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# Adsorption of calcium cations on glauconite concentrate from aqueous solutions containing sulfate and nitrate anions

V.I.Vigdorovich<sup>1</sup>, L.E.Tsygankova<sup>2\*</sup>, I.V.Morschina<sup>1</sup>, N.V.Shel<sup>3</sup>, M.N.Esina<sup>2</sup>, A.A.Uryadnikov<sup>2</sup>

<sup>1</sup>All-Russian Scientific Research Institute of Use of Equipment and Oil Products of the Russian Academy of Sciences, 392022, Tambov, (RUSSIA)

<sup>2</sup>Derzhavin State University, 392000, Tambov, (RUSSIA)

<sup>3</sup>Tambov State Technical University, 392000, Tambov, (RUSSIA)

E-mail: vits21@mail.ru

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**Abstract :** Adsorption ability of 95% glauconite concentrate of Bondar deposit (Russia) has been studied with respect to Ca<sup>2+</sup> ions from the chloride media. Influence of the initial concentration of Ca<sup>2+</sup>, additives of sodium sulfate and potassium nitrate and their concentration, sorption duration, adsorbent amount on the equilibrium time and efficiency of adsorption has been studied. Ca<sup>2+</sup> specific adsorption decreases with increasing ionic strength of the solution because of extraneous salts insertion. The isotherm model which best represented the data obtained was the Langmuir model.

Langmuir parameters for Ca<sup>2+</sup> adsorption on the glauconite concentrate from the chloride solutions in the absence and presence of the extraneous salts were calculated.

Characterization of the glauconite concentrate was achieved by X-ray diffraction, FTIR spectroscopy and thermogravimetry.

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**Keywords :** Glauconite; Calcium cation; Adsorption; Ionic strength.

## INTRODUCTION

Adsorption processes have been widely applied for the removal of contaminants from water and wastewaters. Natural sorbents can be considered highly promising materials at least for two technical applications, e.g. for drinking water purification and sorption sewage treatment, and as bioindicators of lithosphere, hydrosphere and atmosphere contamination. In first case, clay minerals are more perspective. Their im-

portant characteristics are widespread, low cost of mining and application and high environmental purity<sup>[1,2]</sup>. Their shortcoming is relatively low maximum adsorption capacity (mmole g<sup>-1</sup>). So, cationic exchange capacity for a number of montmorillonites, vermiculites and caolinities fluctuates between 0.01 and 0.80<sup>[3]</sup>. Additionally, the clay minerals in different deposits substantially differ in chemical composition, physico-chemical properties and therefore in sorption capacity. These shortcomings are easily compensated with

nominal value of natural sorbents and simplicity of regeneration. Modification of such sorbents makes it possible to multifold increase of capacity. So, chitosan modified calcium silicate hydrate exhibits highly efficient adsorption behavior toward heavy metal ions of  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ . Their maximum adsorption amounts are equal to 406, 400, 796, 425 and 578 mg/g, respectively<sup>[4]</sup>.

The specific surface area of this modified sorbents is equal to  $356 \text{ m}^2\text{g}^{-1}$ . Modification, of course, heightens a cost of the mineral. Such effects are characteristic for aluminum modified hematite, zeolitic tuff and calcite<sup>[5]</sup> applicable for the removal of fluoride ions from water. Modification of montmorillonite with ester-containing Gemini surfactant substantially increases sorption of triclosan<sup>[6]</sup>.

Special interest is connected with adsorption of cations of heavy metals at their joint presence. In<sup>[7]</sup> the adsorption of Cd (II), Cu(II), Pb (II) and Zn(II) onto kaolinite was studied in single- and multi-element systems. Adsorption isotherms at pH=6.0 in the multi-element systems showed that there is competition among various metals for adsorption sites on kaolinite at their equal concentrations. In<sup>[8,9]</sup> kinetics of Cu(II) and Zn(II) sorption onto kaolinite/ montmorillonite, kaolinite/goethite and montmorillonite/ goethite mixed sorbents was studied from aqueous solutions as function of solution composition and aging. Mineral mixing reduced the exchange of protons for sorbing ions and the acidity of the reactive sites, thus impeding Cu and Zn removal by proton exchange. In addition, the transfer rate of Cu relative to the single mineral suspensions is reduced<sup>[8]</sup>. But enhanced Cu sorption on the montmorillonite/ goethite as age increased is attributed to increased hydroxylation of the mineral surface resulting in the formation of new reactive sites<sup>[9]</sup>. In<sup>[10]</sup> importance of assessment of thermodynamic parameters for adsorption equilibrium of heavy metals and dyes is noted. In<sup>[11]</sup> the ability of untreated bentonite to remove Cd(II) and Zn(II) from aqueous and acid solutions at different pH values has been studied for different metal concentrations by varying the amount of adsorbent, temperature, stirring speed, and contact time. The highest adsorption for Zn and Cd was 99.85 and 96.84%, respectively. Ultrasonic desorption for these metals was 66.57 and 51.37%, respectively. Results of study of exchange

of the clinoptilolite tuff cations with hydrogen ions from HCl solution of concentration  $0.1 \text{ mmol/cm}^3$  and ammonium ions solutions of concentration 0.0071 to  $2.6 \text{ mmol/cm}^3$  are presented in<sup>[12]</sup>. The obtained results show that at ammonium ion concentration lower than  $0.1 \text{ mmol/cm}^3$  the exchange capacity decreases in the row:  $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ . At ammonium concentration from 0.2 to  $1 \text{ mmol/cm}^3$  the order is  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ . At concentration higher than  $1 \text{ mmol/cm}^3$  the order is  $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ . During decationization of the clinoptilolite in acid solution, best exchanged are  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions, while exchange of  $\text{K}^+$  ions is the poorest.

