiene Norm. In some cases, where fluoride levels are higher than required in water intended for human consumption, the health of consumers can be affected negatively (Du Plessis 1995). In this case, the execs of fluoride can induce dental and/ or skeleton fluorosis.

The main objective of defluoridation is to remove the excess of fluoride from drinking water, and to decrease it to acceptable limits. Adsorption techniques and membrane separation processes (nanofiltration and reverse osmosis and electro-dialysis) are the most common methods to deal with this issue; other processes are also used for defluoridation such as, coagulation–precipitation and ion exchange (Agarwal *et al.* 2003; MenkouchiSahli *et al.* 2007). Each method has their advantages and disadvantages, the cost effective and reliable processes are investigated globally and locally (Mohapatra *et al.* 2009). All the above mentioned approaches, which are investigated by many scientists, are represented in the following references. The concentrate or the rejected water represents one of the residual of a membrane filtration process, which means that treatment of concentrate is necessary to avoid negative affect on the environment (Vithanage, Bhattacharya 2015).

Methods and materials

Through experiments the most common sorbents were researched: natural opoka from Lithuania, artificial polonite from Sweden. The sorbents adsorbing properties were compared with other globally used sorbent with the same or similar properties.

To perform the laboratory experiments a fluoride compounds rejected by membranes filtration from groundwater of Kretinga region water treatment plants were used. Groundwater quality can be seen from Table 1.

Table 1. Groundwater quality in Kretinga (Lithuania)

Parameters	Units	Max value	Min value
pH	–	7.95	7.61
Conductivity	µS·cm-1 at 25°C	735	650
Fe total	µg.L-1	1100	450
Mn	µgL-1	24	10
F-	mgL-1	2.7	1.55
NH4+	mgL-1	0.36	0.01
SO4	mgL-1	23.4	15.7
Cl-	mgL-1	10.2	10.2
NO3	mgL-1	3.9	3.9
COD	mgO2L-1	0.8	0.8
Al	µg L-1	1.7	1.7
As	µg L-1	2.8	2.8
Cd	µg L-1	0.2	0.2
Cr	µg L-1	0.42	0.42
Ni	µg L-1	0.56	0.56
Pb	µg L-1	3.12	3.12
Cu	mgL-1	0.01	0.01
Na	mgL-1	39.6	32.9

Investigation of microstructure was carried out by employing Scanning Electronis Microscope SEM "Quanta" 250 with SE detector.

Adsorbents, before the first experiment, were crushed and sieved through a sieve with pore width being 0.63 mm. With such a method the size of sorbents adsorbing surface area is maximized. All absorbents before the experiments were dried for 24 hours in the drying oven in a constant 105 °C degrees as to remove of residual moisture. After drying sorbent powder was hermetically kept in desiccator.

Equal amount of 500 ml membrane rejected water was poured into a cone-shaped 1000 ml capacity flask, adding 5.0 g dry sorbent and obtained mixture was mixed in the mixer for 120 rotations per minute.

After 0.5 h of absorbing, obtained solution in static conditions was filtered through paper "Wathman No 5" filter and "GF/A Wathman" filter. Collected filtrate was immediately analysed.

In first stage laboratory research, seeking to determine sorption efficiency depended on pH, the pH of water was measured before and after the sorption.

1. To get statistically reliable data every experiment was repeated 5 times. Statistically unreliable data was rejected and for calculation only the reliable results were used.
2. In the second research stage data was collected in laboratory conditions to determine selected for research sorbent adsorption isotherms by adsorbing fluoride compounds from membrane rejected water.

Adsorption isotherms were created by evaluating the initial fluoride concentration in the solution and 1 g adsorbent's adsorbed fluoride quantity. Freundlich absorbance isotherm equation parameters are calculated by using the experiment research results.

Absorbance isotherms are done at water temperature near 10 °C±0.5 °C (ground water temperature).

According to this stage laboratory research data absorbance isotherms are made for these absorbents: 1 – opoka, particle size smaller than 0.63 mm; 2 – polonite, particle size smaller than 0.63 mm.

Sorption isotherms are created (Fig. 1) also with real ground water pH values: pH = 6.0, pH = 6.5, pH = 7.0, pH = 7.5, pH = 8.0.

To determine the most appropriate absorbent dosages when preparing groundwater according to the required quality drinking water such a proposed scheme (e. g. see Fig. 1) is used: 1 – fluoride sorption curve when the fluoride concentration is highest in membrane rejected water; 2 – the same when the fluoride concentration in rejected water is the lowest.

