Natural Zeolite-Based Filter for the Treatment of Well Water

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Abstract: *In many cases, the quality of the well water intended for human consumption does not meet the standards to be directly consumed by humans. Well water can be affected in the underground both by the interaction with minerals from aquifers and by contamination caused by anthropogenic activities. The objective of the study was to produce and test a filter containing an efficient and cost-effective filtering material based on thermally activated clinoptilolite-type natural zeolites from Romania to remove dissolved ammonium ion and metallic cations from water. The XRD patterns of the zeolitic materials displayed the presence of clinoptilolite as the main phase. The best results for the removal efficiency of contaminants were obtained when the natural zeolite with the particle size of 0.5 – 1.25 mm thermally activated at 300 C was used, but in general, all types of materials were efficient to decrease the concentrations of contaminants below the maximum admitted concentrations established by the EU Drinking Water Directive.*

Keywords: *Natural zeolite, drinking water, water treatment, clinoptilolite, heavy metals, ammonium*

1. Introduction

Groundwater is one of the most important sources of drinking water, and in many regions worldwide it represents the sole source of drinking water. Because of the interactions between groundwater and aquifers, as well as due to contamination from anthropogenic sources, some chemical parameters can be affected, making the quality of water inadequate for drinking [1-4]. In particular, the contamination with ammonium due to agricultural practices and domestic activities [5], or with metals and metalloids coming both from the mineral matrix of aquifers or from industrial activities are of high concern [6,7].
The human right to safe drinking water is recognized as part of the international law by the UN General Assembly and the Human Rights Council in 2010 [8,9]. According to the World Health Organization (WHO), the "Safe drinking water" represents the water which does not pose any substantial health risk due to its consumption [10]. It is estimated that around 2.3 billion people worldwide are at risk of diseases caused by contaminated drinking water due to the lack of adequate water treatment and the absence of a proper distribution system [10].
In order to protect human health, the EU Drinking Water Directive demand the control of public water systems to ensure that the water produced for human consumption can be safely consumed, but a scarce water supply is a foremost challenge in rural areas, where domestic wells are the key drinking water sources [11]. The estimated amount of necessary drinking water is at least 20 litres of water per person per day, up to 1 km radius of the user's home [12]. On the other hand, it is appraised that, in rural areas of Romania, almost 50% of households have their own wells as a primary source of drinking water [12]. In general, it is recognized that many groundwaters in Romania are contaminated by ammonia and metals, mainly Fe and Mn [5,13].
Accordingly, there is a high demand to develop methodologies to treat well water to meet the required quality standards for drinkability. The proposed solutions should consider both the costs of treatment and the efficiency in producing safe drinking water, by the removal of as many as possible contaminants using a single filtering material.
Porous materials can be used as cost-efficient and sustainable adsorbents to remove cations for water treatment. In this class, natural zeolites are ecologically and economically adequate materials. They are aluminosilicate materials with extraordinary ion-exchange and adsorptive

properties. Their unique properties are conferred by the tree-dimensional porous structure with a negative charge on the surface, resulting from the isomorphic replacement of Si by Al in the framework structure. Many studies have confirmed their outstanding performance in removing cations from waters [13-16].
The work aims to develop and test a filter for water treatment based on clinoptilolite type natural zeolite from Chilioara, NW of Romania, as an adsorbent material. The zeolitic tuff was characterized from structural and physico-chemical point of view. Four materials were produced (two different particle sizes, 0.5 – 1.25 mm and 1.25 – 3.00 mm), each of them thermally activated at two temperatures: 200 °C and, respectively 300 °C, and were tested in order to evaluate their adsorption properties for ammonia and metals removal from aqueous solutions.

