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Sorption of Cd^{2+} Ions by Silicate Materials of Different Origins

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Abstract—The sorption capacity of silicate materials with respect to Cd^{2+} ions was studied, and the kinetics and mechanism of the sorption process were determined.

Keywords: Calcium silicate hydrates, silicate sorbents, sorption, cadmium ions.

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INTRODUCTION

Cadmium is a toxic microelement and one of the main environmental pollutants. Regardless of the aggregation state (dust, cadmium oxide fume, vapor, fog), cadmium compounds are poisonous. The toxicity of cadmium approaches that of mercury or arsenic [1]. Cadmium is discharged into the environment via airborne and waterborne transport from mining and processing facilities, due to fuel combustion and incineration of municipal wastes, with wastewater from electroplating shops and those producing silver–cadmium rechargeable batteries, as well as due to wearing of cadmium-containing goods. Most airborne cadmium originates from the production of cadmium metal and scrap recycling. Unlike zinc, cadmium is very difficult to remove from a living organism. It was found that virtually all cadmium is retained in a living body, residing mainly in liver, kidneys, and duodenum. The biological half-life of cadmium is estimated at about 40 years. Therefore, even the presence of a small concentration of cadmium in the environment leads to its continuous accumulation in an organism [2–4].

Taking into account the above stated, an important problem is search for new efficient and "green" sorbents for the extraction of cadmium(II) ions, specifically from aqueous medium. Among a broad series of materials used for this purpose, of particular interest are those based on natural and synthetic calcium silicates $n\mathrm{CaO}\cdot m\mathrm{SiO_2}$ and silicate hydrates $n\mathrm{CaO}\cdot m\mathrm{SiO_2}\cdot p\mathrm{H_2O}$, as well as other minerals (e.g., tobermorite, xonotlite, wollastonite) [5–10]. Some authors [5, 9, 10] synthesized calcium silicates for sorption of Cd^{2+} ions from various calcium- and silicon-containing waste materials.

In the present work we examined sorption of Cd^{2+} ions from aqueous cadmium chloride solutions by calcium silicates (CS) obtained from the multicomponent systems $CaCl_2$–Na_2SiO_3–H_2O and $\mathrm{CaSO_4}\cdot 2\mathrm{H_2O}$–$\mathrm{SiO_2}\cdot n\mathrm{H_2O}$–KOH–$H_2O$ where $\mathrm{CaSO_4}\cdot 2\mathrm{H_2O}$ and $\mathrm{SiO_2}\cdot n\mathrm{H_2O}$ are components of wastes in the borogypsum production.

EXPERIMENTAL

The conditions of synthesis, phase compositions, and specific surface areas of the calcium silicate sorbents used are presented in Table 1. Sorption experiments were carried out at 20°C under static conditions using aqueous solutions of $\mathrm{CdCl_2}\cdot 2.5\mathrm{H_2O}$, which were shaken on a laboratory shaker at a frequency of 200 min^{-1} over a period of 3 h. Cadmium chloride solutions with definite concentrations were prepared by dissolving a precisely weighed sample of analytical grade $\mathrm{CdCl_2}\cdot 2.5\mathrm{H_2O}$ in distilled water.

The sorption isotherms were obtained as follows. A set of test tubes were charged each with 0.5 g of the corresponding sorbent, 20 mL of aqueous cadmium

Table 1. Synthesis, phase composition, and specific surface area of sorbents **I** and **II**

Sorbent	Starting materials and conditions of synthesis	Phase composition		Specific surface area, m^2/g
		before roasting	after roasting at 900°C	
I	Solutions of sodium silicate Na_2SiO_3 (chemically pure, silica modulus SiO_2/Na_2O = 1) and calcium chloride ($CaCl_2 \cdot 2H_2O$ content of no less than 98.3%). Synthesis at 20°C.	Amorphous phase, $CaCO_3$	$CaSiO_3$, CaO	100
II	Borogypsum (content, wt %: SiO_2, 32.2; CaO, 28.4; CO_3, 31.3; Fe_2O_3, 2.7%) and aqueous potassium hydroxide of analytical grade. Synthesis under a pressure of 1.7 atm (2 h)	Amorphous phase, SiO_2, $CaCO_3$, $CaSO_4 \cdot 2H_2O$	$CaSiO_3$, SiO_2, $CaSO_4$	22

chloride with a concentration of 0.89 to 88.9 mM was added, and the test tube was shaken for 3 h. In blank experiments, the same sorbent was placed into a vessel charged with distilled water, and the mixture was shaken concurrently with the cadmium chloride-containing samples. In addition, similar experiments were performed under the same conditions with the borogypsum samples from which calcium silicates were synthesized and calcium carbonate of chemically pure grade. The sorbent was then removed by filtration, and the filtrate was analyzed for Cd^{2+} and Ca^{2+} ions.

