



INFLUENCE OF Fe^{+2} IONS ON THE PROCESS OF BIOLOGICAL REMOVAL OF MANGANESE IN ROCK FILTER

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ABSTRACT

An efficient removal of manganese from polluted waters was achieved by means of a laboratory-scale rock filter. The rock filter consisted of three cells connected in a series with a total volume of about 12 l. The cells were filled with mix of limestone and gravel with a particle size of about 20-50 mm. Experiments for treatment of synthetic Mn-containing waters have been carried out using laboratory installation, containing biofilms of Mn-oxidizing bacteria. The oxidation of manganese was connected with the bacterial production of hydrogen peroxide and enzyme catalase. The Mn^{2+} was then precipitated as MnO_2 . The concentration of dissolved manganese in the filter effluents was less than 0.8 mg/l and this was achieved within residence times of about 72 hours. It was determined that the higher concentrations of Fe^{2+} , lead to negative effects in the rock filter related to reduction of Mn^{4+} to Mn^{2+} and its reversible mobilization in the water.

Keywords: Acid mine drainage, passive treatment, manganese, rock filter, constructed wetlands, heavy metals.

INTRODUCTION

The manganese is definitely the most refractory to precipitation among the heavy metals. In strongly alkaline solutions it precipitated as MnCO_3 , and at negative redox potentials and pH around the neutral point can be precipitated as MnS . The oxidation of the bivalent manganese to the tetravalent state decreases considerably the solubility of the manganese and follows to its precipitation as MnO_2 . However, very few chemical oxidizers towards the Mn^{2+} are available in the natural ecosystems. Some heterotrophic bacteria are able to oxidize Mn^{2+} in the presence of dissolved organic monomers and at around the neutral point. These bacteria produce peroxide compounds, which are the real oxidising agent. Some of these bacteria produce also the enzyme catalase to degrade peroxide and to prevent its toxic effect.

The presence of some algae facilitates the growth and activity of the Mn^{2+} -oxidising bacteria (1). The positive effect of algae is connected with the consumption of CO_2 from the waters which increase their pH to the levels optimal for the above-mentioned bacteria, as well as with the production of solid organic compounds, which are used by the bacteria as sources of carbon and energy. Some passive treatment systems, namely the natural and constructed wetlands and the rock filters, are very suitable for bioremediation of water polluted with manganese (2).

The rock filters are intended mainly for the removal of manganese but can remove also iron and organic compounds. These filters can be used individually but in most cases are constructed as a final component of multistage systems, because manganese, especially when is present at high concentrations (sometimes higher than 50 mg/l), is the most difficult metal for removing from polluted waters (3).

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The main aim of this report is to indicate the influence of presented Fe^{2+} ions at treating of polluted with Mn water. It is known the possibility for reduction of Mn^{+4} to Mn^{+2} from the precipitated pyrolusite on the rock filter in the presence of Fe^{2+} (4). This process could be avoided at aerobic condition in the rock filter, pH over 7.0 and consecutively oxidation of Fe^{+2} and Mn^{+2} .

MATERIAL AND METHODS

The laboratory installation (Figure 1) includes rock filter, vessel for the feed solution, peristaltic pump and collector vessel. To realize this experiment a two-sectional laboratory installation was constructed with working volume of 12 dm³,

where the two identical parallel cameras are filled up with mixture of limestone and river gravel in ratio 1:1. The particle average diameter is about $d \approx 20-50$ mm as the gravel(limestone) are preliminary purified from particles with diameter bigger than 60 mm and less than 10 mm. The cameras are located in cascade way which allows the water to flow freely through the filter. In the filter end there is a vessel with buffer volume of 1.0 dm³, which average the initial waters from the precipitation camera. After averaging the treating waters enter in a collector reservoir. The incoming solution is passed by peristaltic pump at lightly regulation of the debit from 1 – 10 dm³/24 hours.

