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Research paper

Sorption characteristics of economically viable silicate sorbents for sequestration of lead ions from aqueous solutions



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ABSTRACT

The adsorption of Pb^{2+} from aqueous solutions by sorbents based on calcium silicates, obtained in multi-component systems $CaCl_2-Na_2SiO_3-H_2O$ (sorbent I) and $CaSO_4\cdot 2H_2O-SiO_2\cdot nH_2O-KOH-H_2O$ (sorbent II), was studied. Surface area of the two sorbents was found to be 100 and 40 m²/g respectively. The sorption capacities of the adsorbent materials were found to be 3.6 l/mmol and 8.4 l/mmol respectively. Characterization of the sorbent materials was carried out. The equilibrium data was fitted in Langmuir's isotherm and the adsorption capacity of the adsorbent materials was determined. The distribution coefficients at Pb^{2+} ions for the sorbents were determined at different ratios of solid and liquid phases.

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1. Introduction

It is well known that lead and its compounds are highly toxic. Lead is regarded as a poison affecting mainly nervous and vascular systems and directly blood [1,2]. Lead has been reported to be toxic to fauna, flora and human beings. Its adverse effects on living beings through its application in leaded paints, gasoline, and many lead-containing products have been documented [3–5] because of its ill health effects, lead products have been banned in many countries of the world. The application of lead in gasoline was prohibited worldwide but it has been regularly used in aero plane fuels [6–9].

Search for efficient and ecologically safe sorbents for extraction of lead ions, in particular, from aquatic sources is rather urgent.

Scientists have reported adsorption of Pb²⁺ ions with calcium silicates of various compositions and structure. The authors [3] have reported dependence of reactions of natural and synthetic tobermorite $Ca_{10}[Si_{12}O_{31}](OH)_6 \cdot 8H_2O$, xonotlite $Ca_6[Si_6O_{17}](OH)_2$ and wollastonite $Ca_6Si_6O_{18}$ with salts of heavy metals, including

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lead nitrate, in the range of ions concentration Pb^{2+} from 100 to 1,000 mg/l with ratio of solid and liquid phases S:L=1:400. It was found that as a result of lead nitrate's reaction with the studied calcium silicates either lead hydroxocarbonate $Pb_3(CO_3)_2(OH)_2$ (hydrocerussite) or lead carbonate $PbCO_3$ (cerussite) is formed. This is acknowledged by X-ray diffraction analysis of samples after they react with lead nitrate: calcite contained in initial samples of wollastonite and tobermorite, tobermorit disappears. As one of possible mechanisms to form lead hydroxocarbonate, the authors suggested hydrolysis and carbonization of hydrolysis products.

The authors [10] studied process of cations exchange between synthetic 1.1 nm tobermorite and solutions containing Pb²⁺ ions in the range of concentrations of Pb²⁺ ions from 100 to 1,800 µg/ml. As a result, it was concluded that reaction of 1.1 nm tobermorite with lead salts, compounds with general empirical formula Ca_{5-x}Pb_xSi₆...nH₂O are formed, where x varies from 0.033 to 0.514. It was concluded on prospective use of tobermorite, stable in neutral and alkaline media, for ions exchange processes. The process of extraction of ions Pb²⁺ with wollastonite from water solutions of lead nitrate with ratio of solid and liquid phases S:L=1:50 was studied [11]. The impact of temperature on sorption kinetics at 20, 30 and 40°C was studied at pH=6.4 and initial concentration of Pb²⁺ ions 6 mg/l. It was found that as the temperature

Table 1Synthesis conditions, phase structure and BET surface area of sorbents used for sorption of Pb²⁺ ions.

Sorbent	Initial substances and	Phase structure	BET surface	
	synthesis conditions	Before heat-treatment	After heat-treatment at 900°C	area, m²/g
I	Solutions of sodium silicate Na ₂ SiO ₃ , CP (silicate module SiO ₂ /Na ₂ O=1) and calcium chloride (CaCl ₂ ·2H ₂ O content at least 98.3%). Synthesis was made at 20°C.	Amorphous phase, CaCO ₃	CaSiO₃, CaO	100.0
II	Borogypsum (containing basic components, mass %: SiO ₂ – 32.2%; CaO – 28.4; SO ₃ – 31.3%; Fe ₂ O ₃ – 2.7%) and potassium hydroxide KOH, <i>pro analysi</i> . Synthesis was made in autoclave at 1.7 atm. within 2 hours.	Amorphous phase, SiO_2 , $CaCO_3$, $CaSO_4 \cdot 2H_2O$	CaSiO ₃	40.0

increases, removal of Pb decreased from 75.5 to 60.0%, which indicated exothermic nature of sorption. The calculated value of energy of activation of sorption process was 8.730 KJ/mol. The analysis of sorption isotherms by Langmuir equation has shown that the value of maximal sorption capacity falls from 0.308 to 0.234 mg/g (from $1.5 \cdot 10^{-3}$ to $1.13 \cdot 10^{-3}$ mmol/g) as the temperature increases.

