Development of Natural Zeolites Regeneration Scheme

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Abstract. In this paper, the research results on the adsorption process of final treatment of wastewater from electroplating production using a model filter with a nominal capacity of 0.3 m³/h are presented. Natural zeolite of the Trans-Baikal deposit heulandite was used as a charge. The processes of sorption and selective desorption of heavy metal ions were studied. Based on the results, the natural zeolites regeneration scheme was developed; the scheme provides the multiple reuse regenerated adsorbents in the processes of final treatment of wastewater from electroplating production, and eluates produced by regeneration can be reused in the manufacture as components for electrolytes used for electroplated coating deposition.

1. Introduction
The existing processes for toxic metals neutralization in industrial wastewater are combined mechanical, chemical, and physico-chemical methods. The key role is played by the final stage of the process providing the maximum purification depth owing to the use of electrochemical, membrane, adsorption, and other technologies.

Among the mentioned technologies, the adsorption methods are characterized by the highest level of environmental safety owing to reduced amount of used reagents, the efficiency of water treatment plants, an opportunity of organizing a closed loop water treatment or water recirculation, and the absence of significant capital costs. The adsorption processes are easy to manage and they can be automated [1].

The main criteria for the selection of material for wastewater neutralization are adsorption characteristics, porous structure, selectivity, strength, and moderate price. Along with highly efficient but expensive synthetic polymer adsorbents, there are developments exploring relatively cheap and available carbon adsorbents, silica, peat and peat processing products, ashes, carbonate-containing industrial wastes, etc. A prominent place in this series is occupied by natural zeolites [2, 3]. Low cost price and large deposits of natural aluminosilicates suggest their wide use in wastewater treatment technologies. Zeolites are easy to regenerate and recover their adsorption properties. In addition, an opportunity to regenerate zeolites and reuse them makes it possible to implement a recycled water supply system at enterprises. It is known that the advanced environmentally sound manufacture can be achieved by optimizing the current technologies [4].

An additional positive effect of the use of zeolites as filter materials is their selectivity towards heavy metal ions [5, 6].

The aim of this work is to study the possibility of selective desorption of heavy metal ions and to develop the natural zeolites regeneration scheme.
2. Materials and methods

The objects of study were natural zeolites of the Kholinskoe deposit whose total reserves are estimated at 300 mln t. According to the X-ray data, the used zeolites consist of 70–75 wt% heulandite \( \text{Ca}_2\text{Al}_2\text{Si}_7\text{O}_{18} \cdot 6\text{H}_2\text{O} \) and contain 25–30 wt% of impurity rock, namely, potassium feldspar \( \text{KAlSi}_3\text{O}_8 \) [7, 8].

According to the D. Breck’s classification, heulandite, as clinoptilolite, refers to the 7th group including so called lamellar zeolites. Such zeolites refer to the class of microporous sorbents with the micropore size of 0.5–1.5 nm [3].

The study of adsorption properties of heulandite towards heavy metal ions was performed using model solutions and wastewater from electroplating production. In the preparations, chemically pure reagents were used: \( \text{NiSO}_4 \cdot 7\text{H}_2\text{O} \); \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \); \( \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \); \( \text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} \); \( \text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O} \), and distilled water. The required pH value of solutions was achieved by addition of minimal volume of dilute sulfuric acid and controlled using an EV-74 ionomer.

The content of heavy metal ions in solutions was determined by spectrophotometric method in accordance with the standard PNDF techniques using a Promekolab PE-5400V spectrophotometer.

The calcium content in heulandite was determined by electron microscopy using a scanning electron microscope (LV-4500 multipath system). The total exchange capacity of heulandite was calculated based on the content of calcium cations in it.

The adsorption process dynamics was studied using a model filter with a nominal capacity of 0.3 m\(^3\)/h. Heulandite fraction of +1 mm was used as a charge. The adsorbent layer height was 0.34 m, the charge volume was 0.0085 m\(^3\). The adsorbate throughput rate through an adsorbent layer was varied in the range of 4–12 m/h.

The dynamic exchange capacity (DEC, mg/g) was calculated:

\[
\text{DEC} = \frac{V_S \cdot c_0}{m},
\]

where \( V_S \) is the pure solvent volume output from a column from the beginning of experiment to the appearance of solved substance, dm\(^3\); \( c_0 \) is the initial concentration of heavy metal ions, mg/dm\(^3\); and \( m \) is the adsorbent weight in a column, g.