The sorption kinetics were studied as follows. A set of test tubes were charged each with 0.5 g of the corresponding sorbant, 20 ml of aqueous cadmium chloride was added, and the rest tubes were shaken for 1 to 90 min. The initial concentration of Cd^{2+} was 1.004 (sorbent **I**) and 1.04 mM (sorbent **II**). The sorbent was separated by filtration, and the concentration of Cd^{2+} in the filtrate was determined. The sorption capacity (A_s, mmol/g) was calculated by the formula:

$$A_s = \frac{(c_0 - c_{eq})}{m} V,$$

where c_0 is the initial concentration of Cd^{2+} in solution, mM; c_{eq} is the equilibrium concentration of Cd^{2+} in solution, mM; V is the solution volume, L; and m is the sorbent weight, g.

The specific surface areas of the sorbents were determined by the low-temperature nitrogen adsorption method with the aid of a Sorbtometr-M instrument. The X-ray diffraction patterns were obtained on a D8 Advance automatic diffractometer by rotating samples under CuK_α irradiation. The X-ray powder diffraction (XRD) analysis was performed using EVA program and PDF-2 database.

The concentration of cadmium and calcium ions in solution was determined by atomic absorption spectroscopy (AAS) using a Solaar 6 M instrument at λ 228.8 and 422.6 nm, respectively. The detection limits were 0.001 µg/mL for cadmium and 0.0005 µg/mL for calcium.

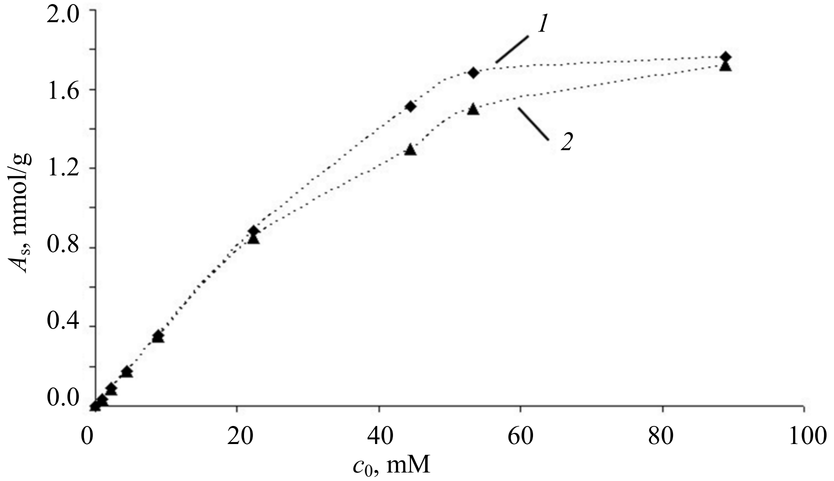

Fig. 1. Plots of the sorption capacity versus initial concentration of Cd^{2+} ions for (*1*) sorbent **I** and (*2*) sorbent **II**.