The subsequent separation of heavy metals cations [12] from a series of solutions containing Pb²⁺, Zn²⁺, Cd²⁺ and Cu²⁺ with calcium hydromonosilicate C–S–H, within the range of initial concentrations of Pb²⁺ ions from 0.127 to 2.68 g/l was studied. The following sequence of cations separation was identified: Cu²⁺, Pb²⁺, Cd²⁺. It is reported [13] that the process of Pb²⁺ ions sorption by synthetic xonotlite and wollastonite obtained from two types of anthropogenic waste – phosphogypsum and silica gel provided significant results. The studies were made with aqueous solutions of Pb at pH=5.0, temperature 25°C, ratio of solid and liquid phases S:L=1:250 within 40 minutes. It was shown that sorption capacity of the silicates studied as related to Pb²⁺ ions is 1.3–1.5 mmol/g for xonotlite and 0.9–1.0 mmol/g for wollastonite.

The sorption characteristics of synthetic composite sorbent based on calcium hydrosilicate C-S-H, amorphous silica dioxide and calcium carbonate were studied [14] at initial concentrations 100-600 mg/l, ratio solid/liquid phases S:L=1:200, pH=6.0-6.5 and temperature 17 °C for 60 minutes. The maximal sorption capacity of the sorbent for removal of Pb²⁺ ions is 94.43 mg/g (0.46 mmol/g). Sorption characteristics of nanosize calcium hydromonosilicate C-S-H were studied [15-17]. Its BET surface area was found to be $462.0 \text{ m}^2/\text{g}$. Adsorption experiments were made by taking a ratio of solid/liquid phases, S:L=1:100, initial concentrations of Pb²⁺ ions 50 mg/l at room temperature. It was shown that a complete removal of lead was achieved within 6 min which indicates that the process of removal is 'fast'. Such an effect can be accounted for a large value of BET surface area of calcium hydrosilicates and cations exchange of Ca²⁺ ions with respective metal ions. From the review of scientific literature, it may be concluded that calcium silicates and materials based on them have been attracting attention of researchers for a long time for their application as sorbents to treat aquatic media containing heavy metals ions including Pb2+ ions. If the chronology of scientific works is taken into account, it may be seen that the concern for studying sorption characteristics of those compounds has been catching impetus continuously.

This paper focusses on removal of Pb ions from aqueous solutions by sorbents based on calcium silicates (hereinafter referred to as silicate sorbents), obtained in multi-component systems CaCl2–Na2SiO3–H2O (sorbent I) and CaSO4·2H2O–SiO2·nH2O–KOH–H2O (sorbent II), where compounds CaSO4·2H2O and SiO2·nH2O are components of boric acid production waste (borogypsum). The sorbents are prepared by 'inexpensive precursors' and though a detailed 'cost analysis' has not been carried out, it is logically understood that the process of removal of Pb on the silicate adsorbents is economically viable.

2. Experimental

2.1. Synthesis of the adsorbents

For synthesis of sorbent 1, solutions of sodium silicate Na_2SiO_3 , CP (silicate module $SiO_2/Na_2O=1$) and calcium chloride (CaCl₂·2H₂O content at least 98.3 %) were prepared in double distilled water and a temperature of 20 °C was maintained during synthesis. Second sorbent was prepared from Borogypsum (containing basic components, mass %: $SiO_2 - 32.2$ %; CaO - 28.4; $SO_3 - 31.3$ %; $Fe_2O_3 - 2.7$ %) and potassium hydroxide KOH. The synthesis was carried out in an autoclave at 1.7 atm pressure and the reaction was carried out for 2 h. The details regarding phase structure and BET surface area have been given in Table 1.

Synthesis conditions, phase structure and BET surface area of the studied silicate sorbents are listed in Table 1.

2.2. Adsorption experiments

Sorption experiments were carried out in batch adsorption mode with solid/liquid phase ratio 1:1000 and temperature 20 °C. The experiments were carried out with initial lead concentrations in 0.02 to 9.09 mmol/l range. A fixed amount of adsorbent was added to Pb solutions of various concentrations (0.02 to 9.09 mmol/l range) and the solutions were shaken on a thermostatic shaking unit 358 S type (Poland) at shaking frequency 200 rpm for 3 h. As initial concentrations of the solutions were of 10^{-3} order, ionic strength of the solutions was maintained at 0.1 M NaClO₄. Besides, simultaneous experiments were run with borogypsum of the said structure being the initial raw material to obtain sorbent II along with the reagents namely calcium carbonate CaCO₃, and calcium sulfate CaSO₄·2H₂O. After 3 h the adsorbents were separated from solutions by filtering through Whatman filter papers. Residual concentrations of Pb and Ca were determined in the aliquot by Atomic Absorption Spectrophotometer (Thermo Electron, the USA).