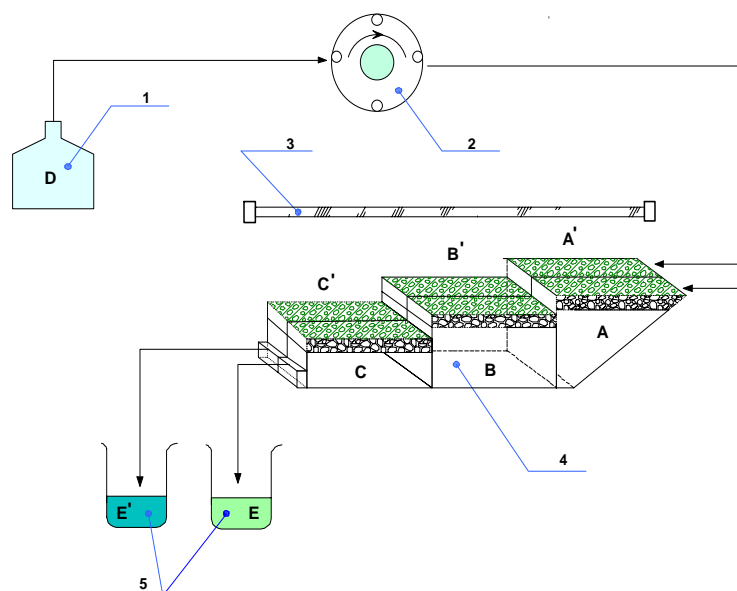


Figure 1. Laboratory installation of rock filter for treatment manganese polluted water. 1– Supply reservoir, 2 – Peristaltic pump, 3 – Artificial light source, 4 – Rock filter, 5 – Collector reservoir, (A,B,C,D,E and A',B',C',D',E') – Sampling points in laboratory installation of rock filter.

Two artificial light sources (luminescent lamps with full spectrum, power 2 x 36 W) are assembled along rock the filter length for more effective proceeding of photosynthesis. A digital light meter type “Pocet – lux – LTM” is used to measure the intensity of illumination in the third cameras of the rock filter. The measured illumination is in the diapason 100 – 25000 lx.

Initially the rock filter is filled with soil solution rich with the typical microflora and additional enriched with sources of phosphorus and nitrogen.

After that the rock filter is inoculated with mixed culture of manganese-oxidizing bacteria, which are preliminary adapted for living in environment with high Mn^{2+} concentration. The soil solution is recirculated by the peristaltic pump for 40 days at debit 5 dm³/24 h and daily adding of water to the system (to compensate the loss from evaporation, which are 0.6 dm³/24 h for each section at ambient temperature 19-21 °C).

The illumination from the two artificial light sources is realized according the scheme 15 hours

light : 9 hours dark. In the end of the 40th daily period in the rock filter is formatted stable microbial population, which is mobilized mainly on the surface of the gravel (limestone).

Chemical analyses for manganese determination in the liquid solution are accomplished modified formaldehyde spectrophotometric method (5). Under control are T^o, pH, Eh, pO₂ and TDS (total dissolved solids) according to the corresponded standard potentiometric methods. There are performed completed ISP cation analyses, as the spectrophotometric data for Mn²⁺ are compared with the ISP data. The concentrations of sulphate, ammonium, nitrate and phosphate ions are determined spectrophotometric. The concentration of dissolved oxygen is determined by polarographic gauge.

The concentration of dissolved oxygen is determined by polarographic gauge. The dissolved organic carbon (C_{org}) is determined by standard method (6). The general physiological groups, identification and quantitative characteristic of

microorganisms are determined by standard microbiological methods (7). There are enough repetitions at all performed analyses.

The distribution of Mn and Fe in the various geochemical fractions of the sediment in the rock filter is determined by applying of sequential extraction procedure (8).

