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Composition, Structure, and Sorption Capacity of Natural Aluminosilicates

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Abstract—Comprehensive study of the composition, structure, and sorption properties of a typical representative of natural aluminosilicates has been performed. The efficiency of extraction of nickel cations from aqueous solutions with a concentration of 10^{-5} to 10^{-2} M has been determined. Such sorbent characteristics as chemical and mineralogical composition, specific surface, porosity, maximum sorption capacity, and number of active sites (as well as its estimate obtained by heterogeneous potentiometric titration) have been found to be mutually consistent.

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Ion-exchange properties of natural aluminosilicates are determined by a combination of interrelated factors, such as chemical and mineralogical composition, crystallinity, number of active sites, porosity parameters, and conditions and results of chemical and thermal treatment. However, studies on sorption properties of particular samples often do not consider the complete set of the aforesaid factors [1–4], especially in adsorption–structural studies, substantiation of the solid/liquid phase ratio, and independent estimation of the number of surface active sites by different methods. As a result, comparison of published data and prediction of sorption properties for particular samples become difficult. The above stated also applies to some extent to solid surface studies. Nevertheless, fairly comprehensive and consistent description and analysis of interrelations of the above properties may be possible within the scope of conventional research practice. This is demonstrated in the present work using as an example a typical representative of natural aluminosilicates, clay from the Lukovskoe deposit in Pskov oblast.

According to the X-ray fluorescence analysis data, the main components of the selected sample are the following oxides (wt %): SiO_2 (55.16), Al_2O_3 (15.52), CaO (6.51), Fe_2O_3 (5.33), MgO (2.73), K_2O (1.0), Na_2O (0.83), TiO_2 (0.81). This composition suggests potential sorption capacity the clay. The [Al] : [Si] ratio is about 1 : 3, which is known [5] to be optimal for ensuring required number and strength of surface acid centers. In the examined sample, these centers are occupied mainly by Na^+ and K^+ cations; efficient exchange of the latter for heavy metal cations that form poorly soluble aluminosilicates in acid medium is quite possible. Therefore, the maximum sorption capacity of the clay may be estimated *a priori*.

It is generally believed that sodium and potassium cations are involved in ion exchange and that Ca^{2+} and Mg^{2+} are structure-forming components of natural aluminosilicates [1, 4, 6]. The overall concentration of Na_2O and K_2O in the clay sample is ~0.24 mmol/g, and we presume that this value reflects the maximum sorption capacity for doubly charged heavy metal cations. To check this assumption let us consider the sorbent structure and specific features of adsorption of Ni^{2+} ions on its surface.

The results of X-ray powder diffraction analysis are collected in table. The degree of crystallinity was estimated at a relatively low level (~9%) by comparing the areas under diffraction peaks and background noise on the X-ray powder diffraction pattern. However, it is important that the major crystalline mineral component is montmorillonite and that kaolinite and muscovite are concomitant phases. The presence of montmorillonite as the major phase (60%) is consistent with the [Al] : [Si] ratio equal to ~1 : 3 [6] which reflects potential ion-exchange capacity of the sorbent.

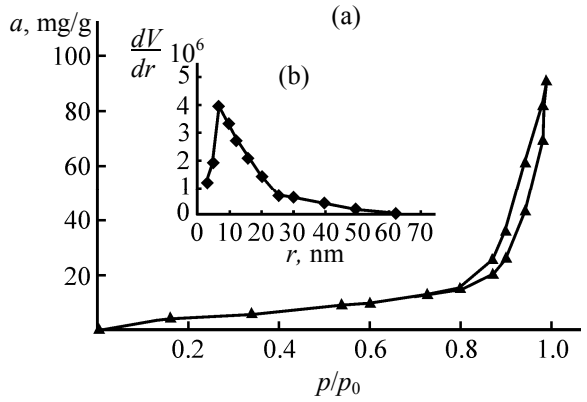

Fig. 1. (a) Isotherm of water adsorption by aluminosilicate and (b) pore size distribution calculated therefrom; p/p_0 is the partial vapor pressure, and r is the pore radius.

The porosity parameters if the sorbent were determined by studying adsorption of water on samples preliminarily dried at 120°C until constant weight. The adsorption isotherm shown in Fig. 1 is typical of microporous adsorbents. The specific surface (S_{sp} = 14 m^2/g) was calculated using the Brunauer–Emmett–Teller equation (1) [7]:

$$S_{sp} = a_m N_A \omega, \quad (1)$$

where a_m = 0.24 mmol/g is the monolayer capacity of adsorbed water, N_A is the Avogadro number, and ω = 10 Å^2 is the adsorption cross section of the adsorbed molecule. From the narrow pore size distribution (Fig. 1) calculated on the basis of the hysteresis loop parameters [7] we obtained the average pore radius ($r \sim 7$ nm).

