Study of iron (III) and nickel (II) ions adsorption from aqueous solutions by basalt fiber

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Abstract. The regularities of iron (III) and nickel (II) ions sorption kinetics on super-thin basalt fiber (STBF) were studied. The correlation between the adsorption rate constants and the ions diffusion coefficients was established. The adsorption equilibrium for the iron (III) ion is well described by the Freundlich model, and for the nickel (II) ion – by the Langmuir model.

1. Introduction

For deep sewage purification from various types of pollution, including heavy metal ions, highly efficient sorption methods are used. The adsorption material must have a high specific surface and adsorption capacity, regenerative capability. If a sorbent does not have regenerative capability, the problem of its utilization arises. The most popular sorbents for sewage purification from heavy metal ions are carbon-containing sorbents; sorbents based on natural or manufactured aluminosilicate minerals; inorganic and organic ion-exchangers; peat and its by-products [1, 2]; and others.

It is more economical to use technogenic wastes, such as metallurgical slags, galvanic sludges, brick, foamed concrete, carbonate-containing wastes [1, 3], vegetal waste, etc. as sorbents. In some cases, sorption properties are found in materials used for other purposes, for example, in fiber-glass materials [4].

Fiber-glass materials include basalt fiber. It is widely known that basalt fiber is used as a reinforcing component in composite materials; as a substitute for glass and heat- and sound-insulating material. In addition, basalt fiber is used in filters for dust and gas emissions purification and in sewage filtration, when impurities are retained on the fiber surface due to mechanical effects. Studies were conducted on the use of basalt fiber as a filler for cation exchange composite materials [5, 6]. The adsorption properties of basaltic rocks were studied [7–9]. The adsorption properties of basalt fibers in relation to heavy metal ions were not sufficiently explored.

In comparison to granular sorbents, fibrous sorbents have a larger specific surface area, greater active centers accessibility, and (as a consequence) a higher adsorption rate [10]. Basalt fiber does not contain impurities of other minerals and is characterized by high chemical and thermal resistance.

The purpose of the study is to explore the adsorption capacity of super-thin basalt fiber (STBF) with respect to iron (III) and nickel (II) ions.

2. Research objects and methods

Staple super-thin basalt fiber (STBF) in the form of mats, panels, or felts is used for thermal insulation of thermal equipment, pipelines, utility systems, and as a heat insulator in the production of liquefied gases.
The material consists of staple fibers layers with a diameter of less than 3 μm, randomly interwoven and fastened together in the form of a mineral wool felt. The chemical composition of the basalt fiber: SiO$_2$ (43-51%), Al$_2$O$_3$ (10-17%), Fe$_2$O$_3$ (10-15%), CaO (8-13%), MgO (4-15%), etc. [11].

The adsorption of iron (III) and nickel (II) ions from simulated aqueous solutions of their sulfates was explored at concentrations ranging from 0.09 to 0.90 mmol/dm$^3$ under static conditions. The contact of the adsorbent with metal salts solutions was carried out by mixing for a certain period of time. The mass ratio of solid and liquid phases is 1:500.

To determine the equilibrium ion concentration in simulated solutions, photocolorimetric method was used.

3. Results and discussions

The ultimate objective of an investigation in the field of kinetics is to identify the mechanism of the process under study. At the beginning of the investigation, kinetic curves, which represent the dependence of the reagent (or reagents) concentration on the time in order to determine the rate constant and the reaction order, are constructed. The cations adsorption kinetic curves construction allows us to conclude that the equilibrium in the system is established in 10–20 minutes.

Assuming that the interaction of ions with the active centers of the adsorbent is inherently an ion exchange, then the process should proceed at high speed. Otherwise, the speed of the process is determined by the speed of the diffusion steps [10].

Since the equilibrium of adsorption is established within 10-20 minutes, we can assume that the speed of the process is determined by the rate of external diffusion. The rate of external diffusion is described by the Fick's equation for steady state diffusion and is proportional to the concentration gradient in the diffusion layer

$$dC/dx = (C_S - C)/\delta$$

$C_S$ is the ion concentration on the surface of the adsorbent, mmol/dm$^3$;
$C$ is the ion concentration in the solution, mmol/dm$^3$;
$\delta$ is the thickness of the diffusion layer, m.

Thus, the rate of external diffusion is described by the kinetic equation of the first order reaction.

