Reduction of excessive heavy metals accumulation in drinking water with natural zeolites

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Abstract. This paper reports on the study of heavy metal removal from groundwater intended for human consumption using natural aluminosilicates of the zeolite group. The natural zeolite material has been extracted from the Sokirnica deposit located in the Zakarpattia Region in Ukraine. The central focus of this study was the course of the heavy metal adsorption process itself, in which natural zeolites were applied for the removal of Cr, Cd, Ni and Pb ions from aqueous solutions in the presence of large amounts of Ca and Mg ions, competing for ion exchange sites. The capacity of zeolite as an adsorbent was assessed with the use of adsorption isotherms prepared for the heavy metals under tests, whereas the mathematical description of the process was provided by Freundlich and Langmuir isotherm equations. The results from the analysis confirm the high efficiency, and thus the applicability, of zeolite deposits in water filtration. The effective Cr, Cd, Ni and Pb removal rate from groundwater intended for human consumption was confirmed even when the content of these metals in water was exceeded by a factor of 10, compared to the permissible limits provided in legal regulations.

1. Introduction
There are over 800 naturally occurring silicate minerals, and the silicate and aluminosilicate mineral content in the rock structure amounts to approx. 75% by weight. Zeolites constitute a large group of aluminosilicate minerals of different chemical composition, properties and crystalline forms. They are typically found as hydrated aluminosilicates of Na and Ca, and less frequency of Ba, Sr, K, Mg and Mn. Derived from Greek etymology, the word “zeolite” comprises two parts “zeo” = cook and “lithos” = stone, which translates to “a boiling stone” [1]. The term was coined in 1756 by a Swedish chemist and mineralogist, Axel Fredrik Cronstedt, following an observation that during heating, the mineral was losing substantial amounts of water. Already in the nineteenth century, the minerals were known to be aluminosilicates, however, it was not until the following century that more accurate analyses and categorisation were carried out. It was then that zeolites were found, by Smith and Beck, to be crystalline, microporous aluminosilicates containing exchangeable cations characterised by their water adsorption/desorption properties. Liebau described these materials as tectonic-silicate minerals built of chambers or channels, which enable them to diffuse the previously adsorbed molecules [2].

Zeolites are crystalline, porous and hydrated metal aluminosilicates of group I and II of the periodic table (Na, K, Ba, Sr). Their simplified structure is given by the formula:

\[ M_{x/n} \left[ Al_x Si_{y} O_{(x+y)} \right] p H_2 O \]  

(1)

where M stands for (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is cation charge; y/x = 1–6, p/x = 1–4. Other formulas also apply, e.g. using patterns of the oxide:
The zeolite skeleton is built by two basic structures, the SiO\(_4\) and AlO\(_4\) tetrahedrons, which are linked by shared oxygen atoms. The Al:Si ratio varies from 1:5 to 1:1. The replacement of the silicon-oxygen group with an aluminium-oxygen group results in the emergence of an excess negative charge in the network, which attracts positive cations Na\(^+\), K\(^+\), Li\(^+\), Cu\(^2+\), etc – as they can move freely. In its aluminosilicate skeletal framework, zeolites contain free spaces storing high-mobility water ions and molecules, which enable cation exchange and reversible dehydration [3].

The tetrahedron, consisting of four oxygen atoms arranged around the central atom of aluminium or any other element with a valence less than 4, is negatively charged and compensated by the off-network cations (figure 1).

\[ M_{2/\alpha} \cdot Al_2O_3 \times SiO_2yH_2O \]  

(2)

**Figure 1.** Schematic structure of the natural zeolite [2].

Currently, there are over 40 known types of natural zeolites, however, only seven of which are used commercially (clinoptilolite, chabazite, mordenite, erionite, ferrierite, analcime, phillipsite). Among the natural zeolites, it is clinoptilolite that is the most widely and frequently studied mineral. This results not only from its common occurrence in nature and the lowest price but also from its unique physicochemical properties [4]. The specific physicochemical properties of zeolites include: high ion exchange selectivity, reversible hydration and dehydration, high gas adsorption capacity, high thermal stability, resistance to aggressive media.

