

CATALYTIC FILTRATION FOR THE IMPROVEMENT OF DRINKING WATER QUALITY

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Received 24 March 2000

Abstract. Model solutions on the basis of Tallinn drinking water containing 3.79 ± 1.34 mg/L of total iron were treated with different filter media, such as *Birm*, *Pyrolox*, *Manganese Greensand* (all based on manganese dioxide), *Crystal Right* (a zeolite), and *sand*. The results of the study indicated that all these filter media removed iron from water and influenced other water quality parameters. *Crystal Right* had the best adsorption capacity among the filter media mentioned above. The sand filter removed also oxidized iron.

Key words: drinking water, catalytic filtration, filter media, ferrous iron, ion content.

INTRODUCTION

Throughout history, the quality and quantity of water available to humans have been vital factors in determining their well-being. Special care has to be taken of the quality of technological and potable water. An ecologically founded system to classify water quality and water use is important for ecosystem-based water management. This system should allow identification of water bodies and their parts that are most sensitive to uses of water resources and that are hence of priority importance for conservation. Ground water is, indeed, one of any country's most valuable natural resources.

Estonian reserves of potable ground water are sufficient to satisfy almost 2/3 of the demand for drinking water in Estonia. The estimated ground-water reserves up to the year 2005 are 1 533 800 m³/d. In recent years, observations relevant to ground-water reserves and quality were made in about 400 wells, within the framework of a ground-water monitoring programme [1]. The monitoring network was divided into seven regions with different hydro-geological conditions and technical feasibilities.

Various parameters of drinking water quality – colour, chemical oxygen demand (COD), turbidity, total dissolved solids (TDS), pH, chloride, sulphate, fluoride, ammonia, nitrite, nitrate, hydrogen sulphide, radon, phenols, and other pollutants – were recently determined by Savitski et al. [2]. Table 1 shows the approximate average values of the main quality parameters for ground water, compared with the MPC of Estonian Drinking Water Standard EVS 663:1995 for the quality classes good (4) and excellent (5). The EU Drinking Water Standard is included as well.

Table 1. Comparison of Estonian ground water quality with the Estonian and EU guidelines

Parameter	Average value	EVS (excellent)	EVS (good)	EU
Colour, deg.	8–50 (100)	5	15	–
Turbidity, NTU	2–30 (100)	1	2	1
COD _{Mn} , mgO/L	1–5	1	2	5
Iron, mg/L	0.05–4.0	0.1	0.3	0.2
Manganese, mg/L	0.02–2.0	0.05	0.1	0.05
Hydrogen sulphide, mg/L	0.003–0.5	0.0	0.05	–
Ammonia, mg/L	< 0.2	0.0	0.5	0.5
Nitrite, mg/L	0.003–0.2	0.0	0.01	0.5
Nitrate, mg/L	0.3–30	1.0	10.0	50
Chloride, mg/L	5–800	100	250	250
Sulphate, mg/L	5–400	100	250	250
Fluoride, mg/L	0–6	1.5 (4.0)	1.5 (4.0)	1.5
Boron, mg/L	2.1–6.6	0.3	0.3	1.0
Barium, mg/L	0.9–9.1	0.7	0.7	–

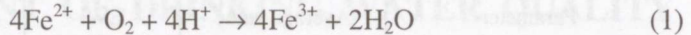
Comparison of the measured values with the Estonian and EU Drinking Water guideline values shows the important areas for quality improvement to be colour, turbidity, the content of iron and manganese, hydrogen sulphide, nitrate, chloride, fluoride, boron, and barium.

Increased content of iron and manganese in ground water of several districts in Estonia (especially, in southern Estonia) is one of the most difficult problems in ground water use for potable water supply. The solution of this problem enables to improve also the colour and reduce turbidity and the corrosion in pipelines. Iron in water imparts a disagreeable metallic taste and, in combination with hydrogen sulphide, produces a black, corrosible film of iron sulphide on the internal surfaces of pipes.

