

Evaluation of the various reagents sorption activity with respect to rare earth elements

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Abstract. Pilot experiments to remove lanthanum and cerium ions from model one-component solutions using reagents: opoka, brucite, amorphous silica, thermovermiculite (500 °C, 2 hours), sawdust, thermally activated brucite (600 °C, 2 hours), activated carbon, zeolite, were carried out. Promising sorbents of rare-earth elements of the light group have been identified, which can be used to purify water with a high content of the elements under consideration or in combined sorption technologies for restoring disturbed lands in the areas of extraction and enrichment of rare metal ores.

1 Introduction

Rare earth elements (REE) are 15 elements from La to Lu, as well as Sc and Y, which have similar chemical properties [1, 2].

The increased content of rare earth elements in environmental components is caused by both natural geological processes (denudation, redeposition) [3] and anthropogenic ones: due to the use of fertilizers containing rare earth elements, mining and processing of rare metal ores, industrial emissions and storage of fuel combustion waste [4], etc.

Recently, they are increasingly considered as emerging pollutants due to their potential risk to humans and the environment [5-7]. The effect of REE on living organisms has been actively studied in recent years.

In industry, ion exchange resins and carbon nanotubes are widely used to extract rare earth elements from process solutions [8]. At the same time, the search for reagents for cleaning ecosystems from REE becomes an urgent task.

The purpose of the study is to evaluate the sorption properties of various reagents with respect to light group REE using the example of lanthanum and cerium.

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2 Objects and methods

Several series of experiments were carried out under laboratory conditions. In the first series of experiments, a list of possible reagents was determined. Concentrated model solutions were prepared from reagents: $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ of analytical grade, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ of chemically pure grade, dissolving 1 g of salt in 1 liter of distilled water.

As potential sorbents, both traditional sorbents and reagents that can be obtained from the waste of the mining complex of the Murmansk region were considered:

- Brucite, commercial reagent, AgroMag, magnesium hydroxide fine powder (particle size $<300 \mu\text{m}$) is obtained from selectively mined natural magnesium hydroxide (ground brucite) by grinding and sorting. The content of the main components is, wt. %: $\text{MgO}/\text{Mg}(\text{OH})_2 - 60.0/87.0$, $\text{CaO} - 3.0$, $\text{SiO}_2 - 3.0$, $\text{Fe}_2\text{O}_3 - 0.5$. Brucite can be obtained from various mining wastes of the Murmansk region: copper-nickel ores, bottom sediments of settling ponds [9].
- Sorbent based on a modified opoka – natural opoka from the Sukholozhskoye deposit (Yekaterinburg) are mined, crushed and activated by heat treatment at a temperature of about $1000 \text{ }^\circ\text{C}$. The content of the main components is, wt. %: SiO_2 up to 84, Fe_2O_3 up to 3.2; Al_2O_3 , MgO , CaO up to 8 [10].
- Amorphous silica is a product of acid decomposition of vermiculite ores, copper-nickel ores [11].
- Sawdust of tree species is a cheap, environmentally friendly "green" sorbent for removing heavy metal ions and organic compounds of various nature from aquatic environments [12, 13].
- Zeolite as a traditional sorbent [14-16].
- BAU-A activated carbon as a traditional sorbent.
- Brucite, thermally activated at $600 \text{ }^\circ\text{C}$ for 2 hours to increase the sorption capacity of the material [9, 17].
- Thermovermiculite – vermiculite of the Kovdor deposit, fired for 2 hours at a temperature of $500 \text{ }^\circ\text{C}$. The content of the main components is, wt. %: SiO_2 , 30.9; MgO , 27.0; Al_2O_3 , 9.6;

1 g of sorbent was added to the prepared solutions and left for 24 hours with occasional stirring. At the end of the experiment, the solutions were filtered through a Vladipor membrane filter of the MFAS-OS-2 type (pore size $0.45 \mu\text{m}$) and submitted for quantitative chemical analysis. The content of elements in the resulting solutions was determined by the method of inductively coupled plasma mass spectrometry (measuring instrument - ELAN 9000 (PerkinElmer, USA) at the Center for Collective Use of the INEP KSC RAS.

