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INFLUENCE OF FILTRATION BED STRUCTURE ON MICROORGANISMS DEVELOPMENT IN THE PROCESS OF MANGANESE AND IRON REMOVAL FROM WATER

Five active materials, recommended for removing manganese from water, were investigated in the study: Purolite MZ-10, G-1, Birm, Hydrocleanit and Defeman. The investigation was carried out in dynamic conditions, using continuous running laboratory filter. Each working cycle of a filter lasted 48 hours and consisted of filtration, rinsing a filter bed and servicing. Results of dynamic research unambiguously show that the effectivenss of the process of manganese removal from the water by beds depends on the kind of filtration mass, which makes the bed appropriate for development of water biocenosis. Removal of manganese and iron from water by mass G-1, Birm and Defeman is first of all controlled by the activity of such microorganisms as *Naumaniella* and *Siderocapsa* and not identified rods with the deposit of Mn(IV) in the form of lamella in central part or cellular wall.

1. INTRODUCTION

Underground waters often include excessive quantity of manganese, which in negative way influences their organoleptic and physicochemical characteristics. In natural waters, manganese appears most often as bivalent ions whose compounds are soluble. In classical method of treating such waters, manganese is oxidize to Mn(IV), then the water is passed through filtration bed. Quartz sand bed is most frequently applied bed. The process of manganese oxidation with oxygen takes place only at high pH. In the presence of oxygen, manganese in the concentration of 10^{-5} mole/dm^3 oxidises at pH > 9.5. Mn(II) oxidation with oxygen at pH values acceptable for drinking water is rather in effective, hence in practice chemical oxidation is applied, e.g. with chlorine gas. This is connected with additional introduction of chemicals into the water and also with formation of bromates, trihalomethanes and other cancerogenous and mutagenous compounds. The problems associated with alkalization or oxidation may be solved by applying ac-

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tive filtration mass. Manganese ores, zeolites or minerals containing calcium carbonate and magnesium carbonate are most frequently used masses.

So, effectiveness of manganese removal from the water depends on different factors. That is why it may be assumed that it is a complexed process. During water filtration through the filtration bed a bacterial jelly is formed, thus biochemical reactions also occur. According to GRABIŃSKA-ŁONIEWSKA [4], [5] under the influence of microorganisms the manganese and iron compounds are oxidized with cellular enzymes and are bound in cellular organelles. Those chemical processes with no doubt depend on water composition and kind of a bed. That is why we aimed at establishing the relationship between biological processes and the removal of manganese and iron from water when it is filtered through active bed.

2. FILTRATION MASSES USED FOR THE RESEARCH

Five active masses [1] recommended for water treatment in filtration process have been tested: Purolite MZ-10, G-1, Birm, Hydrocleanit and Defeman. Purolite mass MZ-10 is aluminosilicate which besides SiO_2, Al_2O_3 contains K_2O, MgO, Fe_2O_3. Purolite MZ-10 requires activating with an oxidizer, e.g. potassium permanganate solution, and should be applied in pH range of 6.5–8.5. Active mass G-1 is produced from imported, highly manganic ore by special treatment according to Polish technology. The filling of a filter consists of 30–100% of that mass, and its remaining part makes quartz sand. In water treatment process, water alkalization is not required. Birm mass contains: manganese dioxide, amorphous and crystalline silica and binding compounds. Hydrocleanit is mineral material containing magnesium and calcium oxides in the amount of approximately 90%. Mass activity is based on water alkalization. The bed, which has been used up, cannot be regenerated nor is resistant to action of acid solutions. Defeman mass is a catalyctic filtration material of natural origin. It does not require working nor regeneration. pH of the water being treated should be contained within 7–8.5.

3. RESEARCH METHOD

The process of Mn(II) and Fe(overall) removal from water was carried out in a dynamic configuration presented in figure 1. Glass filtration columns were 1200 mm high with internal diameter of 25 mm. Filtration bed of the height of 700 mm was supported by a layer of filter gravel 80 mm thick and 3–5 mm graining. Treated water was poured into the bed with the pump Ecoline VC-360 made by Ismatec. Purolite mass MZ-10, as recommended by the producer, before starting the test was activated for 30 minutes with 0.3% solution of $KMnO_4$ flowing through the bed at the speed of 4 m/h. The bed was rinsed counter-currently with tap water at the speed of 6 m/h for 30 minutes. Filtration speed of treated water was constant and amounted to 5 m/h.

