

EFFECT OF FULVIC ACIDS ON THE PROCESS
OF WATER PURIFICATION ON FILTRATION BEDS

ANNA M. ANIELAK, MARIUSZ WOJNICZ

Technical University of Koszalin, Department of Water and Wastewater Technology
ul. Śniadeckich 2, 75-453 Koszalin, Poland**Keywords:** Fulvic acids, zeolites, water purification, infiltration waters, filtration.

Abstract: This study examined the process of filtering of infiltrated water containing excessive amounts of iron, manganese, and fulvic acids through two filtration beds-sand and zeolite-exhibiting catalytic properties. The fulvic acids that were added to the filtered water were extracted from mud in Kolobrzeg. The zeolite bed was modified with manganese oxide using our own technology and required periodic regeneration using 0.3% KMnO_4 solution. Our study showed the fulvic acids' negative effect on the process of water purification. The zeolite bed reduces this effect and is more effective than the quartz sand bed.

INTRODUCTION

Infiltrated water develops from the infiltration of artificial or natural water known as waterside water (it is most often obtained from wells dug along the waterside of a river or lake). Examples of such water intakes include Krajkowo near Poznań, Gruba Kaśka in Warsaw, Dębina in Poznań, SUW in Wasilkowo (Podlasie Voivodeship), Czyzykowko in Bydgoszcz, and Bielany in Krakow. Besides impurities typical of groundwater (e.g. iron, manganese), this water also contains large amounts of ammonia nitrogen and naturally occurring organic substances. Infiltration removes microorganisms, suspended matter, and colloidal particles, and only solutes remain in the water. The concentration of oxygen may reach $2.0 \text{ mg O}_2/\text{dm}^3$, and the concentration of humic substances is between 2 and $7 \text{ mg C}/\text{dm}^3$. Fulvic acids pose a special problem in the treatment of this water. Along with manganese and iron, they form soluble organic complexes, lower the pH of water, give color to it, and in the processes of oxidation and disinfection they are precursors to toxic, carcinogenic, and mutagenic substances.

Humic substances are widely present in surface waters. In rivers, their concentration can be as high as $6 \text{ mg}/\text{dm}^3$ and in swamp waters may exceed $18 \text{ mg}/\text{dm}^3$. They reach the surface waters mainly from the soils of the drainage area. They have a strong coloration from brown to black and hence give color to water. In water solutions they assume spherical shapes. Their aliphatic elements become hydrated, creating chains that are stretched and directed outwards, with polar functional groups: hydroxyl (-OH), carboxyl (-COOH), methoxyl (-OCH₃), methyl (-CH₃), methylene (-CH₂) groups. The hydrophobic fragments are from the aromatic and heterocyclic rings like benzene, furan, pyridine, and also naph-

thalene, anthracene, indole, and quinoline. The model described by Gonet [7] was tested and confirmed using magnetic resonance [5, 6].

Humic substances exhibit a great ability to complex with metal ions, especially Fe^{3+} , Al^{3+} , and Cu^{2+} [9]. They are resistant to biodegradation, and practically are never decomposed by activated sludge in a biological treatment plant. The discharge from sewage treatment (facilities) plant is characterized by high levels of humic substances. These substances are decomposed by microorganisms adapted to the scarcity of organic compounds. They are the eubacteria (*Agrobacterium sp.*, *Bacillus sp.*, *Clostridium sp.*, *Pseudomonas sp.*, *P. fluorescens* and others), myxomycetes, actinomycetes (*Actinomyces sp.*, *Micromonospora sp.*, *Rhodococcus sp.* and others), yeast-like fungi (*Rhodotorula sp.*), moulds (*Aspergillus sp.*, *Cladosporium cladosporioides*, *Penicillium sp.* and others) [8].

In the light of the structure and characteristics of fulvic acids, it is reasonable to expect that they would hinder the process of water treatment. That is why we decided to study the effect of humic substances on the removal of select substances from infiltrated water during its high-rate filtration independently through two filtration beds, manganese-modified zeolite and quartz sand.