2.3. Kinetic experiments

To study the dependency of lead distribution factor (K_d) from the ratio of solid/liquid phases (1:40, 1:100, 1:400, 1:1,000) sorption of Pb²⁺ ions with silicate sorbents, different amounts of adsorbent were added to 20 ml solutions of lead of different initial concentrations: 0.21 mmol/l (in experiments with sorbent I) and 0.13 mmol/l (in experiments with sorbent II). As control experiments, sorbent sample weights were put into vessels with distilled water and shaken simultaneously with the studied samples.

The study effect of pH on removal of Pb²⁺ ions, experiments were conducted in pH range from 1.2 to 4.4 with solid/liquid ratio S:L=1:1000 by making a series of solutions. The required value of pH solutions was maintained by adding 0.1N solution NaOH or HCl.

To obtain kinetic curves of sorption, sorbents were added in a series of beakers, poured with solution of lead chloride and shaken at various time intervals – from 1 to 60 minutes. The initial concentration of Pb²⁺ ions was 1.8 mmol/l (in experiments with sorbent I) and 1.6 mmol/l (in experiments with sorbent II and borogypsum). S:L ratio was 1:1,000 (in experiments with sorbent I) and 1:40 (in experiments with sorbent II and borogypsum). Via certain time spans, solutions were separated from sorbents via filtering and the residual concentration of Pb²⁺ ions in aliquot was determined.

Sorption capacity $(A_c, mmol/g)$ of the samples studies was calculated using following expression [9]:

$$A_s = \frac{(C_{in} - C_e)}{m} \cdot V,\tag{1}$$

where $C_{\rm in}$ – initial concentration of Pb²⁺ ions in solution, mmol/l; $C_{\rm e}$ – equilibrium concentration of Pb²⁺ ions in solution, mmol/l; V – solution volume, l; m – sorbent mass, g.

Degree of extraction of Pb²⁺ ions (α , %) was calculated by the formula [8]:

$$\alpha = \frac{(C_{in} - C_e)}{C_{in}} \cdot 100\% \tag{2}$$

Coefficient of interphase distribution $(K_d, ml/g)$ was determined as follows [8,9]:

$$K_d = \frac{(C_{in} - C_e) \cdot V}{C_e \cdot m} \tag{3}$$

2.4. Characterization of the sorbents

X-ray patterns of the sorbents were taken by automatic diffractometer D8 ADVANCE rotating samples in CuK_{α} -radiation. X-ray diffraction analysis was done using EVA search software with powder databank PDF-2. The quantitative content of calcium carbonate in initial sorbents (on dry sample weight basis) was found by gas volumetric method based on measuring gas volume released from solid sample weights [14].

The BET surface area of silicate sorbents was found via low temperature nitrogen adsorption using Sorbtometer-M device.

The content of Pb^{2+} and Ca^{2+} ions in solutions after sorption was determined by atomic absorption spectrophotometry on two-ray spectrometer Solaar M6 (Thermo Electron, the USA) by analytical lines 283.3 and 422.6 nm respectively. The limit of finding lead in water solutions is 0.07 μ g/ml, calcium – 0.0005 μ g/ml.

pH of the solutions was measured by pH-meter/ionometer Multitest IPL – 102 with glass electrode ESK – 10601/7, standardized by buffer solutions.

3. Results and discussion

3.1. Characterization of the adsorbents

As seen from Table 1, the phase structure of studied sorbents is characterized by amorphous phase and crystalline phases of calcium carbonate in calcite modifications (for both the sorbents) and aragonite (for sorbent I). It was found that the quantity of CaCO₃, found as per Alekseyevskiy et al. [14], is 20.6% for sorbent I and 12.6% for sorbent II. Besides, in sorbent II, crystalline phases of quartz and calcium sulfate were identified. After heat-treatment of the sorbents at 900 °C for 1 h, the diffractograms of both sorbents displayed typical diffraction peaks related to triclinic modification of wollastonite, which evidences transition of amorphous hydrated calcium silicates into crystalline phase of wollastonite.

Table 2Parameters of Langmuir equation in sorption of Pb²⁺ ions with silicate I and II.

Sorbent	k, l⋅mmol ⁻¹	A _m , mmol⋅g ⁻¹	\mathbb{R}^2
I	3.6	$\begin{array}{c} 4.3 \pm 0.86 \\ 2.73 \pm 0.546 \end{array}$	0.9809
II	8.4		0.9980

3.2. Adsorption studies

On the basis of experimental data on Pb^{2+} ions sorption by the silicate sorbents, the dependence of sorption capacity on initial concentrations of Pb^{2+} ions was determined and has been given in Table 1. For efficient sorbents having high values of sorption capacities, when initial concentrations of ions (C_{in}) are higher than equilibrium concentrations (C_e) , it is unfeasible to build sorption isotherm as the dependency of sorption value (A_s) on equilibrium concentration (C_e) . It is because the visibility at which values of initial concentrations we have, the respective values of sorption is lost.