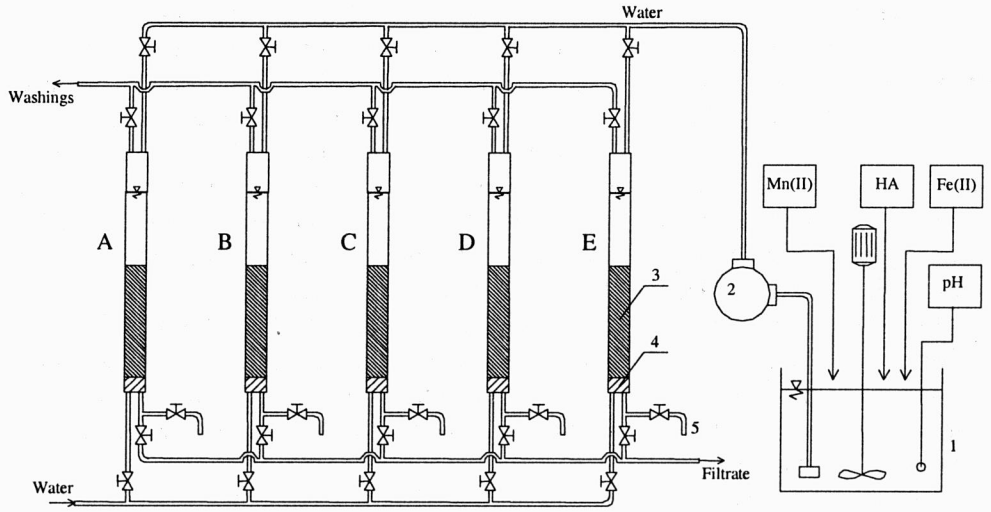

Fig. 1. Experimental set-up: 1 – raw water tank, 2 – dosing pump, 3 – filtration layer (active mass), 4 – supporting layer, 5 – point of taking samples, A – filtration column with the Purolite MZ-10 filler, B – filtration column with the G-1 filler, C – filtration column with the Birm filler, D – filtration column with the Hydrocleanit filler, E – filtration column with the Defeman filler

Operating cycle of the filters lasted 48 hours and consisted of rinsing and filtration. The beds were rinsed with tap water keeping 40% expansion. Rinsing time was 15 minutes.

The filtrate obtained was analyzed for manganese and overall iron. The research lasted 136 days.

On the 136th day of work of the bed the samples of filter filllers drawn from the top layer were tested. In order to wash off the bacterial biocenosis from the filler surface, sodium pyrophosphate at pH = 8.0 was applied. Water slurry was shaken for 30 minutes in the shaker at the speed of 250 rot/min.

Total number of saprophytic bacteria was counted with the Koch dish method on agar medium (MPA), culturing bacteria at the temperature of 26 °C for 7 days in accordance with PN-75/C 04615.03. The result of counting was given as UMC (Units Making Colonies) in 1 g of filling.

A total number of microscopic fungi were counted with the Koch dish method on selective medium according to Martin. Fungi were cultured at the temperature of 26 °C for 7 days. The result of counting was given as UMC (Units Making Colonies) in 1 g of filling.

Autotrophic nitrifying bacteria were counted in the fluid medium according to Winogradzki (PN-77/C 04615.20) after the 14th day of incubation at 26 °C. The result was given as MPN (Most Probable Number) with distinguishing bacteria of the 1st and the 2nd phases in 100 g of a filling.

Bacteria from the *Siderocapsaceae* family oxidizing Mn(II) and Fe(II) were counted in the medium according to Winogradzki containing manganese octane and ferric ammonium citrate as the sources of Mn(II) and Fe(II), respectively. Compounds of Fe(III) and Mn(IV) in bacteria cells were stained according to the method recommended by Rodina. Bacteria were observed in a contrast-phase microscope made by Opton. The species of bacteria were identified on the basis of Bergey's key. The results of counting were given as MPN (Most Probable Number) in 100 g of filling.

The content of treated water was nearly constant. The water being tested was prepared as follows: such amounts of $MnSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot H_2O$ were added to tap water that the manganese and iron concentrations reached 1.0 and 1.4 mg/dm^3, respectively. Assuming that ground water infiltrated into underground water, humic substances consisting of fulvic acids (60%) and humic acids (40%) were added. Concentration of humic substances in water amounted to 5 mg/dm^3. Average content of treated water was presented in table 1.

Humic acids (fulvic and humic) were extracted from the bottoms of the Dzierżęcinka river [2], [3].

Table 1

Average coposition of the water treated using active filtration masses

Index	Unit	Value
Reaction	pH	7.5
Manganese	mg/dm^3	1.0
Overall iron	mg/dm^3	1.4
Oxygen consumption	mg/dm^3 O_2	1.6
Turbidity	mg/dm^3	1.0
Colour	mg Pt/dm^3	5.0
Aroma	–	2.0
General hardness	mval/dm^3	7.0
Alkalinity	mval/dm^3	3.5
Chlorides	mg/dm^3	35.8
Ammonia nitrogen	mg/dm^3	0.01
Nitrate nitrogen	mg/dm^3	0.05
Humic substances	mg/dm^3	5.0
Electrolytic conductivity	μS/cm	594

4. DISCUSSION OF THE RESULTS

4.1. EFFICIENCY OF FILTRATION BEDS

Both manganese and iron were removed from water for 136 days. The results obtained on the 24th and the 126th days of filtration show that better results are obtained after ripping the filtration beds.

Analysis of the results presented in figure 2 shows that all masses except Hydrocleanit efficiently remove manganese from water, which can be attributed to the covering of the surface of the latter with adsorbed substances. In an initial stage of bed operation, they form a layer that makes penetration of calcium and manganese ions into a water impossible, thus increasing water pH.

