

## Article

# Modifying Natural Zeolites to Improve Heavy Metal Adsorption

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**Abstract:** Problems with increasing heavy metal contents in natural waters are becoming a global issue. At the same time, improved methods for water treatment are becoming increasingly important. In this context, natural zeolites can be used to purify polluted water. In this paper, we investigated how the adsorption capacity of natural zeolites can be improved. Natural zeolites from the Shankanay district, Almaty, Kazakhstan, were used as adsorbent material for experiments on improving the water treatment of heavy metals. We found that the adsorption capacity for heavy metals was increased greatly by thermal activation using furnace treatment. The optimal thermal activation condition was about 550 °C for a duration of 2 h. However, the improved adsorption capacity for different heavy metals varied depending on the heat treatment temperature. Adsorption by the heat-treated zeolites at a temperature of 550 °C was 87% for nickel, 99% for copper and cadmium, and 100% for lead. Adsorption by heat-treated zeolites at a temperature of 500 °C was 78% for nickel, 98% for copper, 83% for cadmium, and 88% for lead. The residual concentration of heavy metals in the filtered water did not exceed the maximum permissible concentrations for drinking purposes. In all experiments, intense adsorption took place during the first 10 min representing 35 to 61% of the metal ions in the water. Adsorption properties were verified using adsorption capacity (BET), IR spectroscopy, and scanning electron microscopy. The study shows that modified Shankanay natural zeolites have great potential as a low-cost adsorbent material for purifying water from heavy metals.

**Keywords:** natural zeolites; adsorption; heavy metals; water treatment; Zhankanay deposits; heat treatment



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## 1. Introduction

During recent decades water pollution has become an increasingly difficult problem for human and environmental health. Increasing water pollution threatens sustainable development and public health [1–3]. For this reason, improved water treatment methods are becoming a global necessity [4–9]. One of the most promising and recently suggested methods is adsorption using natural or modified zeolites [10]. Zeolites have a high porosity and naturally occur at a low cost. In general, there are more than 60 types of natural zeolites [11]. Natural zeolites can be used to reduce turbidity and color and degrade ammonium, heavy metal cations, and other cationic pollutants [12]. Various efforts are being made to improve the adsorption potential of zeolites using different modifying methods. Through the modifying methods, zeolite water treatment capacity can be substantially increased for different pollutant types [13–19].

Many industrial processes, e.g., fuel and energy production, iron and steel manufacturing, metallurgy, and metal surface treatment, produce waste containing various heavy metals. In many countries, these are still released into the environment without subsequent treatment [20]. Heavy metals are deposited, assimilated, or aggregated into water sediments and aquatic ecosystems that pose a threat to human health and ecosystems [21]. Therefore, finding improved and cost-effective methods to treat contaminated water from heavy metals are the main priorities for sustainable industrial processes at present. Contaminated industrial water may, for example, contain the following common heavy metals: Cr, As, Pb, Zn, Cu, Ni, Cd, Mn, U, etc. [22,23].

Natural zeolites have greatly varying adsorption properties depending on clay-type content and physicochemical properties. Consequently, modified natural zeolites also have varying adsorption properties depending on both the modification process and origin. Recent reviews have shown the ability of natural zeolites to clean heavy-metal polluted water, e.g., [11,16,18,19,24]. The most applied natural zeolite to remove heavy metals is clinoptilolite. However, each geological origin of clinoptilolite has different adsorption properties [18]. Natural zeolites may have a cation exchange capacity of 2–4 meq/g and a selectivity for heavy metals according to  $Pb > Cu > Zn > Cd > Ni$  (clinoptilolites) [18]. However, this may also vary depending on geological origin. Treatment of natural zeolites may include acid, base, or salt treatment, cationic surfactant modification, or metallic functionalization. Here, we can also add low- and high-temperature thermal treatment. All these adjustments modify the structure of the zeolite and increase adsorption properties. Treatment using HCl appears to be the most used acid modification [16]. For example, [25] notes that HCl treatment increased the specific surface area of natural clinoptilolites from 13 to 78 m<sup>2</sup>/g. In theory, zeolites could be used many times for adsorption purposes. However, in practice, the adsorbing material would need desorption to maintain its efficiency [16].

The pH of the solution to be treated affects the cation exchange capacity. However, the pH of raw water for drinking purposes does not vary that much and does not affect the removal processes to a great extent. For example, [26] noted that maximum adsorption was accomplished at a solution pH of 6 for several heavy metals.