TESTING METHODOLOGY

The tests were conducted at the testing station depicted in Figure 1. There were two high-rate filters with two different beds. The first was a modified zeolite, and the second was quartz sand. The active height of each bed was 0.7 m, and the height of the supporting layer was 0.1 m. The filtered water flowed downstream through the beds at a speed of $v = 5$ m/h. The filter washing was upstream, every 48 hours, with a speed ensuring an 80% expansion of the bed. Rinsing of the bed lasted 15 minutes. Rinsing was performed every 48 hours.

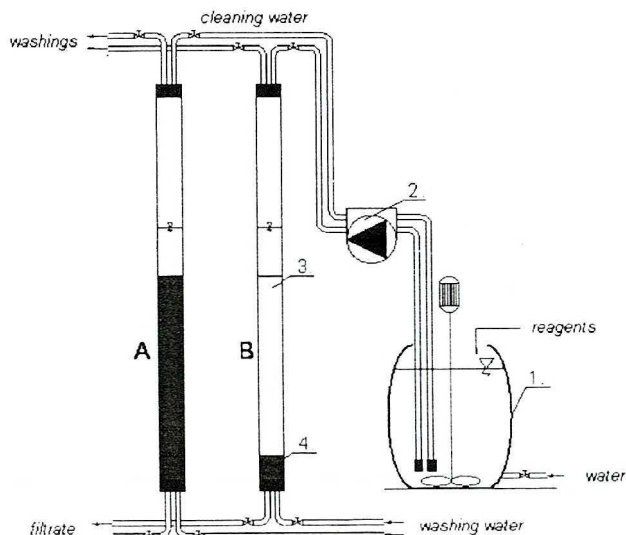


Fig. 1. Layout of the (testing) research station: 1 – treated water reservoir, 2 – dosing pump, 3 – actual filtration layer, 4 – supporting layer, A – zeolite filtration column, B – quartz sand filtration column

Manganese modified bed was regenerated every 14 days with 0.3% KMnO_4 solution. Regeneration lasted 10 minutes, and the speed of solution flow was 4–5 m/h. The chosen regeneration time [4] ensured an adequate catalytic capacity of the bed and a high level of filtration.

FILTRATION BED CHARACTERISTICS

The filtration beds used in the study contained grains with a granularity of 0.5–1.0 mm. The results of the granulometric analysis of the beds are shown in Figure 2. The analysis of the grain composition curves shows that the zeolite bed contained more grains with a diameter greater than 0.63 mm (37%) than the quartz sand bed (21%). Roughly speaking, the size of the grains in the beds was similar.

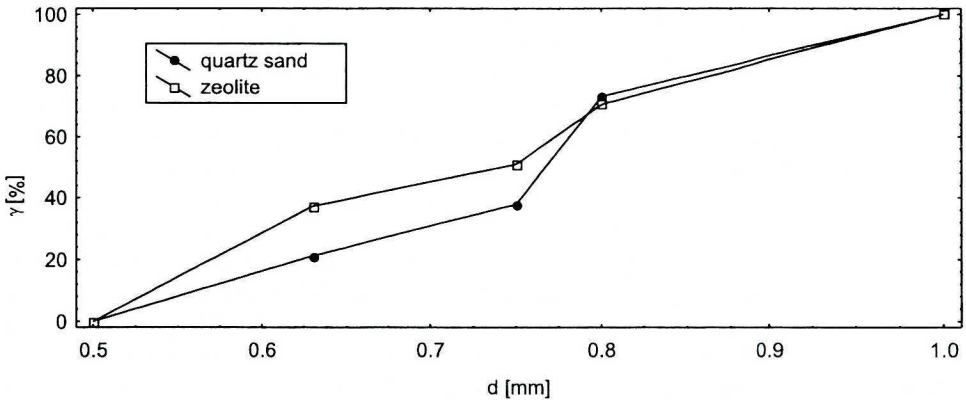


Fig. 2. Curve of the grain composition of the filtration beds

The natural mineral contained 55% clinoptilolite, 26% ash and volcanic glass, 13% montmorillonite, and 6% quartz. The modified zeolite contained 80 mg/g Mn, 295 mg/g Si and 55 mg/g Al [3]. Figure 3 shows a photograph of the manganese-modified zeolite grains. A detailed description of this mineral can be found in [1].