The limit dynamic exchange capacity (LDEC) was determined, mg/g:

\[
\text{LDEC} = \frac{V_{\text{Sol}} \cdot c_0}{m},
\]

where \( V_{\text{Sol}} \) is the solution volume output from a column from the beginning of experiment to the appearance of solved substance with the initial concentration \( c_0 \).

Experiments on desorption were performed under static and dynamic conditions. Dilute sulfuric acid solutions with the concentrations of 0.005–0.6 M were used as eluents.

The degree of desorption (R, %) was calculated by the following formula

\[
R = \frac{c_i \cdot V_i}{m \cdot OE} \cdot 100\%,
\]

where \( c_i \) is the metal concentration in eluate, mg/dm\(^3\); \( V_i \) is the eluent volume passed, dm\(^3\); \( m \) is the zeolite weight, g; and \( OE \) is the exchange capacity, mg/g.

3. Results and discussion

It is known that the technological adsorption processes are mainly performed dynamically, i.e., by directed passing of wastewater through a fixed or backflow adsorbent layer [1]. Thus, for the development of treatment technology for wastewater from industrial manufacture, it is highly important to study the adsorption process under dynamic conditions. The pilot tests of a model filter were performed using aqueous solutions and reagent-treated wastewater with pH 6.5–8.5.
In Fig. 1 and 2, the dependences characterizing the dynamic activity of adsorbent by the volume of aqueous solutions passed from the beginning of adsorbate filtration to its breakthrough are presented.

![Figure 1](image1.png)

**Figure 1.** Volume of aqueous solutions passed depending on the breakthrough ion concentration value ($Ni^{2+}$, $Cu^{2+}$ and $Zn^{2+}$).

![Figure 2](image2.png)

**Figure 2.** Volume of aqueous solutions passed depending on the breakthrough ion concentration value ($Cr^{3+}$ and $Fe^{3+}$).

From the presented data (Fig. 1), it can be seen that the maximum passed volume of about 4 dm$^3$ corresponds to a solution containing $Ni^{2+}$ ions.

In Table 1, the determined exchange capacities of natural zeolites from the Kholinskoe deposit are presented.
Table 1. Exchange capacities of natural zeolites from the Kholinskoe deposit in a neutral medium.

| HMI  | DEC, mg/g | DEC, mg-eq/g | LDEC, mg/g | LDEC, mg-eq/g | OE, mg/g [10] | OE, mg-eq/g [10] |
|------|-----------|--------------|------------|---------------|---------------|----------------|
| Ni²⁺ | 4.1       | 0.14         | 6.1        | 0.21          | 5.9           | 0.20           |
| Cu²⁺ | 3.4       | 0.11         | 4.9        | 0.15          | 4.8           | 0.15           |
| Zn²⁺ | 2.0       | 0.09         | 2.8        | 0.13          | 2.7           | 0.12           |
| Cr³⁺ | 1.6       | 0.09         | 2.1        | 0.12          | 2.0           | 0.12           |
| Fe³⁺ | 1.2       | 0.06         | 2.0        | 0.11          | 1.9           | 0.10           |

From the presented data, it can be seen that, based on the exchange capacity values, the studied heavy metal ions form the following series:
\[ Ni^{2+} > Cu^{2+} > Zn^{2+} > Cr^{3+} > Fe^{3+}. \]

The highest dynamic exchange capacity value during adsorption with heulandite is shown by Ni²⁺ ions. It is known that, the higher the hydration capacity of ions is, the lower their exchange capacity is [2].

The adsorption technologies are efficient only upon condition of multiple reuse of adsorbent. The experiments on desorption were performed under static and dynamic conditions. Sulfuric acid solutions of different concentrations in the range of 0.005–0.6 M were used as eluents. In Table 2, the results obtained under static conditions are presented.