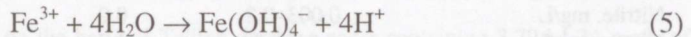
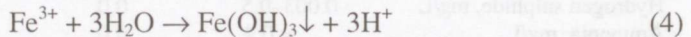
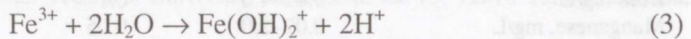
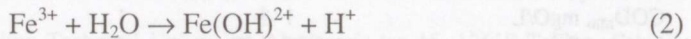
Total iron content in Estonian ground-water samples was usually in the range of 0.05–2.0 mg/L, in some wells even 5–6 mg/L. Iron and manganese are present in natural waters in their most reduced and most soluble forms: Fe²⁺ and Mn²⁺, respectively. Most of the iron in ground water is usually present in the form of bicarbonate Fe(HCO₃)₂. Part of the soluble iron can be in the form of quite stable humic and fulvic acid or colloidal silicon acid complexes. These complexes are very stable, therefore their removal from the ground water is a complicated problem.

Iron may be removed from water by different methods, depending upon the amount and form of iron present. Filtration with a suitable catalytic filter medium used is one of the most promising methods.

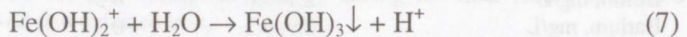
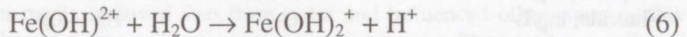
Nowadays a variety of catalytic filter media enable to oxidize Fe^{2+} to Fe^{3+} during filtration. Among them are *Birm*, *Pyrolox*, and *Manganese Greensand* based on manganese dioxides. Mn(III,IV) oxides are strong oxidants and mediate heterogeneous electron-transfer reactions from a wide range of sorbates, including phenols, humic substances, and polyvalent metals such as Cr(III), Fe(II), Mn(II), and Co(II) [3]. The basic reaction, which takes place in the filtering layer, can be written as follows [4]:



Ferric iron readily participates in hydrolysis reactions and produces a whole series of complex ions:



The further hydrolysis leads to the formation of $\text{Fe}(\text{OH})_3$:



Oxidative filters can remove up to 10 ppm of both ferric and ferrous iron. However, for successful operation of these filters the content of dissolved oxygen in ground water must be at least 15% of the iron content, and the pH must be higher than 6.8. Very often the oxygen concentration in ground water is close to zero, which is why pre-aeration is needed [5].

Sand filters are widely used in water treatment technological schemes for the reduction of turbidity, providing a means of removing different forms of iron from water. When iron containing water passes through the sand layer a catalytic film of Fe(III)–O–Fe(II) is formed on the surface of the sand particles. The catalytic film actively affects the oxidation and precipitation of iron from water. The film is permanently renewed due to the additional formation of Fe(III) oxide [3]. Similarly to the manganese containing filters the stable removal of iron with a sand filter can be achieved only in the presence of dissolved oxygen. In practice this makes the purification process more complicated.

Ion exchange is the most expensive and on the other hand the most effective method for iron removal. Such materials as *Crystal Right* can often remove iron, manganese, and small amounts of H_2S . It also adsorbs ammonia, decreases hardness, and elevates low pH. *Crystal Right* can also filter organic contaminants and capture insoluble inorganics. Zeolite differs from classical filtration products

because iron is removed through ion exchange. Therefore iron and manganese may not be oxidized [6].

The existence of a variety of filter media based on different principles and chemical processes gives an opportunity to choose a suitable one according to the local conditions. The aim of the present study was to compare the efficiency of different filter media for iron removal from Estonian potable water.

EXPERIMENTAL

Filtration experiments were carried out with Tallinn drinking water as a model solution. The main parameters of this water are given in Table 2.

