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Research Article

RESEARCH ON THE INFLUENCE OF TEMPERATURE ON THE ACTIVATION OF SELECTED POROUS MNO_2 BEDS

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ABSTRACT
Rising demands concerning water treatment and conservation make it necessary to search for more effective as well as cheap and ecologically safe solutions. During the filtration process quartz sand is replaced by filter materials which also have a strong effect on account of reactions taking place on a bed's surface. Today's technologies for groundwater and seepage water treatment in rapid filters make use of oxidation beds. They are able to effectively remove manganese (II) and iron (II) compounds based on heterogeneous oxidation catalysis. The main catalyst of the manganese removal process in terms of its catalytic oxidation in filtration beds is manganese dioxide. This compound is used as an oxidizing agent in many processes. The research conducted as part of this paper was aimed at creating a product with the qualities similar to a popular Greensand bed protected by patent. The authors tested washed quartz sand varying in granulation which was subject to activation in 10% $KMnO_4$ solution. Grains of quartz sand after covering them with a permanent coat of manganese oxide developed the superficial oxidation layer. While performing the tests, a temperature of the process served as a variable. The beds produced as a result of the experiment enable the removal of iron and manganese from water without prior alkylation. Furthermore, they are an effective method of purifying water of organic pollutants and ammoniacal nitrogen. They function as oxidizing and filtering masses.

Keywords: water treatment, iron, manganese, groundwater

INTRODUCTION

Iron and Manganese are the most common elements found in the earth's crust. Groundwater easily gets contaminated by these compounds. Despite being essential trace elements for humans, their presence in groundwater, if it exceeds a prescribed level, makes water unsuitable for use, mainly for aesthetic reasons. Water with an elevated concentration of iron shows a lot of negative features such as discolorations, metallic taste, smell, turbidity, coloring of underwear and sanitary facilities. In addition, it is conducive to the growth of "iron bacteria" which create silty sediment covering water supply conduits. In accordance with the Regulation of Minister of Health of 20 April 2010 concerning the quality of water intended for human consumption the content of iron cannot exceed 2 mg Fe/l, 0.05 mg Mn/l and the content of ammonia cannot be higher than 0.5 mg NH_4^+/l. The effectiveness of removing manganese compounds in the groundwater treatment processes is of particular importance in view of the recent reports on the influence of manganese ions on the human nervous system, however, *neurotoxicity* of manganese absorbed together with the air has been documented much earlier [Ljung and Vahter 2007]. The latest toxicological studies have shown a correlation between a development of human brain's functions and the ability to learn in children consuming water with the increased content of manganese [Wasserman et al. 2006]. This calls for the use of effective methods of water treatment.

The basic process of removing manganese and iron compounds from water is based on filtration usually preceded by aeration. This is an effective, simple and relatively cheap method since the removal of easily precipitated iron and manganese does not pose any difficulties. Water treatment becomes more economical only when it is conducted as a single-stage filtration; therefore the use of an appropriate filter material is a vital element determining the acquisition of high efficiency of water treatment [Kaleta et al. 2011]. Beds should be effective in removing contaminations from water and simultaneously should not create any operational problems. Besides, the economic aspect is significant. Apart from the price of a bed, operational costs related to the length of filtration cycles, durability of filter material, required amount of wash water, necessity to use air, etc. should be taken into consideration [Sozański and Huck 2007]. Filtration beds which are most commonly used include: quartz, anthracite quartz and oxidation beds [Jeż-Walkowiak 2000]. The term "oxidation beds" denotes filter materials on the surface of which there are processes of catalytic and heterogeneous oxidation of iron and manganese removed from water [Sommerfeld 1999]. The compound which catalyzes iron and manganese oxidation is MnO_2 – a strong oxidizer being a part of external layers of filter material grains [Faust et al. 1998].

Consequently, the search for new solutions or the improvement of the existing ones is constantly conducted in order to find the ones which would ensure the optimum conditions for the whole process. Therefore, research on very uncommon or completely new filtration beds seems to be utterly justified. The purpose of the studies referred to in this paper was the creation of the product with the features similar to popular Greensand bed protected by patent. The test concerned washed quartz sand varying in granulation which was next activated with the use of 10% $KMnO_4$ solution.

MATERIAL AND METHODS

The research was conducted at the Technical University of Białystok in the Department of Environmental Protection and Engineering. It consisted in using sand as a filter material. The bed was available in two granulations, i.e. coarse sand 4.0–8.0 mm (Fig. 1) and fine sand 0.5–1.0 mm (Fig. 2).

