Study of ion exchange at test solutions purification from nickel (II) ions with gabbro-diabase from abzakovo deposit

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Abstract. The paper presents the results of the study of ion exchange processes during the purification of model solutions from nickel ions with gabbro-diabase from the Abzakovo field. The features of the minerals structure that make up gabbro-diabase predetermine their sorption and cation-exchange properties. During the studies, the course of sorption processes was established, as well as the presence of a suspension effect in the system. By determining the concentration of exchangeable cations (Ca²⁺, Mg²⁺, Al³⁺) in the crystal lattices of gabbro diabase and Ni²⁺ cations contained in the model solution, the phenomenon of cation exchange purification has been proved. The treatment of gabbro diabase powder with electromagnetic radiation increases the mobility of exchange cations and water treatment efficiency.

1. Introduction

At present such innovative area in environment protection as using natural mineral compounds (NMC) as reactants for removing pollutants from water medium has been gaining popularity in the world society.

The carried-out research has determined that the promising NMCs for removing heavy metals ions (HMI) from wastewaters are alumino-silicate minerals [1,2], mostly bentonite clays (montmorillonite [3,4] and beidellite [5]), kaolinite [3,5-6], biotite [7], vermiculite [8-9], palygorskite [10-11] and others. The adsorption activity of minerals is determined by the peculiarities of their crystalline structure, as well as by their chemical and mineralogical composition. As a rule, the specific surface of clay minerals is 15-500 m²/g [12].

The clayish natural sorbents are presented with highly-dispersed polymeric systems with complex chemical composition, %: 40-72 - SiO₂; 5-33 - Al₂O₃; 1,2-15 - Fe₂O₃; up to 8 - MgO; 4-5 – oxides of alkaline metals and other metals [13-14], which have the developed surface and good sorption properties. Clay minerals, as well as zeolites, are characterized with physical and molecular sorption along with ion exchange. The physical sorption is conditioned by the presence of certain excess negative charge on crystal faces and the surface acidic and basic hydroxyl groups, which can be ionized. The presence of OH-groups also predetermines the certain anion-exchange capability which is observed in layered minerals. At the molecular sorption the adsorbed substances are arranged between the packs’ planes, disrupting the initial aquo-complexes without changing the layers’
structure. With that the distance between layers is increased, as clay minerals are swelled intralaminarily, unlike zeolites, unable of swelling [13].

In many technological processes, including wastewater treatment processes, dispersed silicas are used, as they are characterized with high strength and porosity, don’t get soaked in water, are low-cost and available in large deposits [14].

Particularly, the works [15-16] describe the use of gaize as component of a new sorption-filtering material for multicomponent wastewaters purification. The research has shown that this material can be used for environmental and analytical purposes, as well as in various processing plants for obtaining recycled water.

In order to expand the resource base for water treatment, we have studied gabbro-diabase from Abzakovo deposit (Republic of Bashkortostan) as a sorption material for HMI removal. Earlier, the possibility of using the latter for oil and colorants extraction was described [17-18].

According to the data of X-ray phase analysis [18], gabbro-diabase consists of such clay minerals as anorthite (feldspars group), kaolinite, oligoclase and illite. The other mineral components of gabbro-diabase are presented with diopside, quartz, α- and β-cristobalite and pyrophyllite. These minerals have been studied as sorption and ion-exchange materials for removing heavy metals ions from water media [3,5-6,19-23]. The formulas of these minerals are given below:

- Anorthite (CaO Al2O3 2SiO2);
- Diopside (CaO-MgO 2SiO2);
- Kaolinite (Al2O3 2SiO2 2H2O);
- Oligoclase (Na2O Al2O3 6SiO2);
- Quartz (SiO2);
- Alpha-cristobalite (SiO2) (high-temperature modification);
- Beta-cristobalite (SiO2) (low-temperature modification);
- Pyrophyllite (Al2O3 4SiO2 2H2O);
- Illite (K4Al2[AlSi3O10](OH)2 nH2O);
- Hornblende (Ca, Na (Mg, Fe)6(Al, Al9O11)(OH)3).

The structure peculiarities of the above-listed minerals predetermine their sorption and cation-exchange properties.

It may be assumed that in the process of test solutions or real waste waters treatment with gabbro-diabase the exchange adsorption takes place. There are several types of active sites in clay minerals: single and pair OH- groups at the borders of tetrahedral and octahedral structural elements; unsaturated pair hydroxides at aluminium atoms. The active elements – broken valency bonds – appear in the process of milling and under the action of water:

\[
\equiv \text{Si-O-Si} \rightarrow \\equiv \text{Si}\text{+O-Si}^- \quad (\text{milling}) \quad \rightarrow \equiv \text{Si-OH} + \text{HO-Si}^- \quad (\text{hydration})
\]

Adsorption centers on a clay mineral’s surface are formed with rings made of six oxygen atoms, with electronic configuration sp (coordination number 2).