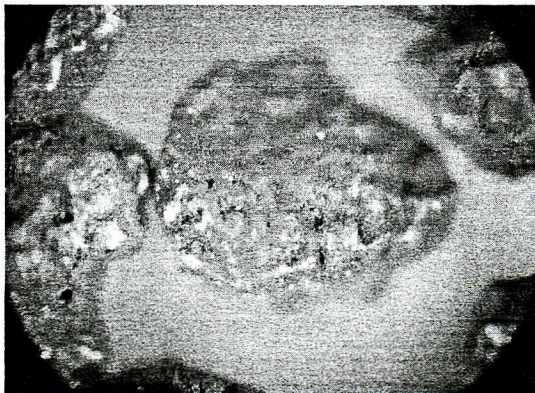


Fig. 3. Natural manganese-modified zeolite

The quartz sand was of the kind widely used in water treatment plant. Its density was 2.65 g/cm^3 , and its hardness on the Mohs scale was 7. It contained 95–99.5% SiO_2 , 0.05% Al_2O_3 , and 0.03% Fe_2O_3 , as well as other trace substances.

CHARACTERISTICS OF TESTED MODELING WATER

The tests were conducted on two water sets, both obtained from the tap. After 24 hours of water standing still, the appropriate amount of salt was added to the settled water to ensure an adequate concentration (1 mg/dm^3) of Mn(II), Fe(II), and ammonium ions. The following salts were dosed: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and NH_4Cl . The second water set additionally contained fulvic acids in the amount of 5 mg/dm^3 .

The fulvic acids were obtained through extraction from Kołobrzeg mud [2]. The content of elementary elements converted into ash-free mass of fulvic acids was as follows: N – 2.56%, C – 45.89%, H – 4.96%, S – 0.40%, O – 46.19%. The amount of ash was 3.89%. The calculated atomic ratio in ash-free mass equals 1.297 and is evidence of the aromatic structure of fulvic acids, the (quotient) ratio $\text{C/N} = 20.92$ are characteristic of a constant humic phase and the (quotient) ratio $\text{O/C} = 1$ corresponds to the fulvic acids present in surface waters [8].

During the course of testing, the concentration of manganese in the water was high but did not exceed 1 mg/dm^3 , and the maximum concentration of iron was 1.16 mg/dm^3 . The basic statistics on the major indicators of both modeling waters is shown in Table 1. In the second modeling water the concentration of Mn (average 0.98 mg/dm^3) and Fe (1.08 mg/dm^3) were similar to the amounts in the first modeling water. Similarly, the concentration of ammonium averaged 1.95 mg/dm^3 for the first modeling water and 1.92 mg/dm^3 for the second. The values for the other indicators were normative. The average concentration of chloride in all water sets was 22 mg/dm^3 . The water sets had an average hardness of 4.20 mval/dm^3 and a solute concentration of 281 mg/dm^3 .

Table 1. Basic statistics on the major indicators of the first and second modeling water

	First modeling water					Second modeling water				
	Mn [mg/dm^3]	Fe [mg/dm^3]	NH_4 [mg/dm^3]	NO_3 [mg/dm^3]	pH [–]	Mn [mg/dm^3]	Fe [mg/dm^3]	NH_4 [mg/dm^3]	NO_3 [mg/dm^3]	pH [–]
Mean	0.89	0.90	1.95	0.27	7.49	0.98	1.08	1.92	0.31	7.39
Median	0.88	0.88	1.96	0.26	7.51	0.97	1.09	1.94	0.29	7.38
Std. dev.	0.04	0.11	0.10	0.05	0.06	0.04	0.10	0.06	0.10	0.09
Minimum	0.80	0.78	1.74	0.19	7.36	0.92	0.93	1.84	0.18	7.28
Maximum	0.96	1.16	2.09	0.35	7.56	1.04	1.19	1.97	0.44	7.55

DESCRIPTION AND ANALYSIS OF TEST RESULTS ASSESSMENT OF THE EFFECTIVENESS OF THE FILTRATION BEDS

The study aimed at analyzing the purification process of water sets of various compositions on zeolite and sand filtration beds. The tests were conducted over a period of more than 250 days, and this article investigates a 60-day subset of that period. The results of the process research, conducted with two prepared modeling waters are shown in Figures 5–13.