Table 2. The main parameters of the water studied

Parameter	Mean \pm SD
pH	7.38 \pm 0.33
Total alkalinity, mg-eq/L	2.49 \pm 0.29
Total acidity, mg-eq/L	0.41 \pm 0.13
Hardness, mg-eq/L	6.03 \pm 0.64
Cl ⁻ , mg/L	21.71 \pm 26.90
SO ₄ ²⁻ , mg/L	61.25 \pm 14.01
NO ₃ ⁻ , mg/L	1.01 \pm 0.63
F ⁻ , mg/L	1.68 \pm 0.55
Silicates, mg SiO ₂ /L	1.15 \pm 0.36

As drinking water had quite a low ferrous ion (Fe²⁺) content, some ferrous sulphate was added before the experiments to bring the initial ferrous iron concentration up to 3.79 \pm 1.34 mg/L.

The experiments of filtration were performed using the laboratory equipment shown in Fig. 1. Water enriched with ferrous sulphate was led through the filtration column (volume 0.12 L, height 68 cm, diameter 1.5 cm). The filtration column was filled with a filter medium, such as *Birm*, *Pyrolox*, *Manganese Greensand*, *Crystal Right*, or sand. The operating conditions of the process are given in Table 3.

Table 3. Operation conditions of the process

	<i>Birm</i>	<i>Pyrolox</i>	<i>Manganese Greensand</i>	<i>Crystal Right</i>	Sand
Effective size, mm	0.5–2.0	0.8–1.0	0.25–0.8	0.5–1.0	0.5–1.0
MnO ₂ content, mg/g	162.2	1000	6.3	0	0
Bed depth, m	0.53	0.55	0.53	0.53	0.56
Bed mass, g	79	200	138	25	178
Oxygen concentration, mg/L	6.20 \pm 0.53	7.28 \pm 2.10	6.28 \pm 0.46	3.48 \pm 1.01	6.62 \pm 1.42
Flow rate, mL/min	33	30	38	38	38
Filtration rate, m/h	11.2	10.2	12.9	12.9	12.9
pH	6.93 \pm 0.14	7.56 \pm 0.19	7.69 \pm 0.14	7.21 \pm 0.20	7.37 \pm 0.14
Temperature, °C	19.41 \pm 2.00	20.74 \pm 1.11	20.37 \pm 0.87	26.44 \pm 1.93	24.11 \pm 2.54

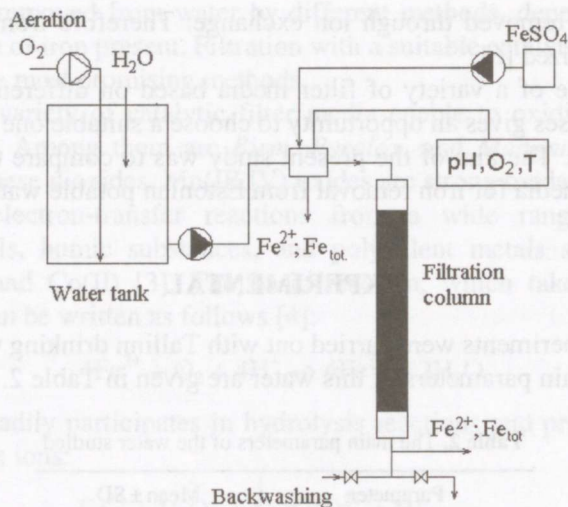


Fig. 1. Scheme of the experimental set.

The oxygen concentration and temperature were measured before filtration with MARVET OXYCOM 4 (ELKE SENSOR Co). Iron (ferrous and ferric) was analysed according to [7] before and after the process. Also the water quality change during adsorption was studied. Water hardness, total alkalinity, total acidity, pH, and SiO_2 content were measured according to [7]. The concentration of chloride, nitrate, sulphate, and fluoride in water were determined by ion chromatography [8].

RESULTS AND DISCUSSION

The changes in main water parameters before and after filtration through the different filter media were monitored.

The experiments on the sorption capacity of filter media were carried out till the iron ions break-through the filter, i.e. the ferrous iron concentration in filtered water reached the Estonian Standard guideline – 0.1 mg/L. The results presented in Figs. 2 and 3 indicate that all filter media remove iron quite successfully. Estimation of the amount of iron adsorbed from water showed that each manganese containing filter medium removed the same amount of iron – approximately 4 g per 1 kg of filter medium (see Fig. 2). The sand filter, removing 3.4 g Fe_{tot} /kg, was somewhat less effective. The sorption capacity of *Crystal Right* was about three times as high as that of the other filter media (11.7 g Fe_{tot} /kg).