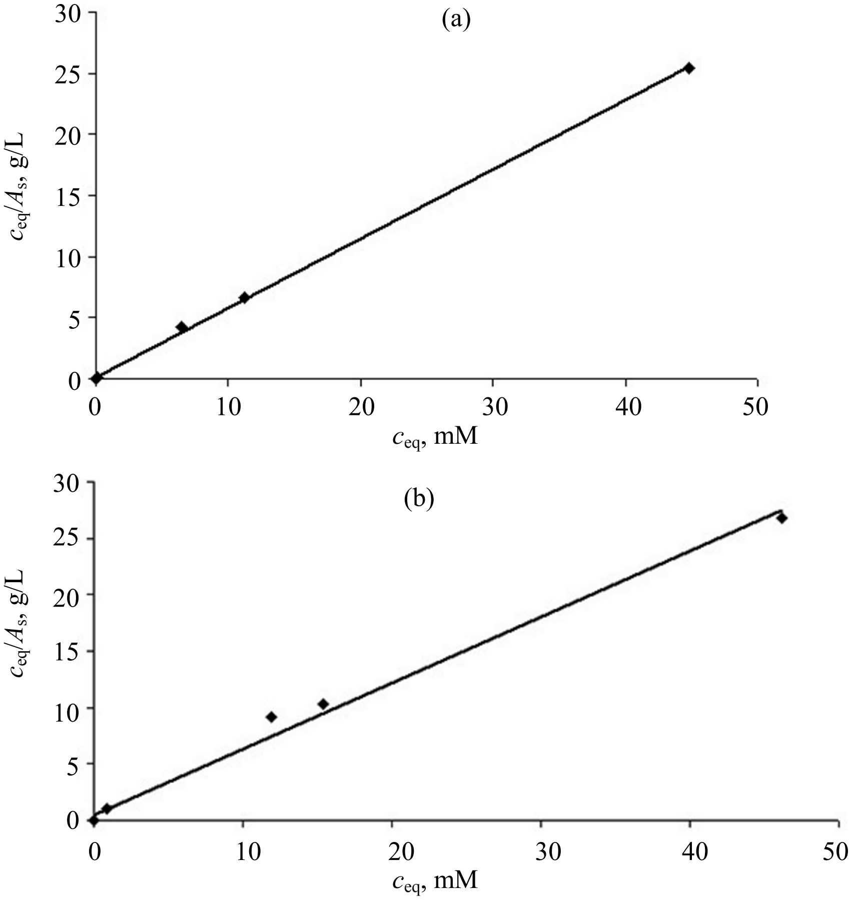

Fig. 2. Plots of c_{eq}/A_s versus c_{eq} according to the Langmuir equation for Cd^{2+} sorption by (a) sorbent **I** and (b) sorbent **II**.

RESULTS AND DISCUSSION

Figure 1 shows the plots of the sorption capacities of silicate sorbents **I** and **II** versus initial concentration of cadmium ions. It is unreasonable to represent sorption isotherms for highly efficient sorbents by plots of A_s versus the equilibrium sorbate concentration; in this case, the dependence is poorly demonstrative. As follows from Fig. 1, the examined silicate sorbents display an insignificant difference in their sorption capacities, and the latter are almost equal at Cd^{2+} concentrations lower than 22.2 mM.

The sorption ability of the silicate sorbents was assessed using the Langmuir equation:

$$\frac{c_{eq}}{A_s} = \frac{1}{A_s k} + \frac{c_{eq}}{A_m}, \qquad (1)$$

where c_{eq} is the equilibrium concentration of Cd^{2+} in solution, A_m is the maximum sorption capacity, and k is the Langmuir constant. The linear dependences of c_{eq}/A_s versus c_{eq} (Figs. 2a, 2b) confirm the validity of the Langmuir model as applied to the process under study and make it possible to determine the parameters A_m and k in Eq. (1) (Table 2).

Figure 3 shows the kinetic curves for sorption of Cd^{2+} ions by silicate sorbents **I** and **II**. No essential differences are observed in the sorption kinetics with sorbents **I** and **II**, and the equilibrium state is achieved in 1 min. The sorption capacities of **I** and **II** are 3.97×10^{-2} and 4.2×10^{-2} mmol/g, respectively (degree of extraction 98.9 and 98.7%). Our results indicate a high rate of Cd^{2+} extraction with sorbents **I** and **II**.

The sorption mechanism was studied by X-ray powder diffraction and atomic absorption spectroscopy. As stated above, both sorbents contained calcite in addition to amorphous phase, while SiO_2 and $CaSO_4\cdot 2H_2O$ were also found in sorbent **II** (Table 1). Thus, sorbents **I** and **II** are multicomponent systems, and possible interactions of cadmium chloride with calcium silicate hydrate, $CaCO_3$, SiO_2, and $CaSO_4\cdot 2H_2O$ must be taken into account while studying the sorption

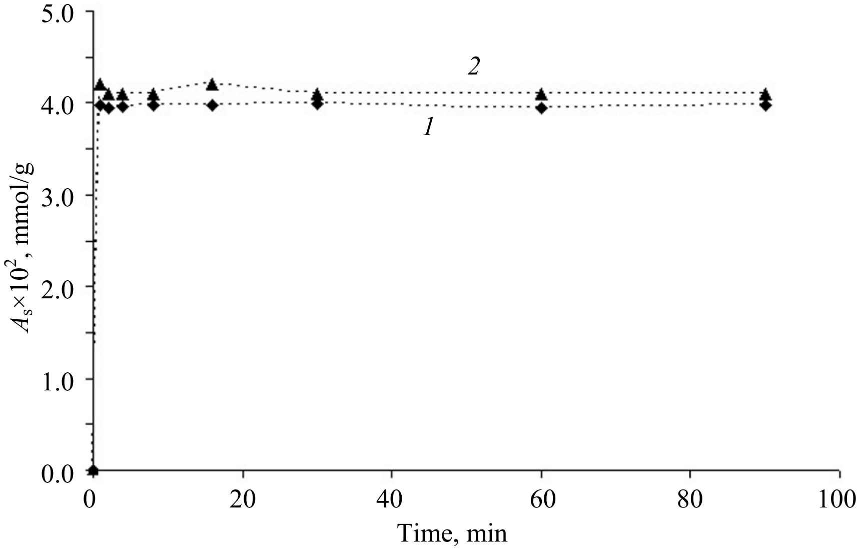

Fig. 3. Kinetic curves for Cd^{2+} sorption by silicate sorbents (*1*) **I** and (*2*) **II**.