Assuming that the adsorption rate is described by the kinetic equation $\nu = k\cdot C^n$; the Van 't Hoff differential method was used to determine the reaction order. Van Goff. Taking the logarithm of this expression, the equation of a straight line in logarithmic coordinates is derived:

$$\lg \nu = \lg k + n \lg C.$$

The reaction order is determined by this straight line inclination angle tangent, and the adsorption rate constant is determined by the value of the y-intercept of the straight line. The results of the construction are presented in table 1.

The reaction order is approximately 0.5. It is possible that the adsorption proceeds in a mixed-diffusion mode or is complicated by chemical reactions on the surface of the sorbent. However, nickel (II) ion adsorption rate is greater than iron (III) ion adsorption rate, thus correlating with the values of ion diffusion coefficients.

| Ion       | $\text{Ni}^{2+}$ | $\text{Fe}^{3+}$ |
|-----------|------------------|------------------|
| $n$       | $k, \text{mol0.5·l·0.5·min}^{-1}$ | $n$ | $k, \text{mol0.5·l·0.5·min}^{-1}$ |
| 0.68      | 0.0062           | 0.57             | 0.0035 |

The external diffusion rate constant “k” is proportional to the ion diffusion coefficient [12]:

$$k = 4D/(d \cdot \delta),$$
where D is the ion diffusion coefficient; d is the fiber diameter; δ is the thickness of the diffusion layer.

Ions diffusion coefficients D0 in infinitely dilute solutions can be calculated through their limiting molar electrical conductivity (mobility) [13]:

$$D_0 = R \cdot T \cdot \lambda_0/(zF^2),$$

where T is the absolute temperature; R is the universal gas constant; z is the particle charge; F is the Faraday constant; $\lambda_0$ is the limiting molar electrical conductivity of an ion.

The diffusion coefficient of the Ni$^{2+}$ ion calculated in this way at the temperature of 298 K is $7.19 \times 10^{-1} \text{ m}^2\text{s}^{-1}$, and that of the Fe$^{3+}$ ion is $6.03 \times 10^{-10} \text{ m}^2\text{s}^{-1}$. The ratio of diffusion coefficients is $D_0(\text{Ni}^{2+}) : D_0(\text{Fe}^{3+}) = 1.2:1.0$.

The diffusion coefficients calculation with consideration of the solution concentration is carried out according to the equation [13]:

$$D = D_0(1 + \Delta n\gamma/\Delta nC) \approx D_0(1 + \Delta n\gamma/\Delta nC),$$

where γ is the ion activity coefficient.

For the solutions with the ion concentration of 50 mg/dm$^3$ (~0.90 mmol/dm$^3$) in comparison with the concentration of 1 mg/dm$^3$ (~0.02 mmol/dm$^3$), $\Delta n\gamma$ were calculated using the Debye–Hückel limiting equation and the diffusion coefficients were obtained: $D(\text{Ni}^{2+}) = 6.76 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ and $D(\text{Fe}^{3+}) = 5.0 \times 10^{-10} \text{ m}^2\text{s}^{-1}$. The ratio of ion diffusion coefficients with increased solutions concentrations in the concentration range under consideration grows $D(\text{Ni}^{2+}) : D(\text{Fe}^{3+}) = 1.35:1.0$. The ratio of adsorption rate constants is $k(\text{Ni}^{2+}) : k(\text{Fe}^{3+}) = 1.77:1.0$.

Table 2 presents the values of the ions adsorption degree and their distribution coefficients. The degree of adsorption ($S,\%$) is the fraction of the adsorbate entered the adsorption layer on the surface of the adsorbent. The decrease in the degree of ions adsorption with increasing concentration is due to the final adsorption capacity of the fiber. Since the iron (III) ion has a pronounced affinity for the surface of the basalt fiber, containing Fe$_2$O$_3$ [11], and a higher charge, its adsorption degree is greater than that of the nickel (II) ion in the entire range of studied concentrations.

The distribution coefficient is equal to the ratio of the specific adsorption to the equilibrium concentration of adsorbate in the solution volume, that is, it characterizes the degree of the ion affinity to the adsorbent surface. Therefore, the distribution coefficient of the iron ion Fe$^{3+}$ is of order $10^2$, and that of the nickel ion Ni$^{2+}$ is of order $10^2$. The ions distribution coefficient also decreases with an increase in their concentration in simulated solutions.