2. Materials and Methods

Natural zeolite (NZ) material was obtained from a quarry located in Chilioara, Salaj County, Romania. Two fractions with particle sizes of 0.50 – 1.25 mm (NZ1) and 1.25 – 3.00 mm (NZ2) were produced by crushing and granulometric separation. Then, both NZ1 and NZ2 fractions were subjected to activation at two temperatures: 200 °C and, respectively 300 °C, to obtain the samples NZ1-200, NZ1-300, and NZ2-200, NZ2-300, respectively.
Major elements (Al, Ca, Mg, K, Na, Fe, Mn) in zeolite samples were measured by inductively coupled plasma optical emission spectrometer Optima 5300DV (Perkin Elmer, Norwalk, CT, USA) after microwave assisted acid digestion USING an Xpert system (Berghof, Eningen, Germany). 0.5 g of the sample was digested with a mixture of HNO_3 65% : HCl 37% : HF 40% (3:9:2, *v:v:v*). The cation exchange capacity (CEC) was obtained by the measurement of the major cations (K, Na, Ca, and Mg) extracted in ammonium acetate solution 1 M using ICP-OES. Three parallel measurements were carried out for each sample analysis.
The X-ray diffraction (XRD) patterns were recorded at room temperature using a D8 Advance (Bruker, Karlsruhe, Germany) diffractometer with CuKα radiation (λ = 1.54060 Å), operating at 40 kV and 40 mA, at room temperature. The morphology of NZ1 200 was observed using a scanning electron microscope (SEM VEGAS 3 SBU, Tescan, Brno-Kohoutovice, Czech Republic) with an EDX detector.

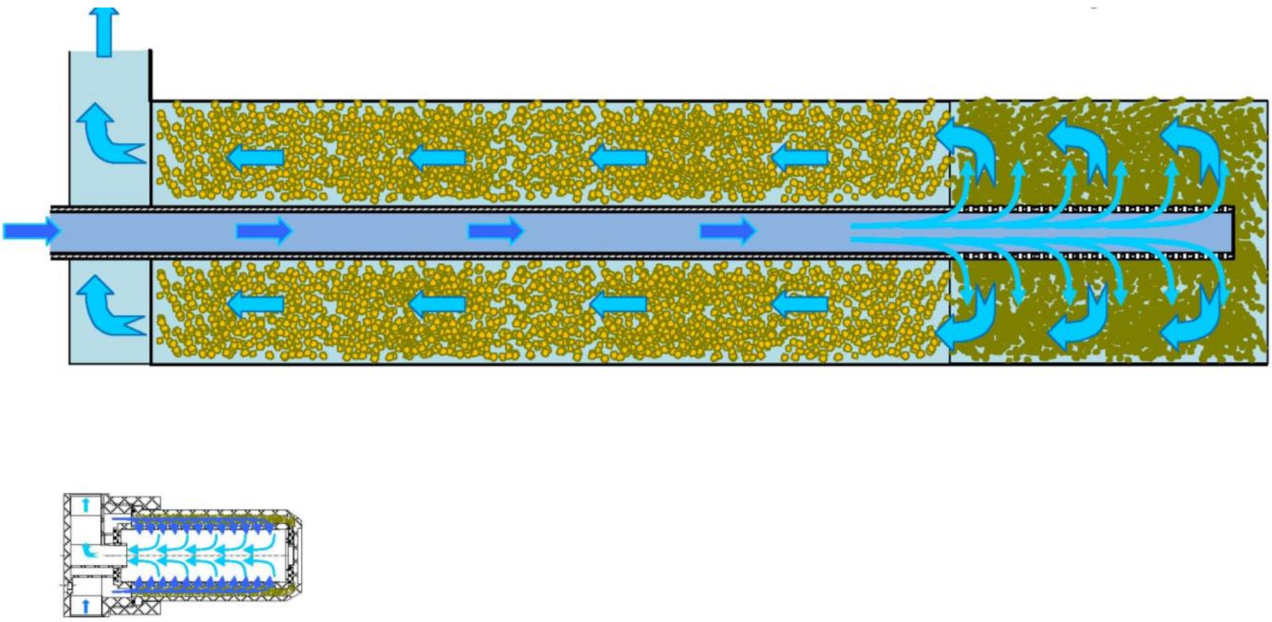

Fig. 1. Design of the natural zeolites-based filter for water filtration

A natural zeolites-based filter, presented in Figure 1, was designed and built at the appropriate dimensions for domestic use, and to assure a maximum efficiency of the filtration process.