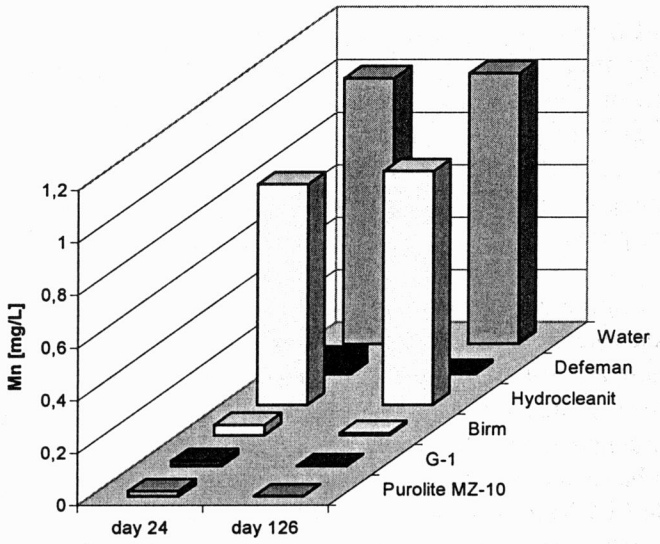

Fig. 2. Manganese concentration in filtrate in chosen days of filtration system operation

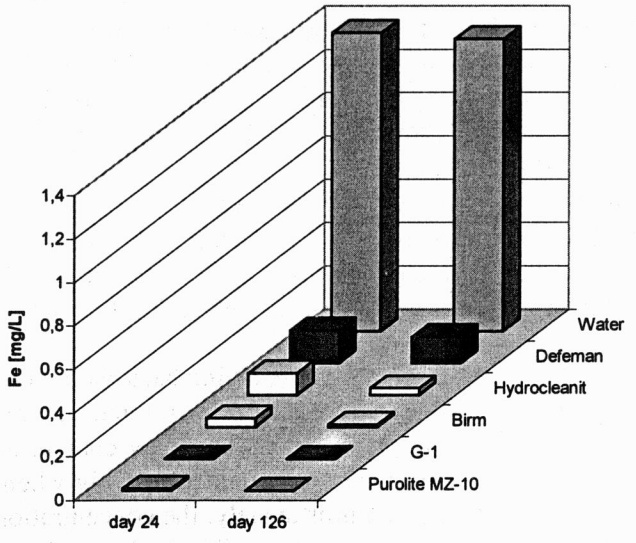

Fig. 3. Iron concentration in filtrate during chosen days of filtration system operation

Iron(III) is a cation that can be easily removed from water. Iron(II) is easily oxidized to Fe(III), e.g. in aeration process. That is why the results presented in figure 3 prove that the process of iron removal occurs regularly in each filtration bed tested.

4.2. MICROBIOLOGICAL TESTS

GRABIŃSKA-ŁONIEWSKA [4], [5] reported that *Naumanniella* sp. from the *Siderocapsaceae* family often accumulates iron and manganese in the form of granularities placed terminally or centrally in the form of the so-called torus, i.e. a thickening of the edges of cells. The shape of torous formed by *Siderocapsa* sp. bacteria resembles a horseshoe. The author divides bacteria oxidizing iron and manganese into bacteria accumulating compounds of Fe(III) or Mn(IV) outside of cells (unicellular bacteria, thready bacteria, purple bacteria) and bacteria accumulating compounds of Fe(III) or Mn(IV) intracellularly.

In practice, manganese and iron most often are removed by one filtration bed. That is why we carried out microbiological tests of biocenosis growing on filtration beds by which iron and manganese are being removed at the same time. Inoculation of the bed in particular with manganese oxidizing bacteria is a long lasting process. For this reason microbiological tests were conducted for the bed after 136 days of its working.

The results obtained allow us to state that manganese removal from water with the usage of Purolite MZ-10 mass is based on biological processes.

Number of saprophytic bacteria was determined as $550 \cdot 10^4$ UMC/g, and that of microscopic fungi as $330 \cdot 10^3$ UMC/g. Fungi were dominated by yeast from the *Rhodotorula* genus. MPN of nitrifying bacteria of the 1st phase ($130 \cdot 10^3$ in 100 g of filling) and of the 2nd phase ($62 \cdot 10^2$/100 g) were found to be huge.

Mn(II) oxidizing bacteria were mainly represented by *Naumanniella* sp. (80%), but the genus of *Siderocapsa* sp. (20%) with characteristic deposit of Mn(IV) salt in central part of the cell was also present. Total MPN in both groups of those bacteria amounted to $63 \cdot 10^3$ in 100 g of filling.

Fe(II) oxidizing bacteria, whose amount in bed was the same as that of Mn(II) oxidizing bacteria (MPN = $62 \cdot 10^3$/100 g), were represented exclusively by the genus of *Siderocapsa*. It should be stressed that those bacteria accumulated Fe(III) mainly in cell wall and like Mn(II) oxidizing *Siderocapsa* they did not create capsules so characteristic of that genus.

The occurrence of both Mn(II) and Fe(II) oxidizing bacteria in one bed proves that in such conditions the bioprocess of manganese and iron removal may be carried out. The presence of nitrifying bacteria proves that water may contain ammonium ions, hence the process of manganese removal may occur effectively when water contains some quantities of ammonia nitrogen. Unfortunately, the concentration of ammonium ions was not determined, therefore it was not possible to define their maximum concentration allowing an effective biological process of manganese removal.

