ROLE OF BIOLOGICAL PROCESSES DURING MANGANESE REMOVAL FROM UNDERGROUND WATER

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Abstract
This article briefly presents the results of the effect of oxidants during filtration of groundwater with high level of manganese compounds. Significant role of biological processes along with physico-chemical at demanganation of groundwater has been noticed. It has been studied that biological processes are dominated in low concentrations of oxidants. At high concentration of disinfectant the role of physico-chemical processes begin to dominate. Thus, there is a significant role of microorganisms in physico-chemical process of manganese removal. Obtained results showed that the oxygen is more efficient oxidizer than sodium hypochlorite for compounds of manganese presented in groundwater.

Keywords: manganese removal, zeolite filter loading, physico-chemical processes, biological oxidizing

1. Introduction

Iron- and manganese containing groundwater is found in almost all regions of Ukraine. The concentration of these elements varies in a very wide range and in some regions reaches 20–30 mg/dm^3 (iron) and 2–3 mg/dm^3 (manganese).

High iron content in water primarily affects its organoleptic properties, causing rusty water color, unpleasant metallic aftertaste and leads to overgrowth of water supply systems and water intake valves. In contrast, manganese may cause destruction of cells liver through prolonged consumption [1]. According to Guidelines for drinking-water quality [2] recommended value for manganese concentration in water for human consumption is 0.1 mg/dm^3. Moreover, epidemiological studies have confirmed that the use of a significant amount of manganese from drinking water can cause neurological effects. At concentration of 0.2 mg/dm^3 manganese will form a coating on pipes, which may slough off as a black precipitate.

In Ukraine physico-chemical removal of iron and manganese is presented at water treatment plants with high capacity (on rapid filters). In contrast, biological treatment is used at low capacity stations [3, 4]. Stations are outdated in most cases. Requirements for water quality are increased due to implementation Water Framework Directive (2000/60/EC) in Ukraine. That is why physico-chemical methods of intensifications iron and manganese removal became more popular.

The role of biological processes in the removal of iron and manganese from water by physico-chemical methods is shown in [5–7]. In [5] indicated that the bacteria *Galionella* on biofilters remove iron effectively at neutral pH and it is shown that the contribution of biological oxidation of iron was more significant than the physical-chemical in complete aeration. In [8] author used an immobilized manganese-oxidizing bacteria embedded in polyvinyl alcohol that was cross-linked with boric acid and then processed with glutaraldehyde and shown the toxicity of the cross linking agent and the preparation condition to bacteria in biological bioactivity.

The purification efficiency of biological removal of iron and manganese was probed by pilot tests. The average removal rate of iron and manganese reached 97.6 % and 90.9 % respectively, the effluent concentration of Fe^{2+} and Mn^{2+} were keep in below 0.1 mg/dm^3 [9]. In [10] authors shown the effectiveness of direct biofiltration of raw surface water for manganese removal (pH=6).

For rapid filter iron and manganese removal technology involves the oxidation of iron and manganese compounds, followed by separation of the precipitate on the filter. Oxygen, ozone and chlorine compounds can be used as oxidants [11, 12]. Silica sand, zeolite (both natural and modi-

fied), kizelgur, manganese ore, sorbent–catalyst based on oxide–carbonate ore, chalcedonite, kaolinite-bentonite ceramics and others can be used as filter loading [7, 13–20].

It should be noted that the processes which occur during physico-chemical removal of iron and manganese are poorly understood from a biological point of view, despite the widespread use of such technologies in water supply practice. However, such technology is widely used in water treatment. For this reason study of the role of physico-chemical and biological processes that occur in the filter loading during iron and manganese removal from water remain relevant. The study of such processes makes it possible to intensify the technology of iron and manganese removal. That is why the definition of the role of physical, chemical and biological processes during manganese removal of underground water was the purpose of this work.

2. Materials and Methods

Real water from the artesian borehole was the object of the experiment. Total manganese concentration varied between 0.33-0.34 mg/dm^3 during the experiments.