Both sections of the installation are supplied with solution contains Mn⁺² with concentration about 20 mg/l. It is water draining from the anaerobic camera for treating of acid mining water. The difference from the initial composition is in the concentration of Fe⁺² in the both filter sections – corresponding at section 1 (testing points A,B,C,D,E) the starting concentration is in the diapason 5,1 – 5,5 mg/l (variant 1), while at section 2 (testing points A',B',C',D',E') the starting concentration is in the diapason 52 – 55 mg/l (variant 2) (**Table 1**). In both variants the initial pH value is adjusted to 6,5. The flow rate in both section ensure residence time about 72 hours.

Table 1. Values of technological parameters in rock filter at both variants of the supplying solution.

Parameter	Before treatment	After treatment	
		Residence time 72 hours	
		Variant 1	Variant 2
pH	6.40 - 6.60	8.6 - 9.3	7.6 - 8.5
Eh, mV	-85 - /-20/	374 - 454	360 - 440
pO ₂ , mg/l	0.1 – 0.5	5.1 – 5.6	5.1 – 5.7
TDS, g/l	1.01 - 1.15	0.86 – 1.05	0.95 - 1.1
Mn, mg/l	19.5- 20.1	0.2 – 0.8	0.5 - 1.3
Fe, mg/l	5.1 – 5.5 * 52 – 55 **	1.2 - 2.4	12 - 20
SO ₄ , mg/l	210 – 300	310 - 450	270 – 400
Dissolved organic carbon, mg/l	130 - 155	25 - 34	31 -39
PO ₄ , mg/l	65 – 82	5.5 - 12.2	10 - 19.2
NO ₃ , mg/l	10 – 25	4 - 8	7 - 10
NH ₄ , mg/l	65.9 - 84.4	12 – 15	16 - 20
K, mg/l	162 - 260	105 - 148	137- 201
Na, mg/l	29 – 45	25.9 - 41.6	32.2 - 54
Ca, mg/l	57 – 90	42.8 - 55.7	61– 91
Mg, mg/l	30 – 55	31.5 - 47	33 - 58
Al, mg/l	0.6 -1.1	0.6 - 1.2	0.3 – 1.0

* - Variant 1

** - Variant

RESULTS AND DISCUSSION

The obtained results from the dynamics of general technological parameters proved the effective work of the rock filter. In the presence of Fe^{+2} at higher concentration (variant 2) in the supplying solution are indicated some negative effects – choking of the rock filter with hydroxide precipitations of Fe , formation of anaerobic zones and reduction of Mn^{+4} to Mn^{+2} . The end concentration of chose residence time is higher at variant 2 in comparison with variant 1 (**Table 1**) – even at the most time of installation work these values are over permissible levels for waters intended for use in the agriculture and/or industry (0.8 mg/l).

The dynamics of pH, Eh, dissolved oxygen and dissolved organic carbon (**Table 1**) explain the negative effect related with the removing of Mn at variant 2. pH values are significantly higher in variant 1, which is explained by neutralization at the higher iron hydroxides concentration in variant 2 and with passivation of the limestone surface in the rook filter. The aerobic conditions of the environment apparent at variant 1 in comparison with 2 – the last could be explain with the deposition of precipitated layer of ferrous hydroxides, which prevent the penetration of oxygen. It is logically the values dynamics at oxidative-reductive potential (Eh), which shows unambiguously oxidative conditions in variant 1. The values of dissolved organic carbon are evidence for this hypothesis.

Related with the dynamic of the microflora at both variant of the rock filter is determined at higher number of the aerobic microorganisms at variant 1, respective for Mn – oxidative bacteria, it is interesting the dynamics of these microorganisms in the nitrogen circle (nitrification and denitrification) – their number at both variant in the rock filter give good characterization of the environment conditions (**Figure.2**).