It is clear from Fig. 1 that at concentrations of Pb²⁺ from 3.5 mmol/l and higher, some differences have been observed in sorption capacity of the sorbents and sorption capacity of sorbent I in relation to Pb²⁺ ions is higher than of sorbent II. At concentrations of Pb²⁺ ions in solution under 2.9 mmol/l, sorbents manifested virtually same sorption capacity.

The experimental data was tried in Freundlich and Langmuir's adsorption isotherm equations but the data fitted Langmuir adsorption isotherm better. The linearized form of Langmuir isotherm equation can be written as follows [8]:

$$\frac{C_{\rm e}}{A_{\rm s}} = \frac{1}{A_m \bullet k} + \frac{C_{\rm e}}{A_m},$$

where C_e (mmol/l), equilibrium concentration of Pb^{2+} ions in solution, A_m (mmol/g) maximal sorption capacity and k (l/mmol) is Langmuir constant.

Linear graphs of dependency $\frac{C_e}{A_s}$ on C_e displayed (Fig. 2) acknowledge the reliability of Langmuir's model to describe the studied process and allow finding parameters A_m and k in Langmuir equation. Values of the parameters have been given in Table 2.

3.3. Effect of pH

The dependence of removal of Pb by the adsorbents on pH value have been presented in Fig. 3. It is clear that as pH of the solution is shifted in the acidic range, sorption capacity of the adsorbents decreases. The highest decrease of sorption capacity and degree of Pb²⁺ ions removal is observed for sorbent I (α falls from 57.3 to 4.9 %) at pH=1.2. For sorbent II, α falls from 57.0 to 22.0 %. Decrease of sorption capacity is explained by instability of calcium silicates and carbonates in acidic range of pH. Experimental data obtained simultaneously in similar conditions for borogypsum used to synthesize sorbent II have shown that within the range of pH from 1.3 to 5.5, the value of borogypsum's sorption capacity virtually does not change.

3.4. Kinetic studies

Kinetic curve of sorption of Pb^{2+} ions with silicate sorbent I at solid/liquid phase ratio 1:1,000, has been displayed in Fig. 4. As seen from Fig. 4, the equilibrium time for the removal of Pb on sorbent I is $\sim \! 16$ min ($A_e \! = \! 1.6$ mmol/g). Kinetic data for sorbent II and borogypsum, obtained at solid/liquid phase ratio 1:40 showed that for those samples, the equilibrium was achieved in less than 1 min and sorption capacity, A_e of sorbent II is 0.64 mmol/g $^{-1}$, and for borogypsum, it was 0.63 mmol/g. High kinetic characteristics

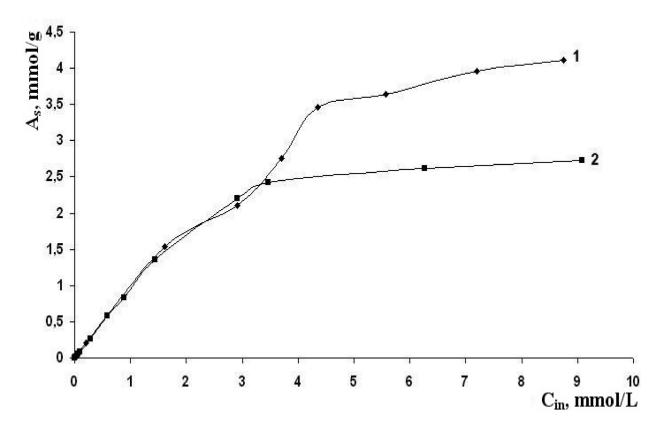


Fig. 1. Dependencies of sorption capacity of silicate sorbents on initial concentration of ions Pb^{2+} : 1 – sorbent I, 2 – sorbent II.

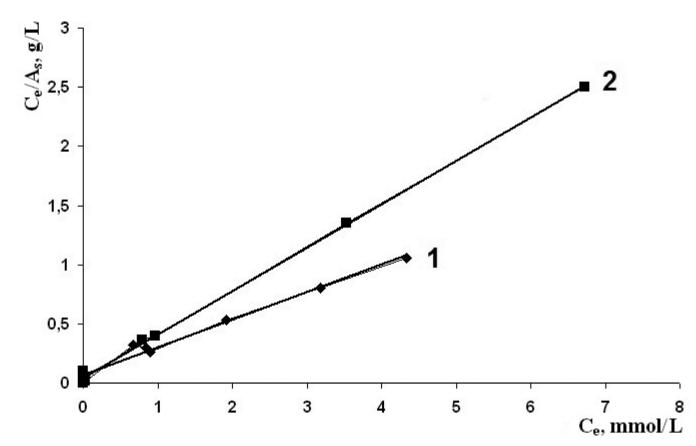


Fig. 2. Dependencies of C_p/A_c ration on C_p , built in compliance with Langmuir equation at sorption of ions Pb^{2+} with sorbent I (1) and sorbent II (2).

