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Original Research

Development of a Fluidized Batch Process Using Natural Powdered Zeolite (Clinoptilolite)

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Abstract

The purpose of this research was to examine water treatment improvement by using natural powdered zeolite (clinoptilolite). Experiments were carried out at a laboratory and in a pilot-scaled water treatment plant. The pilot-scaled plant was fed with groundwater containing a high level of organic compounds from the existing waterworks in Lithuania's Neringa Region. The content of organic substances in the groundwater – characterized by chemical oxygen demand (COD), varied between 5.0 – 40.0 mg O_2 l^{-1} and the permanganate index (oxidation by potassium permanganate) 4.0 – 8.0 mg O_2 l^{-1} was determined during this case study. There was no significant reduction using conventional water treatment. Laboratory analysis of water quality showed: total iron, ammonium, aluminium residual concentrations, pH, colour (Pt scale), turbidity, COD and permanganate index. The drinking water had an undesirable colour, taste and odour due to high concentrations of organic substances in the groundwater. A fluidized batch process and adsorption of natural powdered zeolite were used for reducing organic substances in the water with the effectiveness of total iron concentration reduction by 96%. Experimental research results are included in the article.

Keywords: groundwater, water treatment, sorption, organic compounds, fluidized batch process.

Introduction

Organic compounds (humic acids, fulvic acids) can form stable complexes with metal ions (iron, manganese etc.) and are responsible for the transportation of many contaminants in drinking water. Organic iron complexes are undesirable in a big amount because of the risk to human health, and aspects such as negative organoleptic parameters (colour, turbidity, odour and taste) [1, 2]. Efforts have been made to develop drinking water purification technologies and to reduce the concentration of organic substances during water treatment processes. Expertise of existing conventional iron, manganese and ammonium removal plants show that iron complexes can interfere with conventional iron removal processes (filtration and biological removal) and make water treatment works insufficient. In the case of surface water resources, use of sorbents for the removal of organic compounds may be economically unacceptable because the sorption process will require a high rate of expensive sorbent material. However, the concentrations of organic compounds in groundwater are much lower and use of natural sorbents can be efficient [3-5]. The organic compounds usually exist in surface water resources but some groundwater can be enriched with organic compounds during natural infiltration processes or anthropogenic activities [3, 6]. According to monitoring data provided by the Lithuanian Geological Survey in 2000-04, the quality of groundwater sources from the case study's place (Neringa Region) was as follows: turbidity 8-28 mg l^{-1} (SiO_2 scale), colour

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80-144 mg l^{-1} (Pt scale), total iron concentration 0.54-3.15 mg Fe l^{-1}, manganese concentration 0.30-0.50 mg Mn l^{-1}, ammonium concentration 0.65-2.60 mg NH_4 l^{-1}, permanganate index (PI) 5.40-6.10 mg O_2 l^{-1}. Also, the water had an undesirable taste and a strong odour. The intense colour, taste and odour of the groundwater are due to the high content of organic substances, e.g. humic acids, fulvic acids and organic iron complexes [7].

The well field at the case study place and the water treatment plant started operations in 1972. The water treatment plant was constructed following traditional designs that used technologies such as aeration of groundwater and filtration in pressure filters with crushed gravel filter media (5-10 mm particle size and 2.10 m high). The existing groundwater treatment equipment did not ensure the required quality of drinking water [8].

The remaining concentrations of organic substances, iron, manganese and ammonium residuals were without any significant changes after the treatment plant process. The previous groundwater analysis showed that iron and manganese compounds are partially in a complex organic substance form. Therefore, iron removal should be based on the organic substances removal process, or it should make use of strong oxidants for breaking the bonds between iron and organic substances [9-12]. Because of the possible negative interference of organic compounds during the next water treatment's step – i.e. filtration – large organic compounds can obstruct the filter media [5]. The organic matter concentration can be considered too high for further use without removal, but too low for using common conventional water treatment methods efficiently. Water treatment plants are becoming more like chemical plants with a complicated control and maintenance using a high-powered consumption rate when strong oxidants are in use [7, 8]. The disposal of waste sludge from treatment plants is becoming more difficult, classifying sludge as hazardous wastes.

The sand-ballasted clarification using a fluidized batch process emerged as a proprietary process in that a ballasting agent (about 100 µm particle sized sand) is added to the stirred suspension together with a coagulant to promote adhesion; there is a constant make-up of fine sand with a close-sized specification. Locally available powdered natural zeolite acceptable for water treatment properties is a by-product from a chicken-feed composition with a certificate for use in drinking water purification processes.