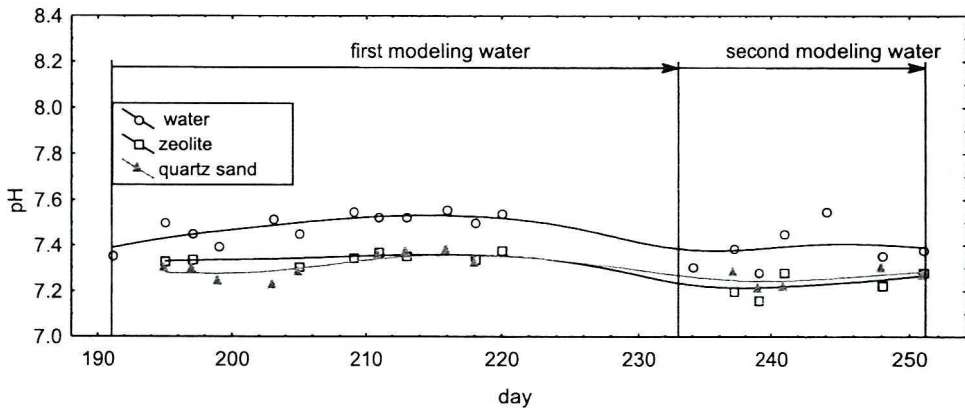


Fig. 4. Reaction of raw water and filtrates on various days of the study

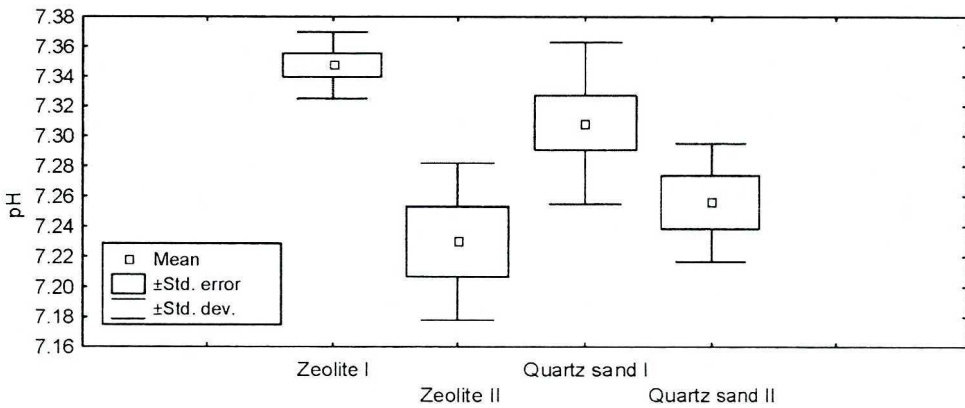


Fig. 5. Basic statistics on the filtrate reactions

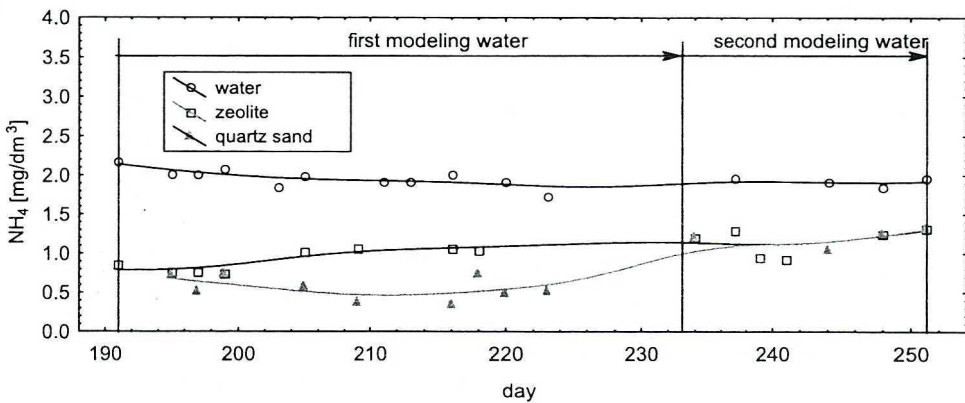


Fig. 6. Ammonium content in raw water and filtrates