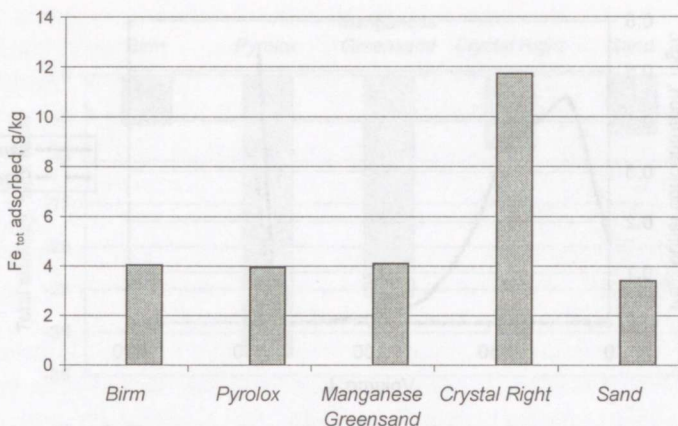


Fig. 2. Iron mass sorption capacity of the tested filter media.

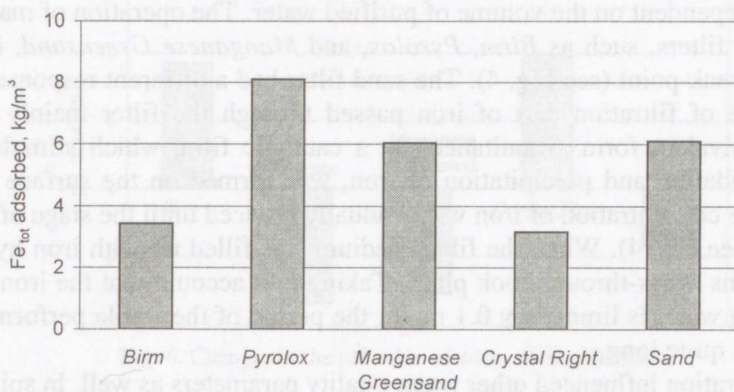


Fig. 3. Specific volumetric sorption capacity of the tested filter media.

Not only the mass sorption capacity of filter media (g Fe_{10t}/kg), but also a volumetric sorption capacity of filter media (kg Fe_{10t}/m³) is needed for designing filtration equipment. Volumetric sorption capacities calculated from the experimental data for different filter media are presented in Fig. 3. It is clear that *Pyrolox* (that is a black-manganese ore – a natural manganese dioxide) possessed the highest volumetric sorption capacity. *Pyrolox* is followed by other natural materials – sand and *Manganese Greensand* (volumetric sorption capacity 6 kg/m³). Light and porous artificial materials such as *Birm* and *Crystal Right* possessed lower volumetric sorption capacity, therefore, technological equipment would have larger dimensions.

For the right choice of technological equipment and the filter medium it is necessary to study the behaviour of the filter medium during the filtration. Figure 4 presents the total iron concentration profile in the water at the outlet of

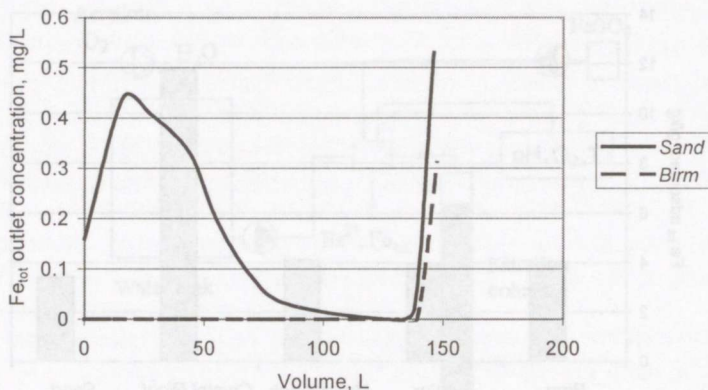


Fig. 4. Iron concentration profile in water after filtration versus volume of purified water.