The degree of extraction of the pollutant from water (E , %) and the static exchange capacity (SEC , mg/g) were calculated using the formulas:

$$E = (C_{in} - C_{eq}) \cdot 100 / C_{in} \quad (1)$$

$$SEC = (C_{in} - C_{eq}) \cdot V/g, \quad (2)$$

where C_{in} is the initial concentration of the element, mg/l ,

C_{eq} is the equilibrium concentration of the element, mg/l ,

V is the volume of the solution, l ,

g is the weight of the reagent sample, g .

The second series of experiments was carried out with reagents selected based on the results of the first stage. A polyelement model solution containing cerium and lanthanum ions was prepared. The weights of metal salts for preparing the solution were taken less than at the first stage, 0.02 g/l , which is due to lower concentrations of elements in the mobile form in the natural environment.

The sorption kinetics of elements from a model polyelement solution by reagents was studied by varying the interaction time (0.5–24 hours), the consumption of reagents was 0.5 g/l.

3 Results and discussion

The results of the chemical analysis of monoelement solutions were processed, the degree of purification and the static exchange capacity of the reagents intended for use were calculated.

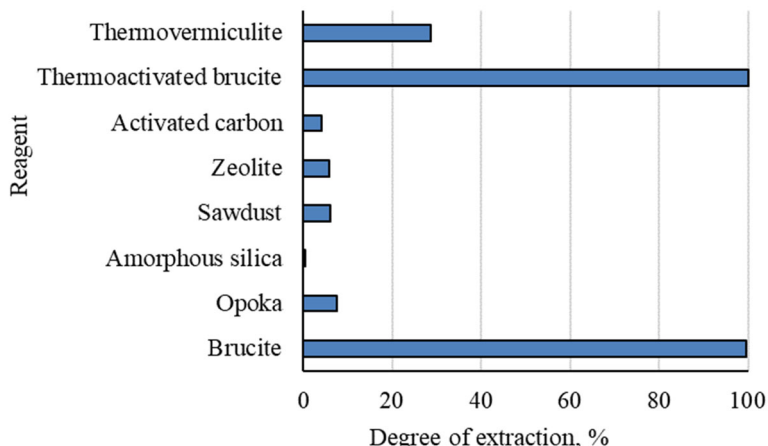


Fig. 1. The degree of purification of the model solution of cerium chloride with reagents.

Figure 1 shows the results of purification of one of the monoelement solutions using cerium chloride as an example.

The best cleaning results were achieved with thermally activated brucite (99.99%), brucite (99.52%), fired vermiculite (28.65%) and opoka (7.45%). The static exchange capacity of thermally activated brucite, brucite, calcined vermiculite and opoka with respect to cerium ions was 359.48 mg g⁻¹, 357.77 mg g⁻¹, 103.00 mg g⁻¹, 26.80 mg g⁻¹, respectively. The results of purification of the model solution of lanthanum chloride were qualitatively similar.

The mechanism of removal of REE ions from aqueous solutions using brucite can be the same as that for the adsorption of heavy metal ions due to the similarity of their properties [19]. Namely, due to parallel processes of adsorption on the surface of the mineral with the formation of bulky aqua and hydro complexes with OH groups and the replacement of Mg²⁺ ions by ions of the sorbed metal [20].

As is known, heat treatment of natural brucite at a temperature in the range of 400–600°C leads to a significant increase in the sorption capacity of the reagent due to an increase in the specific surface area and a “defective” crystal structure [21]. Unfortunately, the purification process was accompanied by a significant increase in the pH of the solution (at the end of the experiment, the pH value was about 10.2 units), which makes it impossible to use this reagent in our further work.

The sorption properties of opoka with respect to ions of heavy metals and metalloids were studied in [10, 22].

Thus, following the results of the first stage, the following were selected for a more detailed study: brucite, opoka and thermovermiculite.