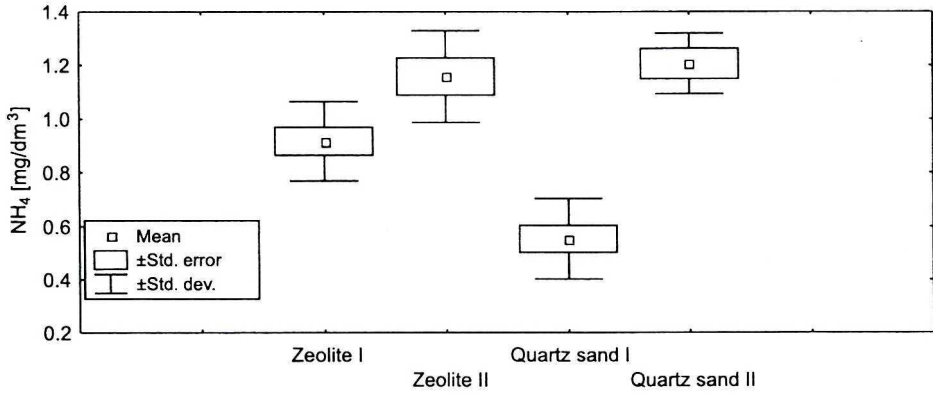


Fig. 7. Basic statistics on the concentration of ammonium in the filtrates

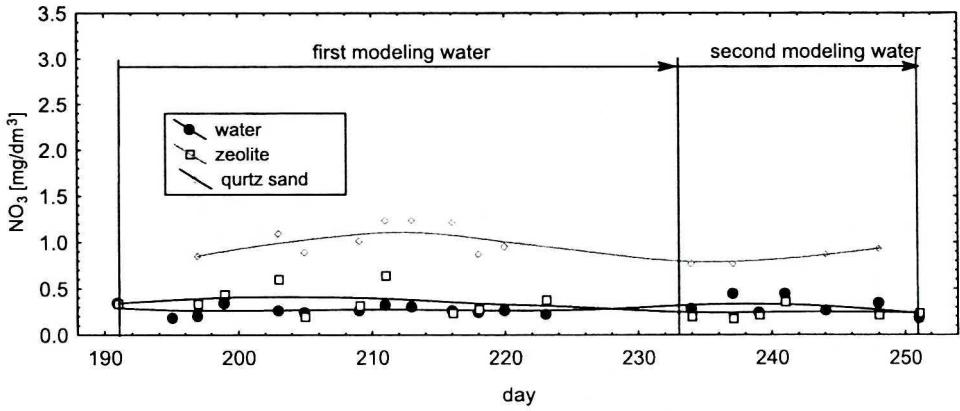


Fig. 8. Nitrogen ion content in raw water and filtrates

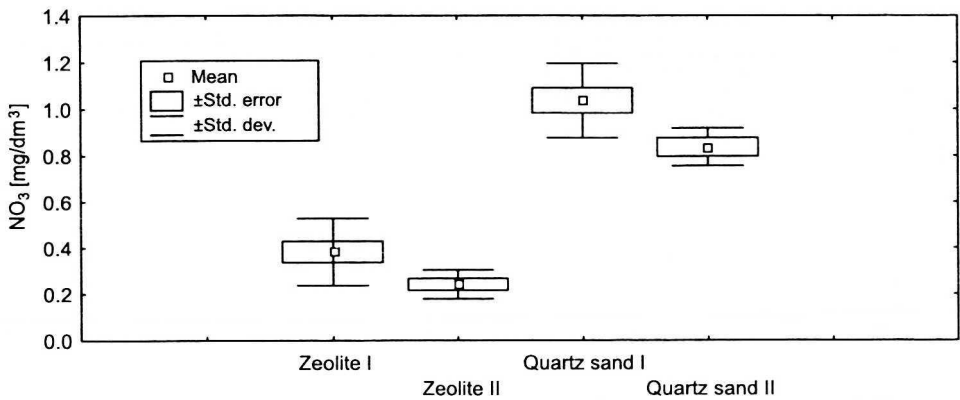