The aim of this research was to evaluate the removal effectiveness of stable organic compounds and organic iron complexes by using a natural powdered zeolite (clinoptilolite) in the fluidized batch process.

Experimental Procedures

Experimental Model

Firstly, the experimental research was started and carried out during the preliminary laboratory study. An experimental pilot plant shown in Fig. 1 was constructed at the existing waterworks, and an investigation was carried out dur-

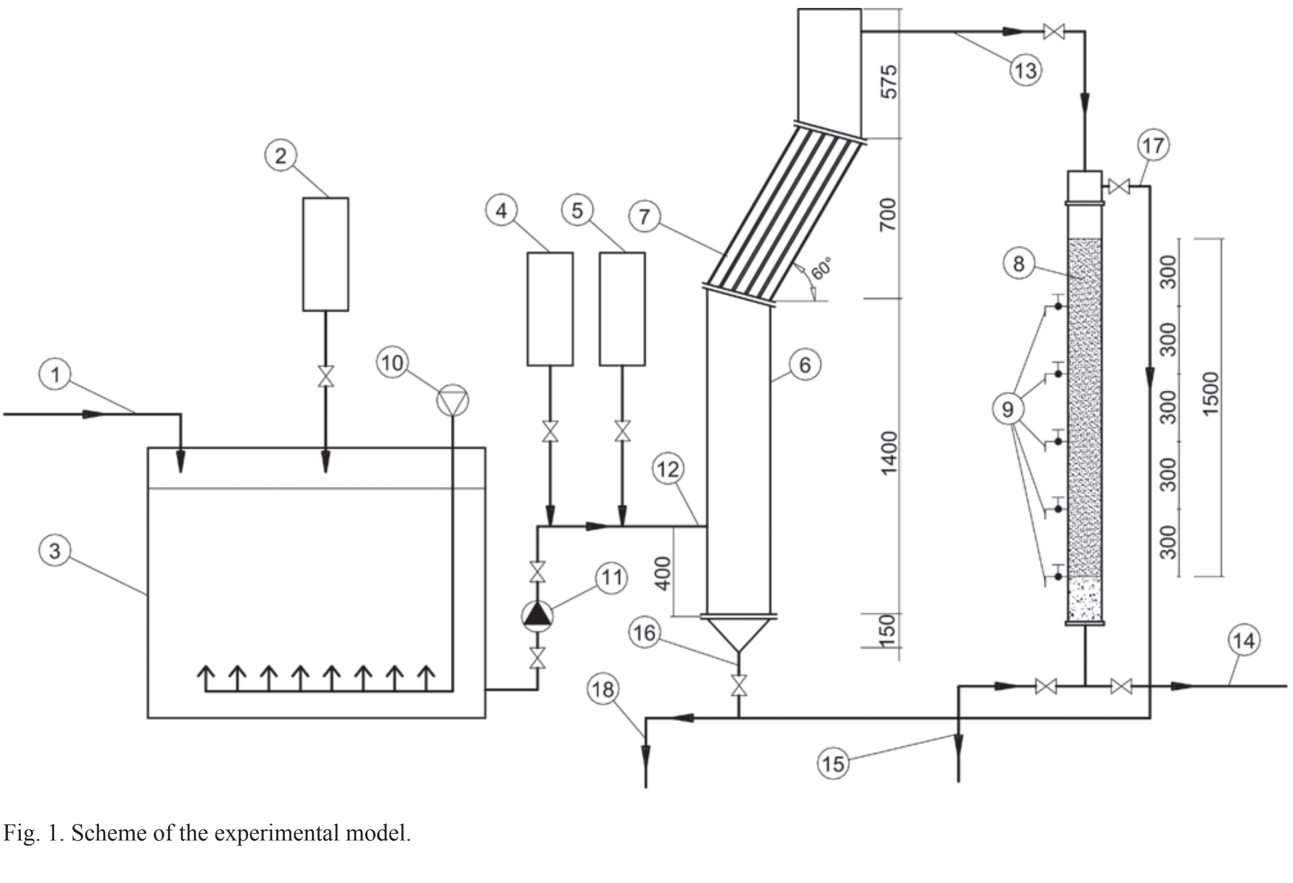

Fig. 1. Scheme of the experimental model.