Microbiological tests showed that biocenosis growing on Purolite MZ-10 bed contained microscopic fungus, *Rhodotorula* sp., whose UMC in 1 g amounts to $330 \cdot 10^3$. The presence of this fungus may be explained by the occurrence of humic substances in water. Those substances are most resistant to biological decomposition, but as Grabińska-Łoniewska reported also actionomycetes from *Nocardia* genus, hypha fungi from *Aspergillus*, *Penicillium*, *Polystictus* and *Spicaria* genera and also yeast-like fungi can take part in that process.

Biocenoses occupying G-1 bed and Purolite MZ-10 bed have similar qualitative composition. However, they distinctly differ in the quantity. It was found that also saprophytic bacteria occurred. After 136 days of bed operation at the depth of 2–4 cm from the surface, their total number expressed in terms of UMC is equal to approx. $380 \cdot 10^4$ in 1 g and was smaller than the number of bacteria in Purolite MZ-10 bed. Among the iron and manganese oxidizing bacteria prevailed heterotrophic species from *Siderocapsaceae* family including Mn(II) oxidizing bacteria (MPN in 100 g was $240 \cdot 10^3$), and Fe(II) oxidizing bacteria (MPN in 100 g was $> 240 \cdot 10^5$). Mn(II) oxidizing bacteria from *Siderocapsaceae* family formed not distinctly identified rods (5 μm in length and 1 μm in width) similar to rods with the deposit of Mn(IV) salt in the form of a lamella in central part or wall cell (photo 1).

Table 2

Results of microbiological tests of biocenosis growing on beds

Symbol	Purolite MZ-10	G-1	Birm	Hydrocleanit	Defeman
Total number of saprophytic bacteria, UMC in 1 g	$550 \cdot 10^4$	$380 \cdot 10^4$	$240 \cdot 10^4$	$120 \cdot 10^4$	$150 \cdot 10^4$
Total number of microscopic bacteria, UMC in 1 g	$330 \cdot 10^3$	$45 \cdot 10^3$	$24 \cdot 10^3$	$154 \cdot 10^2$	$25 \cdot 10^2$
Nitrifying bacteria, 1st phase	$130 \cdot 10^3$	$240 \cdot 10^4$	$240 \cdot 10^4$	210	$240 \cdot 10^4$
MPN in 100 g 2nd phase	$62 \cdot 10^2$	230	< 50	< 50	< 50
Mn(II) oxidizing bacteria from *Siderocapsaceae* family, MPN in 100 g	$62 \cdot 10^3$	$240 \cdot 10^3$	$240 \cdot 10^3$	$21 \cdot 10^2$	$240 \cdot 10^3$
Fe(II) oxidizing bacteria from *Siderocapsaceae* family, MPN in 100 g	$62 \cdot 10^3$	$> 240 \cdot 10^5$	$> 240 \cdot 10^5$	$24 \cdot 10^2$	$> 240 \cdot 10^5$

UMC – units making colonies.
MPN – most probable number.

Fe(II) oxidizing bacteria from *Sidrocapsaceae* family in 85% belonged to the genus of *Naumanniella* sp. which accumulates Fe(III) salt in polar parts of the cell. Remaining 15% made bacteria from *Siderocapsa* sp. accumulating compounds of Fe(III)

in the central part of the cell. Among microscopic fungi no mould fungi were found. Yeast-like fungi prevailed ($45 \cdot 10^3$ UMC/g). The bed was grown with nitrifying bacteria of the 1st and the 2nd phases (for both phases MPN in 100 g was $240 \cdot 10^4$ and 230, respectively). It was proved that quantitative composition of biocenosis found on active bed depended on the kind of growing medium.

The results of the tests allow us to state that biological processes encouraging manganese removal from water with the usage of the given mass are very intensive.

The number of saprophytic bacteria defined in terms of UMC per gram reached $240 \cdot 10^4$. No mould fungi were found. Microscopic fungi were dominated ($24 \cdot 10^3$ UMC/g) by yeast-like fungi.

Nitrifying bacteria in the 1st phase were characterized by a high value of MPN, i.e., $240 \cdot 10^4$/100 in 100 g of filling, while those in the 2nd phase displayed much lower value (<50) of MPN, i.e. 230/100 g.

MPN of Mn(II) oxidizing bacteria was established as $240 \cdot 10^3$ in 100 g of filling. Those bacteria were mainly represented by *Naumanniella* sp. (80%) accumulating Mn(IV) in polar parts of the cells. In a smaller quantity (20%), *Siderocapsa* sp. occurred.

Fe(II) oxidizing bacteria (95%) were dominated by *Naumanniella* sp. accumulating Fe(III) in polar parts of the cells. Remaining 5% made bacteria from the *Siderocapsa* genus, which accumulated Fe(III) in central parts of the cells. Total MPN of those bacteria amounted to $>240 \cdot 10^5$/100 g.

Quantitative and qualitative characteristics of the biocenosis growing on Birm bed were similar to these on G-1 bed.

Analysis of microbiological tests of biocenosis on Hydrocleanit bed showed that the number of all groups of microorganisms were the lowest compared to the number of microorganisms found on other filtration beds. This means that biochemical changes in the bed are the least intensive.

The number of saprophytic bacteria was assessed as $120 \cdot 10^4$ UMC/g. Among microscopic fungi ($154 \cdot 10^2$ UMC/g) yeast-like fungi from the genus *Rhodotorula* dominated. Fungi from that genus are usual components of such biocenosis as, e.g., biologically active carbon filters used for removing manganese and iron from underground waters, but their ability to oxidize manganese and iron has not been proved so far [4].