Natural zeolites contain adsorbed water molecules in their micro-cavities in addition to ion-compensators of excess negative charge. Zeolite water molecules are removed from zeolite at 100–110 °C without any noticeable change in the mineral structure. Infrared spectroscopy data show that coordination-bonded water molecules start to be removed at 150 °C. Their complete removal from the mineral occurs at 350–380 °C. Depending on the peculiarities of their structure, natural zeolites can be divided into seven different types. The theoretical cation exchange capacity of natural zeolites ranges from 2.6 to 5.8 meq/g. The real cation exchange capacity is usually lower. This is mainly due to the presence of non-zeolite impurities in natural ion-exchanger samples.

Regeneration methods for used zeolites can be divided into three types, namely chemical, low-temperature thermal, and thermal. Chemical regeneration refers to the treatment of the sorbent with liquid or gaseous organic or inorganic reagents at a temperature usually not exceeding 100 °C. Both carbon and non-carbon sorbents are chemically regenerated. As a result of this treatment, the sorbate is either desorbed unchanged or the products of its interaction with the regenerating agent are desorbed. Chemical regeneration often takes place directly in the adsorption apparatus. Most methods of chemical regeneration are applicable to sorbates of a certain type. The simplest method of regenerating a sorbent is to heat it in some volume of water. This leads to an increase in the degree of dissociation and solubility of the sorbate and, eventually, to the desorption of part of the sorbate. Thus, in the regeneration of active carbon, water is heated and filtered through the active carbon. The effect of such regeneration, however, is not so high, normally 20–40%. Low-temperature thermal regeneration is the treatment of the sorbent with steam or gas at 100–400 °C. This procedure is quite simple and, in many cases, it is performed directly in adsorbers. Due to its high enthalpy, water steam is most often used for low-temperature thermal regeneration.

It is safe and available in production. Chemical and low-temperature thermal regeneration does not provide a complete recovery of adsorption coals. For a deeper recovery, high-temperature thermal regeneration is performed. However, high-temperature thermal regeneration is a very complex, multi-stage process that affects not only the sorbate but also the sorbent itself.

Natural zeolites from the Shankanay deposit have previously been investigated regarding their adsorption properties [27–29]. However, further systematic studies are needed to elucidate the effects of different modifying processes on treatment capabilities for different kinds of pollutants. For example, several processes are involved in the thermal treatment of natural zeolites and resulting adsorption outcomes need to be further studied [30,31]. In view of this, the main objective of the present study was to improve the understanding of how natural Shankanay zeolites can be modified to enhance heavy metal treatment capabilities from a raw water supply. For this purpose, we used thermally treated natural Shankanay zeolites as a main innovation. Consequently, this study presents methods and ways of preparing modified Shankanay zeolites and the resulting heavy metal adsorption capacity for polluted water. Overall, it is our belief that this study leads to a deeper understanding of zeolite modification and a comprehensive perspective for future heavy metal removal applications especially on raw water for drinking water purposes.

## 2. Materials and Methods

Natural zeolites of the Shankanay deposit in Almaty, Kazakhstan, were used as raw material for adsorption experiments. The host rock is tuff and ignimbrite of the rhyolite-dacite composition of the Permian Zhaltyr formation. The mineralization is represented by horizontally embedded deposits of zeolites. Its average thickness is about 25 m. The general mineral composition of the zeolite ores is clinoptilolite, laumontite, and analcime. Open pit mining at a maximum mining depth of 20 m has been performed since 1996. Figure 1 shows the sampling of natural zeolites from the deposit. About 100 kg of natural zeolites were collected and later homogenized to arrive at representative samples for further analyses.



**Figure 1.** Zeolite sampling from Shankanay deposit, Almaty, Kazakhstan.

The modification of the experimental zeolite samples in this study included acid and high-temperature thermal treatment [16–19]. The high-temperature thermal treatment was done in an argon environment. The experimental installation included a steam production and dosing unit, a container, a peristaltic dosing pump, and an evaporator. The installation also included an air dosing unit with a compressor and shut-off and control valves. The unit had an inert gas supply unit (argon) for supplying it to the working zone of the heat treatment reactor, including a cylinder, a reducer, shut-off and control valves. The modified zeolite was obtained through the following successive stages:

1. Zeolite samples were prepared by grinding and sieving to obtain a size fraction of 0.2–3.0 mm diameter. The sieved raw material was washed from impurities by distilled boiled water and water vapor at a temperature of 100–120 °C and dried in an oven at a temperature not exceeding 105 °C. The Shankanay zeolite belongs to the heulandite–clinoptilolite group and includes impurities such as quartz, feldspar, and montmorillonite [27].
2. The samples were then demineralized through acid treatment. The acid treatment changes the structure of the zeolites by increasing the volume of effective pores, leading to an increase in sorption capacity. The zeolite samples were placed in glass containers covered with lids and filled with a mixture of 20% nitric acid (ratio 1:2). The mixture was boiled for 60 min and after boiling the mixture was left overnight for more complete demineralization. After this, the used nitric acid was drained by decantation and the demineralized sorbent was transferred to another container and washed several times by boiling to establish a neutral environment. The activated sorbents were dried under normal conditions in an oven.
3. Prepared sample sorbents were dosed on a dosing scale and loaded into a heat treatment reactor in an argon environment. The argon feed rate (5 L/min) was controlled depending on the weight of the zeolite and the temperature (450–600 °C). The samples were subjected to constant movement along the reactor. The thermal treatment volatilizes and/or oxidizes adsorbed molecules. Thus, heat treatment changes the morphological properties of the zeolite as well as the adsorption properties.

The thermal activation reactor was a 12X18H10T (equivalent to AISI321 material) material stainless steel pipe. Outside, on the furnace body, there was a wire heater made of X27105T alloy, located on a pipe in a layer of electrically insulating refractory coating. Outside, the electric furnace was thermally insulated (wrapped) with felt from mullite–silicon fiber and placed in a casing. A screw feeder was placed inside the reactor. The reactor was equipped with receiving hoppers for loading raw material and unloading the modified zeolite. Temperature regulation and control was carried out using a 2TRM1 m-regulator device.

Studies of the adsorption of heavy metal ions were carried out on original and modified zeolite samples. The adsorption experiments using heavy metal ions in water were complemented by adsorption capacity (BET) and scanning electron microscopy (SEM). Analysis of the morphological structure and elemental analysis of the obtained samples were carried out using a Quantum 3D 200i scanning electron microscopy (SEM) (Dual System, Riverside, CA, USA) and a TM 4000 Plus[V1] microscope (Hitachi, Tokyo, Japan). The Hitachi TM4000Plus microscope was equipped with an optional low-vacuum secondary electron detector, which allows for efficient examination of the surface of samples with low contrast in back-scattered electrons.

Zeolite samples were tested to evaluate the efficiency in the adsorption of heavy metal cations (Cu, Cd, Pb, and Ni). To study the adsorption properties, standard solutions of metal ions were prepared with a concentration exceeding the maximum permissible concentration for human consumption by about 10 times (Cu = 10.52 µg/mL, Cd = 10.35 µg/mL), and Pb = 11.02 µg/mL). The sorption experiments were carried out as batch tests. In these, sorption was studied by placing 1 g of zeolite in glass beakers with 50 mL of prepared metal solutions. At 10, 20, 30, 40, and 50 min after the start of experiments with continuous mixing, the solutions were filtered and analyzed for metal concentrations. Sorption tests were repeated 5 times to estimate variation and potential error levels.

Metal concentrations were analyzed using atomic absorption spectroscopy on a PerkinElmer PinAAcle 900T AAS-IN atomic absorption spectrometer. The detection limit for this device on Cd, Cu, Pb, and Ni is about 0.014, 0.002, 0.05, and 0.07 µg/L, respectively.

### 3. Results and Discussion

The physicochemical characteristics of the natural zeolites are presented in Table 1. As seen from the table, the clay mineral type is clinoptilolite, which is the most common

zeolite mineral. The mass fraction of zeolite in the Shankanay deposit is between about 50 and 84%. The gelling agent in Table 1 refers to the colloidal mixture that has a loosely cohesive internal structure similar to a liquid.