Among various bioindicators, mosses are widely used because their capacity to reflect the chemical composition of the surrounding atmosphere is due to the fact of absence of root<sup>[13]</sup>. Their sorption efficiency is considered both in the earliest studies<sup>[14-19]</sup> and in the investigations of recent years<sup>[20-22]</sup> including studies of heavy metal adsorption<sup>[23,24]</sup>. Biosorbents are too applicable for sewage treatment. So, the rice bran has been successfully utilized for the removal of Cr(VI) from wastewater<sup>[25]</sup>. The maximum removal was found to be 99.4% at pH=2 and initial Cr(VI) concentration of 200 mg/L.

The aim of present work is study of cations  $\text{Ca}^{2+}$  sorption on glauconite concentrate of Bondar deposit (Russia) from the chloride solution and in the presence of sodium sulfate and potassium nitrate. Sum mass of the deposit is equal to 400 million t, therefore it is attractive raw materials base. In addition, this sorbent is effective in adsorption of aniline and phenol<sup>[26]</sup>. Sorption of phenol on glauconite has been studied most in detail<sup>[27-32]</sup>. Efficiency of phenol sorption from the aqueous solutions on 95 % glauconite concentrate obtained after initial mineral concentration has been studied. Effect of fractional composition, contact time, previous heat treatment of adsorbent was studied<sup>[27]</sup>. Thrice –repeated sorption from stirring irremovable solutions with new portion of sorbent allows to remove 99 %  $\text{C}_6\text{H}_5\text{OH}$ . Effect of linear speed of solution stream, pH value, sorbent layer thickness has been studied. The highest adsorption was 99.98% at the optimal conditions<sup>[28,29]</sup>. Desorption of adsorbed phenol was made by ethyl- and butyl acetate<sup>[31]</sup>. Effect of temperature (20 –  $400^\circ\text{C}$ ) on crystal lattice param-

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eters of glauconite was studied<sup>[32]</sup>. Patent for adsorption of iron cations from drinking and sewage water on glauconite was taken out<sup>[33]</sup>. In<sup>[34]</sup> adsorption of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$  ions from aqueous solutions on glauconite of Karinsky deposit was studied. The isotherm model which best represented the data obtained was Langmuir one. Corresponding values of maximum adsorption ( $q_{\text{max}}$ , mmole/g) are equal to:  $0.129 \pm 0.009$  ( $\text{Ca}^{2+}$ );  $0.107 \pm 0.009$  ( $\text{Mg}^{2+}$ );  $0.163 \pm 0.012$  ( $\text{Fe}^{3+}$ );  $0.121 \pm 0.010$  ( $\text{Mn}^{2+}$ );  $0.159 \pm 0.016$  ( $\text{Zn}^{2+}$ ); (pH=6). Obtained data in<sup>[1]</sup> and<sup>[34]</sup> conform to each other.

## EXPERIMENTAL

### Characterization of glauconite

95% glauconite concentrate was used with chemical composition, wt.%:  $\text{K}_2\text{O}$  9.5;  $\text{Na}_2\text{O}$  - 4.1;  $\text{Al}_2\text{O}_3$  - 14.8;  $\text{Fe}_2\text{O}_3$  - 11.5;  $\text{FeO}$  - 5.3;  $\text{SiO}_2$  - 48.1;  $\text{H}_2\text{O}$  - 6.7.

The characterization of glauconite was achieved by X-ray diffraction (instrument Dron-3,  $\text{CuK}_\alpha$ -radiation with wavelength equal to 0.154 nm, Ni filter). X-ray reflection values corresponding to the interfacial distance, nm, and their relative intensities (% , in brackets) are 0.995 (22); 0.498 (200); 0.331 (100); 0.319 (32); 0.246 (32); 0.224 (8); 0.199 (40); 0.194 (3).

FTIR spectrum of glauconite (spectrometer Infracum FT-801) is shown in Figure 1.

A band of absorption observed between 3930-3690  $\text{cm}^{-1}$  is assigned to OH-stretching vibration modes in water molecules and Si-OH groups. Such OH groups are as a rule connected with  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  cations too<sup>[1]</sup>. Partly they are caused with a presence of molecular H-bonds between water molecules. The bands corresponding to 600 and 685  $\text{cm}^{-1}$  can be assigned to deformation vibrations of OH-groups. Poor bands at 1000 and 1100  $\text{cm}^{-1}$  is assigned to valence vibrations of Si-O bonds. The bands at 1570 and 1380  $\text{cm}^{-1}$  are characteristic for the glauconite and are not observed for other lamellar materials<sup>[1]</sup>.