Along with ion exchange, the processes of physical and molecular sorption are also typical for clay minerals. The physical sorption is conditioned by the presence of certain excess negative charge on crystal faces (broken bonds) and the surface acidic and basic hydroxyl groups, which can be ionized by the following schemes:

At pH=11,4-11,9: =Si-OH ↔ =SiO^-+H^+

and at pH=2,5: =Al(Fe,Mg)OH ↔ =Al(Fe,Mg)^+-+OH^-.

At the molecular sorption the adsorbed substances are arranged between the packs’ planes, disrupting the initial aquo-complexes without changing the layers’ structure. With that the distance between layers is increased, as clay minerals are swelled intralaminarily.

The acidity of SiOH-groups is increased, if the SiO3(OH) tetrahedron on the side face or edge is linked with the AlO4 tetrahedron through a bridging oxygen atom. The negative charge, which appears on the AlO4-tetrahedron, is mostly compensated by either the excess positive charge or by the metal ion; simultaneously the end group OH* is polarized.

At the alteration of the medium from acidic to alkaline the clay particles change their charge: in the acidic medium the potential-determining particles are positive aluminium cations, and in the alkaline medium – the negatively charged AlO2^- radicals. In the acidic medium the diffuse layer of clay
particles is sign-variable: on the base surface it is formed with positive ions, and on the lateral surface – with negative ions. In the alkaline medium the diffuse layer of base and lateral chippings of particles have the same polarity.

As it has been determined by means of X-ray phase analysis [18], gabbro-diabase contains quartz particles (SiO2), the surface of which [14] is known to be negatively charged.

So, in this system the sorption interaction of physical adsorption type between SiO2- particles and hydrolyzed and non-hydrolyzed heavy metals ions is also possible according to the scheme (Figure 1):

![Figure 1. The scheme of physical adsorption interaction.](image)

Based on the above, the experiments in studying the opportunity of using gabbro-diabase powder for extracting Ni\(^{2+}\) ions from test solutions were carried out. This choice is conditioned by the fact that the nickel ions are present in electroplating industry wastewaters as the prevalent pollutant.

2. Experimental

To determine the efficiency of wastewater purification from Ni\(^{2+}\) ions by means of powdered gabbro-diabase the fraction with particle size from 0.14 mm to 0.25 mm was used. The sorption properties of gabbro-diabase were determined with the static method. Test solutions with Ni\(^{2+}\) ions concentration from 5 to 10 mg/L were prepared by means of dilution; pH was adjusted up to values, which would exclude hydrates formation, i.e. the reactant purification. The sorption material (gabbro-diabase) weighing 0.32g was placed into a retort and poured over with 50 cm\(^3\) of solution with a certain concentration of Ni\(^{2+}\) ions. The mix was stirred for 1 hour. After 24 hours gabbro-diabase was filtered and the residual concentration of Ni\(^{2+}\) ions in the initial solution and in the filtrate was determined by means of photocolorimetric method with «KFK-2 MP» photocolorimeter according to standard procedure (PNDF 14.1:2.52-96).

The sorption properties of gabbro-diabase were evaluated by the isotherms, which characterize the dependence of sorption capacity of the gabbro-diabase under study on the sorbate concentration in the solution at constant temperature.

Comparing the value of Ni\(^{2+}\) ions initial concentration in the solution with the residual concentration of metal ions after the solution’s contact with gabbro-diabase, we can make a conclusion about the adsorption capacity of the latter for Ni\(^{2+}\) ions.

The value of Ni\(^{2+}\) ions adsorption on the surface of gabbro-diabase was calculated through the Eq. (1):

\[
G = (C_{in} - C_{eq})V_{sol} / m_{gabbro-diabase},
\]

where \(C_{in}\) – the initial concentration of Ni\(^{2+}\) cations in the solution, mole/L; \(C_{eq}\) – the equilibrium concentration of Ni\(^{2+}\) cations in the solution, mole/L; \(V_{sol}\) – the volume of solution, L; \(m_{gabbro-diabase}\) – the weight of gabbro-diabase, used for the adsorption process, g.
3. Results

According to the obtained data, the isotherm of Ni$^{2+}$ ions adsorption on the gabbro-diabase was plotted (Figure 2). In the course of the research, a suspending effect at adding gabbro-diabase to the water medium, which displays itself in the difference between the pH values of the suspension and the filtrate, has been observed (Eq. (2)):

$$\Delta pH = pH_s - pH_f,$$

where $pH_s$ and $pH_f$ – the pH values of the suspension and the filtrate, respectively.

By the $\Delta pH$ value we can judge about the polarity sign on the surface of the dispersed particles. At studying the suspending effect in gabbro-diabase-containing water systems, the finely-dispersed gabbro-diabase powder was added to 100 cm$^3$ of distilled water, the suspension was stirred for 10 minutes, and then the pH values were determined. After measurements the suspension was filtered through paper filter, and the pH value was determined again for the filtrate.

