Efficiency of using the Kazakhstan zeolites for the purification of water from iron ions

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Abstract. The problem of provision of the population with high-quality drinking water is currently one of the most topical in connection with the unsatisfactory technical condition of the existing water supply systems and pollution of the water sources. Natural zeolites, which have a sufficiently high sorption capacity, cation-exchange properties, relatively low cost and availability, are increasingly being used in recent times for water purification. The mineralogical properties of natural zeolites of the Tayzhuzgen and Shankanai deposits have been investigated. A comparative study of the sorption properties of the natural and modified zeolites of the Kazakhstan deposits has been carried out on model solutions, containing iron ions (Fe²⁺). The exchange mechanism and the degree of extraction of ions from the solutions have been established. The efficiency of the municipal water purification in the Auezovskiy district of Almaty with zeolites of the Shankanai field has been equal to 85.94%. This suggests a possibility of using these zeolites to purify water from iron ions with the purpose of water treatment in the dairy industry.

1. Introduction
For the provision of the population and industry with milk, both full and powdered milk is used. The seasonality of milk production in agriculture is the main reason for the partial replacement of the full milk for powdered milk. To restore the milk powder, water is used, which should meet the requirements of the Technical Regulations of the Customs Union “On food safety” [1]. Apart from the general requirements to drinking water, in the production of dairy products, the water, used for technological needs, should meet a number of specific requirements regarding hardness, the presence of nitrate and nitritions, chlorine ions, heavy metals, etc. [2]. It has been established that the chemical composition of water affects the solubility of milk powder [3]. The main methods of water treatment in the food production are filtration, coagulation, deferrization, disinfection, ion exchange, electrodialysis, and reverse osmosis. These methods, along with the positive aspects, have also disadvantages. Besides, along with the hardness ions it is required to extract from the water, entering the production processes of the dairy products, more hazardous components, such as heavy metal cations, radioactive isotopes, organochlorine and surfactants, pesticides, etc. Accounting for the properties of these pollutants, those filter materials are promising, which have the pronounced sorption and ion-exchange properties [4]. At the same time, these materials should be chemically resistant and mechanically strong. Natural zeolites meet almost all of these requirements. Extensive studies have
shown that zeolites meet all the requirements and are unique in their high content of exchangeable iron ions, fine dispersion and swelling in water [5]. This work aims at studying the sorption of metal ions $\text{Fe}^{\text{total}}$ by Kazakhstani deposit zeolites.

2. Materials and methods
In the experiments, a pre-sieved fraction of zeolites from the Tayzhuzgen and Shankanai deposits of Kazakhstan with a size of 0.5 and 1 mm were used. To increase the exchange capacity of natural zeolite and improve its sorption properties, natural zeolites from the Tayzhuzgen and Shankanai deposits were subjected to “hard” modification. For modification, a 4% solution of 1 N hydrochloric acid was used, which was prepared from a 37% concentrated hydrochloric acid solution with a density of 1.198 g/cm$^3$.

X-ray diffraction analysis was carried out using DRON-3 Automated Diffractometer with $CuK\alpha$ radiation, $\beta$-filter. Diffractogram scanning environment: $U = 35$ kV; $I = 20$ mA; scanning – 0-20; detector – 2 DPM. The semiquantitative X-ray phase analysis was carried out using diffractograms of powdered samples by the method of equal weighted quantities and artificial mixtures. Quantitative ratios of crystalline phases were determined. Diffractograms were interpreted using data from the ICDD and diffractograms of impurity-free minerals. The component content was calculated for the major phases.

In order to achieve the goal, analyses were conducted with the use of standardized test solutions. Standardized test solutions were prepared from state standard reference samples of $\text{Fe}^{2+}$ using distilled water with 2.5 mg/l concentration of $C(\text{Fe}^{2+})$. Once the standardized test solution was filtered at a rate of 4 ml/min, each filtrate was selected and the $\text{Fe}^{2+}$ concentration was determined using KFK-2 photocolorimeter. After positive results, further similar experiments were carried out using tap water. The resulting filtrate was examined on the spectrometer “KVANT-Z.ETA”.

3. Results and discussion
The quality of water is assessed not only in terms of the impact on the technological processes, the quality of the finished products, but also on the hygienic food safety indicators [6]. Currently, much attention is paid to the environment and the internal environment of the human body from the ever-increasing action of chemicals of natural and anthropogenic origin, in particular heavy metals.

Heavy metals are highly toxic substances and pose a danger to human health [7]. At the same time, macro- and microelements are indispensable factors of nutrition, which, on the one hand, makes it possible to normalize their content in the diet and food products, on the other hand, dictates the need for such rationing under the conditions of environmental pollution [8].

The sources of heavy metals, which enter the human body, can be air, food, and water [9]. All of these factors take place especially in the industrialized regions.

It has been of interest to study the sorption of a number of heavy metals from the aqueous solutions of their salts using materials, based on zeolites from the Tayzhuzgen and Shankanai deposits.