Fig. 9. Basic statistics on the concentration of nitrogen ions in the filtrates

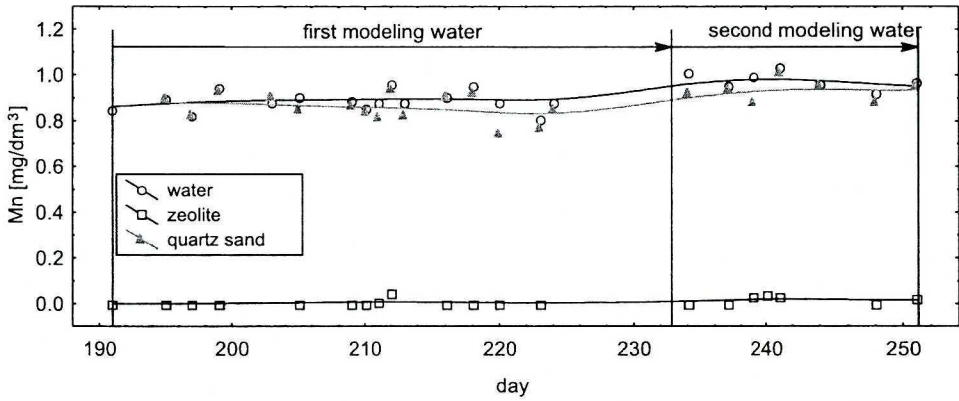


Fig. 10. Manganese ion content in raw water and filtrates

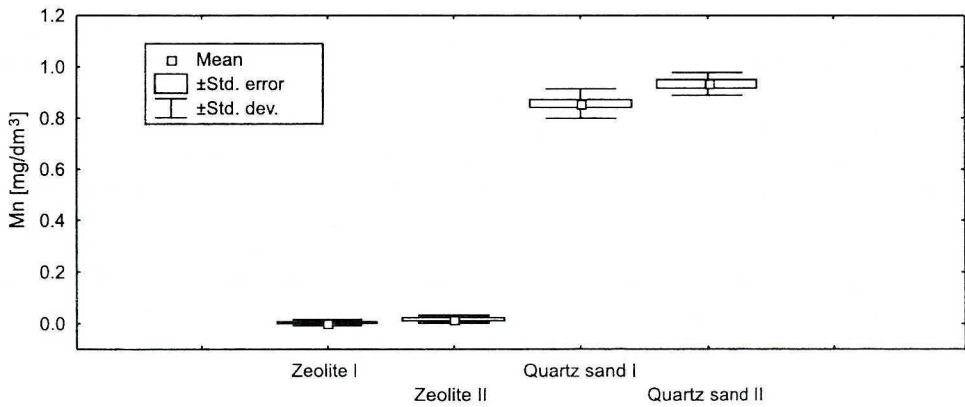


Fig. 11. Basic statistics on the concentration of manganese ions in the filtrates