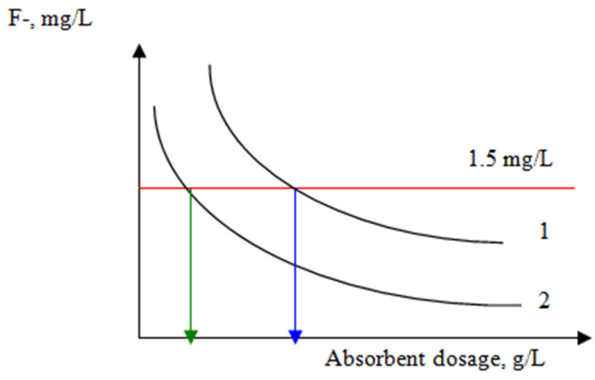

Fig. 1. Optimal sorbent dosage determining scheme

When preparing one or another sorbent to use for water treatment it is important to pay attention not only to the sorption capacity but also the sorbent cost efficiency, its exploration properties, regeneration possibilities and etc.

With a steady temperature (14±10 °C) and using the same amount of absorbent, the amount of fluorides was changed and, using spectrophotometer "Spectronic Genesys 20" as well as calibration curve, the absorbed fluoride amount was determined. By using obtained results following sorbent adsorption capacity was evaluated as well as Freundlich equation parameters. Mathematical sorption isotherm expression is provided in Formula 1:

$$q_s = a_F C_s^{b_F}, \tag{1}$$

where: q_S – absorbed fluoride amount, mg/g of absorbent; C_S – balance of absorbed material's concentration in solution, mg/L; a_F and b_F – Freundlich constants, a_F is absorbent sorption capacity, ml/g; b_F – constant unit-less, describing sorbent's chemical composition homogeneity (value fluctuates between 1 and 0, when homogeneity lowers the constant's value approaches zero).

Results and discussions

SEM instrument provided enlarged pictures of sorbent surface and some composition of compounds (e. g. see Fig. 2). In this stage performed laboratory research, all obtained results give enough information about researched absorbent amount required for reducing fluoride concentration to the required limits and their shared absorbance capacity. The absorbent particle size was smaller than 0.63mm. It can be seen in the Figure 2 that every absorbent particle is covered in small crystals, mainly flat form crystals, which size is about 1 micrometer. Small flat form crystals on particle surface enlarge every particle's surface area.

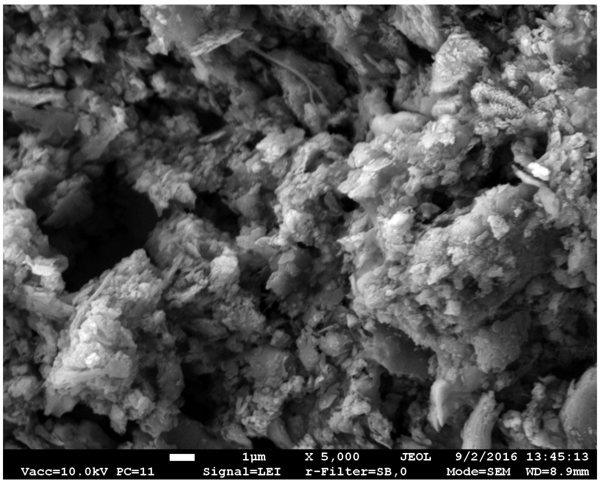

Fig. 2. SEM picture with enlarged adsorbent surface

Here all results in weight % according to processing option when all elements analyzed (normalized): O – 50.16; Al – 4.98; Si – 30.94; K – 1.40; Ca – 10.45; Cu – 2.07.

Two sorption isotherms are presented In Figure 3, when polonite was used as an absorbent, while fluorides in one instance were determined in artificially prepared water, in other – in membrane rejected water. In later instant it was attempted to determine what influence to the sorption process does the attenuation of different ions.

While creating absorption isotherms according to Freudlich equation, for every curve constants a_F and b_F were calculated. The bigger a_F value, the better absorption results.

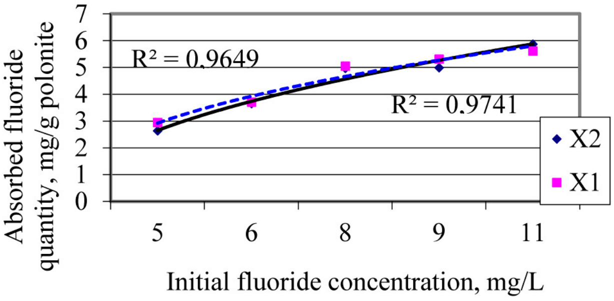

Fig. 3. Sorption isotherms, when polonite is used (particle size <0.63 mm):
X1 – sorption in artificially prepared water, X2 – sorption in membranes rejected water

In prepared water (curve X1) and membranes rejected water (curve X2) Freundlich's absorption formulas have such expression:

$$q_s = 2.925 \cdot C_s^{0.425}, \qquad (2)$$

$$q_s = 2.654 \cdot C_s^{0.495}, \qquad (3)$$

When absorbing fluorides in prepared water a_F = 2.925 ml/g, while in membrane rejected water a_F = 2.654 ml/g, that is to conclude, in distilled water polonite sorption capacity is about 11% higher.