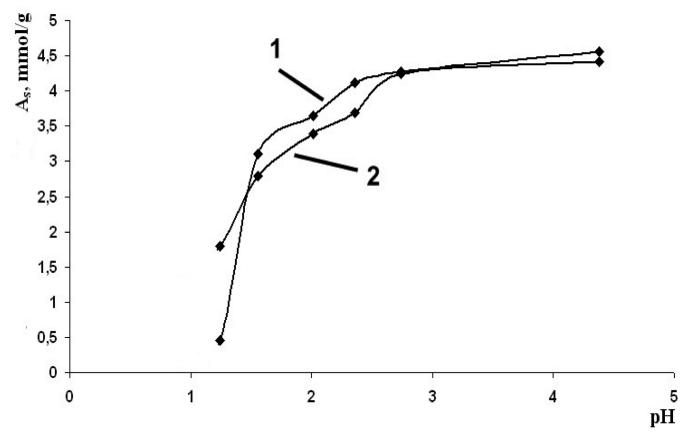
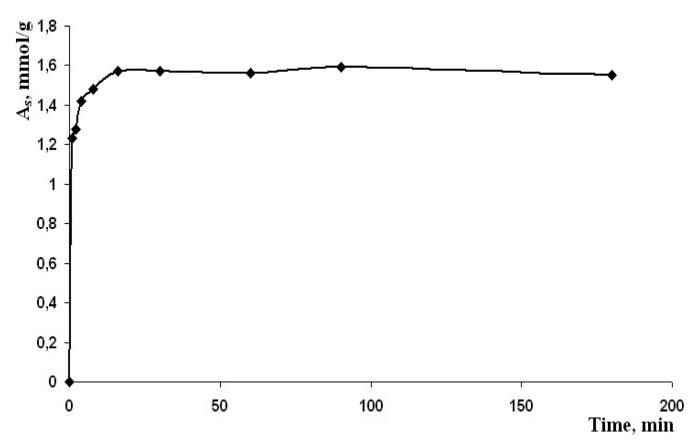


Fig. 3. Dependencies of degree α of extraction of ions Pb²⁺ on pH value with silicate sorbents: 1 – sorbent II, 2 – sorbent II.



 $\textbf{Fig. 4.} \ \, \textbf{Kinetic curve of sorption of ions } Pb^{2+} \ \, \textbf{with silicate sorbent I.}$

Table 3 Data on dynamics of Ca^{2+} ions concentration in filtrates after sorption.

Experiment	Concentration of Pb ⁺² in initial solution, mmol/l	Concentration of Pb+2 in solution after sorption, mmol/l	Concentration of Ca^{+2} in solution after sorption, mmol/l
Sorbent I			
1	0.21	0.003	2.3
2	1.62	0.0063	2.4
3	2.91	0.67	3.1
4	3.71	0.84	3.54
5	4.35	0.9	3.72
6	5.57	1.92	3.91
7	7.2	3.18	3.95
8	8.75	4.34	4.12
9	0 (control)	_	2.4
Sorbent II			
1	0.021	0.002	0.72
2	0.048	0.003	0.9
3	0.06	0.006	0.98
4	0.088	0.002	0.83
5	0.28	0.004	1.2
6	0.58	0.0043	1.3
7	0.89	0.003	1.9
8	1.44	0.025	2.86
9	2.91	0.79	2.6
10	3.46	0.96	2.94
11	6.26	3.53	3.1
12	9.09	6.73	3.2
13	0 (control)	_	0.68

of samples are conditioned by values of the product of solubility of the compounds formed.

Table 3 contains the data on dynamics of Ca^{2+} ions concentration in filtrates upon sorption. It is seen from the table that as the initial concentration of Pb^{2+} ions in solution increases, the concentration of Ca^{2+} ions in filtrates after sorption grows as well. However, if we compare the change of initial and equilibrium concentration of Pb^{2+} ions with concentration of Ca^{2+} ions which occurred in solution after sorption, it may be concluded that the process of involvement of Pb^{2+} ions in the studied multicomponent systems is related to cations exchange and formation of less-soluble compounds $(Pb_3(CO_3)_2(OH)_2$, and $Pb(OH)_2$).