Extraction of Ni^{2+} ions by the clay from acidic (pH 2) aqueous $Ni(NO_3)_2$ solutions ($c = 10^{-5}$ to 10^{-2} M) was studied under static conditions at a constant sorbent to liquid phase ratio (0.4 g of the sorbent per 10 mL of solution; 1 : 25). Acid medium favors the sorbent to act in its native cationic form due to neutralization of alkali released into the solution during ion exchange process. Examination of the sorption kinetics showed that, despite vigorous sorption in the initial period, in all cases the equilibrium state was reached only after 24 h. An appreciable diffusion inhibition is determined by the presence of fine pores in the sorbent (Fig. 1). Nevertheless, about 70–80% of the equilibrium amount of Ni^{2+} is adsorbed within the first 5–6 h of contact with solution.

Concentrations of crystalline minerals in the aluminosilicate sample

2θ, deg	Montmorillonite, %	Muscovite, %	Kaolinite, %	Miller indices
21.8776	6.51	–	–	(1 1 1)
27.5849	43.84	–	–	(1 1 3)
30.3512	9.90	–	–	(1 1 16)
35.9450	–	–	5.13	(2 0 0)
37.4696	–	5.05	–	(2 0 4)
43.3330	–	–	5.73	(1 2 3)
51.0537	–	10.37	–	(2 2 6)
60.9342	–	6.77	–	(1 3 11)
69.2444	–	6.69	–	(2 2 11)

An important parameter which is often not optimized while studying ion-exchange processes is the sorbent-to-solution (solid/liquid) ratio S/L. Just this fact hinders comparison of the results of different studies performed with the same substrate. Figure 2 shows that increase in the sorbent amount, the solution volume remaining constant ($c = 6.2 \times 10^{-4}$ M) is accompanied by expected reduction of the amount of adsorbed Ni^{2+} per gram of the sorbent. However, the degree of extraction of Ni^{2+} ions rapidly increases, attains 97% at S/L = 1/25, and then almost does not change (Fig. 2).

The experimental dependence of the amount of adsorbed Ni^{2+} ions (Q) on the concentration of $Ni(NO_3)_2$ is described by the first type isotherm (Fig. 3), and it becomes linear in the Langmuir coordinates [Eq. (2)] [7].

$$1/Q = 1/Q_{max} + 1/Q_{max}\, b\, c. \quad (2)$$

We thus determined the maximum sorption capacity (Q_{max} = 0.11 mmol/g), the sorption/desorption equilibrium constant (b = 176.34), and the corresponding Gibbs energy (ΔG = –12.6 kJ/mol). The change in the free energy indicates a steady process leading to firm fixation of Ni^{2+} cations on the aluminosilicate surface in acid medium. It is interesting to compare the experimental maximum sorption capacity for Ni^{2+} (Q_{max} = 0.11 mmol/g) with the prediction made on the basis of the sorbent composition (0.24 mmol/g; see above). Presumably, accessible active surface of the sorbent contains approximately a half of the total amount of alkali metal cations, and just those active sites on the surface involved in ion exchange process determine the observed sorption capacity. As a result, the degree of extraction of Ni^{2+} is 95–97% at low Ni^{2+} concentration in solution ($c = 10^{-5}$–10^{-4} M), the S/L ratio being greater than or equal to 1/25.

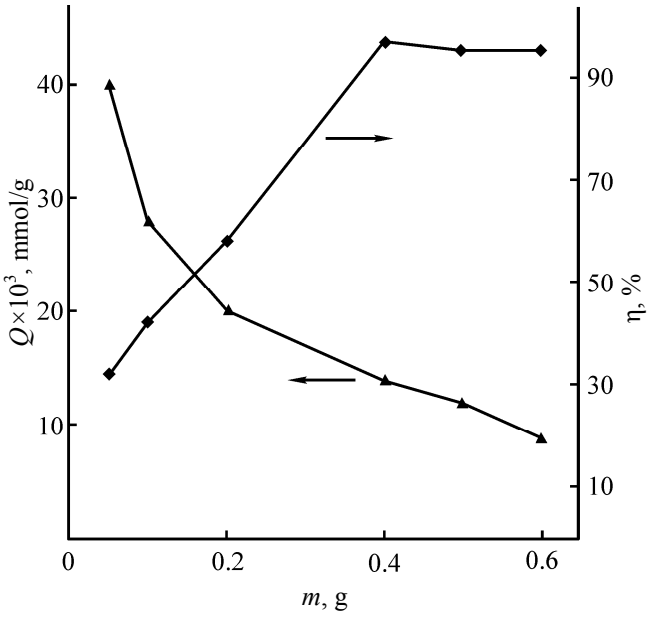

Fig. 2. Plots of the (*1*) amount of adsorbed Ni^{2+} ions (Q) and (*2*) degree of their extraction (η) from an aqueous solution of $Ni(NO_3)_2$ ($c = 6.2\times10^{-4}$ M) versus the sorbent amount (m).