Their particular properties determine that zeolites provide a suitable solution in a wide range of environmental, scientific and industrial problems. Since their discovery in 1756, zeolites have been a considerably popular object of scientific studies. Axel Fredrik Cronstedt has found them to be highly effective adsorbents, ion exchangers and molecular sieves. In particular, this is their last application (molecular sieves) that is the most widespread in engineering. Zeolites are used to separate straight-chain hydrocarbons from branched ones [2], as chemical sensors [5] in the control of industrial processes, monitoring indoor air quality and environmental quality, wastewater control and in automatic flue gas treatment. The application of natural zeolites for water and wastewater treatment has been continuing and studied for years. With respect to their industrial application, zeolites were first implemented as water softeners in high-pressure boiler plants; on the other hand, their water softening properties in groundwater treatment have been studied to date [6]. However, in recent decades, natural zeolites have been under scrutiny considering their capacity for the removal of heavy metals from wastewater [7, 8, 9]. Numerous researches have been undertaken to improve the process by chemical or thermal activation of natural zeolites [10, 11]. Considering water treatment, the issues that are typically approached by researchers are the removal of ammonia and humic compounds [12], seawater desalination [13] or Mn and Fe filtering [12, 14]. In addition to the Mn removal, zeolites’ purification efficiency has been confirmed in other heavy metals, such as Pb and Zn [15, 16, 17, 18].

Despite the technological progress, which has led to the partial replacement of natural zeolites with synthetic ion exchangers in the second half of the 20th century, the minerals of the zeolite group remain irreplaceable in a wide range of processes, e.g. removal of ammonia from water. The high-quality, easily available and cost-effective natural zeolite is a leading solution currently in use in water and wastewater treatment technologies, heavy metal filtration from wastewater and Fe, Mn and ammonia removal from water. In response to the progressive contamination of groundwater with
heavy metals, this study attempts to investigate the use of natural zeolite as a fully ecological material for the removal of excessive heavy metal accumulation in drinking water.

The central aim of the presented investigation is the assessment of zeolite potential as a natural ion-exchange adsorbent to remove heavy metal excess (Cr, Cd, Ni and Pb) from groundwater intended for human consumption.

2. Materials and methods

The natural zeolite sample has been purchased from Andalusia Group (Warsaw, Poland) and originally extracted from the Sokirnica deposit located in the Zakarpattia Region in Ukraine. The main component of the zeolite material is clinoptilolite (70-75%), and its detailed composition is presented in Table 1.

| Chemical composition of natural zeolite | wt. % zeolite |
|----------------------------------------|---------------|
| SiO$_2$                                | 67.7          |
| Al$_2$O$_3$                            | 12.6          |
| Fe$_2$O$_3$                            | 2.0           |
| Na$_2$O                                | 0.35          |
| K$_2$O                                 | 2.8           |
| CaO                                    | 2.6           |
| MgO                                    | 1.0           |
| SO$_4^{2-}$                            | 0.43          |

The material subjected to testing was the commercial zeolite powder (particle size 1.5-2.0 mm, bulk density 1.04 g/cm$^3$). The tested groundwater was sampled from an individual water intake on a private property in the suburbs of Lublin, from a depth of approx. 45 m. The pH of the water was neutral, pH = 7.1, and it was characterised by a high content of Ca and Mg, 100 mg/dm$^3$ and 18 mg/dm$^3$, respectively. From the ICP-OES analysis, employed to determine the Cd, Cr, Ni and Pb content, it was shown that the content of metals in question is below the limit of detection (Cd < 2, Cr < 5, Ni < 10, Pb < 5 ppb).

The solutions with a metal content of 0.01 mol/dm$^3$ were prepared by dissolving their respective salts in double-distilled water: Cr(NO$_3$)$_3$·6H$_2$O, CdCl$_2$·3H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Pb(NO$_3$)$_2$. Pure reagents for analysis were used to prepare the working solutions of the analysed metal substrates.

The concentration of metals in all test samples was determined by means of the inductively coupled mass spectrometry in inductively coupled plasma ICP-OES JY 238 Ultrace (Jobin Yvon-Horriba France).

2.1. Adsorption isotherms

The adsorption of heavy metal cations (Cr, Cd, Ni, Pb) onto zeolite material is known to depend on the equilibrium concentrations of these metals in aqueous solutions; therefore, to obtain in-depth information on the relationship between the two, the static method of separate sampled portions was employed. The test procedure was as follows: 100 ml plastic flasks were filled with 95 ml of groundwater water (containing competitive adsorption Ca and Mg ions) with the addition of 1 g of zeolite and subjected to shaking for 12 hours. Subsequently, working solutions of the Cr, Cd, Ni and Pb were added to the mix.