During the study, following mean values were measured: concentration of oxygen and sodium hypochlorite, concentration of manganese at initial and output of units. For measure standard methods were used [21, 22].

Sodium hypochlorite of grade A (supplier PE "Ukrokomfort", Zaporizhzhya, Ukraine) was used in experiments. An initial concentration is 112 g/dm^3.

The role of biological processes was established by comparison changes in the efficiency of manganese removal after washing filter with water with disinfectants (sodium hypochlorite) and without it.

3. Experimental procedures

First experiment was conducted at the unit (**Fig. 1**), which consists of contact tank and pressure filter. Water from the well and oxidant (sodium hypochlorite/oxygen) move to a contact tank. There the interaction of compounds of manganese with oxidants is taken place. Then water goes to the pressure filter, where is actually the oxidation of iron compounds and manganese, and manganese oxides are delayed.

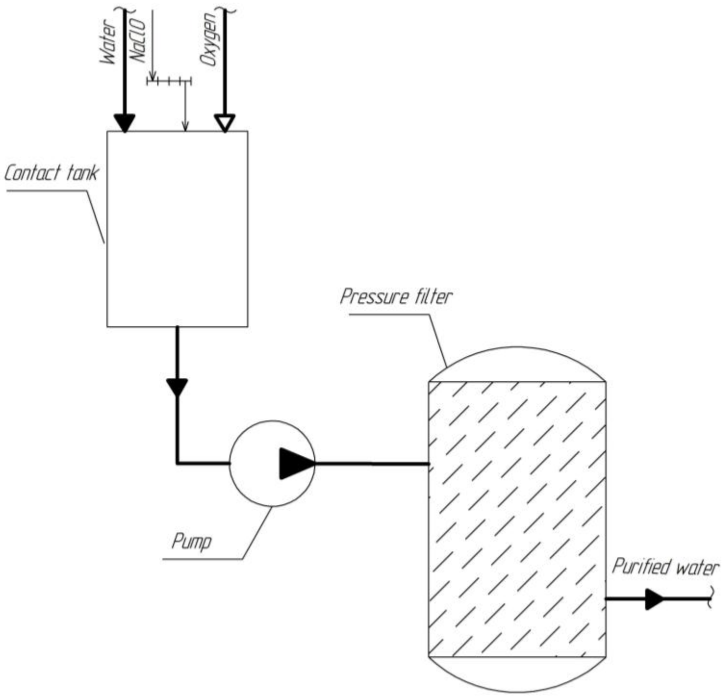

Fig.1. Unit for iron and manganese removal

Second experiment was conducted using the semi industrial installations, which included sample pressure factory production filter. Filter unit was made of fiberglass and coated inside of the non-toxic polyethylene layer. A fully automated filter; output to washing was performed with increasing resistance of filter loading. Installing worked in two modes: washing with purified water and purified water with sodium hypochlorite dose of 2–3 mg/dm^3.

4. Results

First experiment results with using sodium hypochlorite as an oxidant for manganese removal are given in **Table 1.**

Table 1

Changes in the concentration of manganese in the filtrate with sodium hypochlorite

Dose of sodium hypochlorite [mg/dm^3]	**Initial concentration of manganese** [mg/dm^3]	**Output concentration of manganese** [mg/dm^3]	**Number of captured manganese** [mg/dm^3]	**Efficiency of manganese removal [%]**	**Ratio of Cl_2 and captured Mn** [mg/mg]
0.2	0.33	0.15	0.18	54.5	1.11
0.5	0.32	0.24	0.08	25.0	6.25
1.0	0.33	0.28	0.05	15.2	20.00
1.5	0.33	0.29	0.04	12.1	37.50
2.0	0.31	0.26	0.05	16.1	40.00
3.0	0.32	0.25	0.07	21.9	42.86
4.0	0.31	0.22	0.09	29.0	44.44
5.0	0.32	0.21	0.11	34.4	45.45
6.0	0.33	0.22	0.11	33.3	54.55
8.0	0.31	0.22	0.09	29.0	88.89
10.0	0.32	0.21	0.11	34.4	90.91

Fig. 2 shows the effectiveness of removing manganese with sodium hypochlorite as oxidant.