Thermogravimetry (TG) of glauconite (Figure 2) was made under air - argon (3:1) atmosphere using thermogravimetric analyzer STA 449F3 Jupiter (Netzsch, Germany). Glauconite, independently from temperature of its previous heat treatment, is characterized with a presence of endothermic effect at 100°C caused by vaporization of water. Intensity of endothermic effect decreases with increasing temperature of previous heat treatment. This is caused by an increase of water vaporization. However, main bulk of water is removed at temperature of endothermic effect. Water removal continues with following growth of temperature, but its contribution is small. So, till temperature of 150°C glauconite loses 4%  $\text{H}_2\text{O}$ , but following growth of temperature up to 500°C causes additional loss of 2%  $\text{H}_2\text{O}$ . Thus, glauconite loses water in all temperature range 25-600°C, but most effectively near 100°C.

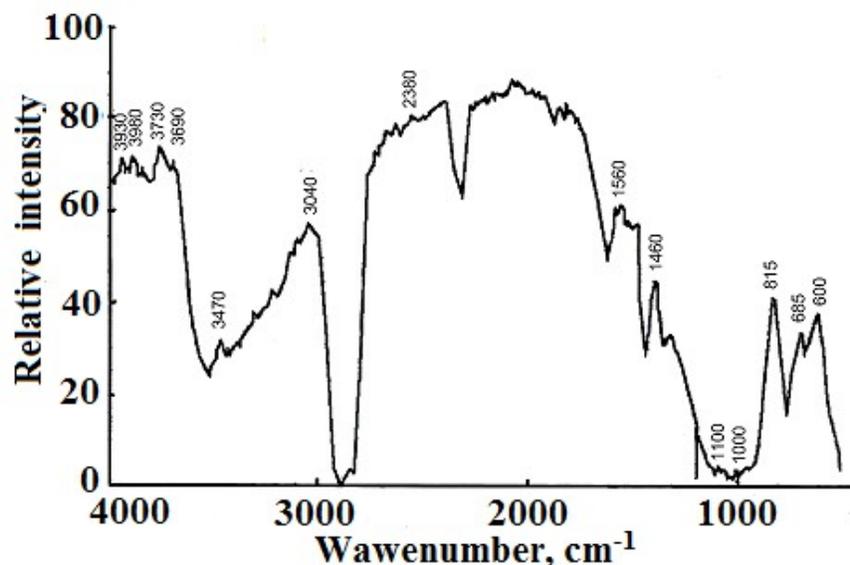


Figure 1 : Infrared spectrum of glauconite concentrate without preliminary preparation.

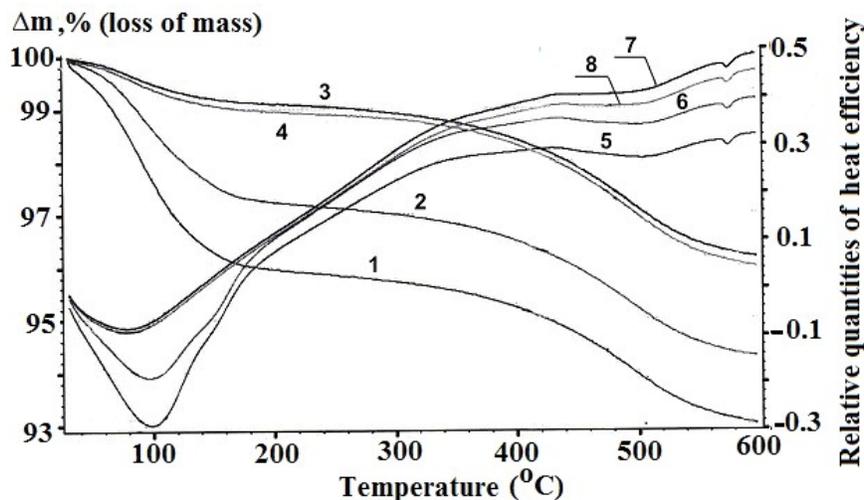


Figure 2 : TG profiles for glauconite concentrate. Dependence of mass loss (1-4) and heat efficiency values (5-8) on temperature. Preliminary thermal treatment (20 min), °C: 1 and 5 – absent, 2 and 6 – 200, 3 and 7 – 250, 4 and 8 -300.

### Chemicals

In the adsorption experiments, analytical-grade  $\text{CaCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KNO}_3$ ,  $\text{NaCl}$  and twice distilled water were used.