In the bed, the MPN of nitrifying bacteria was low both in the 1st and the 2nd phases (respectively 210 and < 50 in 100 g of filling). This means that this filtration bed does not promote their development, and nitrifying processes are heavily dependent upon the kind of a bed.

Small amounts of manganese and iron oxidizing bacteria in filtration bed with the Hydrocleanit mass prove that biological removal of both manganese and iron from water is inefficient. This is confirmed by the results of the test carried out in dynamic conditions (the mass practically does not remove manganese from the water).

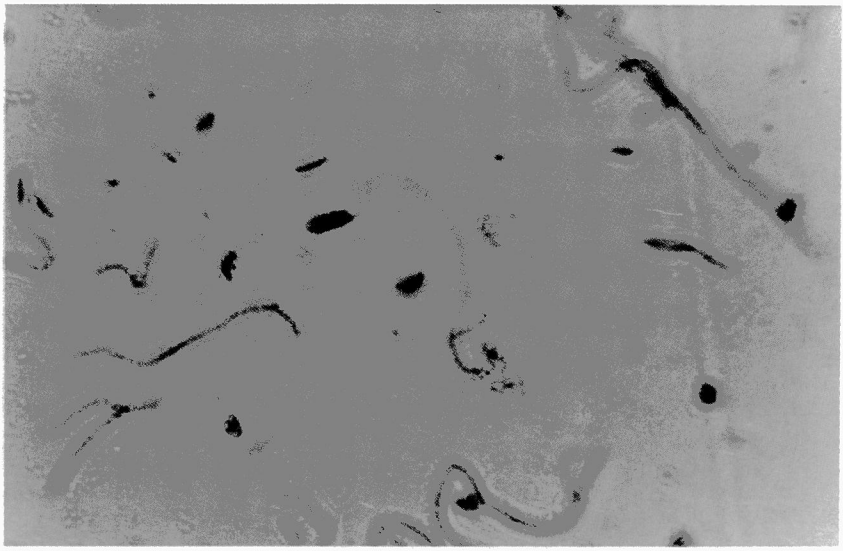

Photo 1. Not identified rods with deposits of Mn(IV) salt
in the form of lamellae in central part of cell or in cell wall

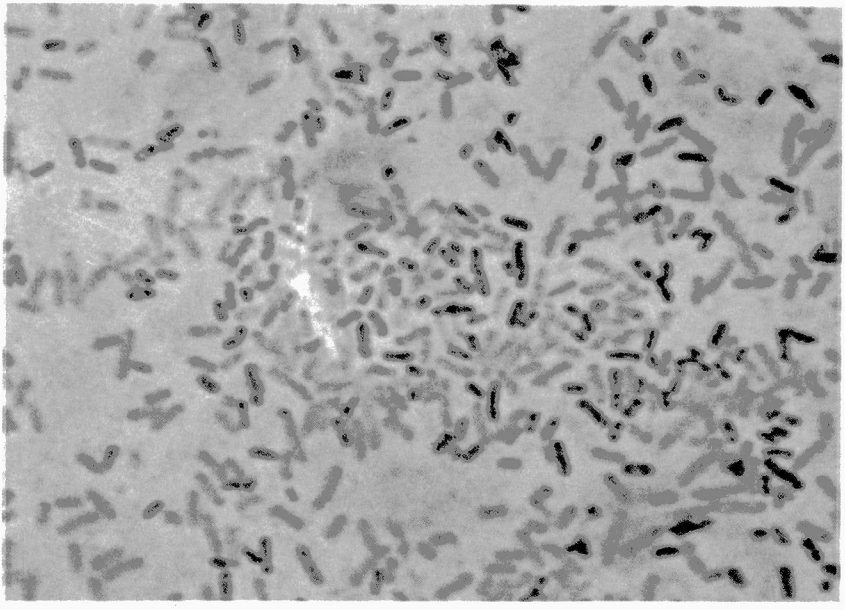

Photo 2. Fe(II) oxidizing bacteria from *Siderocapsaceae* family (*Naumanniella* sp.)
on the medium according to Winogradzki with ferric ammonium citrate.
Microscopic enlargment approx. 1000×. The arrows show dark violet deposits of Fe(II)
in the form of granules being stained