the filter dependent on the volume of purified water. The operation of manganese containing filters, such as *Birm*, *Pyrolox*, and *Manganese Greensand*, is stable until the break-point (see Fig. 4). The sand filter had a different response. At the early stage of filtration part of iron passed through the filter mainly in non-oxidized bivalent form. Simultaneously a catalytic film, which stimulated the further oxidation and precipitation of iron, was formed on the surface of sand grains. The concentration of iron was gradually reduced until the stage of its total sorption (see Fig. 4). When the filter medium was filled up with iron hydroxide the iron ions break-through took place. Taking into account that the iron content in drinking water is limited by 0.1 mg/L, the period of the stable performance of the filter is quite long.

The filtration influenced other water quality parameters as well. In spite of the fact that there are no direct guidelines for total acidity and total alkalinity of drinking water they both influence the water (consumer) quality reducing or increasing the corrosion in pipelines. It can be noticed that total alkalinity was reduced by all filter media, especially by *Pyrolox* and *Manganese Greensand* (see Fig. 5). The same filter media increased the total acidity and decreased the pH value of water (see Fig. 6). Although no processes involving the formation of H^+ ions can take place during filtration through the sand filter, some increase in the acidity and decrease in the pH value was noticed also in this case. The filtration through *Crystal Right* was accompanied by enrichment of water with Na^+ ions; therefore, a decrease in total acidity and an increase in the pH value of water were observed (see Figs. 6 and 7). As the guidelines allow large variation in the drinking water pH (for example, pH value 6.5–8.5 for Estonian guidelines for quality class “excellent” [9]), the changes in the pH value during filtration by 10–15% can be neglected.

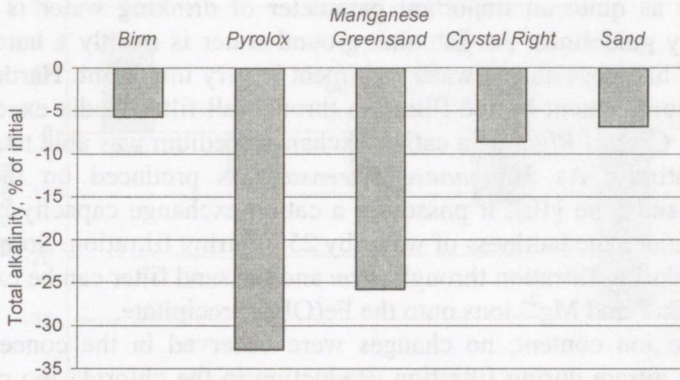


Fig. 5. Changes in the total alkalinity of water during filtration.

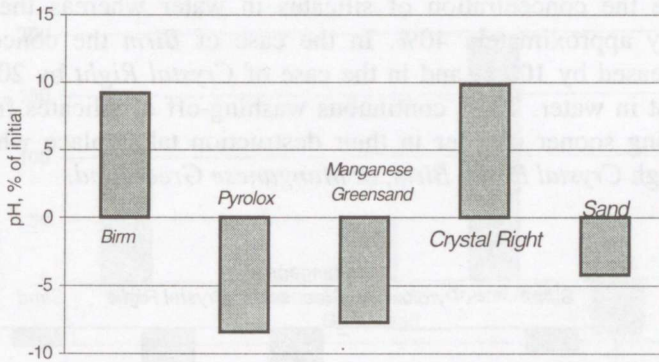


Fig. 6. Changes in the pH value of water during filtration.

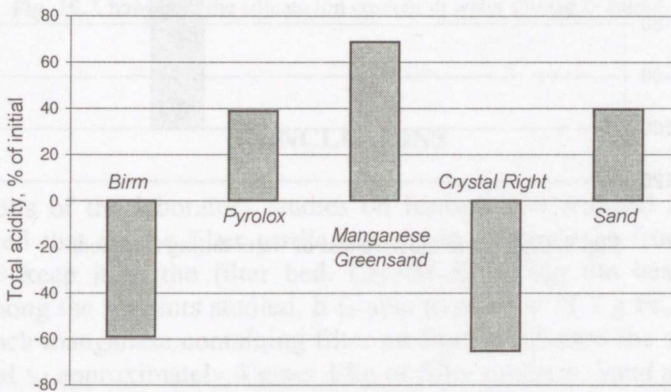


Fig. 7. Changes in the total acidity of water during filtration.