At this stage of the work, both natural and hydrochloric acid-modified zeolites of the Tayzhuzgen (the Tarbagatai district of East Kazakhstan region) and Shankanai (the Kerbulak district of Almaty region) deposits have been used, the main mineral composition of which has been determined by the X-ray diffraction method. It has been found that clinoptilolite is the basis of the mineral composition of zeolites. The X-ray phase analysis data are presented in Table 1.

In general, the chemical composition of zeolites is described by the formula: $\text{Me}_{2n}O\cdot \text{Al}_2\text{O}_3\cdot x\text{SiO}_2\cdot y\text{H}_2\text{O}$, where $n$ is the valence of the metal cation, $x$ is the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $y$ is the number of moles of water. The total volume of cavities and channels in zeolites is about 50% of the volume.
The frame of zeolites is negatively charged, as a result of which charge-compensating counterions can be replaced by protons or other cations (Figure 1). The negative charge on the surface of zeolite promotes the adsorption of the polar particles [10].

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![Figure 1. Adsorption of metal ions on the zeolite frame.](image-url)

To analyze the sorption properties, the samples of the zeolite materials have been crushed in a jaw crushe...
a glass, poured with a 4% solution of hydrochloric acid in a ratio of 2:5 and stirred for 1 hour at the room temperature, then zeolite has been separated from the acid, washed with water and dried at 60 °C in a drying cabinet. To determine the conditions for purifying water from iron ions in a dynamic mode, water has been passed through a column filled with a sorbent at a rate of 4 ml/min. The concentration of Fe$^{2+}$ ions has been determined by the photocolorimetric method (photocolorimeter KFK-2). The results are presented in Table 2, Table 3, Table 4 and Table 5.

**Table 2.** The results of reducing the content of iron ions in the model solutions in a dynamic mode, when using natural zeolite of the Tayzhuzgen deposit.

| No. | Fraction, mm | Sample weight, g | The volume of passed water, ml | Fe$^{2+}$ concentration in the model solution, mg/l | After passing through a zeolite filter, mg/l | Purification degree α, % |
|-----|--------------|------------------|-------------------------------|---------------------------------|---------------------------------|------------------|
| 1   | 0.5          | 4                | 20                            | 2.5                             | 1.1                             | 56               |
| 2   | 0.5          | 4                | 30                            | 2.5                             | 0.95                            | 62               |
| 3   | 0.5          | 4                | 30                            | 2.5                             | 0.75                            | 70               |
| 4   | 0.5          | 4                | 30                            | 2.5                             | 0.6                             | 76               |
| 1   | 1            | 5.0              | 20                            | 2.5                             | 1.0                             | 60               |
| 2   | 1            | 5.0              | 30                            | 2.5                             | 0.9                             | 64               |
| 3   | 1            | 5.0              | 30                            | 2.5                             | 0.9                             | 64               |
| 4   | 1            | 5.0              | 30                            | 2.5                             | 1.05                            | 58               |

As can be seen from the presented data, in the dynamic mode at the tested rate of water passing through the column with the load of 4 g, with the fraction of 0.5 mm, the degree of purification increases up to 76%, and when used with the load of 5 g, with the fraction of 1 mm, the degree of purification has reached 64%.

**Table 3.** The results of reducing the content of iron ions in the model solutions in a dynamic mode, when using modified zeolite from the Tayzhuzgen deposit.

| No. | Fraction, mm | Sample weight, g | The volume of passed water, ml | Fe$^{2+}$ concentration in the model solution, mg/l | After passing through a zeolite filter, mg/l | Purification degree α, % |
|-----|--------------|------------------|-------------------------------|---------------------------------|---------------------------------|------------------|
| 1   | 0.5          | 3.7              | 20                            | 2.5                             | 0.95                            | 62               |
| 2   | 0.5          | 3.7              | 30                            | 2.5                             | 0.92                            | 63.2             |
| 3   | 0.5          | 3.7              | 30                            | 2.5                             | 1.05                            | 58               |
| 4   | 0.5          | 3.7              | 30                            | 2.5                             | 1.1                             | 56               |
| 1   | 1            | 5.0              | 20                            | 2.5                             | 0.95                            | 62               |
| 2   | 1            | 5.0              | 30                            | 2.5                             | 0.95                            | 62               |
| 3   | 1            | 5.0              | 30                            | 2.5                             | 0.9                             | 64               |
| 4   | 1            | 5.0              | 30                            | 2.5                             | 1.2                             | 52               |

It is shown that as a result of the modification, the sorption capacity of zeolite in the dynamic mode at the tested rate of water passing through the column with the load of 3.7 g, with the fraction of 0.5 mm, increases up to 63.2%, and when used with the load of 5 g, with the fraction 1 mm up to 64%.
Table 4. Results of reducing the content of iron ions in the model solutions in a dynamic mode, using natural zeolite from the Shankanai deposit.