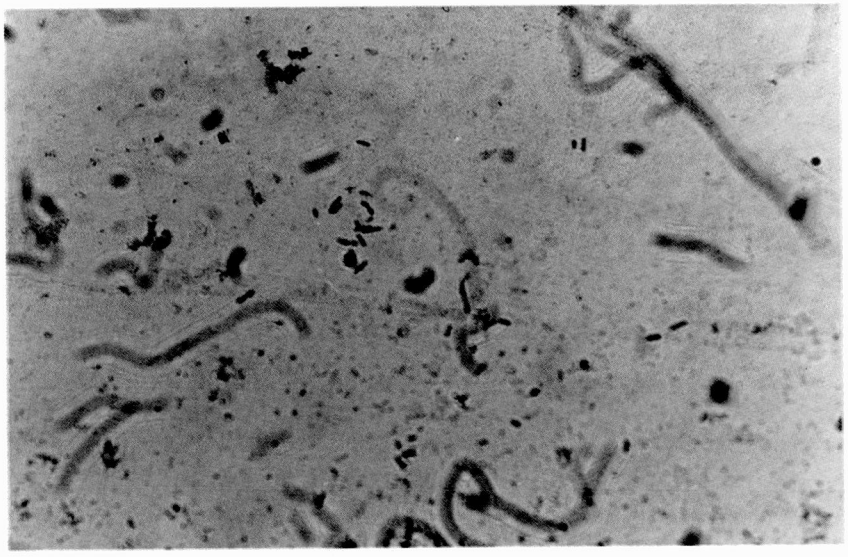

Photo 3. Mn(II) oxidizing bacteria from *Siderocapsaceae* family (*Naumanniella* sp.) on the medium according to Winogradzki with manganese citrate.
Microscopic enlargement approx. 1000×.
Bacteria with deposits of Mn(IV) in the form of granules in terminal part of cells (marked with arrows)

Most of Mn(II) oxidizing bacteria (80%) are represented by *Naumanniella* sp., and some of them belong to the *Siderocapsa* genus, which has characteristic deposits of Mn (IV) salt in the central part of the cell. It should be stressed that in such circumstances those bacteria did not produce capsules, which are characteristic of them. MPN of those bacteria (*Naumanniella* sp. and *Siderocapsa*) was $21 \cdot 10^2$ in 100 g of filling.

Fe(II) oxidizing bacteria were found in the amounts comparable to those of Mn(II) oxidizing bacteria. They were represented exclusively by the genus of *Siderocapsa*. Those bacteria accumulated Fe(III) mainly in the cell wall and did not produce capsules like Mn(II) oxidizing *Siderocapsa*.

Total number of saprophytic bacteria growing on Defeman bed was determined as$150 \cdot 10^4$ UMC in 1 g. In total number of microscopic fungi expressed as $25 \cdot 10^2$ UMC/g no mould fungi were found. MPN of nitrifying bacteria in the 1st phase was as high as $240 \cdot 10^4$/100 g. However, this index in the case of nitrifying bacteria in the 2nd phase was small (<50/100 g of filling).

Mn(II) oxidizing bacteria were represented exclusively by *Siderocapsa* sp. accumulating Mn(IV) in the central part of the cell. MPN of those bacteria amounted to $240 \cdot 10^3$ in 100 g of filling. Most of Fe(II) oxidizing bacteria were identified as *Naumanniella* sp. (95%). Some of such bacteria were also represented by *Siderocapsa* sp. (5%), the species accumulating Fe(IV) in the central part of the cell. Total MPN of those bacteria approached $> 240 \cdot 10^5$/100 g.

Quantitative and qualitative characteristics of the microorganisms found in Defeman bed are similar to characteristics of microorganisms in Birm and G-1 beds. The manufacturers of all beds tested declare that the beds are manganese ores. Approximate characteristics of biocenosis of these ores show that water treatment proceeds according to the same mechanism. Vigorous development of biocenosis proves that biological treatment is the basic process of iron and manganese removal from water. Such bacteria as *Siderocapsa* sp. and *Naumanniella* sp. are involved in oxidation and fixation of iron and manganese. Those bacteria accumulate iron and manganese intracellularly. Arrows in photo 2 show dark purple deposits of Fe(III) in the form of granules in terminal parts of cells. Arrows in photo 3 show deposits of Mn(IV) also in the form of granules in the terminal part of cells. The characteristics of those bacteria are compatible with the characteristics reported in many papers by Grabińska-Łoniewska. The occurrence of the above bacteria testifies to biological processes in water being treated. However, it should be stressed that Fe(II) and Mn(II) oxidizing bacteria occur in much smaller amounts in biocenosis growing on Purolite MZ-10 and Hydrocleanit beds. That is why one may conclude that development of microorganisms depends not only on water content, but also on the kind of the bed, its chemical structure and the way of its exploitation. Purolite MZ-10 bed was periodically regenerated with 0.3% solution of $KMnO_4$. Hydrocleanit bed is mineral composite of calcium and magnesium. Chemical contents of other filtration beds are similar. Hence it may be concluded that materials that are manganese ores (Birm, G-1, Defeman) create advantageous conditions for the development

of microorganisms. At the same time the results of water treatment in dynamic conditions showed that the beds which are manganese ores effectively removed iron and manganese. This testifies to the convergence between the results of chemical analyses and microbiological analysis.

In the beds tested, Mn(II) and Fe(II) oxidizing bacteria from *Siderocapsaceae* family were found, which proved that each bed removed both manganese and iron. This statement contradicts the opinion presented by Mouchet. The occurrence of nitrifying bacteria on all the beds testified to the presence of the ammonia ions in water. These ions were introduced into the water together with humic acids. The presence of nitrifying bacteria and simultaneous effective manganese removal from water prove that nitrification takes place. Therefore, it may be stated that the process or manganese removal is effective at some concentration of nitrogen in water. The occurrence of yeast-like fungi may be explained by the presence of humic acids, which participate in their biodegradation.

4.3. CHEMICAL ANALYSIS OF FILTRATION BEDS AFTER THE PROCESS OF MANGANESE REMOVAL

The purpose of research was to assess the adsorption efficiency of filtration beds which retain iron and manganese ions removed from water during its treatment. The concentrations of these cations in the beds before water filtration were considered as reference point.