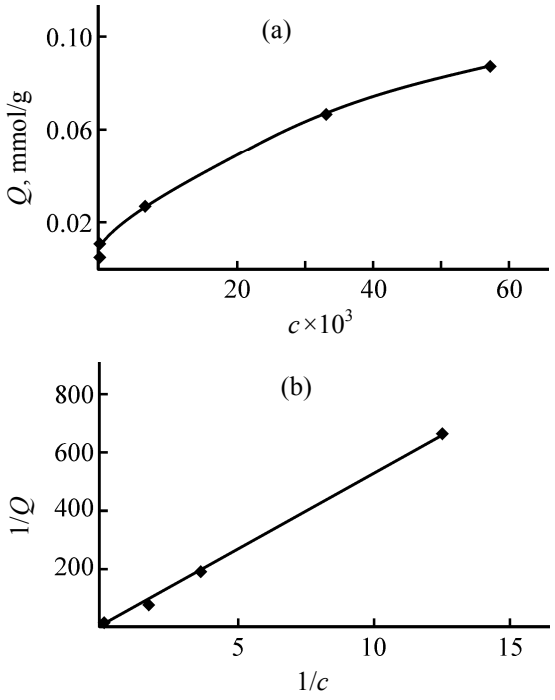

Fig. 3. (a) Plot of the amount of adsorbed Ni^{2+} ions (Q) vs. concentration of aqueous $Ni(NO_3)_2$ solution and (b) its linearization in the Langmuir coordinates.

It is seen that the maximum sorption capacity (Q_{max} = 0.11 mmol/g, 0.22 mequiv/g) is consistent with the water monolayer capacity (a_m = 0.24 mmol/g). Obviously, surface active sites accessible to water vapor are almost equally accessible to nickel cations in solution, which may be regarded as an indirect support for high degree of occupation of the sorbent surface by Ni^{2+} ions. In addition, estimation of the adsorption cross section of Ni^{2+} by Eq. (3) assuming Q_{max} = 0.11 mmol/g gave a value of ~0.2 nm^2 which matches well with the hydrated nickel ion size.

$$\omega(Ni^{2+}) = S_{sp}\, Q^{-1}\, N_A^{-1}. \quad (3)$$

Finally, Fig. 4 shows the potentiometric titration curve of an aqueous suspension of the sorbent (Fig. 4). The initial pH value equal to 9.65 reflects equilibration between the glass electrode and alkaline surface of solid particles. The amount of acid necessary to adjust the suspension to a neutral pH value is 0.22 ± 0.03 mmol/g, which coincides with the maximum sorption capacity for Ni^{2+} (Q = 0.22 mequiv/g) and is close to the monolayer capacity of adsorbed water (a_m = 0.24 mmol/g). The observed agreement between independently determined parameters indicates high surface coverage of the aluminosilicate sorbent with alkali metal cations and reflects their activity in both ion exchange and adsorption processes. Characteristically, the subsequent titration of the suspension (pH < 7.0) requires considerably longer time for equilibration of the system, and an inflection point is clearly observed on the titration curve (Fig. 4). Presumably, this step corresponds to gradual extraction of difficultly accessible Na^+ and K^+ cations from the near-surface layer. Thus, acid titration of a suspension of aluminosilicate sorbent in its native cationic form

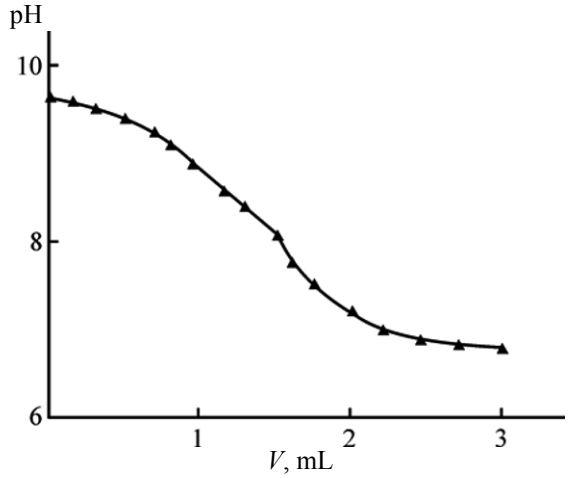

Fig. 4. Titration of an aqueous aluminosilicate suspension with hydrochloric acid (s = 0.1 M, V is the titrant volume).

provides a useful tool for preliminary estimation of its ion-exchange capacity.

EXPERIMENTAL

The elemental composition of the sorbent was determined with the aid of an X–Art M X-ray fluorescence analyzer equipped with appropriate software for data processing. The X-ray powder diffraction analysis was performed using a DRON-7 diffractometer with a copper anode (λ 1.5406 Å).

The sorption capacity was determined from the reduction of Ni^{2+} concentration which was measured by the photometric method implying formation of a colored complex with dimethylglyoxime [8].

Adsorption of water was studied at room temperature; the partial vapor pressure p/p_0 was set using sulfuric acid solutions. Samples of the sorbent were preliminarily dried at 120°C until constant weight (to remove adsorbed water) and were then placed in succession in a series of desiccators with increasing humidity. The equilibration time was about 24 h. After saturation (p/p_s = 0.99), desorption branch of the isotherm was obtained by gradually reducing the partial vapor pressure.

Potentiometric titration of an aqueous aluminosilicate suspension was performed with aqueous hydrochloric acid (c = 0.1 M) under continuous vigorous stirring.

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