The concentration of the solutions was 0.01 M in 0.1 to 1 cm$^3$. The flasks were shaken for 2 hours, upon which time, a 10 ml sample was taken for analysis and 0.2 ml of nitric acid (V) was added. Thus obtained test samples were, finally, shaken for 1 hour, after which the heavy metal concentration in the solution was determined. The amount of adsorbed metal was calculated from the difference between the introduced and the analysed amount of the adsorbate. The collected data were interpreted in the form of adsorption isotherms.
2.2. Heavy metal removal from water

The removal of heavy metal cations from water was performed under dynamic conditions by filtering the water at a speed of 2 m/h through a 75-cm-high zeolite bed. The filtration process was continued, and the heavy metal content (Cr, Cd, Ni and Pb) was increased at 24-hour steps. For the first day, the tested groundwater was filtered without Cr, Cd, Ni or Pb, and the following day, water with the addition of permissible heavy metal content levels for drinking water (Cr 50 µg/l, Cd 5 µg/l, Ni 20 µg/l, Pb 10 µg/l). Over the next three 24-hour filtration cycles, the heavy metal concentration was increased by 2, 5 and 10 times, respectively. In each filtration cycle, after 6, 12, 18 and 24 hours, 50 cm$^3$ of filtered water samples were collected. The 24-hour average sample was analysed for heavy metal content.

3. Results

The tests set out to determine the adsorption rate of Cr, Cd, Ni and Pb cations by natural zeolite depending on the heavy metal concentration in aqueous solutions, containing high levels of competitive Ca and Mg ions. The collected results provided data for the sorption isotherms presented in figures 1-4. The experimentally determined amounts of adsorbed heavy metals ($q_e$), depending on their equilibrium concentration in the solution ($C_e$), provided the data for Freundlich and Langmuir equations, thus delivering the description of the investigated adsorption process. The constants in the mathematical models, as well as the error of their determination, were established by the Gauss-Newton method for solving nonlinear least-squares regression problems, with the use of Statistica software package [19]. The values of adsorption isotherm coefficients of the tested heavy metals onto natural zeolite are presented in table 2.

| Isotherm      | Formula                          | Coefficient | Cd    | Cr    | Ni    | Pb    |
|--------------|---------------------------------|-------------|-------|-------|-------|-------|
| **Freundlich** | $q_e = aC_e^k$                  | a           | 0.119 | 0.140 | 0.205 | 0.091 |
|              |                                  | k           | 1.073 | 0.631 | 0.547 | 1.036 |
|              |                                  | R           | 0.923 | 0.823 | 0.892 | 0.926 |
| **Langmuir**  | $q_e = aC_e/(1+kC_e)$            | a           | 0.121 | 0.211 | 0.363 | 0.085 |
|              |                                  | k           | -0.019| 0.465 | 0.696 | -0.016|
|              |                                  | R           | 0.922 | 0.836 | 0.901 | 0.929 |

From the table, it emerges that there is a rectilinear relationship between the adsorption rate and Cd and Pb ion content, hence, in practice, the adsorption rate of the said heavy metals onto zeolite rises proportionally to the increase in their concentration in the solution (figures 2, 5).

**Figure 2.** Relationship between the amount of adsorbed Cd onto zeolite bed and its equilibrium concentration in groundwater (model adsorption isotherms: F – the Freundlich isotherm, L – the Langmuir isotherm).
Figure 3. Relationship between the amount of adsorbed Pb onto zeolite bed and its equilibrium concentration in groundwater (model sorption isotherms: F – the Freundlich isotherm, L – the Langmuir isotherm).

Figure 4. Relationship between the amount of adsorbed Cr onto zeolite bed and its equilibrium concentration in groundwater (model sorption isotherms: F – the Freundlich isotherm, L – the Langmuir isotherm).

Figure 5. Relationship between the amount of adsorbed Ni onto zeolite bed and its equilibrium concentration in groundwater (model sorption isotherms: F – the Freundlich isotherm, L – the Langmuir isotherm).
In terms of Cr and Ni ions, the amounts of these metals adsorbed by natural zeolite decrease as their concentration in the water phase increases (figures 1, 4). The two applied mathematical models, i.e. Freundlich or Langmuir equations, describe the course of Cr, Cd, Ni and Pb adsorption on natural zeolite from Ca- and Mg-ion-rich aqueous solutions.

The error of equilibrium adsorption constants, determined with the use of Freundlich or Langmuir equations, are in the range of 0.82 to 0.93. Thus, it can be concluded that the heavy metal ion removal observed in our tests occurs as a result of two activities, the adsorption in micropores and the monolayer adsorption in the surface region [20]. Although similar studies report a considerably higher degree of compliance of the mathematical model with the experimental data, this applies to situations where adsorption of heavy metal ions on zeolite occurs from monometal ion solutions in the absence of competing ions [16].