Addition of  $\text{Na}_2\text{SO}_4$  and  $\text{KNO}_3$  was used for an estimation of the extraneous salts influence on  $\text{Ca}^{2+}$  adsorption. The used concentration of sulfate ions in parallel experiments was equal to 16.5 and 1.65 mmole/L and did not admit deposition of  $\text{CaSO}_4$  in accordance with its value of  $L_p$  equal to  $6.10 \cdot 10^{-5}$ <sup>[36]</sup> and  $9.01 \cdot 10^{-5}$ <sup>[37]</sup>. Ionic strength of used solutions ( $\mu$ ) was in the range of 0.00425 – 0.06454 and activity coefficient  $f_{\pm}$  equal to 0.624 – 0.870 in accordance with second Debye approach

$$\log f_{\pm} = -0.506Z_+Z_- \sqrt{\mu} / (1 + \sqrt{\mu}),^{[38]}$$

nevertheless could not promote  $\text{CaSO}_4$  salting out. Concentration of nitrate ions was 5.0 and 0.5 mmole/L in the experiments.

Before the experiments, 95 % glauconite concentrate was wash off from  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions with 3M  $\text{NaCl}$  solution.

### Adsorption studies

The adsorption experiment were performed in polypropylene flasks continuously agitated with a Teflon coated magnet stirrer at  $20 \pm 2^\circ\text{C}$ . The initial  $\text{Ca}^{2+}$  concentration was 2.5mmole/L and diluted twofold, fourfold, sixfold and eightfold at the constant concentration of  $\text{Cl}^-$  ions that was achieved by insertion of calculated quantity of  $\text{NaCl}$ .

For the adsorption kinetic experiment, 100 mL of solution and 1, 2, 3 or 5 g of the adsorbent were added in each flask. After agitation for 5 – 60 min the adsorbent was removed by paper filtration and the respective solutions were analyzed by titration with EDTA solution in the presence of eriochrome black T at  $\text{pH}=10$ .

The adsorption capacity, expressed as the amount of  $\text{Ca}^{2+}$  adsorbed per gram of adsorbent ( $\text{mg g}^{-1}$ ) was calculated as follows

$$q_{\tau} = V(C_0 - C_{\tau})/m,$$

where  $q_{\tau}$ ,  $C_0$ ,  $C_{\tau}$  are the amount of  $\text{Ca}^{2+}$  adsorbed ( $\text{mg g}^{-1}$ ) at contact time  $\tau$ , the initial concentration of  $\text{Ca}^{2+}$ , and its concentration ( $\text{mg L}^{-1}$ ) at contact time  $\tau$  in the solution respectively.  $V$  is the volume (L) of the solution in the flask and  $m$  (g) is the dosage of adsorbent.

Efficiency of adsorption ( $\rho$ , %) was calculated as ratio of the  $\text{Ca}^{2+}$  amount adsorbed for certain time of contact and its initial amount in the solution.

The solution pH was equal to 5.8-5.9 because of contact with  $\text{CO}_2$  of air.

## RESULTS AND DISCUSSION

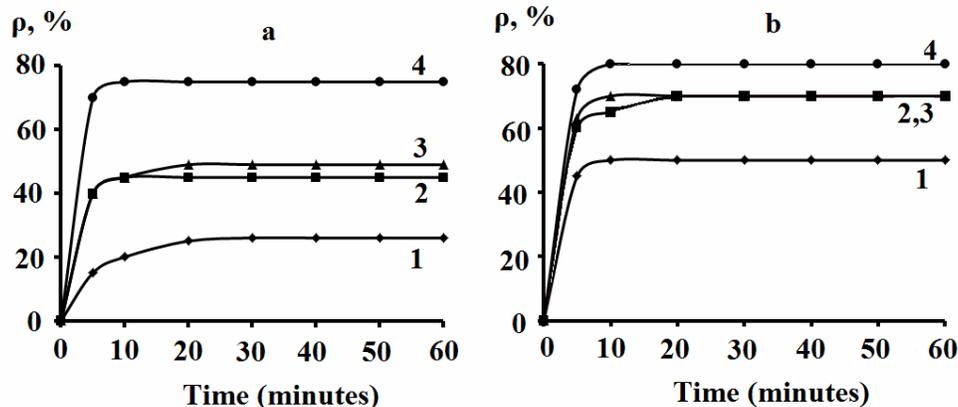
### Adsorption from chloride solutions without other anions

The adsorption kinetics curves showed that the equilibrium time is sufficiently small (Figure 3). Efficiency of adsorption increases with increasing adsorbent amount. So, insertion of 1 g adsorbent into the

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solution containing 2.5 mmol/L  $\text{Ca}^{2+}$  permits to obtain  $\rho$  value equal to 26%. Growth of the adsorbent amount up to 5 g results in  $\rho$  value equal to 74%. (Figure 3a). One can see that  $m_5/m_1 > \rho_5/\rho_1 = 2.8$  (where lower index corresponds to the adsorbent amount). Twofold decrease of initial  $\text{Ca}^{2+}$  concentration leads to  $\rho_5/\rho_1 = 1.5$  at the same value of  $m_5/m_1 = 5$ . This picture can be explained with adhesion of adsor-

bent particles inducing a decrease of their effective specific surface  $S_{sp}$ . Growth of adsorbent amount in the stirred solution induces an increase of quantity of adsorbent particles in unit of solution volume and frequency of their collisions. This causes their adhesion and  $S_{sp}$  decrease. The same picture is observed and at fourfold (Figure 3b) and at eightfold decrease of  $\text{Ca}^{2+}$  concentration in the initial solution.