| No. | Fraction, mm | Sample weight, g | The volume of passed water, ml | Fe$^{2+}$ concentration in the model solution, mg/l | After passing through a zeolite filter, mg/l | Purification degree $\alpha$, % |
|-----|--------------|------------------|-----------------------------|-----------------------------------------------|---------------------------------|---------------------|
| 1   | 0.5          | 15               | 30                          | 2.5                                           | 1.15                            | 54                  |
| 2   | 0.5          | 15               | 40                          | 2.5                                           | 0.9                             | 64                  |
| 3   | 0.5          | 15               | 40                          | 2.5                                           | 0.85                            | 66                  |
| 4   | 0.5          | 15               | 50                          | 2.5                                           | 0.45                            | 82                  |
| 1   | 1            | 15               | 30                          | 2.5                                           | 1.1                             | 56                  |
| 2   | 1            | 15               | 40                          | 2.5                                           | 0.9                             | 64                  |
| 3   | 1            | 15               | 40                          | 2.5                                           | 0.7                             | 72                  |
| 4   | 1            | 15               | 50                          | 2.5                                           | 0.5                             | 80                  |

Table 5. Results of a decrease in the content of iron ions in the model solutions in a dynamic mode, when using the modified zeolite of the Shankanai deposit.

| No. | Fraction, mm | Sample weight, g | The volume of passed water, ml | Fe$^{2+}$ concentration in the model solution, mg/l | After passing through a zeolite filter, mg/l | Purification degree $\alpha$, % |
|-----|--------------|------------------|-----------------------------|-----------------------------------------------|---------------------------------|---------------------|
| 1   | 0.5          | 10               | 30                          | 2.5                                           | 0.9                             | 64                  |
| 2   | 0.5          | 10               | 40                          | 2.5                                           | 0.82                            | 67.2                |
| 3   | 0.5          | 10               | 40                          | 2.5                                           | 0.8                             | 68                  |
| 4   | 0.5          | 10               | 50                          | 2.5                                           | 0.5                             | 80                  |
| 1   | 1            | 15               | 30                          | 2.5                                           | 0.92                            | 63.2                |
| 2   | 1            | 15               | 40                          | 2.5                                           | 0.92                            | 63.2                |
| 3   | 1            | 15               | 40                          | 2.5                                           | 0.7                             | 72                  |
| 4   | 1            | 15               | 50                          | 2.5                                           | 0.65                            | 74                  |

Table 4 presents the results before and after passing water through a column with natural zeolite with the filtering mass of 15 g, with the fraction of 0.5 mm, the purification is achieved by 82%, and with the load of 5 g, with the fraction of 1 mm, by 80%. Table 5 shows that when using the modified zeolite with the mass of 10 g, with the fraction of 0.5 mm, the degree of purification increases up to 80%, and with the load of 15 g with the fraction of 1 mm, up to 74%.

As can be seen from the data obtained, the extraction of iron ions by zeolites is ambiguous. Based on all these data, we can conclude that it is possible to improve the cleaning performance in a dynamic mode with an increase in the mass of zeolite.

The analysis of iron content in drinking water of Almaty before and after its processing with natural zeolites by atomic-absorption spectrometry method on the spectrometer “KVANT-Z.ETA” (Table 6, Table 7) has been carried out.

Table 6. Results of the study of the content of iron ions before and after passing through zeolite of the Tayzhuzgen deposit.

| Sample weight, g | Fe$^{2+}$ concentration in the model solution, mg/l | Purification degree $\alpha$, % |
|------------------|-----------------------------------------------|---------------------|
| 3.2              | 23.076                                        | 3.37                | 85.94                                            |
Table 7. Results of the study of the content of iron ions before and after passing through zeolite of the Shankanai deposit.

| Sample weight, g | Fe$^{3+}$ concentration in the model solution, mg/l | Fe$_{\text{total}}^{3+}$ concentration in the model solution, mg/l | Purification degree $\alpha$, % |
|------------------|-----------------------------------------------|-------------------------------------------------|-----------------|
| 3.2              | 23.076                                        | 3.486                                           | 84.89           |

Table 6 and Table 7 shows that before and after the purification of municipal water with zeolites of the Tayzhuzgen deposit from Fe$_{\text{total}}$ has been 85.94%, and with zeolites of the Shankanai deposit - 84.89%.

4. Conclusion

The mineralogical composition of natural zeolites of the Tayzhuzgen and Shankanai deposits has been studied. The main component of the zeolite-containing rock is clinoptilolite. At the initial concentration of iron ions Fe$^{3+}$ (2.5 mg/L), when passing the model solution through a filter on the basis of natural zeolite of the Tayzhuzgen deposit, the removal efficiency has been 76%, and that of the Shankanai deposit - 82%. And when the model solution has been passed through a modified zeolite filter, the removal efficiency of Fe$^{3+}$ has been 80%. The results of the study before and after purification of the municipal water with zeolites of the Tayzhuzgen deposit from Fe$_{\text{total}}$ has been 85.94%, and with zeolites of the Shankanai deposit - 84.89%. It has been found that iron ions interact with zeolites by the ion exchange mechanism, i.e. its extraction by zeolite is possible. The recovery increases depending on the weight of zeolite.

Thus, the studies carried out allow us to speak of the efficiency of using zeolites of the Tayzhuzgen and Shankanai deposits in the water treatment system in the dairy industry in order to ensure its technological indicators.

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