**Table 1.** Main physicochemical characteristics of the investigated natural zeolites of the Shankanay deposit, Kazakhstan.

| No. | Indicator                                                                                                                                                                                                                                            | Unit | Characteristics                                                                                                                                       |
|-----|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|-------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1.  | Ocular appearance                                                                                                                                                                                                                                    |      | Free-form granules with dark brown color without impurities                                                                                           |
| 2.  | Mass fraction of zeolite                                                                                                                                                                                                                             | %    | 50–84                                                                                                                                                 |
| 3.  | Mineral type                                                                                                                                                                                                                                         |      | Clinoptilolite                                                                                                                                        |
| 4.  | Mohs hardness                                                                                                                                                                                                                                        |      | 4.5                                                                                                                                                   |
| 5.  | Associated minerals:<br>clay<br>dolomite                                                                                                                                                                                                             | %    | 3.0–6.0<br>0.5–2.0                                                                                                                                    |
| 6.  | Mass fraction of gelling agents                                                                                                                                                                                                                      | %    | 0.9–1.8                                                                                                                                               |
| 7.  | Organic content                                                                                                                                                                                                                                      | %    | 0                                                                                                                                                     |
| 8.  | Chemical composition:<br>SiO <sub>2</sub><br>Al <sub>2</sub> O <sub>3</sub><br>TiO <sub>2</sub><br>Fe <sub>2</sub> O <sub>3</sub><br>MnO<br>MqO<br>CaO<br>Na <sub>2</sub> O<br>K <sub>2</sub> O<br>P <sub>2</sub> O <sub>5</sub><br>H <sub>2</sub> O | %    | 60.0–74.0<br>14.0–15.0<br>0.070–0.700<br>1.40–5.83<br>0.067–0.199<br>0–2.120<br>0.130–6.400<br>0.610–5.450<br>0.660–4.030<br>0.012–0.173<br>0.0–4.090 |
| 9.  | Ratio of SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>                                                                                                                                                                                            |      | 4.00–5.28                                                                                                                                             |

Natural zeolites are porous hydrated minerals with an anionic skeleton, a crystalline structure consisting of silicon (aluminum) and oxygen tetrahedrons, and its pores are formed by a combination of different tetrahedra [32]. Zeolites normally have a dominant micropore size of 0.5–1.5 nm not exceeding 10 nm. Zeolites can exchange cations and lose or adsorb water molecules in their structures [33]. The pollutant removal mechanisms of natural zeolites are (a) ordered and connected pores or channels in the crystalline interior [32] and (b) excess negative charges of the zeolite framework can be balanced by monovalent or divalent cations (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) [11].

The specific surface area (*S*) is important for adsorption properties. Thus, *S* was first determined depending on thermal processing. Untreated zeolite had an *S* corresponding to about 15 m<sup>2</sup>/g. The *S* was compared to processing temperature, time of heat treatment, and supply of inert gas. Firstly, zeolites were processed at a temperature of 400, 450, and 550 °C at 120 min (Table 2).

**Table 2.** Characteristics of the modified zeolite samples obtained at different temperature conditions.

| Name                     | Characteristics        | Processing Condition | <i>S</i> , m <sup>2</sup> /g |
|--------------------------|------------------------|----------------------|------------------------------|
| Modified natural zeolite | Brown color, size 3 mm | 400 °C, 120 min      | 20.07                        |
| Modified natural zeolite | Brown color, size 3 mm | 450 °C, 120 min      | 19.60                        |
| Modified natural zeolite | Brown color, size 3 mm | 550 °C, 120 min      | 54.23                        |

Depending on the conditions of the temperature in the processing reactor, *S* was found to change (Table 3). Thus, the optimal temperature for the thermal treatment of natural zeolite was determined, equal to a processing temperature of 550 °C. The maximum *S* (92.21 m<sup>2</sup>/g) was found for 550 °C and 60 min heat treatment (Table 3).

**Table 3.** Characteristics of modified zeolite samples depending on time of heat treatment.

| Name                     | Characteristics        | Processing Condition | <i>S</i> , m <sup>2</sup> /g |
|--------------------------|------------------------|----------------------|------------------------------|
| Modified natural zeolite | Brown color, size 3 mm | 550 °C, 60 min       | 92.21                        |
| Modified natural zeolite | Brown color, size 3 mm | 550 °C, 90 min       | 85.24                        |
| Modified natural zeolite | Brown color, size 3 mm | 550 °C, 120 min      | 80.18                        |

The next step of the investigation was to test the adsorption of heavy metals by the modified zeolites. Figure 2 and Table 4 show the results of the adsorption of Ni ions on the modified zeolites as a function of temperature. From the figure it is seen that a heat-treated zeolite at a temperature of 550 °C has the highest adsorption capacity.