**Figure 3 :** Dependence of efficiency of  $\text{Ca}^{2+}$  adsorption ( $\rho$ , %) from the chloride solutions containing 2.50 (a) and 0.625 (b) mmol/L of  $\text{Ca}^{2+}$  on contact time and the adsorbent amount, g: 1–1; 2–2; 3–3; 4–5.

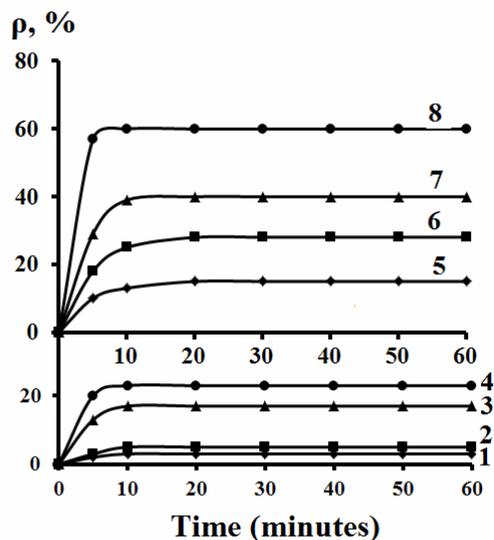
One can see rather small adsorption capacity of glauconite concentrate characteristic for clay minerals<sup>[1,2,34,40,41]</sup>.

## Adsorption from chloride solutions containing sodium sulfate

Insertion of 16.5 mM  $\text{Na}_2\text{SO}_4$  into the 2.5 mM  $\text{CaCl}_2$  solution increases ionic strength and substantially decreases activity coefficient  $f_{\pm}$ . This leads to a decrease of efficiency of  $\text{Ca}^{2+}$  adsorption ( $\rho = 22\%$  in the presence of 5 g adsorbent) (Figure 4, curves 1-4). Tenfold decrease of  $\text{Na}_2\text{SO}_4$  concentration and lowering of ionic strength of the solutions, that is equal to 0.015 and 0.016 in the absence and presence of  $\text{Na}_2\text{SO}_4$  respectively, substantially increase of  $\text{Ca}^{2+}$  adsorption ( $\rho = 63\%$ ) (Figure 4, curves 5-8).

Such an effect is caused with fourfold decrease of the initial  $\text{Ca}^{2+}$  concentration (Figure 5). In the presence of 16.5 mM  $\text{Na}_2\text{SO}_4$   $\rho = 50\%$  at  $m = 5$  g. Tenfold decrease of  $\text{Na}_2\text{SO}_4$  concentration increases  $\rho$  value up to 77%. However, in this case, effect of lowering of  $\text{Na}_2\text{SO}_4$  concentration is less than in more concentrated  $\text{CaCl}_2$  solution (Figure 4 and 5). At the same time, the equilibrium time does not practically depend on the

concentration of  $\text{Ca}^{2+}$  and  $\text{Na}_2\text{SO}_4$  (Figure 4, 5). This time is near 20 min.



**Figure 4 :** Dependence of efficiency of  $\text{Ca}^{2+}$  adsorption ( $\rho$ , %) from 2.5 mM  $\text{CaCl}_2$  solutions containing 16.50 (1-4) and 1.65 mM (5-8)  $\text{Na}_2\text{SO}_4$  on contact time and the adsorbent amount, g: 1 and 5–1; 2 and 6–2; 3 and 7–3; 4 and 8–5.

## Adsorption from chloride solutions containing potassium nitrate

Insertion of 5.0 mM  $\text{KNO}_3$  into the 2.5 mM  $\text{CaCl}_2$

solution decreases the equilibrium value of  $\rho$  substantially less than maximum studied  $\text{Na}_2\text{SO}_4$  concentration (Figure 3 and 6). This picture is practically observed in the presence of all glauconite amounts from 1 to 5 mg. Simultaneously a growth of ionic strength of the solution  $\mu$  because of insertion of 5.0 mM  $\text{KNO}_3$  is appreciably less ( $\Delta\mu=0.005$ ) than in the presence of 16.5 mM  $\text{Na}_2\text{SO}_4$  ( $\Delta\mu=0.495$ ).

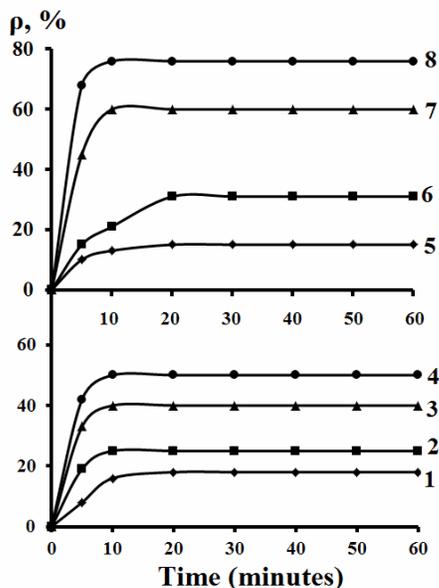


Figure 5 : Dependence of efficiency of  $\text{Ca}^{2+}$  adsorption ( $\rho$ , %) from 0.625 mM  $\text{CaCl}_2$  solutions containing 16.50 (1-4) and 1.65 mM (5-8)  $\text{Na}_2\text{SO}_4$  on contact time and the adsorbent amount, g; 1 and 5 – 1; 2 and 6 – 2; 3 and 7 – 3; 4 and 8 – 5.

