Enhancing the Sorption Activity of Gaize by Thermal and Chemical Modifying

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Abstract

On the basis of opal-cristobalite rock (gaize) a sorbent is obtained for the sorption of heavy metal cations from aqueous medium. The increase in the sorption activity of gaize was achieved via thermal and chemical modification, as well as *via* immobilization by means of r-aminopropyl triethoxysilane. Optimum conditions for increasing the sorption activity of gaize have been determined. The sorption of Cu^{2+}, Ni^{2+}, Zn^{2+} on the samples obtained has been realized and the values of their SEC, TDEC with respect to the mentioned cations have been determined. The kinetics as well as the sorption dependence on the solution pH value and on background electrolyte concentration have been studied for Cu^{2+}, Ni^{2+}, Zn^{2+} cations sorption onto modified gaize from aqueous solutions.

Key words: opal-cristobalite rock − gaize, thermal activation, chemical modifying, immobilization by γ-aminopropyl triethoxysilane, Cu^{2+}, Ni^{2+}, Zn^{2+} cations sorption from aqueous medium

INTRODUCTION

One of the priority lines of activity in the field of hydrosphere protection and aquatic resources conservation consists in the prevention of the hydrosphere pollution with heavy metals. The application of various (reagent-based, electrochemical, coagulating) methods in order to extract the cations of heavy metals from waste water is expensive enough, at the same time being not necessarily the case for providing any required purification level [1]. In this connection the development of sorption methods for wastewater treatment with the use of naturally occurring materials, in particular opal-cristobalite rocks, is of currently central importance.

In the papers devoted to the sorption of heavy metals onto opal-cristobalite rocks, the authors mainly consider native sorbents, whereas the question of increasing the sorption activity, as a rule, still remains with no attention.

The opal-cristobalite rocks (diatomite, gaize, tripoli) belong to mineral wealth with a wide range of valuable properties and thus they are promising for a wide application [2].

It is known that sorption properties of the opal-cristobalite rocks are determined by the specific surface area and the sorption space volume [3].

Thermal and chemical methods of activation use to be applied in order to increase the sorption activity of naturally occurring raw material. The thermal activation results in the removal of adsorbed water and, consequently, gives rise to an increase in the adsorption space. The essence of chemical activation methods consists in the chemical interaction of a reagent with surface groups of the sorbent structure, whereby the chemical composition and porosity character (the volume and size of pores, the specific surface area) [4] are varied.

The sorption activity of the opal-cristobalite rocks could be increased to a considerable ex-

tent by means of organosilicon modifiers. The main advantage of this immobilization method consists simplicity, the possibility of obtaining a considerable amount of a grafted target substance and well as the uniformity of adsorption centres [5].

This work is devoted to considering the sorption of Cu^{2+}, Ni^{2+}, Zn^{2+} cations onto opal-cristobalite rock (gaize), thermally and chemically modified and immobilized by means of γ-aminopropyl triethoxysilane.

EXPERIMENTAL

In the experiments we used opal-cristobalite rock (gaize) from the Bogdanovichi deposit (Sverdlovsk Region). Gaize represents light, dense, fine-pored the rocks consisting mainly of the finest (<0.005 mm) silica particles. The mean density of these rocks amounts 1100–1600 kg/m^3, the porosity value amounting to 45 %. The coloring of gaizes varies from light grey up to dark grey [3]. The gaize from the Bogdanovichi deposit is characterized by the following chemical composition, mass %: SiO_2 85.2, MgO 0.65, Fe_2O_3 4.0, and Al_2O_3 4.81.

Gaize (1–2 mm sized fraction) was subjected to thermal activation *via* calcination during 3 h at the temperature ranging within 200–800 °C.

Acidic processing was carried out via boiling the gaize during 3 h in the solutions of hydrochloric and nitric acids (with a ratio of 1 : 3) whereby Fe^{3+} cations were washed out of the samples. The solution of the acids containing Fe^{3+} cations was then neutralized. The experiments were carried out with concentration of acids ranging from 0.5 to 6 mol/L, the content of Fe_2O_3 being monitored. The concentration of iron was determined by means of a photocolorimetric method with sulphosalicilic acid.