**Table 2.** Distribution coefficients and iron (III) ions and nickel (II) ions adsorption degrees on STBF.

| C$_0$, mg/dm$^3$ | Fe$^{3+}$ | | | Ni$^{2+}$ | | |
|-----------------|-----------|-----------------|-----------|-----------------|-----------|
|                 | S, %      | Kd, ml/g        | S, %      | Kd, ml/g        |
| 5               | 86.2      | 3118            | –         | –               |
| 10              | 79.9      | 1981            | 50.0      | 500             |
| 20              | 57.7      | 681             | 35.7      | 277             |
| 30              | 45.8      | 423             | 28.7      | 201             |
| 40              | 57.7      | 337             | 31.4      | 229             |
| 50              | 33.9      | 257             | 29.6      | 210             |
| 75              | –         | –               | 27.8      | 192             |
| 100             | –         | –               | 25.1      | 168             |

Understanding of the nature of heavy metals ions adsorption process on the basalt fiber can be obtained through adsorption isotherms. In order to determine adsorption equilibrium constants, the Langmuir, Freundlich and Temkin adsorption isotherm equations were used. The Langmuir model describes monomolecular adsorption proceeding on active centers with the same adsorbent-adsorbate
interaction energy. The Temkin and Freundlich models take into account the dependence of the adsorption energy on the degree of surface occupation. The Temkin model is based on the assumption of a linear nature of the dependence of the adsorption energy on the fraction of occupied active centers. The Freundlich empirical equation provides a good description of the adsorption cases when the adsorbent-adsorbate interaction energy dependence on the occupied active centers fraction is exponential. The results of the determination are presented in Table 3.

**Table 3. Constants in the adsorption isotherms equations.**

| Constants in the adsorption isotherm equation of | Ion | Fe³⁺ | Ni²⁺ |
|-----------------------------------------------|-----|------|------|
| Langmuir A∞·10⁴, mol/g                       |     | 0.18 | 0.59 |
| Kₗ·10⁻³, dm³/mol                              |     | 9.9  | 0.6  |
| Determination coefficient R²                  |     | 0.925| 0.995|
| Temkin 1/α·10⁻², mol/g                        |     | 298.0| 5.0  |
| K₅·10⁻⁹, dm³/mol                              |     | 0.03 | 0.13 |
| Determination coefficient R²                  |     | 0.988| 0.978|
| Freundlich Kᵢ·10⁻⁴, mol/g                    |     | 1.2  | 16.6 |
| 1/n                                           |     | 0.028| 0.66 |
| Determination coefficient R²                  |     | 0.9942| 0.972|

Ion exchange can be complicated by chemical reactions [10]. For example, on complex ion exchangers, ion exchange is accompanied by the formation of the coordination bond, in addition to the ionic one, between an adsorbed cation (complexing compound) and the functional group (ligand). Ligands are carboxylic, glyoximate, phosphonate, mercapto groups, etc. [14]. When iron (III) and nickel (II) ions are adsorbed on clays, ion exchange and the formation of complex compounds with surface hydroxyl groups of the mineral occur simultaneously [14, 15].

The adsorption process on the surface of aluminosilicate basalt fiber takes place with the participation of the following groups ≡Si−OH, =Al−OH, ≡Si−O−Al=., as well as oxygen atoms. Apparently, in the process of heavy metals ions sorption on basalt fiber, two sorption mechanisms are realized: ion exchange and the formation of complexes with surface hydroxyl groups.

The adsorption of Ni²⁺ ions on the surface of basalt fiber is well described by the Langmuir model and the adsorption of Fe³⁺ ions – by the Freundlich model. The adsorption of nickel (II) ions occurs on energy equivalent active centers, iron (III) ions – on the active centers with different sorption energy. The adsorption equilibrium constant in the Langmuir equation Kₗ(Fe³⁺) is an order of magnitude greater than Kₗ(Ni²⁺), which indicates stronger adsorption of the iron (III) ion. This may be due to its higher charge and stronger ability to form complex compounds.

4. Conclusion
It was established that STBF exhibits adsorption activity towards iron (III) and nickel (II) ions. The higher value of the nickel ion adsorption rate constant is due to its larger diffusion coefficient. The adsorption of Ni²⁺ ions on the basalt fiber surface is well described by the Langmuir model and the adsorption of Fe³⁺ ions – by the Freundlich model.

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