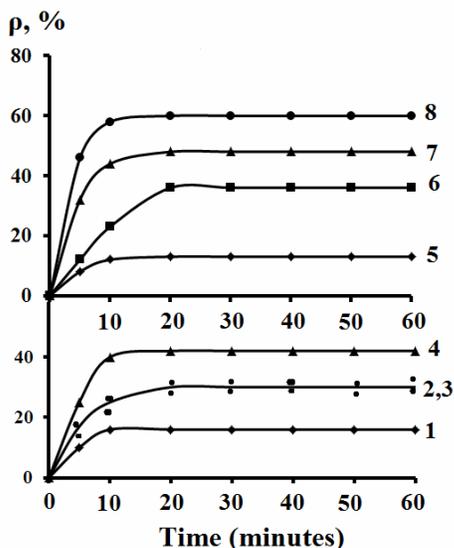


Figure 6 : Dependence of efficiency of  $\text{Ca}^{2+}$  adsorption ( $\rho$ , %) from 2.5 mM  $\text{CaCl}_2$  solutions containing 5.0 mM (1-4) and 0.5 mM (5-8)  $\text{KNO}_3$  on contact time and the adsorbent amount, g; 1 and 5 – 1; 2 and 6 – 2; 3 and 7 – 3; 4 and 8 – 5.

However, sorption ability depends not only on the solution ionic strength, but on the anion nature too. The results of  $\text{Ca}^{2+}$  sorption from the solutions containing 0.625 mM  $\text{CaCl}_2$  at the constant  $\text{KNO}_3$  content testify about this (Figure 7). So, tenfold decrease of  $\text{KNO}_3$  concentration, when a change of ionic strength is not large (6%),  $\rho$  value increases more than twice (from 16 to 40 %, Figure 7, curves 1 and 5).

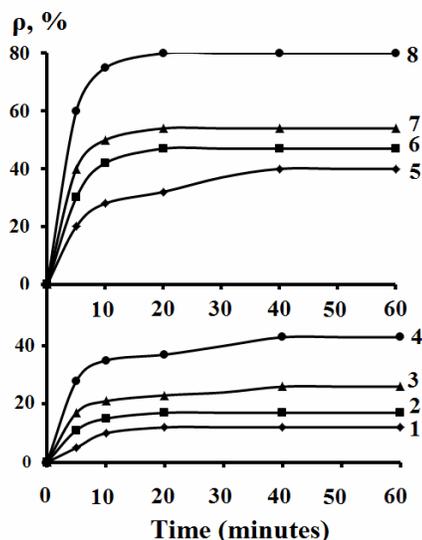


Figure 7 : Dependence of efficiency of  $\text{Ca}^{2+}$  adsorption ( $\rho$ , %) from 0.625 mM  $\text{CaCl}_2$  solutions containing 5.0 (1-4) and 0.5 mM (5-8)  $\text{KNO}_3$  on contact time and the adsorbent amount, g; 1 and 5 – 1; 2 and 6 – 2; 3 and 7 – 3; 4 and 8 – 5.

### Adsorption isotherm

View of adsorption isotherms as a function of  $\text{Ca}^{2+}$  concentration in solution and a nature of inserted salts in the  $\text{CaCl}_2$  solution is shown in Figure 8. Decrease of indifferent salts content increases specific adsorption (Figure 8, curves 1 and 2, 3 and 4). At that, effect of  $\text{KNO}_3$  is less, than influence of  $\text{Na}_2\text{SO}_4$ , this can be connected, in first approach, with corresponding decrease of ionic strength value.

To identify the models that best fit the experimental data the Freundlich, Langmuir and Temkin isotherms were considered.

### Freundlich adsorption isotherm

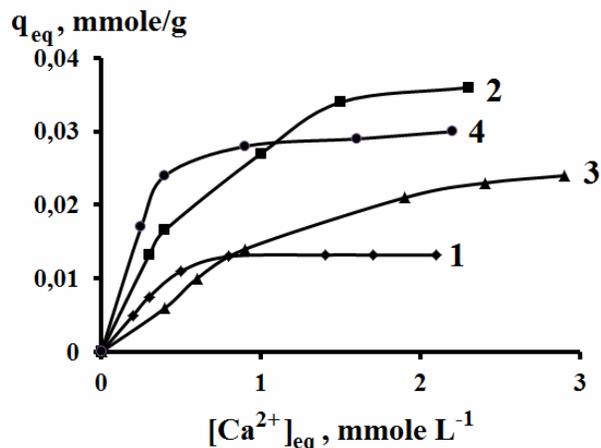
The Freundlich isotherm model is given by

$$q_{\text{eq}} = k_{\text{F}} C^{\frac{1}{n}} \quad (1),$$

where  $q_{\text{eq}}$  is specific adsorption at equilibrium,  $C$  – is the solute concentration at equilibrium,  $k_{\text{F}}$  and  $1/n$  are Freundlich adsorption isotherm constants. The

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Freundlich isotherm model takes multilayer and heterogeneous adsorption into account<sup>[42,43]</sup>.