The flow direction of the fluid is parallel to the permeable porous medium, the liquid "sweeping" through the flow, the surface of the filter. Tangential filtration is a dynamic process; the fluid flow is parallel to the surface of the filter element, thus preventing the formation of a layer of impurities above the filter surface through agglomeration. Hence, the filter's functionality is maintained by reducing the jamming effect. The pressure drop and fluid flow remain constant over time. With tangential filtration, recirculation filtration can be performed in a closed circuit, an important advantage for specific energy consumption.
For each batch experiment, 50 L of distilled water was contaminated with known quantities of contaminants: ammonium, Al, Cd, Cr, Cu, Mn, Ni, Fe, Mn, Na and Zn. The solutions were filtered in four different experiments using the four zeolitic materials (NZ1-200, NZ1-300, and NZ2-200, NZ2-300). The concentrations of metals in the resulted solutions were measured by ICP-OES, while the ammonium concentration was measured using a Lamda-25 Perkin Elmer UV-Vis spectrophotometer.

3. Results and discussion

3.1 Characteristics of the natural zeolites

The chemical composition in terms of the major oxides and total CEC of the thermally activated natural zeolites with different particle size zeolites is presented in Table 1.

Table 1: Chemical composition (wt. %) and CEC of the thermally activated natural zeolites

Zeolite	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3	MnO	CEC
	%								mEq $100g^{-1}$
NZ1-200	65.2	12.3	0.27	2.46	1.64	1.09	1.23	0.04	120
NZ1-300	66.9	12.4	0.25	2.51	1.48	1.17	1.31	0.04	107
NZ2-200	64.8	12.2	0.28	2.33	1.63	1.21	1.22	0.03	126
NZ2-300	65.1	11.9	0.29	2.24	1.55	1.08	1.17	0.04	112

According to the SiO_2/Al_2O_3 ratio, the natural zeolite from Chilioara belongs to the group of super silicic materials. The grain sizes and the activation temperature do not significantly influence the chemical composition of the materials.

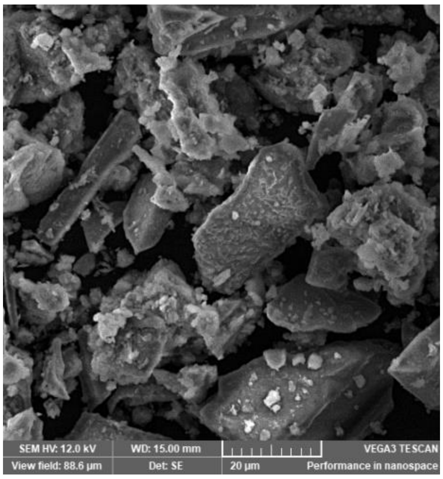

Fig. 2. SEM images of the NZ1 200 zeolite sample

The Scanning Electron Microscopy (SEM) image of the NZ1 200 zeolite is shown in Figure 2. The rough surfaces were favourable for the adsorption of metals.