The immobilization of the activated gaize samples was carried out using 5 % γ-aminopropyl triethoxysilane solution during 30 min at 220 °C [5]. The dependence has been investigated for the amount of grafted γ-aminopropyl groups on previous thermal and acidic processing. The γ-aminopropyl triethoxysilane grafting process proceeds according to the scheme

$$\equiv SiOH + (Eto)_3Si(CH_2)_3NH_2 \rightarrow \ _\equiv SiOSi(CH_2)_3NH_2 + EtOH$$
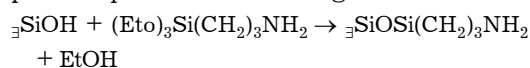
The possibility of the sorbent application depends on the porosity character, pore-size distribution, sorption space volume and specific surface area. The specific surface area and mesopore adsorption volume have been determined for the samples obtained. The textural characteristics of the samples were studied basing on the adsorption of a standard gas (nitrogen) at 77.4 K; the measurements were carried out at the Boreskov Institute of Catalysis, SB RAS (Novosibirsk).

The sorption of Cu^{2+}, Ni^{2+}, Zn^{2+} cations on the samples obtained was carried out at each modification stage. The concentration of metal cations were determined using photocolorimetry methods: Cu^{2+} with sodium diethyldithiocarbamate, Ni^{2+} with dimethylglyoxim, Zn^{2+} with dithizon.

For the tentative assessment of the sorption capabilitiy of the samples obtained with respect to the cations of metals we determined the sorption exchange capacity (SEC) *via* the contact of weighed sample (1 g) with about 50 mL of a modelling solution of metal salt during 24 h under static conditions.

The total dynamic exchange capacity (TDEC) was determined by filtering the solution containing a known concentration of metal ions under investigation through a column of 1 cm in diameter, packed with 30 g of a sample. The filtering flow rate of the solution amounted to 100 mL/h. The filtration was carried out till equal metal concentration values obtaining for the initial solution and for the filtrate.

The dependence of heavy metal cations sorption on the pH value for the medium represents one of the basic characteristics of the sorption from aqueous solutions. For establishing the dependence of the sorption process on the solution pH we chose the values of pH ranging within 2.5–6.8. The experiments were carried out under static conditions with the sample exposed to thermal treatment (200 °C), acidic treatment as well as the immobilization by means of γ-aminopropyl triethoxysilane.

The influence of electrolytes (Na_2SO_4, $CaCl_2$, $Al(NO_3)_3$) upon the sorption level was studied under static conditions at pH 6 when the sorption level is maximal.

An effect of the concentration of metal ions on the sorption level for the metal has been

TABLE 1

Fe_2O_3 washing out dependence on previous thermal and acidic activation

T_{calc}, °C	Mixture	Fe_2O_3 content, %
200	HNO_3 (6 mol/L) + 3HCl (6 mol/L)	0.63
300	HNO_3 (6 mol/L) + 3HCl (6 mol/L)	0.68
400	HNO_3 (6 mol/L) + 3HCl (6 mol/L)	0.71
400	HNO_3 (1 mol/L) + 3HCl (1 mol/L)	0.97
400	HNO_3 (0.5 mol/L) + 3HCl (0.5 mol/L)	0.8
500	HNO_3 (6 mol/L) + 3HCl (6 mol/L)	0.76
800	HNO_3 (6 mol/L) + 3HCl (6 mol/L)	0.97

Note. Here and in Tables 2−5: T_{calc} is the temperature of calcination.

TABLE 2

Dependence of grafted γ-aminopropyl groups amount on the conditions of thermal and acidic modifying

T_{calc}, °C	Acidic treatment	nNH_2, mol-eq/g
200	HNO_3 (6 mol/L) + 3HCl (6 mol/L)	0.36
400	HNO_3 (6 mol/L) + 3HCl (6 mol/L)	0.34
800	HNO_3 (6 mol/L) + 3HCl (6 mol/L)	0.25
−	−	0.22

considered at a constant pH value equal to 5.5. The studies on the kinetic laws for the sorption of Cu^{2+}, Ni^{2+} cations was carried out with the samples calcinated at 200 °C and immobilized by means of γ-aminopropyl triethoxysilane, whereas for Zn^{2+} the studies were performed with the sample calcinated at 200 °C.

RESULTS AND DISCUSSION

We have investigated the dependence of Fe_2O_3 washing out on previous thermal and acidic activation of samples (Table 1).

The content of Fe_2O_3 in native gaze amounted to 4 %. After acidic treatment a minimal content of Fe_2O_3 (0.63 %) has been revealed for the sample calcinated at 200 °C and processed by means of acids with the concentration of 6 mol/L. For the sample calcinated at 800 °C the content of Fe_2O_3 has amounted to 0.97 %, which could be connected with structural water removal. Gaize treatment with the solutions of acids with the concentration values of 0.5 and 1 mol/L exerted no considerable influence upon the content of Fe_2O_3.