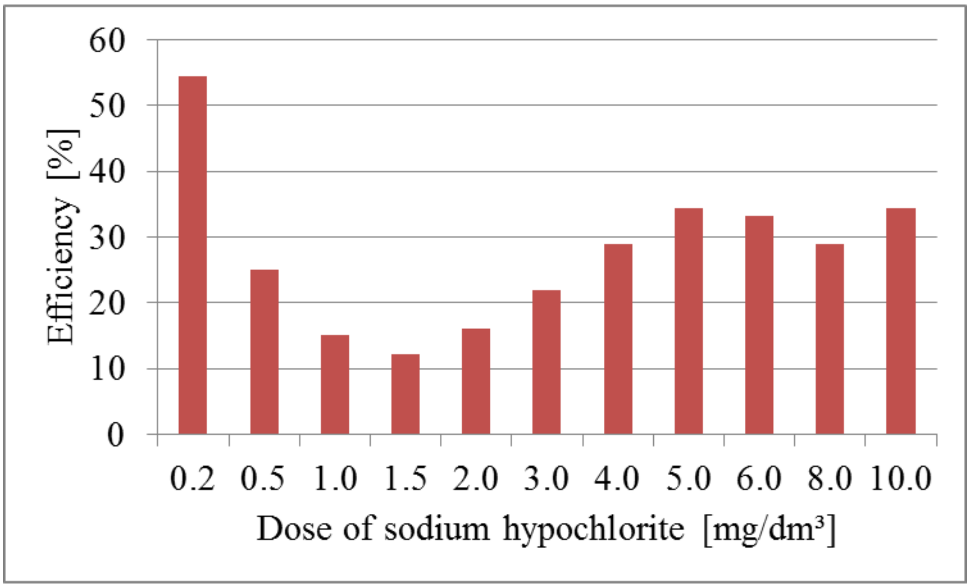

Fig. 2. Efficiency of manganese removal with sodium hypochlorite as oxidant

According to the chart on **Fig. 2** high efficiency of manganese removal is observed from the beginning of the experiments with low doses of sodium hypochlorite. With increasing concen-

tration of sodium hypochlorite to 2 mg/dm^3 efficiency decreases, and further, since the concentration of sodium hypochlorite 3 mg/dm^3, efficiency increases slightly.

It is known that the theoretical consumption of sodium hypochlorite for oxidation of 1 mg of manganese (II) is about 1.3 mg/mg. This condition is satisfied for sodium hypochlorite in dose of 0.2 mg/dm^3. At low doses high efficiency removal of manganese is observed. This fact can be explained by a significant contribution of biological removal of manganese. Taking into consideration that sodium hypochlorite is not only oxidant, but also a strong disinfectant, an increase of its dose leads to the suppression and destruction of microorganisms. Consequently, it is observed a sharp decrease in the efficiency of cleaning. That is why at doses of 0.5-3.0 mg/dm^3 there is a minimum efficiency. With increasing of the dose the effectiveness of chemical oxidation with sodium hypochlorite of manganese are increased. Thus, during increasing the concentration of sodium hypochlorite transition from biological to chemical removal of manganese from the water take place.

Next experiment was carried out with oxygen as an oxidant for manganese removal. Results are given in **Table 2.**

Table 2
Changes in the concentration of manganese in the filtrate with oxygen

Dose of oxygen [mg/dm^3]	**Initial concentration of manganese** [mg/dm^3]	**Output concentration of manganese** [mg/dm^3]	**Number of captured manganese** [mg/dm^3]	**Efficiency of manganese removal** [%]	**Ratio of O_2 and captured Mn** [mg/mg]
0.2	0.33	0.25	0.08	24.2	2.50
0.5	0.32	0.24	0.08	25.0	6.25
1.0	0.33	0.22	0.11	33.3	9.09
1.5	0.33	0.14	0.19	57.6	7.89
2.0	0.31	0.12	0.19	61.3	10.53
3.0	0.32	0.11	0.21	65.6	14.29
4.0	0.31	0.08	0.23	74.2	17.39
5.0	0.32	0.08	0.24	75.0	20.83
6.0	0.33	0.07	0.26	78.8	23.08