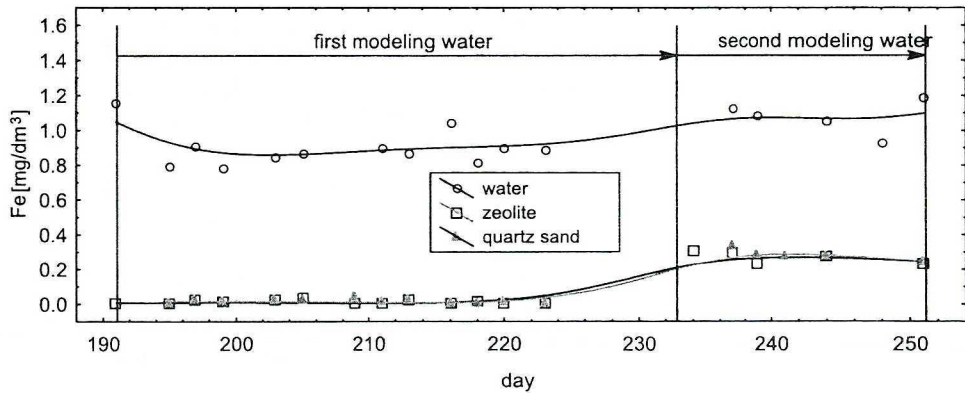


Fig. 12. Iron ion content in raw water and filtrates

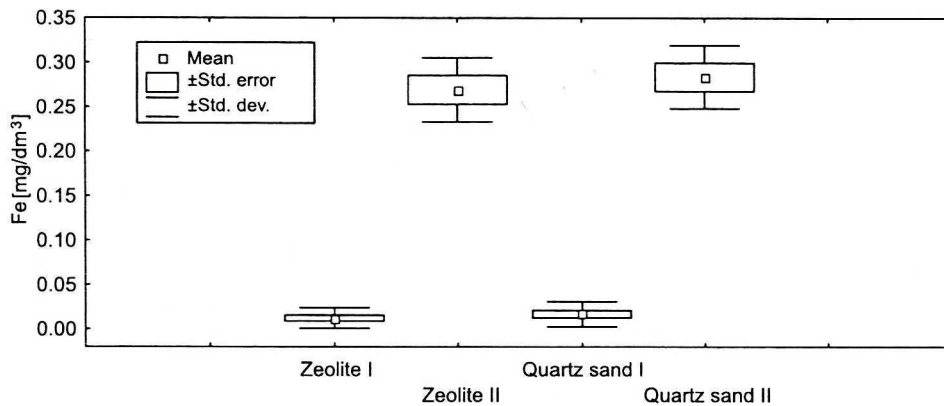


Fig. 13. Basic statistics on the concentration of iron ions in the filtrates

The analysis of the reaction of the modeling waters (Figs 5 and 6) reveals that the pH of the sand bed filtrate of the first modeling water was 7.31, whereas the reaction of the second modeling water was 7.26. The results were similar for the zeolite bed; the filtrate of the first modeling water had an average pH of 7.35, and that of the second modeling water had pH of 7.23. The lower pH of the filtrate from the second modeling water was caused by the humic acids, whose reaction is slightly acidic. The standard deviation and standard error of the average pH values (Fig. 5) indicate high measurement accuracy.

The amount of ammonium in the first raw water was 1.95 mg/dm³. The analysis of the amount of ammonium in the tested filtrates indicates that with the first modeling water nitrification is more efficient in the sand bed than in the zeolite bed, whereas with the filtration of the water containing humic acids, nitrification takes place at the same level in both beds (Figs 6 and 7). There are various mechanisms of removing ammonium (as well as iron and manganese ions) in the tested beds. While in sand bed the formed bacterial film and growing microflora are responsible for oxidation of ammonia compounds to nitric and nitrite, in zeolite bed these ions are removed in physico-chemical processes of oxidation and sorption. The zeolite bed was periodically regenerated with potassium permanganate solution to restore its catalytic properties. This solution is also a strong oxidizing agent and had a disinfecting effect on the filtration bed, which limited the growth of microorganisms. On the sand bed could grow the autotrophic chemosynthetic bacteria *Nitrosomonas*, *Nitrosocystis*, *Nitrosolubus*, *Nitrosospira*, *Nitrococcus*, *Nitrospira* and *Nitrobacter*, which is why we observe a decrease in the concentration of ammonium in the filtrate. The nitrification process happens in two stages: first, *Nitrosomonas* oxidizes ammonium into nitrites, and then *Nitrobacter* converts the nitrites into nitrates. The second stage usually happens very rapidly, that is why the nitrites are not shown.