TABLE 3

Specific surface area and mesopore adsorption volume depending on the conditions of modifying

T_{calc}, °C	Acidic treatment	Immobilizing by APTES	S_{sp}, m²/g	Pore volume, cm³/g
Initial sample			132	0.28
200	−	−	135	0.28
400	−	−	136	0.28
800	−	−	114	0.28
200	+	−	138	0.27
400	+	−	137	0.30
800	+	−	138	0.30
200	+	+	93	0.30
400	+	+	87	0.23
800	+	+	99	0.27

Note. Here and in Tables 4, 5: APTES is γ-aminopropyl triethoxysilane.

TABLE 4

Gaize SEC dependence on modifying conditions for Cu^{2+}, Ni^{2+}, and Zn^{2+} cations

Modifying conditions			SEC, mg/g		
T_{calc}, ^{o}C	Acidic treatment	Immobilizing by APTES	Cu^{2+}	Ni^{2+}	Zn^{2+}
Initial sample			3.0	4.5	3.8
200	–	–	4.8	6.2	6.0
400	–	–	3.8	7.0	4.7
800	–	–	2.04	5.1	2.9
200	+	–	0	0	0
400	+	–	0	0	0
800	+	–	0	0	0
200	+	+	5.6	7.3	3.7
400	+	+	5.4	7.1	2.7
800	+	+	4.3	5.0	2.3

Note. For designations see Tables 2, 3.

Table 2 displays the data obtained for the immobilization of activated samples. One can see that the process of γ-aminopropyl groups grafting onto the surface of gaize proceeds most effectively for the samples calcinated at the temperature of 200 ^{o}C (nNH_2 = 0.36 mol-eq/g). For sample calcination temperature amounting to 800 ^{o}C the amount of grafted γ-aminopropyl groups is equal to 0.25 mol-eq/g, which could be connected with the condensation of a part of silanol groups with the formation of siloxane groups.

Table 3 demonstrates the data on the specific surface area and mesopore adsorption volume are resulted depending on the conditions of modifying. One can see that the modifying does not exert any significant influence upon the variation of these parameters.

In Table 4 the results are displayed for the studies on gaize SEC with respect to Cu^{2+}, Ni^{2+}, and Zn^{2+} depending on the conditions of modifying. One can see that the maximum SEC value for Cu^{2+} and Ni^{2+} cations is inherent in the samples calcinated at 200 ^{o}C, exposed to acidic activation and immobilization by γ-aminopropyl triethoxysilane, whereas in the case of Zn^{2+} cations the maximum SEC value is observed

TABLE 5

Dependence of total dynamic exchange capacity (TDEC) on modifying conditions for Cu^{2+}, Ni^{2+}, and Zn^{2+} cations

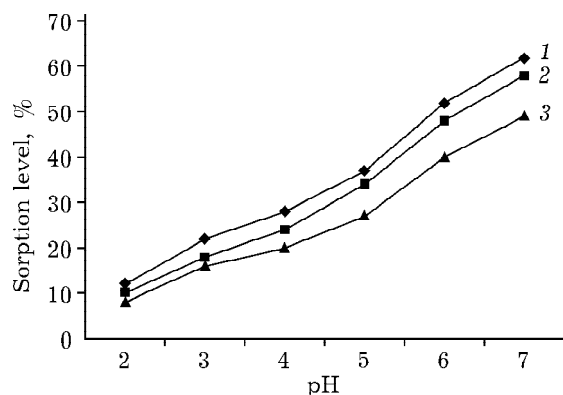| Modifying conditions			TDEC, mg/g		
T_{calc}, ^{o}C	Acidic treatment	Immobilizing by APTES	Cu^{2+}	Ni^{2+}	Zn^{2+}
Initial sample			1.6	2.1	1.7
200	–	–	2.3	3.1	2.8
400	–	–	1.7	3.4	2.2
800	–	–	0.98	2.5	1.3
200	+	–	0	0	0
400	+	–	0	0	0
800	+	–	0	0	0
200	+	+	2.7	3.7	1.7
400	+	+	2.4	3.6	1.2
800	+	+	2.1	2.6	1.1

Note. For designations see Tables 2, 3.