Fig. 3 shows the effectiveness of removing manganese with oxygen as oxidant. The dependence on Fig. 3 differs significantly from that with sodium hypochlorite (**Fig. 2**). The efficiency of manganese oxidation increases gradually to 78.8 % when the dissolved oxygen content is 6.0 mg/dm^3.

Dependence change under the replacement of the reagent is explained with fact that oxygen does not show disinfectant properties unlike sodium hypochlorite, and there is no transition from biological to chemical oxidation process. There is a gradual increase in the efficiency of process with increasing concentration of oxidant.

Comparison of data from **Table 1** and **Table 2** shows that the efficiency of manganese removal with oxygen is higher than with sodium hypochlorite - 54.5 % against 78.8 %, respectively. Thus, biological manganese removal is more efficient than chemical.

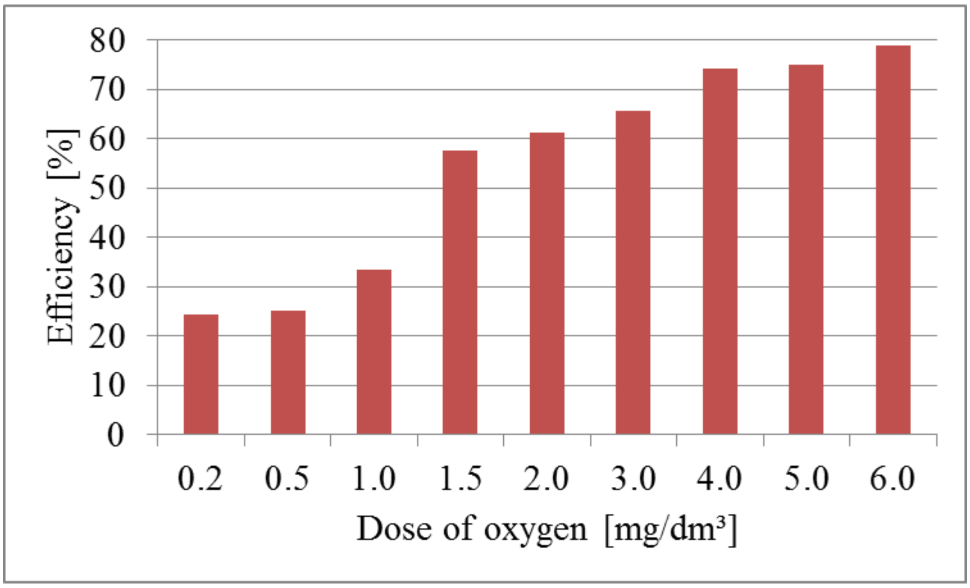

Fig. 3. Efficiency of manganese removal with oxygen as oxidant

At the next step of experiments identifying the role of microorganisms in the process of manganese removal was carried out. Experiments included several filter cycles with oxygen as oxidant. In one cycle, flushing of filter loading was carried out with purified water and with chlorinated water (sodium hypochlorite) in the other. **Fig. 4** illustrates the change in the efficiency of removal manganese during filter flushing with water with sodium hypochlorite and without it.