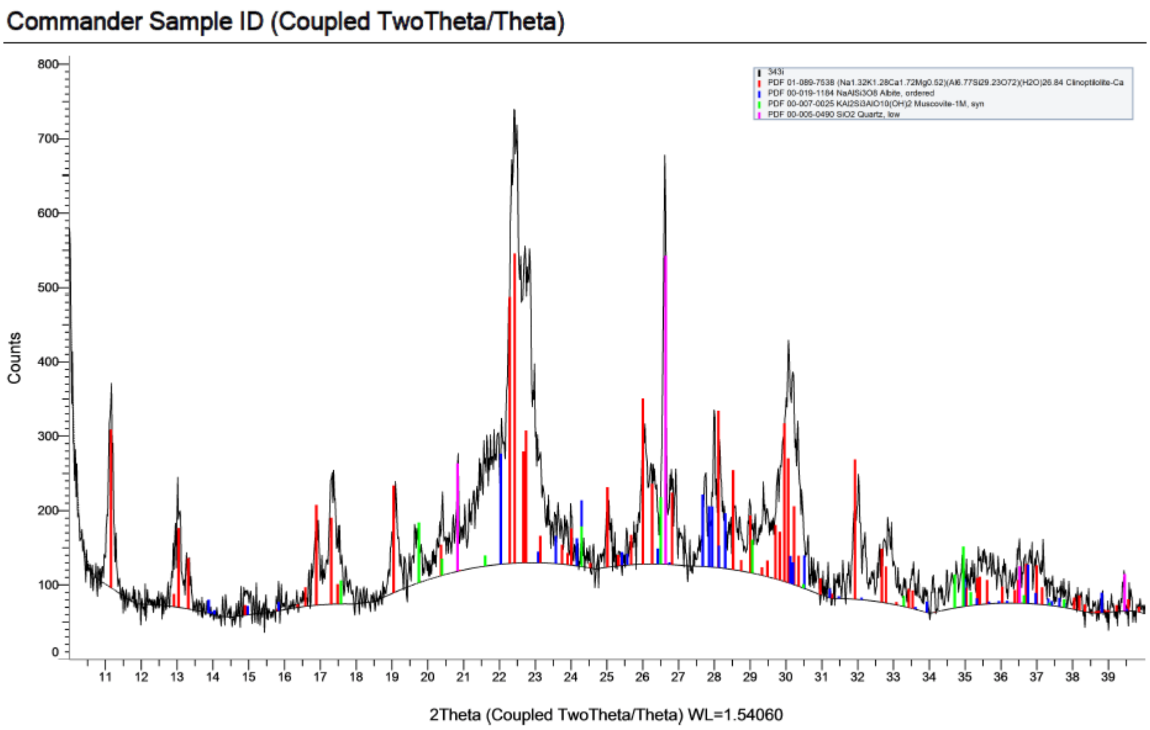

Fig. 3. XRD pattern of the NZ1 200 sample

The XRD patterns of the zeolitic tuffs presented in Figure 3 display the presence of clinoptilolite as the main phase, joined by muscovite, albite, orthoclase, quartz, and montmorillonite. The RIR (Reference Intensity Ratio) method, employed for the quantitative phase analysis, indicates a clinoptilolite content of about 65%.

3.2 Adsorptive characteristics of the filter filled with the four types adsorbent materials

In Table 2 are presented the concentrations of cations of metals and ammonium before and after the filtration of the contaminated solutions using the filtering material NZ1-200.

Table 2: Concentrations of pollutants before and after the filtration of contaminated solutions using the filtering material NZ1-200

Parameter	MAC*	Initial concentrations	Concentrations after filtration
Al	200 µg/l	400 µg/l	150 µg/l
Cd	5.0 µg/l	10 µg/l	3.5 µg/l
Cr	50 µg/l	100 µg/l	36 µg/l
Cu	0.1 mg/l	0.2 mg/l	0.05 mg/l
Ni	20 µg/l	40 µg/l	13 µg/l
NH_4^+	0.50 mg/l	1 mg/l	0.33 mg/l
Fe	200 µg/l	400 µg/l	110 µg/l
Mn	50 µg/l	100 µg/l	28 µg/l
Na	200 mg/l	400 mg/l	132 mg/l
Zn	5 mg/l	10 mg/l	8.2 mg/l

MAC* maximum admitted concentrations according to Drinking Water Directive [17]

In Table 3 are presented the concentrations of contaminants in the contaminated solutions before and after the filtrations using the filtering material NZ1-300.