3.5. Mechanism of removal

To assess the sorption mechanism of Pb²⁺ ions with silicate sorbents, X-ray phase analysis and atomic absorption spectroscopy were applied. As shown in Table 1, in the structure of both sorbents, besides amorphous phase, calcite phase was present and in the structure of sorbent II, the quartz and calcium sulfate dihydrate phases were also present. Thus, the studied sorbents are multicomponent systems and in course of studying sorption mechanism, it is required to account for possible reaction of lead chloride with calcium silicate, CaO·SiO₂·nH₂O, CaCO₃, SiO₂ and CaSO₄·2H₂O. It was ascertained by determination of the values of Gibbs free energy for respective chemical reactions. The values of Gibbs free energies for the reactions were determined and were found to be as follows: for interaction of lead chloride with hydrosilicate ($\Delta G^{\circ}_{x,p} = -210.6$ KJ/mol), carbonate ($\Delta G^{\circ}_{x,p} = -194.2$ KJ/mol) and sulfate ($\Delta G^{\circ}_{x,p} = -188.4$ KJ/mol) of calcium forming respective lead salts. The values showed thermodynamic feasibility of the reactions.

Thermodynamic calculations approve the data of X-ray phase analysis of residual matters after sorption. On sorbent I diffractograms, crystalline phases $PbCO_3$, $Pb_3(CO_3)_2(OH)_2$ and $Pb(OH)_2$ were identified. Similar results were reported by other workers [3]. In sorbent II, $PbSO_4$ and $Pb_3(CO_3)_2(OH)_2$ phases were identified (Fig. 5).

The lead hydrosilicate $PbSiO_3 \cdot nH_2O$ formed in reaction of lead chloride with calcium hydrosilicate is amorphous, it is impossible to identify it in residual matter by X-ray phase analysis. It was acknowledged as a result of synthesis and study of so called the 'model' lead silicate from reagents, sodium silicate Na_2SiO_3 and $PbCl_2$. Diffractogram of residual matter obtained as a result of synthesis contains typical diffraction peaks related to hydrocerussite $Pb_3(CO_3)_2(OH)_2$ and amorphous phase.

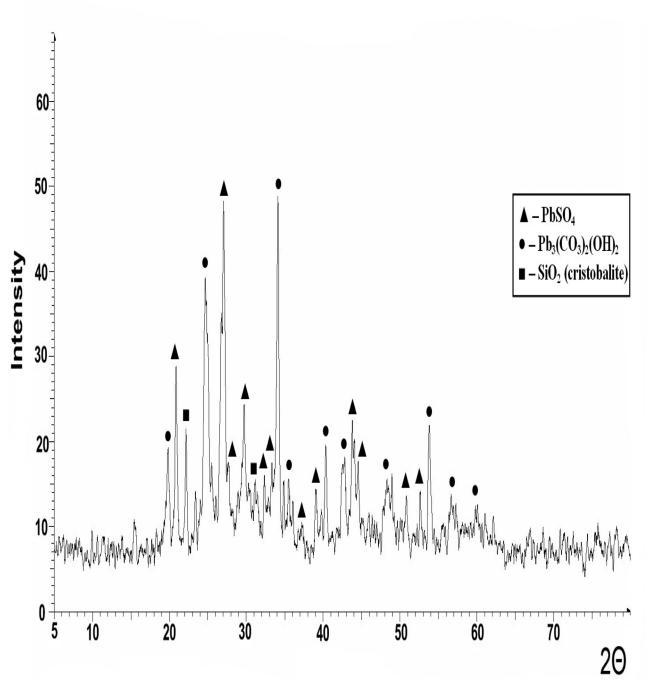
The reaction of cations exchange of lead chloride with sorbents components (CaCO $_3$ (for sorbents I and II) and CaSO $_4\cdot 2H_2O$ (for sorbent II) is evidenced by control experiments using reagents CaCO $_3$ and CaSO $_4\cdot 2H_2O$ (CP qualification) and borogypsum of which sorbent II was synthesized (Figs. 6 and 7).

It is seen from Fig. 1 that borogypsum contributes directly to sorption of Pb^{2+} ions to form lead sulfate, $PbSO_4$, which is acknowledged by X-ray phase analysis data. In concentrations of Pb^{2+} ions in solution under 1.4 mmol/l, sorbent II and borogypsum show the same sorption capacity. In concentrations of Pb^{2+} from 2.9 mmol/l and higher, sorption capacity of borogypsum related to Pb^{2+} ions is higher than of sorbent II. Similar results were obtained for calcium sulfate $CaSO_4\cdot 2H_2O$ (CP qualification). The process of Pb^{2+} ions sorption [16,17] with natural gypsum was studied, similar data were obtained and it was concluded on the prospect of application of gypsum in treatment of aquatic media from lead ions.

As seen from Fig. 7, calcium carbonate also takes part in Pb²⁺ ions extraction and at concentration of Pb²⁺ ions equaling 10.4 mmol/l, the value of sorption capacity CaCO₃ is 0.46 mmol/g.