ing two kinds of water treatments: 1 – with only coagulants and 2 – with coagulants plus natural adsorbent powdered zeolite, which were applied during the research. Powdered zeolite (clinoptilolite) was added to the reactor – contact time was approximately 45 min. This natural zeolite was a hydrated aluminosilicate mineral, with a porous structure and with valuable physicochemical properties such as cation exchange, molecular sieving, catalysis, and sorption. Natural clinoptilolite is a zeolite of the heulandite group; Transcarpathian origin clinoptilolite was used in this case study. Multiple uses of natural zeolites are based on their physicochemical properties, as mentioned above, and this explains their wide range of applications in numerous agricultural and industrial areas [3-6, 13, 14]. Natural zeolite-clinoptilolite is the most abundant in nature and is readily available from more than forty species of natural zeolites. Transcarpathian natural zeolite-clinoptilolite is superior to other natural zeolites due to its greater acid-stability, thermal resistance and mechanical strength. Natural clinoptilolite has the formula $[AlSi_5O_{12}]_2(K_2,Na_2,Ca)\cdot(H_2O)_8$, where the Si/Al ratio in the zeolite structure influences the adsorption properties of clinoptilolite.

All contents (groundwater (1) and powdered zeolite (2)) of the fluidized batch reactor's (3) volume were continuously mixed to avoid sedimentation of the powdered zeolite. The mixture of water and powdered zeolite was supplied from the mixing unit (10) to the reaction tank (6). To achieve better water treatment efficiency, coagulants, i.e. solutions of Al_2SO_4 (4) and Na_2CO_3 (5) were added during this water treatment step [15]. After the sorption treatment approximately 30% of the used zeolite was removed from the water (16, 18) into the Lamella settlement unit (7). The remaining part, approximately 70% powdered zeolite, was then recycled into the fluidized batch reactor unit. Pretreated water was supplied (13) into the final water treatment step filter (8) for the removal of iron, manganese, ammonia and other residual substances. Quartz sand was used as a filter media, the height was 1.50 m, and the size of sand particles was 1.0 mm to 2.5 mm. Water sampling taps (9) were arranged in the test filter column at different heights every 0.3 m. Special valves, pipes (12-18), water pump (11) were arranged to regulate the operation of the experimental pilot plant.

During the final water treatment step of the filtration process filter media pressure losses were registered continuously. The filtration rate was controlled, according to the situation. The water supply was interrupted when higher filter media pressure losses occurred, then the filtration rate was registered and a backwashing process was restarted. Samples of untreated water (1), water outlet from the sedimentation tank (13) and water after filtration (14) were also continually recorded.

Water Quality Analysis

A water quality analysis was made and certain technological parameters were determined for the control and evaluation of technolgical processes using international standard methods: total iron concentration, mg Fe l^{-1}; manganese concentration, mg Mn l^{-1}; ammonium concentration, mg NH_4 l^{-1}; residual aluminium concentration, mg/L Al; filtration rate, m/h; backwash time, min; adsorbent (zeolite) rate, g/L; coagulants (Al_2SO_4, $FeCl_3$) rate, mg/L and other relevant parameters (e.g. odour, taste, colour, turbidity). The quantitative results are presented as the arithmetic mean of six independent measurements (x±SD, n=6). Significant differences ($p<0.05$) were removed from the results estimations and the measurements were analyzed once again.

The data from the experimental investigation was statistically calculated from the registered analyses. The concentration of substances (Fe, Mn and NH_4) was measured 11 times in raw water, in taps of filters and in filtered water. The average concentration at typical points was:

$$\overline{c} = \frac{1}{n}\sum_{i=1}^{k} c_i m_i \qquad (1)$$

where: c_i – concentration of substances at typical points, m_i – probability at the occurrence of concentration; n – number of days; k – number of different values of the concentration.

The average concentrations of substances, mentioned above, at the characteristical point were also calculated. The standard statistical estimation error of the arithmetic average was approximatly 11%.

Results

Conventional Coagulation

Groundwater supplied to the existing waterworks was used for research at the pilot plant. Two kinds of coagulants (Al_2SO_4 and $FeCl_3$) were used for the initial evaluation of water treatment efficiency. Na_2CO_3 was added to insure optimal conditions (pH range) for the formation of large floccules with a high sedimentation rate. Analysis results show that a better sedimentation rate was obtained by using Al_2SO_4. Other reasons for using aluminium sulphate's are as follows: Al_2SO_4 coagulant is produced locally, it is cost effective. Aluminium sulphate is most often successfully applied in water treatment processes. The results of water quality improvement during the different dosage rate of Al_2SO_4 are presented in Table 1. During research the optimal coagulant dosage rate of 15 mg l^{-1} was obtained. This dosage was used during the following experimental research with the enhanced fluidized batch process using natural powdered zeolite. Higher rates, such as overdosing, were avoided because of the increased turbidity and residual aluminium values. The residual of aluminium into the treated water was controlled according to safe and permitted values for drinking water, i.e. according to the World Health Organization 2004, European Commission Council 1998 [1, 2].