Table 3: Concentrations of pollutants before and after the filtration of contaminated solutions using the filtering material NZ1-300

Parameter	MAC*	Initial concentrations	Concentrations after filtration
Al	200 μg/l	400 μg/l	42 μg/l
Cd	5.0 μg/l	10 μg/l	0.9 μg/l
Cr	50 μg/l	100 μg/l	22 μg/l
Cu	0.1 mg/l	0.2 mg/l	0.03 mg/l
Ni	20 μg/l	40 μg/l	7 μg/l
NH_4^+	0.50 mg/l	1 mg/l	0.12 mg/l
Fe	200 μg/l	400 μg/l	50 μg/l
Mn	50 μg/l	100 μg/l	12 μg/l
Na	200 mg/l	400 mg/l	44 mg/l
Zn	5 mg/l	10 mg/l	4.6 mg/l

In Table 4 are presented the concentrations of contaminants in the contaminated solutions before and after the filtrations using the filtering material NZ2-200.

Table 4: Concentrations of pollutants before and after the filtration of contaminated solutions using the filtering material NZ2-200

Parameter	MAC*	Initial concentrations	Concentrations after filtration
Al	200 μg/l	400 μg/l	175 μg/l
Cd	5.0 μg/l	10 μg/l	4.7 μg/l
Cr	50 μg/l	100 μg/l	44 μg/l
Cu	0.1 mg/l	0.2 mg/l	0.1 mg/l
Ni	20 μg/l	40 μg/l	19 μg/l
NH_4^+	0.50 mg/l	1 mg/l	0.41 mg/l
Fe	200 μg/l	400 μg/l	175 μg/l
Mn	50 μg/l	100 μg/l	50 μg/l
Na	200 mg/l	400 mg/l	175 mg/l
Zn	5 mg/l	10 mg/l	7.9 mg/l

In Table 5 are presented the concentrations of contaminants in the contaminated solutions before and after the filtrations using the filtering material NZ2-200.

Table 5: Concentrations of pollutants before and after the filtration of contaminated solutions using the filtering material NZ2-300

Parameter	MAC*	Initial concentrations	Concentrations after filtration
Al	200 μg/l	400 μg/l	180 μg/l
Cd	5.0 μg/l	10 μg/l	4.6 μg/l
Cr	50 μg/l	100 μg/l	50 μg/l
Cu	0.1 mg/l	0.2 mg/l	0.09 mg/l
Ni	20 μg/l	40 μg/l	19 μg/l
NH_4^+	0.50 mg/l	1 mg/l	0.4 mg/l
Fe	200 μg/l	400 μg/l	180 μg/l
Mn	50 μg/l	100 μg/l	48 μg/l

Parameter	MAC*	Initial concentrations	Concentrations after filtration
Na	200 mg/l	400 mg/l	184 mg/l
Zn	5 mg/l	10 mg/l	8.2 mg/l

According to the data presented in Tables 2-5, the best results for the removal of contaminants from water were obtained when the natural zeolite with the grain size of 0.5 – 1.25 mm thermally activated at 300 °C was used for the filtration. Generally, the use of all types of natural zeolites was proved to be efficient since the concentrations of contaminants in water decreased below the maximum admitted concentrations established by the EU Drinking Water Directive.

4. Conclusions

This paper investigated the simultaneous removal of ammonium ion and metal cations using natural zeolite form Chilioara as filtering material. The XRD patterns of the zeolitic materials showed the presence of clinoptilolite as the main phase in a content of about 65%, which explains the excellent adsorbtive and ion-exchage properties of the material. The rough surface of the thermally activated natural zeolite, as shown by the SEM images, favors the adsorption of contaminants. The best results for the removal efficiency of contaminants were obtained when the natural zeolite with a grain size of 0.5 – 1.25 mm thermally activated at 300 °C was used, but in general, all types of materials were efficient to decrease the concentrations of contaminants below the maximum admitted concentrations established by the EU Drinking Water Directive. The obtained results demonstrate the possibility of using activated natural zeolite from Chilioara querry to simultaneously remove cations from aqueous solutions, including producing drinking water from contaminated wells.

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