Table 4 visually displays the results of X-ray phase analysis of sorbents I and II, borogypsum and control reagents ($CaCO_3$ and $CaSO_4\cdot 2H_2O$ CP qualification) after sorption of Pb^{2+} ions from lead chloride solution.

As seen from Table 4, in the course of Pb²⁺ ions sorption, for sorbent I the formation of low-soluble compounds as lead carbonate and hydroxide is typical and for sorbent II, formation of lead sulfate and hydroxocarbonate is typical. Lead hydroxocarbonate may be formed in both the cases: with interaction of lead chloride with calcium chloride contained in initial sorbent and with hydrolysis of PbCl₂ and further by carbonization of the compounds



 $\textbf{Fig. 5.} \ \ \text{Diffractogram of sorbent II after sorption (initial concentration of ions Pb$^{2+}$-6.3 mmol/l)}$

Table 4X-ray phase analysis of sorbents I and II, borogypsum and control reagents (CaCO3 and CaSO4-2H2O CP qualification) after sorption of Pb²⁺ ions from lead chloride solution.

№	Sorbent	Initial concentration of Pb^{2+} ions, $mmol \cdot l^{-1}$	Phase composition of sample (product of compound solubility)
1	Sorbent I	2.9	PbCO ₃ (7.5·10 ⁻¹⁴), Pb(OH) ₂ (5·10 ⁻¹⁶)
2	Sorbent II	2.9	$PbSO_4$ (1.6·10 ⁻⁸), $Pb_3(CO_3)_2(OH)_2$ (3.5·10 ⁻⁴⁶), SiO_2 (crystobalite)
3	Borogypsum	2.9	PbSO ₄ , PbCO ₃ , CaSO ₄ ·2H ₂ O
4	CaCO ₃ of CP qualification	7.6	PbCO ₃
5	CaSO ₄ ·2H ₂ O of CP qualification	8.6	PbSO ₄

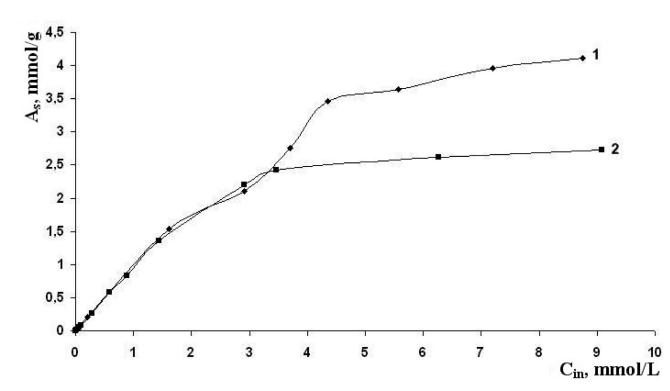
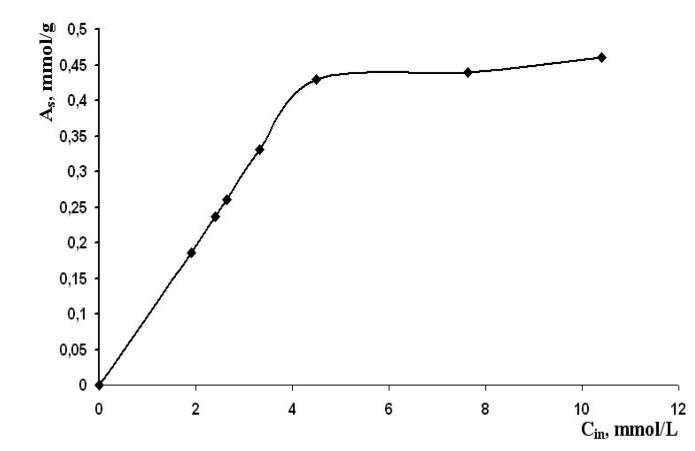


Fig. 6. Dependencies of sorption capacity of sorbent II and borogypsum on initial concentration of ions Pb^{2+:} 1 - borogypsum, 2 - sorbent II (S:L=1:1000).



 $\textbf{Fig. 7.} \ \ \text{Dependency of sorption capacity value of calcium carbonate CP qualification on initial concentration of ions Pb$^2+ (S:L=1:100).$

Table 5 Distribution coefficients at Pb^{2+} ions for sorbents I, II and borogypsum at various S:L ratios.

Ratio of solid and liquid phases (S:L)	K_d , ml/g Samples		
	sorbent I	sorbent II	borogypsum
1:40	3892	2771	587
1:100	14616	3513	1049
1:400	49633	19221	1243
1:1000	62582	22146	1278

formed. As a result of borogypsum and lead chloride interaction, lead sulfate and carbonate are formed. Lead carbonate formation in that case relates to microelements in form of calcium contained in borogypsum, which is not incompletely decayed in the course of sulfuric acid treatment of datolite concentrate. Reaction of calcium carbonate and sulfate with lead chloride follows to form lead carbonate and sulfate respectively. Values of distribution coefficients (K_d) of Pb^{2+} ions on sorbents I, II and borogypsum at solid/liquid phase ratio 1:40, 1:100, 1:400 and 1:1,000 are displayed in Table 5.