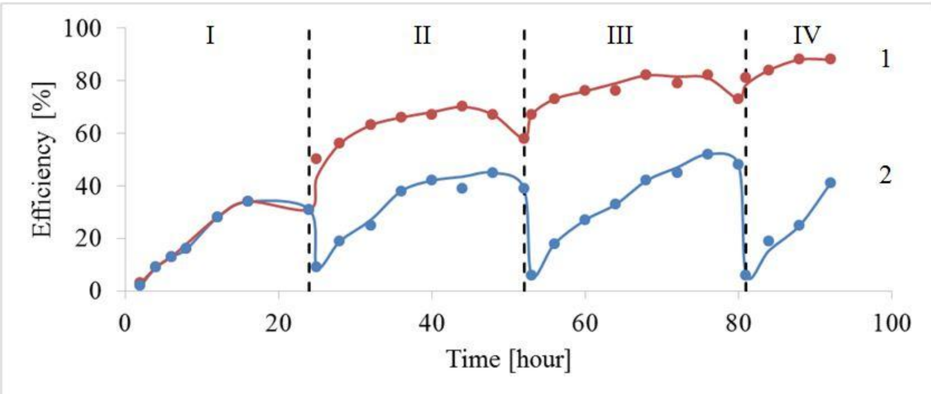

Fig. 4. The efficiency of removing manganese compounds during flushing (1) with sodium hypochlorite during flushing and (2) without sodium hypochlorite. I, II, III, IV - filtration cycles

Analysis of Fig. 4 fully confirms the hypothesis concerning important role of microorganisms in the process of manganese removal from water. According to graph on **Fig. 4** the effectiveness of demanganation increases gradually to maximum in the first filtration cycle (approximately 18 h).

If in the case of flushing water with disinfectant actually the patterns of first filtration cycle are repeated, then without reagent in each filtration cycle a gradual increase of efficiency of manganese removal are observed. Taken into consideration that sodium hypochlorite is not strong enough substance to influence on the catalytic activity of manganese, a significant impact due its nothing like disinfectant action. That, in a case of flushing filter with water without disinfectant, there is gradual growths of biomass of bacteria that can oxidize manganese are observed. In the

presence of disinfectant biomass does not grow, which leads to low efficiency of demanganation process in general.

5. Conclusions

In this paper the influence of oxidants - sodium hypochlorite and oxygen – on the processes of filtering underground water with high content of manganese has been studied. It was found that along with chemical processes biological play significant role.

It is shown that at low concentrations of oxidants biological processes are dominated, while in higher chemical process are more important. Moreover, the use of chlorine compounds (which can be also disinfectants) as oxidants leads to the replacement of one process by another (biological to chemical). At the same time, efficiency with oxygen is increased gradually with its contents for both processes.

It is shown that flushing filter with water containing sodium hypochlorite leads to prevent the growth of microorganisms. This fact is affected negatively the removal of manganese in the early hours of filtration cycle. Flushing water without disinfectant are not caused such adverse effects.

Experimentally determined that the using of water with disinfectants for filter flushing do not allow deep removal of manganese compounds. This follows from the fact that the time required to biomass growths of bacteria (capable of removing manganese) longer than filtration cycle.

All the above facts demonstrate the significant role of microorganisms in the process of manganese removal.

In practical terms, the obtained results showed that the oxygen in the air compared to sodium hypochlorite is more efficient oxidizer for compounds of manganese presented in groundwater. In addition, the expediency of using for demanganation filters flushing water, untreated disinfectants.

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MATHEMATICAL MODELING OF THE SULFURIC ACID DROPS EVAPORATION

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Abstract

The evaporation process of sulfuric acid solution has been analyzed in the hollow apparatus of column type under direct contact between acid drops and hot gas. On the basis of the mathematical model the main parameters have been calculated: evaporation time, distance passed by a drop and its evaporation temperature. The mathematic dependencies of evaporation time of water and sulfuric acid drops on their initial diameters and air temperature have been developed. The drop diameter of $\leq 0.5\cdot10^{-3}$ m was found to be necessary to carry out the evaporation with the rate sufficient for the industrial columns. The obtained results are proposed to be used to determine the effect of intensifying parameters on the evaporation process of sulfuric acid waste solutions and development of their recycling technology.

Keywords: sulfuric acid, evaporation, mathematical model.

1. Introduction

Sulfuric acid (SA) is an important large-tonnage industrial product. A great bulk of SA weak solutions are obtained at many technological processes, in particular at the pigment titani-