Table 2. Effect of sulfuric acid concentration on the desorption of heavy metal ions.

| (H₂SO₄)₃ | Ni²⁺ ions | R, % | Cu²⁺ ions | R, % | Zn²⁺ ions | R, % |
|----------|-----------|------|-----------|------|-----------|------|
| C        | in eluate | mg/dm³ | C        | in eluate | mg/dm³ | C        | in eluate | mg/dm³ |
| 0.61     | 25.8      | 43.8 | 24.9      | 51.9 | 13.2      | 49.0 |
| 0.30     | 25.6      | 43.3 | 28.5      | 59.3 | 18.0      | 66.7 |
| 0.15     | 27.8      | 47.1 | 32.0      | 66.8 | 15.3      | 56.8 |
| 0.07     | 33.4      | 56.5 | 30.3      | 63.0 | 15.1      | 55.9 |
| 0.04     | 33.9      | 57.4 | 31.4      | 65.5 | 14.9      | 55.1 |
| 0.02     | 31.7      | 53.7 | 30.7      | 63.0 | 14.2      | 52.5 |
| 0.01     | 18.6      | 31.5 | 29.3      | 61.1 | 14.4      | 53.3 |
| 0.005   | 21.4      | 36.3 | 16.5      | 34.3 | 9.8       | 36.5 |

From the presented data (Table 2), it follows that Ni²⁺, Cu²⁺, and Zn²⁺ ions can be desorbed with sulfuric acid of a lower concentration compared to the recommended concentration of 0.7–1.0 M.

The preliminary experiments on the desorption of Cr³⁺ and Fe³⁺ ions show that the deepest desorption of these ions is provided when using 1.0 M sulfuric acid solution as eluent.

The throughput rates of the selected eluates were determined under dynamic mode (Table 3). In addition, the results show that regenerated zeolites can be reused many times in the treatment technologies.
Table 3. Effect of eluent throughput rate on the degree of desorption of heavy metal ions.

| HMI | C (H₂SO₄), mol/dm³ | Degree of HMI desorption, % (for different eluent throughput rates) |
|-----|---------------------|---------------------------------------------------------------|
|     | 0.75 dm³/min | 1.0 dm³/min | 1.2 dm³/min | 1.5 dm³/min | 2.0 dm³/min |
| Ni²⁺ | 0.04     | 97         | 97         | 97         | 97         |
| Cu²⁺ | 0.15     | 95         | 95         | 95         | 94         |
| Zn²⁺ | 0.30     | 92         | 92         | 92         | 90         |
| Cr³⁺ | 1.0      | 89         | 89         | 87         | 85         |
| Fe³⁺ | 1.0      | 89         | 89         | 87         | 84         |

From the presented data, it follows that, in the case of Ni²⁺ ions, the change in the eluent throughput rate from 0.75 to 2 dm³/min does not affect their degree of desorption, which is 97%; Ni²⁺ ions can be desorbed at a throughput rate of 2 dm³/min, which corresponds to the linear throughput rate of 1.5 m/h.

The desorption of Cu²⁺ ions is better at an eluent throughput rate of 1.5 dm³/min, which corresponds to 1.2 m/h. Under further increase in the throughput rate to 2 dm³/min, the degree of desorption decreases to 94%. It is recommended to desorb Zn²⁺ ions at a throughput rate of 1.2 dm³/min, which corresponds to 1.0 m/h. The corresponding degree of desorption is 92%.

The separation of Cr³⁺ and Fe³⁺ ions does not occur under dynamic conditions because both ions are desorbed simultaneously with 1 M sulfuric acid solution. The deepest recovery of Cr³⁺ and Fe³⁺ ions is provided at a throughput rate of 1.0 dm³/min, which corresponds to 0.85 m/h.

Based on the performed integrated study on desorption of spent zeolites, their regeneration scheme was developed (Fig. 3); the scheme provides the separation of ions of divalent metals under desorption.

Figure 3. Zeolites regeneration scheme.
First, 0.04 M sulfuric acid solution was passed as eluent through spent zeolite at a rate of 1.5 m/h. As a result, eluate containing nickel sulfate was produced. Further, 0.15 M sulfuric acid solution was passed through zeolite at a rate of 1.2 m/h. As a result, eluate containing copper sulfate was formed. After that, 0.3 M sulfuric acid solution was passed through regenerated zeolite at a rate of 1.0 m/h. The resulting eluate was zinc sulfate.

Finally, Cr\(^{3+}\) and Fe\(^{3+}\) ions are desorbed simultaneously with 1 M sulfuric acid solution at the throughput rate of 0.5 m/h. The resulting eluate contains chromium sulfate and ferrous sulfate.

4. Conclusion
The practical implementation of the developed regeneration scheme provides the multiple reuse of natural zeolites in the wastewater treatment processes, and eluates produced by regeneration (nickel sulfate, copper sulfate, and zinc sulfate) can be reused in the manufacture as components for electrolytes used for electroplated coating deposition.

5. References
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