The coefficient \( a \) in Freundlich and Langmuir adsorption isotherm equations, which expresses the heavy metal adsorption capacity of natural zeolite, indicates a comparable adsorption rate for Cd and Cr, and a notably higher zeolite affinity for Ni, and, finally, relatively low efficiency in Pb ion removal. Compared with the research data from other studies, it becomes clear that the filtration capacity of the investigated material emerging from our study is, admittedly, quite low. This discrepancy should be attributed to the fact that the reported studies investigated different sorption materials, which was, furthermore, analysed in test conditions excluding the impact of competitive ions, which decrease the sorption efficiency of zeolite [10, 17].

Furthermore, considering the same adsorbent, as shown by our previous studies, the presence of Ca and Mg ions in the solution has a profoundly negative effect on the natural zeolite’s adsorption capacity in relation to the heavy metals in question. The adsorption capacity of the natural zeolite used in the study was exponentially higher in monometal solutions [21]. Therefore, competitive adsorption in the presence of considerable amounts of Ca and Mg ions substantially reduces the adsorption capacity of natural zeolite for Cr, Cd, Ni and Pb ions. However, the heavy metal filtration efficiency was proved sufficient for the zeolite material to be subjected to drinking groundwater purification tests. The results from the subsequent tests are summarised in table 3.

| No. of 24-hour filtration cycle | Cd  | Cr  | Ni  | Pb  | Cd  | Cr  | Ni  | Pb  |
|--------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| 1                              | < 2 | < 5 | < 10| < 5 | < 2 | < 5 | < 10| < 5 |
| 2                              | 5   | 50' | 20' | 10' | < 2 | 6.1 | < 10| < 5 |
| 3                              | 10  | 100 | 40  | 20  | < 2 | 11.2| < 10| < 5 |
| 4                              | 25  | 250 | 100 | 50  | 2.7 | 27.6| 14.2| 9.4 |
| 5                              | 50  | 500 | 200 | 100 | 3.6 | 44.3| 15.7| 12.2|

< - heavy metal content below the limit of detection,
* - permissible heavy metal content levels for drinking water, as per the Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption.

The most obvious finding emerging from the analysis is that the natural zeolite bed exhibits high efficiency in the removal of heavy metal ions from drinking water. At the lowest of the tested toxic heavy metal concentrations in water, i.e. not exceeding the permissible limits provided in the respective legal regulations, the filtration was shown to reduce their levels below the lower limit of detection, characteristic of the employed analytical method; it was only in the case of Cr that analytically detectable concentrations of this metal were recorded. Following filtration on zeolite, the Cr concentration in water showed a 10-fold decrease compared to the levels measured prior to the water treatment. Simultaneously, the increased content of tested heavy metals in raw water results in their higher
concentration in the filtrated water. However, it was proved that even when the permissible norms are exceeded five times, the resulting Cr, Cd, Ni and Pb concentrations in the treated water are within the standard for drinking water. Even in extreme scenarios and the most severely polluted water, a 5th filtration cycle solves the heavy metal pollution problem, successfully reducing Cr, Cd and Ni concentrations below the acceptable threshold [22]. It was only in the case of Pb that the concentration in the filtered water was above the permissible limit, of 10 µg/dm³, having reached 12.2 µg/dm³. This stems from the adsorption properties of the tested zeolite, which shows low Pb adsorption capacity; furthermore, similar trends were also observed for other natural zeolites [16,17]. The experimental data suggest that the issue could be resolved by proper optimisation of the filtration process conditions, e.g. by increasing the filter bed height or reducing the filtration speed, although further work is planned to confirm these assumptions.

4. Conclusions
1. Adsorption isotherms for the Cr, Cd, Ni and Pb ion heavy metal adsorption in aqueous solutions, despite the presence of substantial concentrations of competitive Ca and Mg ions, confirm that the natural zeolite is an effective ion exchange adsorbent.
2. The course of ion-exchange adsorption of Cr, Cd, Ni and Pb onto natural zeolite is described at high accuracy by Freundlich and Langmuir isothermal models.
3. The values of the natural zeolite ion exchange capacity for Cr, Cd, Ni and Pb ions under competitive adsorption conditions obtained from the tests prove that natural zeolite exhibits sufficient effectiveness to be considered as a filtering bed material, which is further accentuated by the fact that this mineral does not require any chemical pre-treatment prior to its application as a filtration medium.
4. The tests conclude that natural zeolite shows high selectivity for Cr, Cd, Ni and Pb ions, which enables effective removal of heavy metal excess from water intended for human consumption.

5. References
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