Fig. 1. Sorption dependence on the solution pH value for Ni^{2+} (*1*), Cu^{2+} (*2*), and Zn^{2+} (*3*) ions.
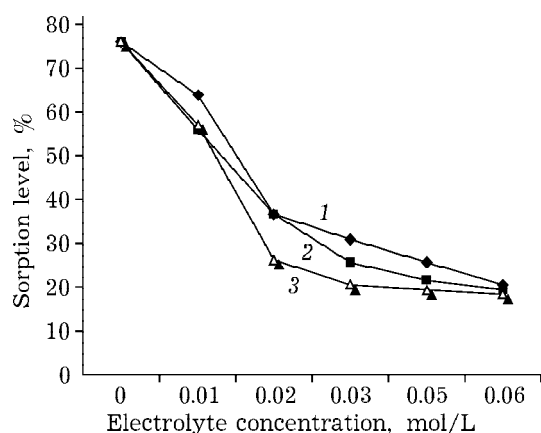
Fig. 2. Nickel sorption dependence on the background electrolyte concentration of Na_2SO_4 (*1*), $ZnSO_4$ (*2*), $Al(NO_3)_3$ (*3*).
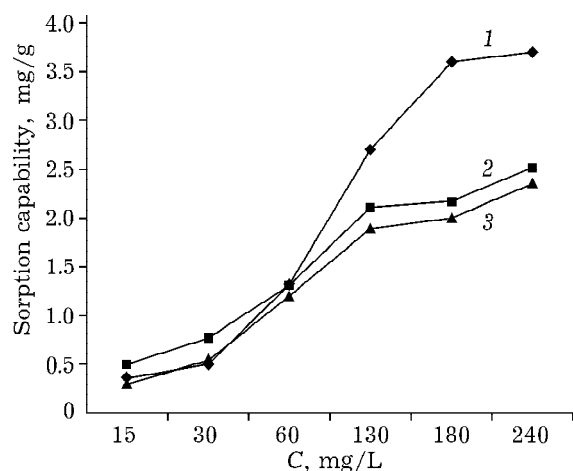
Fig. 3. Sorption isotherm for Ni^{2+} (*1*), Cu^{2+} (*2*), and Zn^{2+} (*3*) ions at pH 5.5 obtained with the sample calcinated at 200 °C.

Fig. 4. Kinetic curve for the sorption of Ni^{2+} (*1*), Cu^{2+} (*2*), and Zn^{2+} (*3*) ions.

for the sample exposed to thermal activation at 200 °C only.

Only 40–45 % of the sample capacity is realized in the dynamic mode as compared to the capacity in the static mode (Table 5).

According to the efficiency of extraction the metals could be ranged in the following order: $Ni^2 > Cu^{2+} > Zn^{2+}$ (Fig. 1). The maximum sorption level is attained at pH 5.5–6.5. Under acidic conditions (pH < 4) the extraction of the metals being in the cationic form, is reduced owing to the competitive action of acid, whereas the formation of hydrolysed forms of metal ions those can be sorbed is observed at pH > 5. It should be noted that the sorption activity of gaize in the neutral media could be also connected with the presence of impurities influencing the sorption level in naturally occurring silica.

Figure 2 displays the curves for nickel sorption level depending on the concentration of background electrolyte. One can see that with the increase in the concentration of electrolyte (as well as the charge of salt cation) the sorption level decreases.

The adsorption isotherms obtained (Fig. 3) indicate that with the increase in the concentration of metals the sorption capability increases in a regular manner and can be described by the Langmuir adsorption isotherm.

For all the three metals the character of kinetic curves has appeared similar to each other (Fig. 4). Within the first four hours the concen-
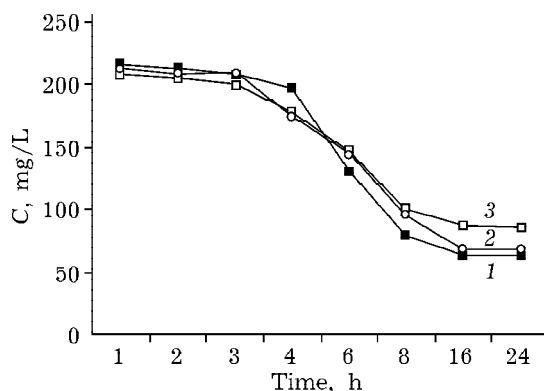
tration of metals exhibits almost no changes, then an abrupt decrease in the concentration is observed and the dynamic equilibrium is attained in 7−8 h. A low sorption rate value, most likely, could be caused by the specificity of the behaviour of metal ions in the solution and their interaction with grafted amino groups.

CONCLUSION

Thus, optimum conditions are determined for thermal and chemical modification of gaize in order to adsorb Cu^{2+} and Ni^{2+} cations (sample calcination temperature of 200 ºC, acidic processing by the mixture of nitric and hydrochloric acid solutions with the concentration of 6 mol/L, immobilization by 5 % aqueous solution of γ-aminopropyl triethoxysilane) as well as Zn^{2+} cations (calcination temperature of 200 ºC). The maximal sorption level for Cu^{2+}, Ni^{2+}, and Zn^{2+} cations is attained at pH 5.5−6.5. The dynamic equilibrium for all the metal cations is established within 7 h.

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