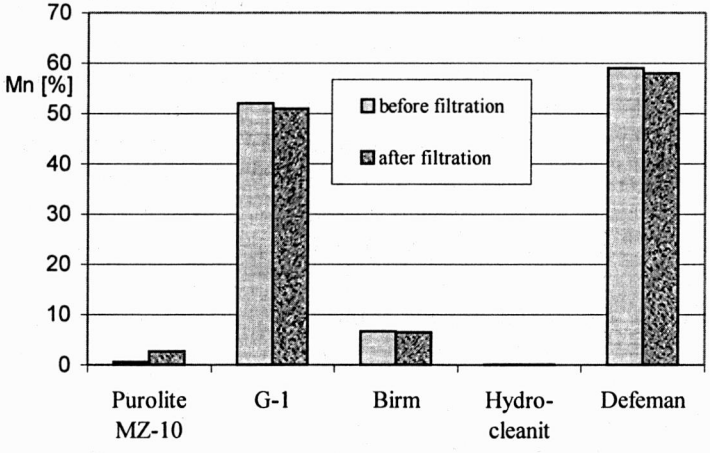

Fig. 4. Manganese percent in active beds before and after filtration process

The test results presented in figure 4 show that the share of manganese in Purolite MZ-10 mass increased from 0.54 to 2.7%. In the Hydrocleanit mass, a slight increase of manganese (from 0.06 to 0.085%) was observed. In other beds (G-1, Birm, Defeman), the concentrations of manganese decreased: in G-1 bed from 52 to 51%, in

Birm bed from 6.7 to 6.5% and in Defeman bed from 59 to 58%. The increase in manganese content in Purolite MZ-10 bed should be explained by temporary activation of ore with potassium permanganate solution and manganese retaining by the ore. The surface of Purolite MZ-10 was covered with smaller number of Mn(II) oxidizing bacteria compared to their MPN in the beds being manganese ores. Regeneration of the bed and lack of manganese in its mineral mass are responsible for this phenomenon.

The test results presented in figure 4 prove that proportion of manganese in active mass of Purolite MZ-10 rose several times after manganese removal. Taking account of the fact that given mass was activated and periodically regenerated by potassium permanganate solution it should be stated that this increasing proportion is due to covering the bed with manganese oxide during its activating with potassium permanganate and manganese removal from water. So, manganese removal is enhanced by catalyctic reactions.

The test results obtained for G-1, Birm and Defeman show that manganese proportion in those beds decreased after 136 days of bed operation. As is well known, our active filtration beds are manganese ores. Manganese oxides, their components, take a key role in biological processes on the phase boundary: the surface of filtration bed–treated water. Such conditions promote development of Mn(II) oxidizing bacteria which use both manganese present in treated water and that contained in given filtration bed. So, we may conclude that manganese is removed from water by means of such filtration materials as G-1, Birm and also Defeman due to biochemical changes on the surface of filtartion bed.

A slight increase of manganese concentration in Hydrocleanit should be explained by a small quantity of Mn(II) oxidizing bacteria growing on this bed.

During periodical rinsing of the bed, removal of some bacteria took place together with manganese accumulation, which results in lamellae formation in central part (G-1) or granularities in terminal part of cells (Defeman, Birm).

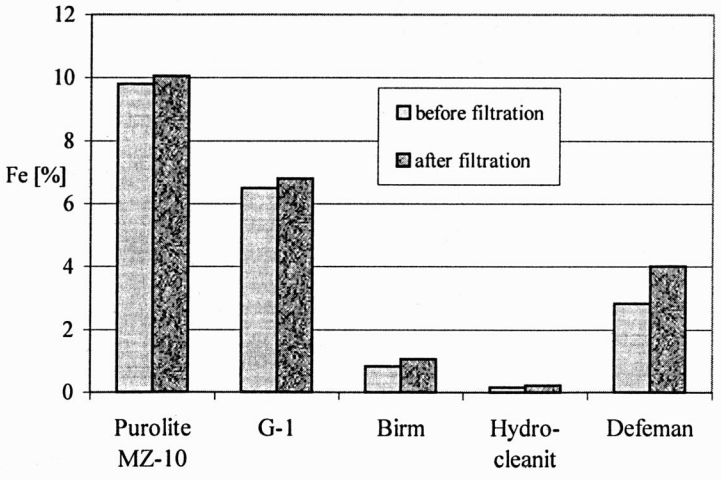

Fig. 5. Iron percent in active beds before and after filtration process

Analysing the test results presented in figure 5 we may state that percentage share of iron in each filtration material examined increases after manganese removal. The explanation is as follows: the concentration of iron in treated water (~1.5 mg/dm^3) is greater than that of manganese (~1.0 mg/dm^3). Because the number of manganese oxidizing bacteria was close to the number of iron oxidizing bacteria, some percent of iron oxidized to Fe(III) penetrated as coloidal hydroxide particles, together with water, into porous grains of activated bed and adsorbed on its negatively charged surface.

5. SUMMARY

The investigation prove that filtration materials differ in their chemical compositions. Defeman and G-1 contain approx. 1% of manganese, while Purolite MZ-10 and Birm comprise, respectively, 0.54 and 0.24% of this element. Those materials also contain iron – its highest concentration (9.8%) was measured in Purolite MZ-10. Trace concentrations of manganese and iron are found in Hydrocleanit, which – as the only one – contains large amounts of calcium and magnesium.