Hardness as quite an important parameter of drinking water is limited by water quality guidelines. As Estonian ground water is mainly a hard water the reduction of hardness during water treatment is very important. Hardness can be reduced to some extent by the filtration through all filter media except *Pyrolox* (see Fig. 8). *Crystal Right* as a cation exchange medium was able to remove the hardness entirely. As *Manganese Greensand* is produced on the basis of glauconite sandstone [10], it possesses a cation-exchange capacity as well and enables to reduce the hardness of water by 25% during filtration. Some reduction of hardness during filtration through *Birm* and the sand filter can be explained by sorption of Ca^{2+} and Mg^{2+} ions onto the $\text{Fe}(\text{OH})_3$ precipitate.

As to the ion content, no changes were observed in the concentration of fluoride and nitrate during filtration. Reduction in the chloride ion content was observed for all filter media except *Birm*. In the case of *Birm* the concentration of chloride ions increased by 15% (see Fig. 9). Changes in the content of water soluble silicates during filtration were also observed (see Fig. 10). *Pyrolox* did not influence the concentration of silicates in water whereas the sand filter reduced it by approximately 40%. In the case of *Birm* the concentration of silicates increased by 100%, and in the case of *Crystal Right* by 200% of their initial content in water. Thus, continuous washing-off of silicates from catalyst grains resulting sooner or later in their destruction takes place when water is filtered through *Crystal Right*, *Birm*, or *Manganese Greensand*.

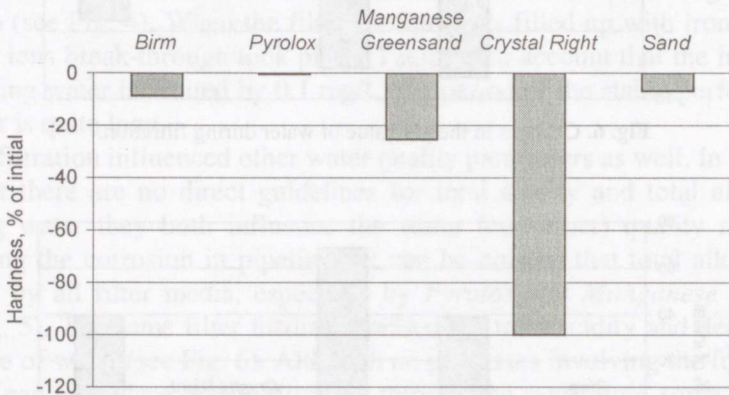


Fig. 8. Changes in the hardness of water during filtration.

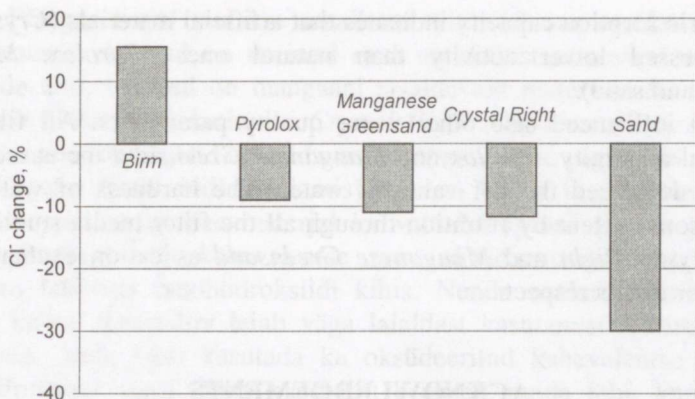


Fig. 9. Changes in the chloride ion content in water during filtration.