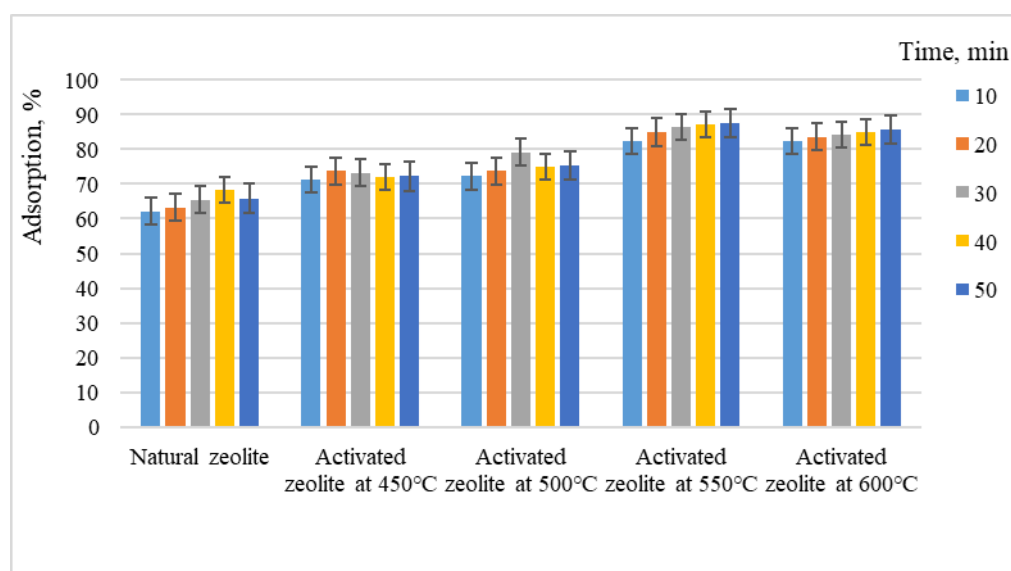


**Figure 2.** Adsorption characteristics of natural and modified zeolites with respect to nickel (Ni) for different temperature treatments (vertical bars indicate approximate error levels).

**Table 4.** Adsorption characteristics of natural and modified zeolites with respect to nickel (Ni) for different temperature treatments.

| Time, min | Adsorption, %   |                             |                             |                             |                             |
|-----------|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|           | Natural Zeolite | Activated Zeolite at 450 °C | Activated Zeolite at 500 °C | Activated Zeolite at 550 °C | Activated Zeolite at 600 °C |
| 10        | 62.2            | 71.3                        | 72.3                        | 82.3                        | 82.4                        |
| 20        | 63.3            | 73.7                        | 73.7                        | 85.0                        | 83.6                        |
| 30        | 65.5            | 73.2                        | 79.2                        | 86.5                        | 84.2                        |
| 40        | 68.2            | 72.1                        | 75.1                        | 87.1                        | 85.1                        |
| 50        | 65.9            | 72.2                        | 75.2                        | 87.5                        | 85.8                        |

Scanning micrographs of the original natural mineral and some of the resulting reaction products are shown in Figure 3. A comparison of micrographs of the original sample and products after activation shows how the mineral surface of the zeolite changes.