The analysis at this investigation was significantly important for determination of ferrous and manganese distribution in the various geochemical fractions of precipitated material in the rock filter (**Table 2**). The proceeded selective dissolving of formed ferrous and manganese hydroxides by the method of sequential extraction give us the opportunity to evaluate the type of the obtained products and the dissolving conditions. At variant 1 ($Mn = 20\text{mg/l}$, $Fe = 5 \text{ mg/l}$) the manganese is distributed mainly in the reducible fraction, i.e. insoluble oxide (generally MnO_2) and manganese hydroxide. This evidence confirms again the mechanism for biological oxidation of manganese. At variant 2 ($Mn = 20 \text{ mg/l}$, $Fe = 50 \text{ mg/l}$) the manganese is distributed mainly in the easy accessible exchanged and carbonate fractions – it could be due the presence of Fe^{2+} in tenfold higher concentration, which is reason for the reduction of Mn^{4+} to Mn^{2+} (**Table 2**). A characteristic feature is that in both variants the contents of Fe and Mn in the oxidisable fractions is less than 1.8 %.

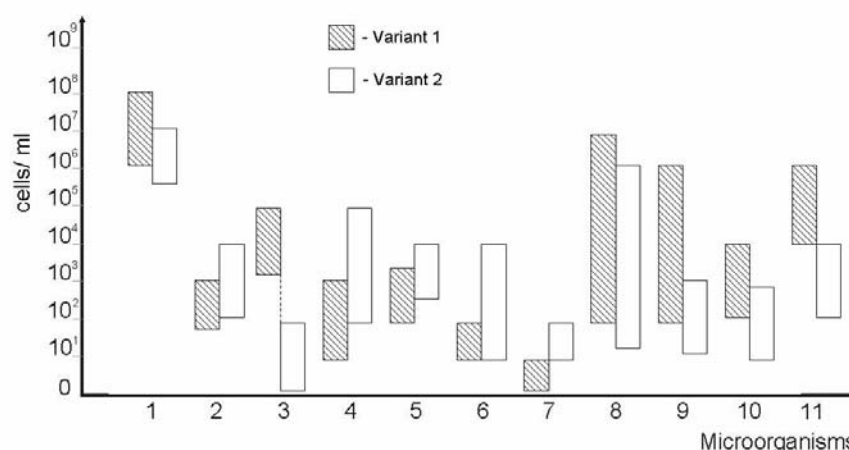


Figure 2. Composition of microflora in the rock filter.

1- Aerobic heterotrophic bacteria, 2- Anaerobic heterotrophic bacteria, 3- Bacteria fermenting sugars with gas production, 4- Cellulose-degrading anaerobic bacteria, 5- Denitrifying bacteria, 6- Fe^{3+} -reducing bacteria, 7- Mn^{4+} -reducing bacteria, 8- Fe^{2+} -oxidising heterotrophs (at pH 7.0), 9- Mn^{2+} -oxidising heterotrophs (at pH 7.0), 10- Nitrifying bacteria, 11- Microscopic algae.

Table 2. Distributions of Mn and Fe in the various geochemical fractions of the precipitated product in the volume of rock filter at both variant of supplied solution.

Fractions	Variant 1 (Mn = 20 mg/l, Fe = 5 mg/l)		Variant 2 (Mn = 20 mg/l, Fe = 50 mg/l)	
	Mn, %	Fe, %	Mn, %	Fe, %
Exchangeable fraction	10.38	15.36	52.25	5.13
Carbonate fraction	11.76	20.75	28.37	8.68
Acid dissolved fraction	16.88	38.62	11.03	22.20
Reducible fraction	60.84	24.23	7.72	62.15
Oxidisable fraction	0.1	1.05	0.6	1.8

CONCLUSION

The higher concentrations of Fe^{2+} lead to negative effects in the rock filter related to reduction of Mn^{4+} to Mn^{2+} and its reversible mobilization in the water. This hypothesis is proved from the results for Mn and Fe distribution in the various geochemical fractions in the precipitated material in the filter. Other negative effect is the higher consummation of ferrous hydroxides in alkaline environment and the formation of its layer on the surface of rock material. This phenomenon lead to degradation of the aerobic conditions in the environment and filter obstruct. Due to these reasons it is necessary to remove preliminary Fe^{2+} from the water contain Mn and Fe before their treatment in the rock filter. The fraction distribution of Fe and Mn in the precipitate proves that the base reason for Mn removing is its biological oxidation by peroxidation mechanism.

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