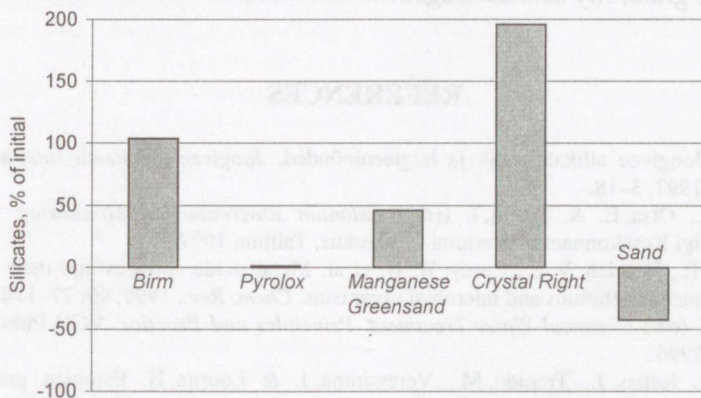


Fig. 10. Changes in the silicate ion content in water during filtration.

CONCLUSIONS

The results of the laboratory studies on ferrous iron removal from ground water showed that all the filter media tested can remove iron from water and successfully keep it in the filter bed. *Crystal Right* has the best adsorption capacity among the sorbents studied. It is able to remove 11.7 g Fe_{tot}/kg of filter medium. Each manganese containing filter medium eliminated the same amount of iron equal to approximately 4 g per 1 kg of filter medium. Sand also removed iron well. The sorption capacity of sand is 3.63 g of total iron per 1 kg of filter medium.

Volumetric sorption capacity indicates that artificial materials (*Crystal Right*, *Birm*) possessed lower activity than natural ones (*Pyrolox*, *Manganese Greensand*, and sand).

Filtration influenced also other water quality parameters. All filter media reduced total alkalinity. *Pyrolox* and *Manganese Greensand* increased the total acidity and decreased the pH value of water. The hardness of water can be reduced to some extent by filtration through all the filter media studied, except *Pyrolox*. *Crystal Right* and *Manganese Greensand* as cation exchange media were superior in this respect.

ACKNOWLEDGEMENTS

The authors would like to thank the Estonian Science Foundation (grant No. 2637) for the financial support. The technical assistance of Mrs. Marina Davydova is gratefully acknowledged.

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KATALÜÜTILINE FILTRIMINE JOOGIVEE KVALITEEDI PARANDAMISEKS

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Paljud Eesti pinnase- ja põhjaveed on rauarikkad. Sellised veed on kahjulikud inimese tervisele ja kõlbmatud kasutamiseks ka mõningates tööstusharudes. Selle tõttu on kahevalentse raua lubatud sisaldus joogi- ja tarbevees väga rangelt

piiratud. Praegusel ajal tuntakse maailmas mitmeid raua eraldamise tehnoloogilisi protsesse. Autorid on uurinud raua eraldamist erinevate teraliste filtermaterjalide abil. Uuritud on mangaani sisaldavaid materjale *Birm*, *Pyrolox* ja *Manganese Greensand*, kationiiti *Crystal Right* ning kvartslüüva. Katseandmed näitavad, et need materjalid eemaldavad veest rauaioone väga hästi. Kõige parem neist on *Crystal Right*, mille neelamisvõime on 11,7 g Fe_{uld}/kg materjali kohta. Samal ajal pehmendab see materjal ka vett. Mangaani sisaldavad materjalid toimivad katalüütiliselt kahevalentse raua oksüdatsioonil ning soodustavad sorptsiooni tekkivas raudhüdrosiidi kihis. Nende neelamisvõime on 4 g/kg materjali kohta. Kvartslüüv leiab väga laialdast kasutamist filtrimismaterjalina veekäitluses. Seda saab kasutada ka oksüdeeritud kahevalentse raua eraldamiseks. Protsessi algul laseb kvartslüüv osaliselt rauda läbi, kuni liivaterade pinnale kasvab piisava paksusega raudhüdrosiidi kiht, mis edaspidi on oksüdatsiooni katalüsaator.

Töö tulemused annavad võimaluse hinnata uuritud filtrimismaterjalide efektiivsust konkreetsetes eksploatatsioonitingimustes.