From Table 5, it is seen that the highest values of distribution factor are observed for all sorbents with solid/liquid ratio S:L=1:1000. For sorbent I, the highest values of interphase distribution coefficient are typical. Thus, treatment of aqueous solutions Pb^{2+} ions using the sorbents occurs both as a result of Pb^{2+} ions sorption processes, cations exchange mechanism and hydrolysis of lead salt forming lead hydroxide and as a result of carbonization of reagents system due to reaction of air with CO_2 forming lead hydroxocarbonate.

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References

- [1] P.N. Lyubchenko, Specifics of medical checkup of lead production workers.

 Guidelines. Moscow. 1985. 15-22.
- 2] Large medical encyclopedia. Moscow: Soviet encyclopedia, 23(1986) 21-25.
- [3] S. Komarneni, E. Breval, D.M. Roy, R. Roy, Reactions of some calcium silicates with metal cations, Cem. Concr. Res. 18 (1988) 204–220.
- [4] S.S. Madan, K.L. Wasewar, S.L. Pandharipande, Modeling the adsorption of benzeneacetic acid on CaO₂ nanoparticles using artificial neural network, Resour. Effic. Tech. 2 (2016) S53–S62.
- [5] M. Ganesapillai, Prithvi Simha, The rationale for alternative fertilization: Equilibrium isotherm, kinetics and mass transfer analysis for urea-nitrogen adsorption from cow urine. Resour. Effic. Tech. 2 (2015) 90–97.
- [6] F. Cai, R.M. Calisi, Seasons and neighborhoods of high lead toxicity in New York city: the feral pigeon as a bioindicator, Chemosphere 161 (2016) 274–279.
- [7] A. Frantz, M.-Á. Pottier, B. Karimi, H. Corbel, E. Aubry, C. Haussy, J. Gasparini, M. Castrec-Rouelle, Contrasting levels of heavy metals in the feathers of urban pigeons from close habitats suggest limited movements at a restricted scale, Environ. Pollut. 168 (2012) 23–28.
- [8] Uma, S. Banerjee, Y.C. Sharma, Equilibrium and kinetic studies removal of malachite green from aqueous solution by a low cost activated carbon, J. Ind. Eng. Chem. 19 (2013) 1099–1105.
- [9] A.L. Srivastava, P.K. Singh, V. Srivastava, Y.C. Sharma, Application of a new adsorbent for fluoride removal from aqueous solutions, J. Hazard. Mat. 263 (2013) 342–352.
- [10] N. Labhasetwar, O.P. Shrivastava, $Ca^{2+} \leftrightarrow Pb^{2+}$ exchange reaction of calcium silicate hydrate: $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$, J. Mater. Sci. 24 (1989) 4359–4362.
- [11] K.P. Yadava, B.S. Tyagi, V.N. Singh, Effect of temperature on the removal of lead (II) by adsorption on china clay and wollastonite, J. Chem. Tech. Biotech. 51 (1991) 47–60.
- [12] G.O. Grigoryan, L.G. Baginova, G.A. Arutyunyan, A.A. Khachatryan, Subsequent separation of heavy metals cations from solutions using calcium hydrometasilicate (CSH), Chem. J. Arm. 52 (1999) 39–42.
- [13] L.V. Akatyeva, Synthesis and physical and chemical properties of xonotlite and wollastonite PhD thesis in chemistry, N.S. Kurnakov Institute of general and inorganic chemistry of RAS, Moscow, 2003.
- [14] Q. Chen, C.D. Hills, M. Yuan, H. Liu, M. Tyrer, Characterization of carbonated tricalcium silicate and its sorption capacity for heavy metals: a micron-scale composite adsorbent of active silicate gel and calcite, J. Hazard. Mat 153 (2008) 775–783
- [15] J. Wu, Y.-J. Zhu, F. Chen, Ultrathin calcium silicate hydrate nanosheets with large specific surface areas: synthesis, crystallization, layered self-assembly and applications as excellent adsorbents for drug, protein, and metal ions, Small 9 (2013) 2911–2925.
- [16] Ye.V. Alekseyevskiy, R.K. Golts, A.P. Musakin, in: Quantitative Analysis, Goskhimizdat, Leningrad, 1953, pp. 574–575.
- [17] J.M. Astilleros, A. Godelitsas, J.D. Rodriguez-Blanco, L. Fernandez-Diaz, M. Prieto, A. Lagoyannis, S. Harissopulos, Interaction of gypsum with lead in aqueous solutions, Appl. Geochem. 25 (2010) 1008–1016.