Crushing the absorbent makes its surface area much more accessible, making absorption capacity increase with it. That is why there were created two more natural opoka isotherms: one for sorbent, which particle diameter is <0.63 mm, and another for sorbent, which particle diameter is <0.14 mm. Isotherms shown in Figure 4 Freudlich formulas accordingly had such expressions:

$$q_s = 2.654 \cdot C_s^{0.495}, \qquad (5)$$

$$q_s = 2.802 \cdot C_s^{0.499}, \qquad (6)$$

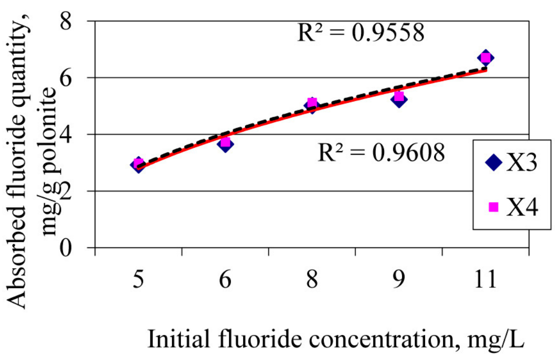

Fig. 4. Sorption isotherms, sorbent with particle size <0.14mm and <0.63 mm 3 – particle size <0.14mm,
X4 – particle size <0.63mm

Here, smaller particle size sorbent efficiency rose slightly (about 5.5%). Polonite (isotherm X4) Freundlich formula has this expression:

$$q_s = 2.871 \cdot C_s^{0.492}. \qquad (7)$$

Comparing absorbent polonite and natural sorbent opoka powder properties a 2.4% absorption capacity increase is determined when using polonite.

In foreign (USA and Scandinavia) scientific-technical literature it has been claimed, that sorption process can be influenced by water's pH. Russian scientists that carried out an experiment with various absorbents didn't determine such influence. Due to contradictory information an extra experiment was carried out by absorbing with opoka powder fluoride's compounds from membrane rejected water with variation from 6 to 8 pH values (these values are conventional for Lithuania's groundwater).

Analysing shown results in Figure 5 water fluorides concentration dependency after absorption due to pH value was determined – absorption's efficiency increased when pH value decreased.

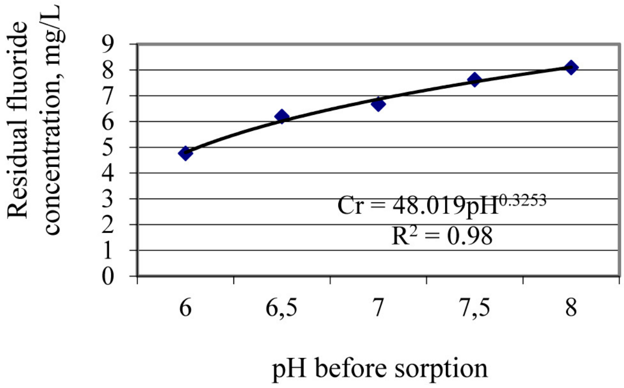

Fig. 5. Residual fluoride concentration dependent on water pH

Membrane rejected water treatment with opoka adsorbent being also investigated in order to improve the adsorption capacity and looking for a better efficiency with natural adsorbent.

Opoka sorbent amount related to different concentrations of fluoride in membrane rejected water can be seen in Figure 6.

From all of the results from membrane rejected water fluoride, approximately similar amounts of fluoride were found in all samples of both removal using opoka and polonite sorbents and it can be used to improve water quality at the outlet of water treatment plants.

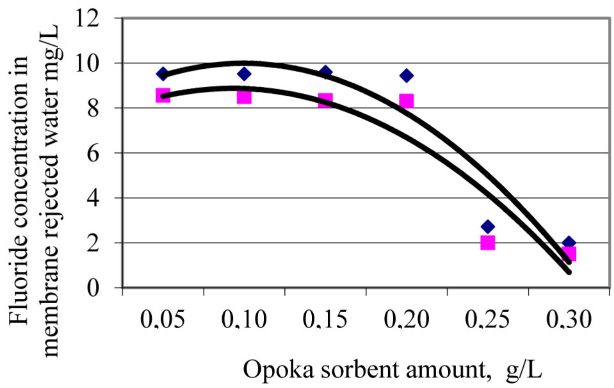

Fig. 6. Opoka sorbent amount used according to different concentrations of fluoride

Conclusions

By analysing research results, it was determined that:

1. researched absorbents (polonite and natural opoka) powder can have a practical adjustment, when it is necessary to remove fluorides from membrane rejected water;
2. natural opoka powder absorption capacity increased as water's pH value decreased;
3. adsorbed fluoride quantity has an influence to membrane rejected water quality, the more various compounds there will be in water, the more smaller absorption efficiency will be in one compound aspect;
4. laboratory research confirmed, that absorption isotherm method, together with Freudlich absorption formula, is very convenient and reliable method (with R^2 more than 0.96) for determining sorbent sorption properties;

5. by comparing opoka and polonite powder sorption properties from fluoride aspect it was determined a 2.4% absorption capacity increase when using polonite. Since the increase is small, it was decided that natural sorbent opoka powder will be accepted and in the future experiments opoka will be used.

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