The experiment included tests on eight samples. Four of them contained fine sand and the remaining ones – coarse sand. The experiment encompassed the preparation of the samples. 1.5 kg of each bed was measured for this purpose. Next the solution of potassium permanganate (10% $KMnO_4$ solution) was prepared to prime the beds. Due to the fact that sand activation time was set for the period of two weeks, the beds were primed for such time during the performance of a series of laboratory tests (Fig. 3, 4)

Drying of the beds constituted the following stage. The beds were dried at various temperatures. This process was conducted in a laboratory dryer. The drying temperatures were 25 °C, 50 °C, 100 °C and 200 °C (Fig. 5).

Figure 1. Coarse sand

Figure 2. Fine sand

Fig. 3. Coarse sand primed with KMnO4 solution

Fig. 4. Fine sand primed with $KMnO_4$ solution

Fig. 5. Filter materials after the drying process

RESULTS

The results of the experiment are presented in the table below (Table 1)

The above table presents the results of the tests performed on filter materials with two different granulations, i.e. coarse sand 4.0–8.0 mm and fine sand 0.5–1.0 mm. There were eight samples used for the experiment. A variable used for the tests was the drying temperature of the beds whereas a constant was the activation time of the samples, which equaled two weeks. All the examined cases had one feature in common. All the grains of the beds were covered with an active layer of MnO_2 (Fig. 6).

As shown in the above graph the dependence of the thickness of oxidation layer on the drying temperature indicates significant differences in MnO_2 quantity in the tested beds. It has been noted that in the temperature of 100 °C the greatest quantity of MnO_2, as much as 3.23 g/kg per dry matter, settled on the grains of coarse sand. Furthermore, only in this temperature coarse sand showed the biggest quantity of MnO_2. In other temperatures the biggest quantity of MnO_2 active layer settled on the grains of fine sand. The test

Table 1. Results of the experiment

Sample no.	Type of filter material	Temperature [°C]	MnO_2 [mg/kg dry matter]	MnO_2 [g/kg dry matter]
1	fine sand	25	986.35	0.99
2	coarse sand		868.23	0.87
3	fine sand	50	1024.00	1.02
4	coarse sand		668.10	0.67
5	fine sand	100	2329.20	2.33
6	coarse sand		3233.70	3.23
7	fine sand	200	1070.60	1.07
8	coarse sand		744.60	0.74

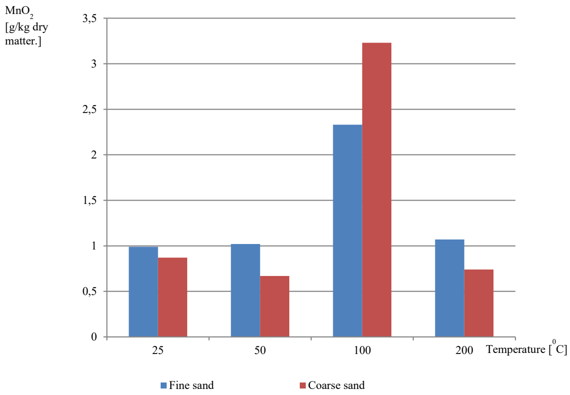

Figure 6. Results of the experiment

of fine sand, during which the greatest quantity of MnO_2 was detected, was also the one during which the drying temperature equaled 200 °C. Drying of the beds in other temperatures i.e. 25 °C, 50 °C, 200 °C allowed a smaller quantity of manganese dioxide (II) to settle both on the grains of fine and coarse sand.

CONCLUSIONS

Based on the assumption adopted in this paper, stating that the performed tests should enable sand activation, it can be claimed that the conducted experiments confirmed its validity. The beds were covered with an oxidizing layer of manganese dioxide which enabled the activation of the bed and its application in the processes of iron and manganese removal.

In the processes of removing iron and manganese, their oxidation based on a classic and nonreagent technology of groundwater treatment occurs as a result of heterogeneous oxidation process on the surface of filter material grains. The oxidation product of manganese found in water that has undergone water treatment is manganese dioxide with a compact structure overlapping the grains of filter material. This compact structure is formed as a result of heterogeneous oxidation of manganese which is assisted by oxidation filter material catalyzing an oxidation process [Faust 1998].

The experiment has shown that sand is susceptible to activation since a compact structure of MnO_2 settled on it. Its method of activation consisting in priming it with $KMnO_4$ solution and next drying it in an appropriate temperature resulted in a ready bed which does not have to be activated. Still the main contested issue is the washing of oxidation beds. In technical literature it is recommended to conduct a process with the use of air and water and washing parameters should be specified on the basis of general principles. Detailed principles concerning the designing of oxidation bed washing should not lead to the loss of an oxidation layer on grains and should ensure their stability.

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