**Figure 8 :** Adsorption isotherms of  $\text{Ca}^{2+}$  on glauconite from  $\text{CaCl}_2$  solutions containing additives of  $\text{Na}_2\text{SO}_4$  (16.50 mM – 1; 1.65 mM – 2) and  $\text{KNO}_3$  (5.0 mM – 3; 0.5 mM – 4).

Linearization of expression (1) gives

$$\log q_{\text{eq}} = \log k_f + \frac{1}{n} \log C \quad (2)$$

## Temkin isotherm

The Temkin model considers adsorption at uniformly heterogeneous surface, when adsorbate - adsorbate interactions induce a decrease of adsorption energy with increasing coverage<sup>[44,45]</sup>. This model is given by

$$q_{\text{eq}} = \frac{1}{f} \log (aC) \quad (3),$$

where  $f$  is Temkin constant,  $a$  is the constant of adsorption equilibrium,  $C$  – is the solute concentration at equilibrium. The dependence of (3) is linear in  $q_{\text{eq}}$ ,  $\log C$  coordinates.

## Langmuir isotherm

The Langmuir isotherm is based on assumption that adsorption takes place at specific homogeneous sites and there is no interaction among adsorbed species. The Langmuir isotherm is given by

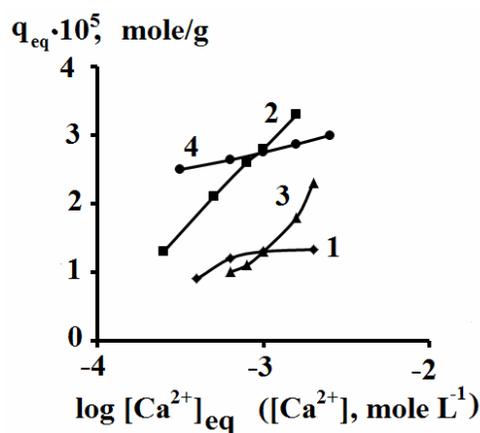
$$q_{\text{eq}} = \frac{k_L q_{\text{max}} c}{1 + k_L C} \quad (4),$$

where  $q_{\text{max}}$  is the monolayer capacity of the adsorbent,  $k_L$  is the constant of adsorption equilibrium. Linearization of expression (4) gives

$$\frac{C}{q_{\text{eq}}} = \frac{1}{q_{\text{max}} k_L} + \frac{C}{q_{\text{max}}} \quad (5)$$

One can see that the dependence of (5) is linear in  $C/q_{\text{eq}}$ ,  $C$  coordinates. Thus, using corresponding coordinates bringing the isotherms to linear appearance according to (2), (3) and (5), one can see which isotherm best represents the data about  $\text{Ca}^{2+}$  adsorption on glauconite. It was found that the dependence in  $\log q_{\text{eq}}$ ,  $\log C$  coordinates is not linear. Therefore, the Freundlich isotherm was excluded of further consideration.

Dependence in coordinates of  $q_{\text{eq}}$ ,  $\log C$  corresponding to Temkin isotherm is linear at the small concentrations of the indifferent salts (1.65 mM  $\text{Na}_2\text{SO}_4$  and 0.5 mM  $\text{KNO}_3$ ) (Figure 9). However, linearity is lost at tenfold increasing concentration of the salts.



**Figure 9 :** Adsorption isotherms of  $\text{Ca}^{2+}$  on glauconite in coordinates of Temkin isotherm (Eq. 3) from  $\text{CaCl}_2$  solutions containing additives of  $\text{Na}_2\text{SO}_4$  (16.50 mM – 1; 1.65 mM – 2) and  $\text{KNO}_3$  (5.0 mM – 3; 0.5 mM – 4).

Dependence in coordinates of  $C/q_{\text{eq}}$ ,  $C$  corresponding to Langmuir isotherm is linear both in the absence of the indifferent salts (Figure 10) and in their presence at all the studied concentrations (Figure 11).

Thus,  $\text{Ca}^{2+}$  sorption is satisfactorily represented by the Langmuir and Temkin isotherms in a number of cases. Such a variability is frequently observed<sup>[43]</sup>. We believe that the best model represented the isotherm curves is the Langmuir isotherm because it corresponds to the largest amount of observed facts. In addition, adsorption of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and also  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  on the nature minerals<sup>[34,40,41]</sup> and biosorbents<sup>[13]</sup> is described by the Langmuir isotherm. Langmuir parameters for  $\text{Ca}^{2+}$  adsorption on the glauconite are given in TABLE 1. In addition, rate constant of adsorption  $k_a$  and value of Gibbs energy of the process ( $\Delta G_{\text{ads}}$ ) are given. Gibbs