![Figure 2. Isotherm of Ni$^{2+}$ ions adsorption on gabbro-diabase surface.](image)

It was found, that the pH of the filtrate is shifted to the area of the acidic media ($pH = 9.8$ for the suspension and $pH = 7.9$ for the filtrate), i.e. H$^+$-ions pass to the filtrate from the mobile external diffusion layer around a gabbro-diabase particle.

So, to determine the possibility of replacing the exchangeable cations (Ca$^{2+}$, Mg$^{2+}$, Al$^{3+}$) in gabbro-diabase crystalline lattices with the Ni$^{2+}$ cations, contained in the test solution, the concentrations of leachable cations in various media were determined [22].

A portion of the powdered sample weighing 1 g was treated with 500 cm$^3$ of distilled water with various pH values at various temperatures. The duration of gabbro-diabase sample’s contact with the water medium was 30 minutes. After filtering the suspension, the concentration of Ca$^{2+}$, Mg$^{2+}$, Al$^{3+}$ cations was determined in the filtrate with photolorimetric method according to standard procedure The findings of the research are presented in Table 1.

| pH | t of water medium, °C | Ca$^{2+}$, mg/L | Mg$^{2+}$, mg/L | Al$^{3+}$, mg/L |
|----|----------------------|---------------|---------------|---------------|
| 7  | 20                   | 1.91          | 0.58          | -             |
| 7  | 40                   | 5.82          | 1.16          | 0.02          |
| 7  | 60                   | 6.79          | 1.74          | 0.06          |
| 2  | 20                   | 7.76          | 3.48          | 0.65          |
| 2  | 60                   | 9.41          | 6.97          | 0.69          |

One of the ways to increase the sorption capacity of natural mineral compounds is treating them with ultraviolet (UV) irradiation. In particular, as it was demonstrated earlier, the UV-treatment of natural clays from Katoka and Kateti deposits results in the increase of their sorption capacity for heavy metals ions [23-24]. This is apparently due to the weakening of chemical bonds between the
metal atoms and oxygen atoms in the layers of NMCs crystalline lattices, which results in the increase of their exchange capacity.

In view of the above, to increase the mobility of exchangeable cations in the crystal lattices of minerals, forming the gabbro-diabase, and to ease their passing to the liquid medium, the gabbro-diabase powder was treated with the UV irradiation for 10 minutes, and then the experiments similar to the above-mentioned ones were carried out. The findings of determining the mobile cations’ concentrations in the filtrate are presented in Table 2.

Table 2. Leachability of exchangeable cations after the UV-treatment of gabbro-diabase.

| pH | t of water medium, °C | Ions, mg/L | Ca²⁺ | Mg²⁺ | Al³⁺ |
|----|---------------------|------------|------|------|------|
| 7  | 60                  |            | 8.95 | 2.16 | 0.08 |
| 2  | 60                  |            | 12.62| 7.23 | 0.82 |

The leachability of all mobile cations is in all cases higher for the UV-treated samples. The ions concentrations were, for the native samples: Mg – 1.74 mg/dm³ (neutral media), Mg – 6.97 mg/dm³ (acidic media), Ca – 6.79 mg/dm³ (neutral media), Ca – 9.41 mg/dm³ (acidic media), for the UV-treated samples: Mg – 2.16 mg/dm³ (neutral media), Mg – 7.23 mg/dm³ (acidic media), Ca – 8.95 mg/dm³ (neutral media), Ca – 12.62 mg/dm³ (acidic media).

As it was mentioned above, the UV irradiation of minerals must cause the weakening of O-Me bonds in the crystalline lattice, which results in the yield of the part of exchangeable cations from the lattice and their replacement with ions, contained in the solution. In order to check this assumption, the portions of the native and UV-treated gabbro-diabase were added to the test solution, containing Ni²⁺ ions in concentration 10 mg/dm³, in amount 3 g for 500 cm³ of the test solution. After 10 minutes of stirring the concentrations of Ca²⁺, Mg²⁺, Al³⁺, Ni²⁺ ions were determined in the filtrate. The findings of the research (Table 3) show that the Ni²⁺ ions concentration is lower in the solution, purified with the UV-treated gabbro-diabase.

Table 3. Cation composition of filtrates.

| Medium to be treated | Cations, mg/L | Efficiency of purification from Ni²⁺, % |
|----------------------|---------------|----------------------------------------|
| Ni²⁺- containing solution, 10 mg/L | Ca²⁺ | Mg²⁺ | Al³⁺ | Ni²⁺ | init. g-d | init. g-d | init. g-d | init. g-d | init. g-d | init. g-d | init. g-d | init. g-d | init. g-d | init. g-d |
| Ni²⁺ | 25.17 | 31.21 | 30.31 | 35.2 | 0.58 | 0.62 | 1.18 | 0.7 | 88.2 | 97.3 |

4. Conclusions

So, the carried-out research has demonstrated that the gabbro-diabase powder can be used as a sorption material for removing heavy metals ions from aqueous media. It has been determined that the sorption characteristics of gabbro-diabase for nickel ions are increased under the UV irradiation. The performed experiments have shown that the main mechanism of extracting Ni²⁺ ions from test solutions is the ion exchange.

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