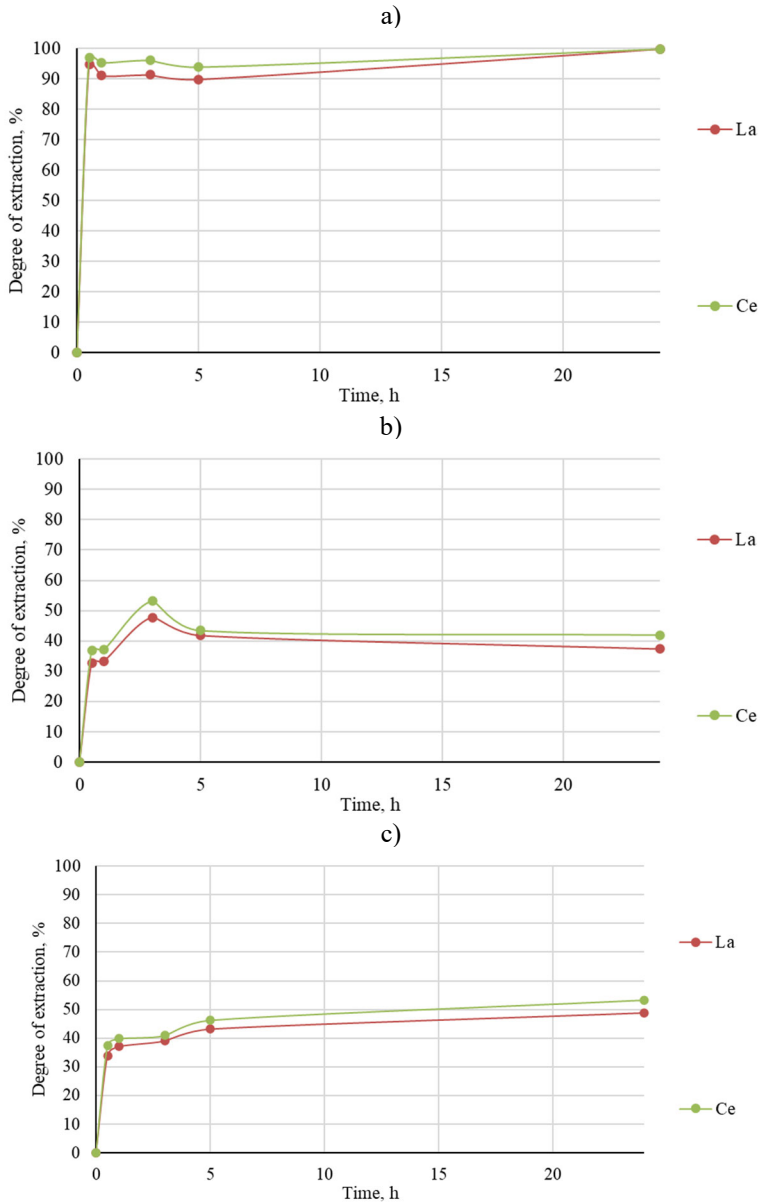


Fig. 2. Curves of sorption kinetics. From top to bottom: brucite, opoka, thermovermiculite.

The curves of the sorption kinetics of elements from a polycomponent solution are shown in Figure 2. It can be concluded that the highest degree of purification is achieved when using (in descending order of efficiency): brucite, thermovermiculite and opoka. All reagents exhibit sorption properties to the pollutants under consideration, decreasing in the series: cerium > lanthanum.

For the opoka, a slight decrease in the cleaning efficiency can be noted, probably caused by the desorption of metals after three hours of interaction.

Vermiculite, which has intermediate values of cleaning efficiency, when used, for example, in reclamation activities, will reduce the content of pollutants, increase the moisture capacity of technozems, and loosen the surface due to the layered structure.

4 Conclusion

Search experiments were carried out to remove lanthanum and cerium ions from model one-component solutions using various reagents: opoka, brucite, amorphous silica, thermovermiculite (500 °C, 2 hours), sawdust, thermally activated brucite (600 °C, 2 hours), activated carbon, zeolite.

Promising REE sorbents of the light group have been identified, namely: brucite, vermiculite and opoka, which can be used to purify water with a high content of REE or in combined sorption technologies for restoring disturbed lands in the areas of extraction and enrichment of rare metal ores.

More detailed studies of the sorption properties of the selected reagents are required.

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