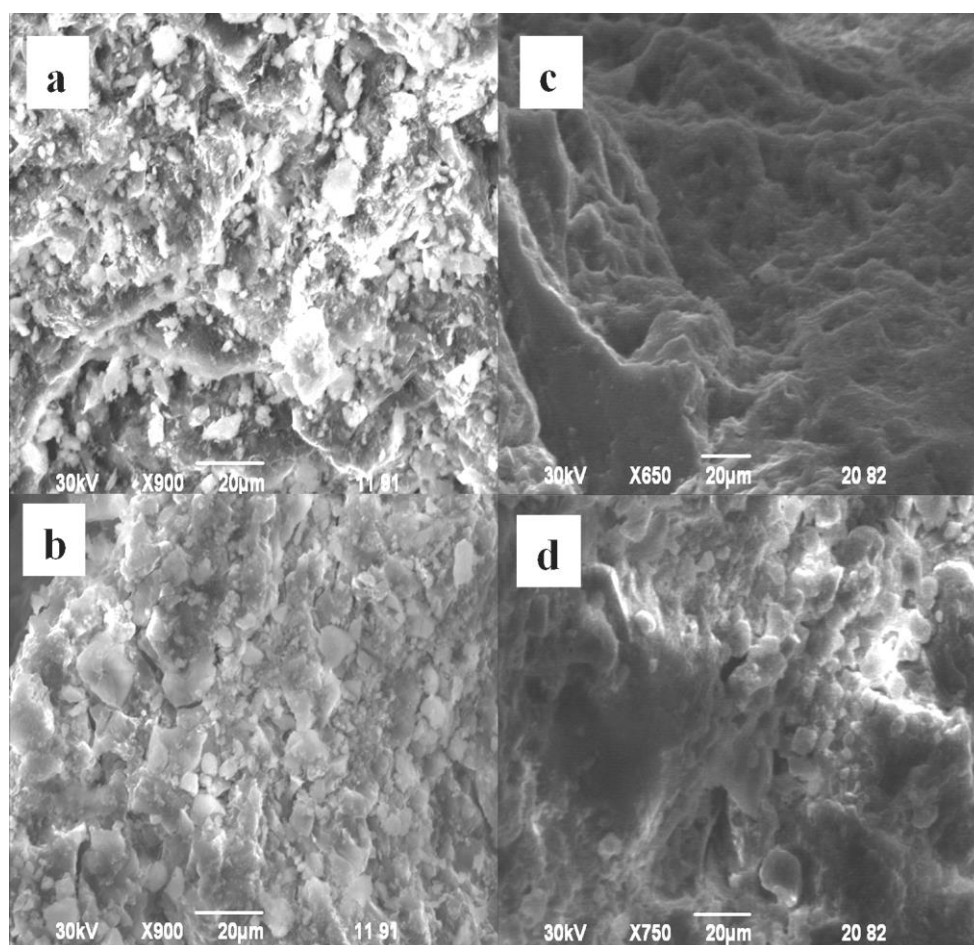


**Figure 3.** Scanning micrographs of zeolite surface: (a) raw, (b) after washing and drying, (c) modified at 500 °C, (d) modified at 500 °C after adsorption (e.g., Ni and Co were adsorbed).

The figure shows that raw and activated natural zeolite surfaces tend to change significantly after treatment. In Figure 3a,b, the rugged and grainy surface of raw natural zeolites appears to change after activation (washing and drying). Figure 3b shows that some of the fine-scale graininess disappear after activation. This indicates the removal of some of the smallest impurities. Figure 3c indicates that after heat treatment the surface changes significantly and becomes smoother indicating significant removal of adsorbed material. Finally, Figure 3d shows that adsorbed material again increases the graininess (Ni and Co were adsorbed). During adsorption in the microporous structure of the zeolite, e.g.,  $\text{Na}^+$  ions are easily displaced from water by, e.g.,  $\text{Pb}^{2+}$  ions.

Experiments were carried out to study the potential adsorption of metals in water, in particular, copper, cadmium, lead, and nickel. The sorption activity of the modified zeolites was studied when individual metals were introduced into the medium in concentrations of Cu ( $C_{\text{in}} = 10.52 \mu\text{g/mL}$ ), Cd ( $C_{\text{in}} = 10.35 \mu\text{g/mL}$ ), Pb ( $C_{\text{in}} = 11.02 \mu\text{g/mL}$ ). Figures 4–6 present the results of adsorption characteristics after different heat treatments of the zeolite.

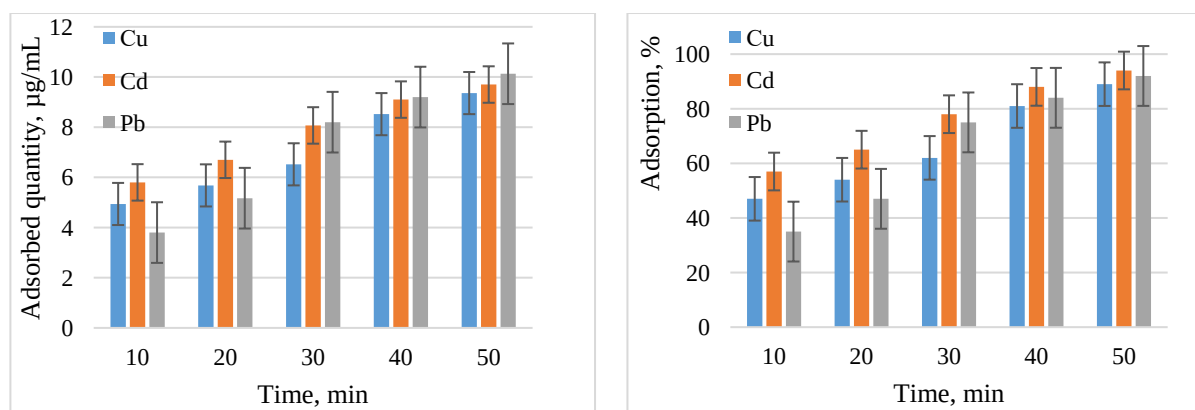


**Figure 4.** Influence of the heat treatment temperature of the zeolite (450 °C) on the sorption of heavy metal ions. The left figure shows the adsorbed quantity and the right figure shows the adsorption in per cent.