Microbiological tests showed that microorganisms took vital part in manganese removal from water. The most probable number of manganese and iron oxidizing bacteria was found on the beds which contained manganese ores (G-1, Defeman, Birm). This proves that the kind of substratum is of a great importance for the intensity of biochemical changes taking place there. Manganese ores promote development of microorganisms that oxidize manganese. The results of manganese removal from water in dynamic conditions testify to high efficiency of manganese ores in water treatment. Activity of manganese oxidizing bacteria is also substantiated by the results of chemical analysis of filtration deposits after manganese removal. As it turned out, such materials as G-1, Birm and Defeman (manganese ores) suffer loss of manganese. This proves that bacteria present in filtration bed need for their development not only manganese from the treated water, but also that in the bed, and that removal of this element from water takes place, among other things, as a result of biochemical changes connected with microorganisms activity. The reactions of manganese(II) and iron(II) oxidizing may be written in the following way [6]:

$$4FeCO_3 + O_2 + 6H_2O \rightarrow 4Fe(OH)_3 + 4CO_2 + 22.6\ J\ ,$$

$$MnCO_3 + H_2O + 0.5O_2 \rightarrow MnO(OH)_2 + CO_2 + 12.9\ J\ ,$$

$$2FeO + 0.5O_2 + 3H_2O \rightarrow 2Fe(OH)_3 + 60.5\ J\ ,$$

$$2MnO + O_2 + 2H_2O \rightarrow 2MnO(OH)_2 + 9.6\ J\ .$$

Oxidation of iron and manganese produced 83.1 J and 22.5 J, respectively. Hence, for the bacteria catalyzing the process of water treatment, manganese is considered to be the source of energy 2–6 times efficient than iron. Those equations explain the

results of chemical determinations of iron and manganese contents in filtration bed before and after 136 days of filtration process. Mn(II) oxidizing bacteria obtain their lacking energy from manganese contained in the bed. This explains a substantial manganese loss in the bed and more abundant development of manganese oxidizing bacteria in biocenosis growing on beds which are manganese ores. Manganese deposits accumulated in bacteria cells were periodically removed together with bacterial jelly during bed rinsing.

The removal of manganese on Purolite MZ-10 bed is governed by different mechanism. The results of biological tests show that the MPNs of manganese and iron oxidizing bacteria on this bed are lower than on the beds comprising manganese ores. Additionally, chemical analysis shows that manganese percent in a given bed increased a few times after manganese removal from water. Purolite MZ-10 was periodically regenerated by potassium permanganate, therefore it should be stressed that manganese removal on a given bed took place, among other things, due to catalyctic activity.

The results of biological tests of the biocenosis growing on Hydrocleanit show that biochemical changes taking place in filtration bed during water treatment are rather small. Also, chemical analysis carried out after 136 days of bed operation did not show any substantial changes in its composition. The results of dynamical investigations lead to the conclusion that Hydrocleanit is not efficient in manganese removal from water.

6. CONCLUSIONS

On the basis of the tests carried out the following conclusions may be drawn:

1. The effectiveness of manganese removal from the water on various beds depends on the kind of filtration material, which makes an appropriate substratum for the development of bacterial biocenosis.

2. Bacteria from the *Naumanniella* and *Siderocapsaceae* genera take part in the process of manganese removal from water. Activity of microorganisms in a great extent depends on the composition of active bed.

3. The greatest number of UMC of saprophytic bacteria and microscopic fungi were found on Purolite MZ-10.

4. The highest MPN of manganese and iron oxidizing bacteria was observed on G-1, Defeman and Birm.

5. The energy necessary for their development manganese oxidizing bacteria take from manganese which is in the water and in the bed.

6. The main factor affecting the process of manganese and iron removal from water on G-1, Birm and Defeman is the activity of microorganisms, mainly *Naumaniella* and *Siderocapsa* and not identified rods with the deposits of Mn(IV) salt in the form of lamellae in central part of a cell or in cell wall.

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WPŁYW BUDOWY PODŁOŻA FILTRACYJNEGO NA ROZWÓJ MIKROORGANIZMÓW W PROCESIE USUWANIA MANGANU I ŻELAZA Z WODY

Przebadano pięć mas aktywnych zalecanych do usuwania manganu z wody: Purolite MZ-10, G-1, Birm, Hydrocleanit i Defeman. Badania przeprowadzono w warunkach dynamicznych, na laboratoryjnym filtrze o pracy ciągłej. Cykl pracy każdego z filtrów wynosił 48 godzin i składał się z filtracji wody, płukania złoża i czynności pomocniczych. Wyniki badań dynamicznych jednoznacznie wskazują, że efektywność usuwania manganu z wody na złożach zależy od rodzaju masy filtracyjnej, która stanowi odpowiednie podłoże do rozwoju biocenozy wodnej. Głównym czynnikiem decydującym o procesie usuwania manganu i żelaza z wody na masach G-1, Birm i Defeman jest aktywność mikroorganizmów *Naumanniella* i *Siderocapsaceae* oraz bliżej niezidentyfikowanych pałeczek ze złogami soli Mn(IV) w postaci blaszki w centralnej części komórki lub w ścianie komórkowej.