When filtering the second modeling water, the removal of ammonium with the zeolite bed worsened slightly (from 0.92 mg/dm³ to 1.16 mg/dm³), whereas on the sand bed this decline was pronounced (from 0.55 mg/dm³ to 1.21 mg/dm³) (Fig. 7). This was the result of the negative, bacteriostatic influence of the fulvic acids, despite the fact that the temperature was between 20 and 30°C and the pH was optimal for nitrification. The effectiveness of nitrification falls by about 50% below a pH of 7.0 and near a pH 9.8.

Due to the superior nitrification, the concentration of the nitrate ions in the filtrate obtained from the sand bed was higher than that from the zeolite bed (Figs 9 and 10). The average concentration of the nitrate nitrogen in the filtrates of the first modeling water filtered by the sand bed was 1.04 mg/dm^3 and in the second 0.84 mg/dm^3 . But for the zeolite bed the concentration of nitrate ions did not exceed 0.4 mg/dm^3 . When treating the water containing the humic acids the nitrification worsened, analogous to the removal of ammonium for the zeolite and sand columns.

While analyzing the amount of manganese in the water it was observed that modeling water composition did not influence significantly manganese ions removal in the zeolite column (Figs 10 and 11). The concentration of manganese ions in the filtrate during the course of the study was 0 mg/dm^3 for the water sets with and without fulvic acid. On the other hand, the removal of manganese ions on the sand bed was small in the case of the first modeling water (0.86 mg/dm^3) and worsened to 0.93 mg/dm^3 in the presence of fulvic acids. It would stand to reason that the fulvic acids impeded the oxidation of Mn(II) to Mn(IV). They could also have combined with Mn(II) into soluble complexes, which are difficult to remove during filtration.

The analysis of the iron content in the filtrates from the zeolite and sand beds as compared to its content in the raw water indicates that the effectiveness of removing this cation was similar for both beds, but different for each modeling water set. For the first modeling water the effectiveness was very high (on the order of 99% for the zeolite bed and 98% for the sand bed). Filtering the water containing the fulvic acids produced filtrates in which the effectiveness of iron removal was considerably lower: 75% for the zeolite bed and 74% for the sand bed (Figs 12 and 13). The drop in effectiveness of the beds with regard to the second modeling water was caused by the creation of soluble complexes of iron and fulvic acids.

CONCLUSIONS

The results of this study lead us to the following conclusions:

1. Humic substances decelerate biochemical processes, inhibiting nitrification.
2. The presence of fulvic acids reduces the removal of Mn(II) and Fe(II) from the water.
3. Manganese-modified zeolite beds are more effective than quartz sand beds at purifying water with and without humic substances.
4. Humic substances lower the pH of water and of the filtrate.

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WPLYW KWASÓW FULWOWYCH NA EFEKTYWNOŚĆ OCZYSZCZANIA WODY NA ZŁOŻACH FILTRACYJNYCH

W pracy przebadano proces filtracji wody infiltracyjnej o nadmiernej ilości żelaza, manganu i kwasów fulwowych przez dwa złoża filtracyjne: piaskowe i zeolitowe wykazujące właściwości katalityczne. Kwasy fulwowe dodawane do filtrowanej wody ekstrahowano z kołobrzeskiej borowiny. Złoże zeolitowe było modyfikowane tlenkami manganu według własnej technologii i wymagało okresowej regeneracji 0,3% roztworem KMnO_4 . Badania wykazały ujemny wpływ kwasów fulwowych na procesy oczyszczania wody. Złoże zeolitowe pomimo trudnych warunków oczyszczania wody jest efektywniejsze od złoża kwarcowo-piaskowego.