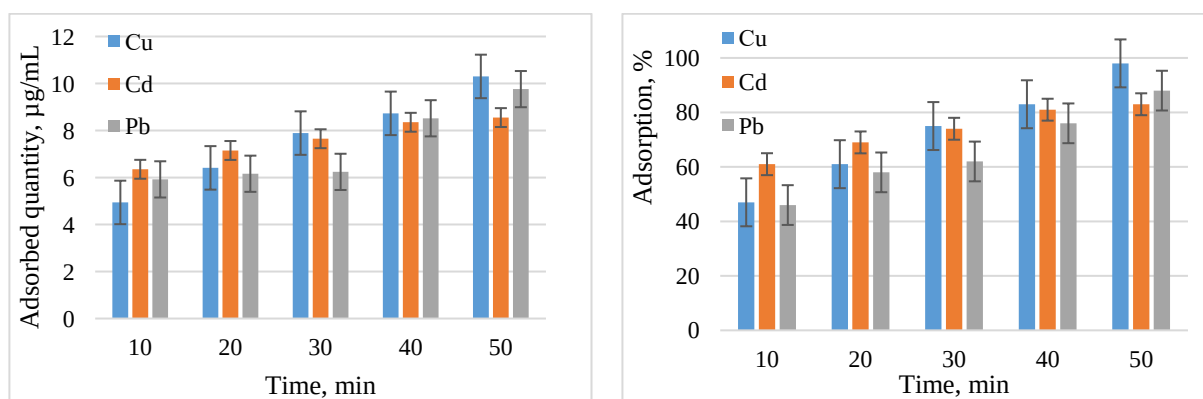


**Figure 5.** Influence of the heat treatment temperature of the zeolite (500 °C) on the sorption of heavy metal ions. The left figure shows the adsorbed quantity and the right figure shows the adsorption in per cent.

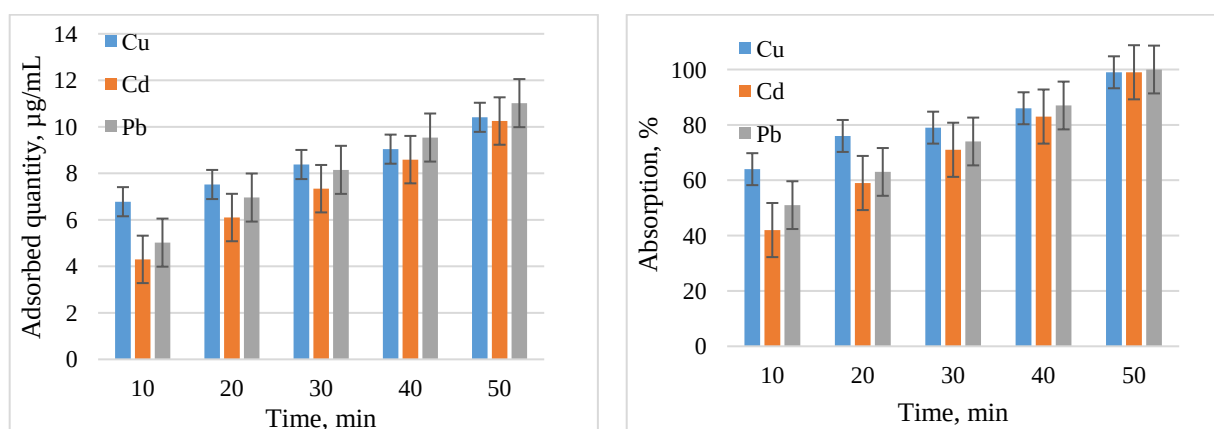


**Figure 6.** Influence of the heat treatment temperature of the zeolite (550 °C) on the sorption of heavy metal ions. The left figure shows the adsorbed quantity, and the right figure shows the adsorption in per cent.

As can be seen from Figures 4–6, with an increase in temperature, the sorption of metals by zeolites treated at a temperature of 550 °C is 99% for copper and cadmium, and 100% for lead. The modified zeolite sorbent treated at a temperature of 500 °C, adsorbs

98% copper, 83% cadmium, and 88% lead. In all experiments, it was observed that intense adsorption takes place during the first 10 min and from 35 to 61% of metal ions are adsorbed by the zeolite during this time.