energy was calculated according to formula

$$\Delta G_{\text{ads}} = -2.3 RT \log k_L,$$

and  $k_a$  value was estimated from the dependence

$$\frac{dq}{d\tau} = k_a (q_{\text{max}} - q_\tau)$$

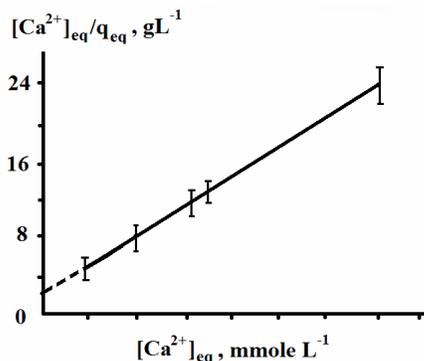


Figure 10 : Linearization of Langmuir isotherm (Eq. 5) of  $\text{Ca}^{2+}$  adsorption on glauconite from  $\text{CaCl}_2$  solutions.

where  $q_\tau$  is the amounts of  $\text{Ca}^{2+}$ , adsorbed at time  $\tau$ ,  $dq/d\tau$  is calculated from the dependence of  $q = f(\tau)$ .

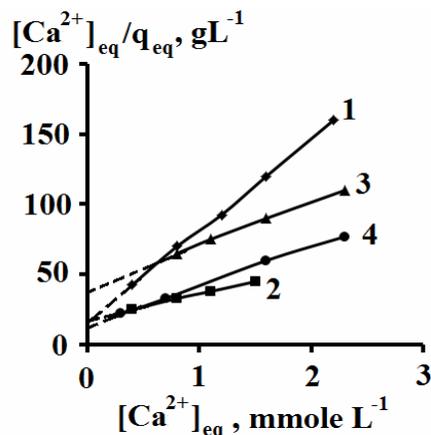


Figure 11 : Adsorption isotherms of  $\text{Ca}^{2+}$  on glauconite in coordinates of Langmuir isotherm (Eq. 5) from  $\text{CaCl}_2$  solutions containing additives of  $\text{Na}_2\text{SO}_4$  (16.50 mM – 1; 1.65 mM – 2) and  $\text{KNO}_3$  (5.0 mM – 3; 0.5 mM – 4).

TABLE 1 : Langmuir parameters for adsorption of  $\text{Ca}^{2+}$  on Bondar deposit glauconite

Solution	$k_L$ , L/mol	$q_{\text{max}}$ , mmol/g	$-\Delta G_{\text{ads}}$ , kJ/mol	$k_a$ , $\text{min}^{-1}$
$\text{CaCl}_2$	3120	0.120	19.5	0.165
$\text{CaCl}_2 + 16.5 \text{ mM Na}_2\text{SO}_4$	3800	0.016	20.0	0.070
$\text{CaCl}_2 + 1.65 \text{ mM Na}_2\text{SO}_4$	1280	0.050	17.4	0.026
$\text{CaCl}_2 + 5.0 \text{ mM KNO}_3$	1110	0.018	17.1	0.087
$\text{CaCl}_2 + 0.5 \text{ mM KNO}_3$	1930	0.040	18.4	0.058

TABLE 2 :  $q_{\text{max}}$  of a number of cations on clay minerals

Cation	Mineral	$q_{\text{max}}$ , mmol/g	Reference
$\text{Ca}^{2+}$	Karinsky deposit glauconite	0.09-0.13	[34]
$\text{Mg}^{2+}$	Karinsky deposit glauconite	0.05-0.11	[34]
$\text{Sr}^{2+}$	Montmorillonite	0.02-0.04	[40]
$\text{Fe}^{3+}$	Karinsky deposit glauconite	0.16	[34]
$\text{Mn}^{2+}$	Karinsky deposit glauconite	0.12	[34]
$\text{Zn}^{2+}$	Karinsky deposit glauconite	0.02-0.16	[34]
$\text{Fe}^{2+}$	Karinsky deposit glauconite	0.06	[34]

Data of  $q_{\text{max}}$  for adsorption of  $\text{Ca}^{2+}$  and a number of other cations on clay minerals are shown in TABLE 2.

One can compare data of TABLE 2 with those obtained in this work (TABLE 1).

## CONCLUSION

Clay minerals show rather low maximum specific adsorption. Its value weakly depends on cation nature and even its charge and is in the range of 0.03 – 0.16

mmol/g. However, sufficiently small adsorption capacity of glauconite is compensated with rich deposits of this mineral, simplicity and high manufacturability of its preliminary preparation.

Sorption of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  on glauconite, its concentrates and fractions does not require of their regeneration. This simplifies recycling of the sorbent.

Most probable isotherm of adsorption of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations and toxic ions of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  on glauconite is Langmuir isotherm. The values of maxi-

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mum specific adsorption of these cations are rather similar. Langmuir parameters for adsorption of  $\text{Ca}^{2+}$  on Bondar deposit glauconite were calculated.

$\text{Ca}^{2+}$  specific adsorption decreases with increasing ionic strength of the solution because of insertion of extraneous salts. However, sorption ability depends not only on the solution ionic strength, but on the anion nature too.

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