Iron, manganese and ammonia concentrations, permanganate index, chemical oxygen demand, colour and turbidity were analyzed using international standard methods.

In the case study experiment, the measured elements concentration, with optimal coagulant dosage rate, showed that the residuals of manganese and aluminium were still too high. Therefore, research was continued using natural powdered zeolite that was applied.

Enhanced Coagulation Using Natural Powdered Zeolite

The results of water quality improvement during different dosage rates of natural powdered zeolite are presented in Table 2. During research the optimal zeolite dosage rate of 5 g l^{-1} was obtained.

The best water quality was obtained when aerated water was treated with coagulant and natural powdered zeolite. After the sorption treatment approximately 30% of the used zeolite could be removed from the treated water into the sedimentation unit and a residual part of approximately 70% of powdered zeolite needed to be recycled into the fluidized batch reactor unit. Concentrations of total iron and ammonium contained in the water, after filtration, met the requirements of the World Health Organization 2004, and the European Commission Council 1998, i.e. when the filtration rate was 10 m/h, the particle size of the filter media was 1.0 mm–2.5 mm, and the depth of the quartz sand filter media was 1.50 m.

According to the research results the optimal rate of coagulant Al_2SO_4 is 15 mg l^{-1} when the total iron concentration in raw water is 0.5-3.5 mg Fe l^{-1}, manganese and ammonium concentrations are 0.3-0.5 mg Mn l^{-1} and 0.6-3.0 mg NH_4 l^{-1}, respectively. It resulted in iron removal

Table 1. Results of groundwater treatment with coagulant.

Measured elements concentration	Study results					
	Raw water	Treated water, when the rate of coagulant Al_2SO_4 is as follows:				
		12 mg l^{-1}	15 mg l^{-1}	18 mg l^{-1}	21 mg l^{-1}	24 mg l^{-1}
Total iron, mg Fe l^{-1}	1.26	0.16	0.14	0.15	0.16	0.16
Manganese, mg Mn l^{-1}	0.453	0.239	0.224	0.258	0.235	0.233
Ammonium, mg NH_4 l^{-1}	0.79	0.28	0.02	0.08	0.09	0.34
Aluminium, mg Al l^{-1}	Not detected	Not detected	0.12	0.24	0.14	0.20
pH	7.2	7.26	7.3	7.29	7.3	7.2
Colour, mg l^{-1} Pt scale	103	74	50	46	59	96
Turbidity, NTU	17	14	10	9	13	19

Note: Treated with coagulant (optimal rate of 15 mg l^{-1}) water taste and odor were acceptable to consumers and no abnormal changes occurred.

Table 2. Study results of groundwater treatment with coagulant and natural powdered zeolite.

Measured elements	Raw water	Water treated with coagulant	Content of elements in water after sedimentation, when natural zeolite rate is as follows:				
			1 g l^{-1}	2 g l^{-1}	3 g l^{-1}	4 g l^{-1}	5 g l^{-1}
Total iron, mg Fe l^{-1}	3.21	0.240	0.200	0.190	0.180	0.170	0.130
Manganese, mg Mn l^{-1}	0.375	0.230	0.220	0.220	0.210	0.210	0.210
Ammonium, mg NH_4 l^{-1}	1.070	1.010	0.660	0.410	0.220	0.110	0.050
Aluminium, mg Al l^{-1}	<0.02	0.420	0.370	0.330	0.300	0.270	0.240
pH	7.2	7.2	7.18	7.16	7.16	7.21	7.20
Colour, mg l^{-1} Pt scale	114	52	48	44	38	27	20
Turbidity, NTU	22	10	10	9	6	4	3

Note: Treated with 15 mg l^{-1}coagulant rate and powdered zeolite water taste and odor were acceptable to consumers and no abnormal changes occurred.

to 96%, manganese removal to 44%, and ammonium removal to 95%.

Data from the experiment showed a dependency between chemical oxygen demand (COD_{Cr}), permanganate index and total iron concentration and was established a logarithmic regression type $COD_{Cr} = 1.9494Ln(Fe_{total}) + 10.167$, $PI = 0.571Ln(Fe_{total}) + 0.4276$ (R^2=0.98) and shown in Fig. 2.