Previous studies of untreated Shankanay zeolites have shown that they can remove about 65% of lead and 50% of copper cations [27]. Sultanbayeva et al. [27] showed that this zeolite treated with  $\text{Na}_2\text{CO}_3$  solution can improve lead adsorption by 99.0% and copper adsorption by 96.6% in phosphoric acid. Thus, the adsorption effects for the two treatment methods by [27] and in this study appear similar. Consequently, for a practical choice between different treatment techniques, a more detailed analysis of cost and industrial applicability is needed. This must be determined in future studies.

#### 4. Conclusions and Discussion

Natural zeolites from the Shankanay deposit in Kazakhstan have unique metal adsorption behavior. This depends on the active clinoptilolite type content and its unique physicochemical properties. To improve the understanding of how these natural zeolites can be modified to enhance heavy metal adsorption capabilities, this study investigated thermal methods to increase the adsorbing properties of the Shankanay zeolites. Crushed and homogenized zeolites with a diameter of 3 mm were separated by sieving. Three different stages of activation were carried out to increase the specific surface area and porosity of the selected zeolite granules (maximum  $d = 3$  mm). In the first stage, zeolite granules were cleaned of contaminants with distilled boiled water vapor at temperatures of 100–120 °C. In the second stage, samples were demineralized through acid treatment. The acid treatment changes the structure of the zeolites by increasing the volume of effective pores, leading to an increase in sorption capacity. In the final stage, the purified zeolite was subjected to a high thermal activation process in an argon flow (5 L/min) in an inert atmosphere in the range of 450–550 °C. The adsorption capacity of the obtained samples with respect to various heavy metal ions dissolved in water was determined from filtration by heavy metal-polluted water. We found that the adsorption capacity for heavy metals increased by thermal activation using the high thermal activation treatment. The optimal thermal condition was 550 °C for about 2 h. The improved adsorption capacity for different heavy metals varied depending on the treatment temperature. Adsorption by the heat-treated zeolites at a temperature of 550 °C was 99% for copper and cadmium, 100% for lead, and 85% for nickel. Adsorption by heat-treated zeolites at a temperature of 500 °C was 98% for copper, 83% for cadmium, and 88% for lead. Nickel displayed adsorption of 78%. In all experiments, it was found that intense adsorption takes place during the first 10 min representing 35 to 61% of the metal ions in water. The residual concentration of heavy metals in the filtered water did not exceed the maximum permissible concentrations for drinking purposes.

The experimental results show that natural zeolite water treatment based on ion-exchange capacity, microporous structure, and adsorption capacity is very effective and allows the removal of heavy metal ions almost completely. This method can be used for wastewater treatment, mainly in the metallurgical industry, as well as for water softening. Natural zeolites obtained from the Shankanay deposit in the Almaty region have a high potential as an economical sorbent for the treatment of heavy-metal polluted water. For the purification of heavily polluted water with the predominance of high concentrations of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions it is economical to use the relatively cheap natural zeolites. The absorption degree of the above pollutants by zeolite is 70–95%. The zeolite of the Shankanay deposit more fully sorbs heavy metal ions (94–98%) at intervals of 30–60 min, after carbonization at a temperature of 500 °C, its sorption capacity is about 1.87 g/100 g.

The thermal treatment in this study resulted in a large increase in specific surface area ( $S$ ). The size of  $S$  indicates the potential of the reactive surface area of the zeolite to adsorb metal ions and thus, the potential efficiency in the treatment of water pollutants. The reported  $S$  for different natural and chemically modified zeolites in the world is in the range of about 5–100  $\text{m}^2/\text{g}$  [16]. The  $S$  in this study was up to approximately 92.2  $\text{m}^2/\text{g}$  for

550 °C thermal treatment during 60 min. Compared to the range in [16], this indicates an S value in the present study in the upper interval. Consequently, this may as well indicate that thermal treatment of zeolites may be more efficient than chemical treatment. However, further studies are needed to confirm this assumption.

Future research in the field of modified zeolites may be based on simultaneous analysis of adsorption by multiple pollutants, and to expand and scale up water and wastewater treatment possibilities. Further studies should also be made available to determine the cost of full-scale industrial treatment processes of the different activation possibilities for zeolites.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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