The removal of organic matter by using natural adsorbent powdered zeolite has a significant impact on decreasing total iron concentration. Stable organic iron complexes were removed according to dependencies of chemical oxygen demand (COD_{Cr}), permanganate index (PI) and total iron concentration (Fe_{total}) (Fig. 2). This dependency proves the efficiency of organic compound removal and the decrease of total iron concentration into treated water.

Discussion of Results

To obtain the required drinking water quality that meets requirements, two different technologies can be applied for water treatment according to this case study's results:

1. A common conventional method with chemical only (using coagulation and filtration);
2. A method with adsorbents and chemicals treatment into the fluidizing batch reactor (using coagulation, adsorbents and filtration).

Both methods have advantages as well as disadvantages and are explained below.

Conventional organic contaminant and organic iron removal from groundwater is generally achieved by coagulation and followed by filtration. During the experimental research the disadvantage of a conventional organic matter removal mechanism was obtained when formed colloidal particles obstructed the filter media. Some flock particles had a diameter 3-5 mm and did not settle down properly into the sedimentation unit. Organic molecules can form complex organic compounds with iron and cause obstructing the filter media. It show that organic iron complexes need to be removed before a filtration process and that is why the authors carried out the research with enhanced coagulation using natural powdered zeolite. In a conventional coagulation process, the floccules formation reduces the run-time of the filters and produces sludge, which must be disposed of very carefully because it is classified as hazardous waste.

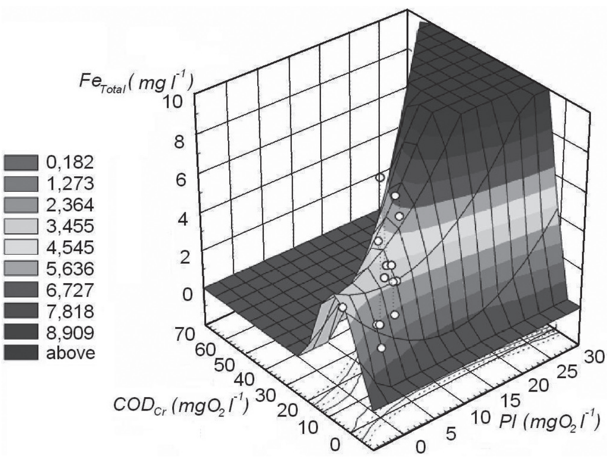

Fig. 2. Dependency between chemical oxygen demand (COD-Cr), permanganate index (PI) and total iron concentration (Fe-total)

Water treatment technology, when coagulation and adsorbents are used in a fluidizing batch, is considered better for an application and is more advanced, compared to a technology that uses only chemicals because a better quality of the treated water can be obtained and water treatment effectiveness following residual total iron concentration is up to 96%. The advantages of using adsorbents are as follows:

- Lower amounts of chemicals need to be added into the natural groundwater. In this research the same dosage of 15 mg Al_2SO_4 l^{-1} resulting treatment effectiveness regarding turbidity approximately 54%, using natural powdered zeolite – up to 86%;
- Compared with a high coagulant dosage of 18-24 mg Al_2SO_4 l^{-1}, when a higher level of the treated water turbidity occurred – up to 19 mg l^{-1}, the adsorbent dosage of even 5 g l^{-1} has only a positive effect on treated water quality. Treated water turbidity decreased to 3 mg l^{-1};
- Powdered zeolite removed from the sedimentation unit can be used for land or forest fertilizing purposes, because according to existing legislation these sediments are not contaminated with inadmissible substances.
- One disadvantage still exists because a water treatment plant will need powdered zeolite storage and dosage equipment.

According to the research results, natural adsorbent zeolites have a positive impact on the removal of organic matter and even on organic metal complexes (iron and manganese) removal from groundwater in a safe ecological way.

The rate of adsorbent natural powdered zeolite in groundwater treated at the waterworks had a positive effect on treated water quality and on the organoleptic parameters (taste, odour, colour, turbidity) of drinking water. A rate of 5 g l^{-1} of natural powdered zeolite, when contact time was 45 min., reduced the concentrations of iron and ammonium respectively by 95-96% after sedimentation. It shows and proves that using powdered natural adsorbent had a positive impact on a fluidizing batch process, compared with conventional chemical treatment.

After aeration and coagulation, as well as the addition of natural powdered zeolite (5 g l^{-1} initial rate) and filtration of the groundwater at 10 m/h via 1.0 mm–2.5 mm particle-sized 1.50 m deep quartz sand filter media, total iron concentration met the requirements of drinking water quality and show the appropriateness of a developed and improved fluidizing batch process for the water purification purpose. However, such processes still need to be proved in more extensive investigations, but these research results could be applied as a basic scenario.

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