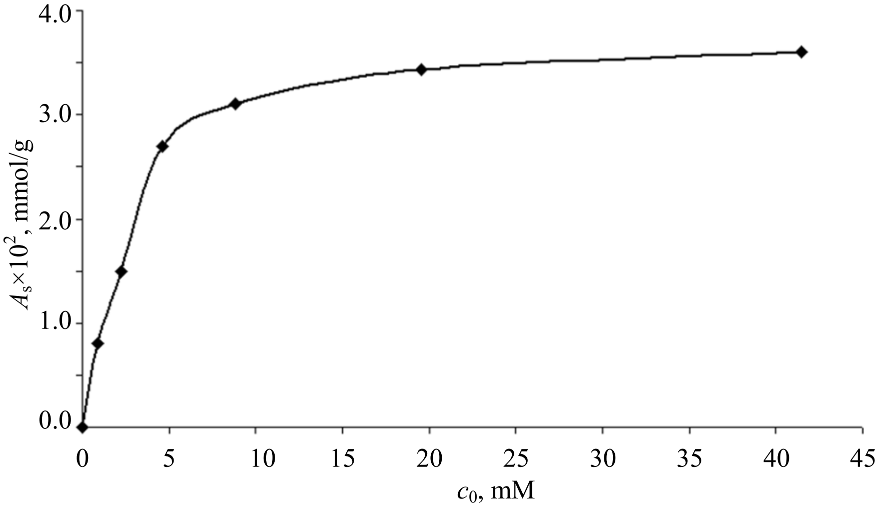

Fig. 4. Plot of the sorption capacity of calcium carbonate versus initial concentration of Cd^{2+} (chemically pure grade reagent).

mechanism. For this purpose, we calculated the Gibbs energies of the corresponding chemical reactions. Positive values of ΔG^0 for the reactions of cadmium chloride with calcium sulfate and silicon dioxide indicated that these reactions are improbable. Interactions of $CdCl_2$ with calcium carbonate (ΔG^0 = –241.7 kJ/mol) and calcium silicate hydrate (ΔG^0 = –254.6 kJ/mol) may be regarded as thermodynamically possible.

Table 2. Parameters of the Langmuir equation for Cd^{2+} sorption by silicate sorbents **I** and **II**

Sorbent	*k*, L/mmol	A_m, mmol/g	R^2
I	4.29 ± 0.858	1.76 ± 0.352	0.9994
II	1.23 ± 0.246	1.7 ± 0.34	0.9924

The X-ray powder diffraction data for sorbents **I** and **II** isolated after the sorption experiments showed the presence of $CdCO_3$ (otavite) starting from a certain Cd^{2+} concentration in the initial solution. The formation of $CdCO_3$ in sorbent **I** was detected at a Cd^{2+} concentration of 2.22 mM and higher, and in **II**, at 44.5 mM and higher. We can conclude that cation exchange in $CaCO_3$ present in both sorbents constitutes a pathway of the Cd^{2+} sorption process. However, it is not the only sorption pathway, as follows from the dependence of the sorption capacity of calcium carbonate on the initial Cd^{2+} concentration, which was obtained under analogous conditions (Fig. 4). It is

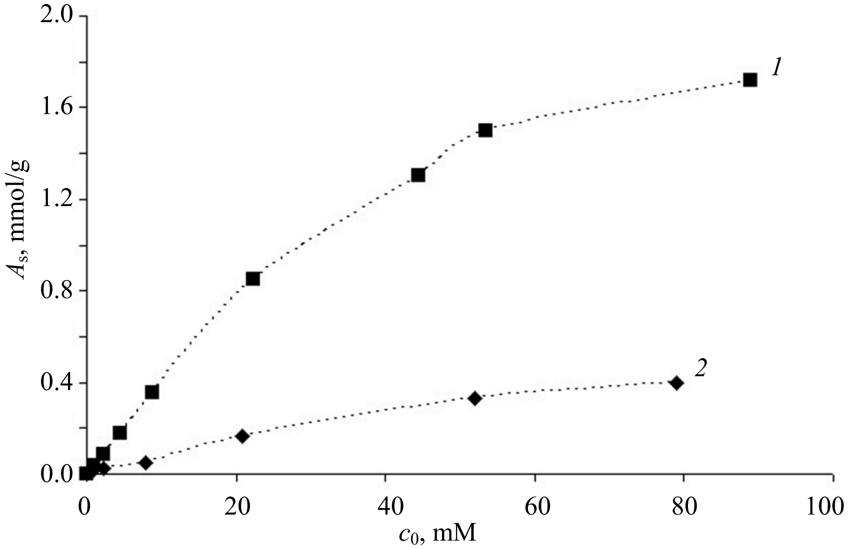

Fig. 5. Plots of the sorption capacity of (*1*) sorbent **II** and (*2*) borogypsum versus initial concentration of Cd^{2+} ions.

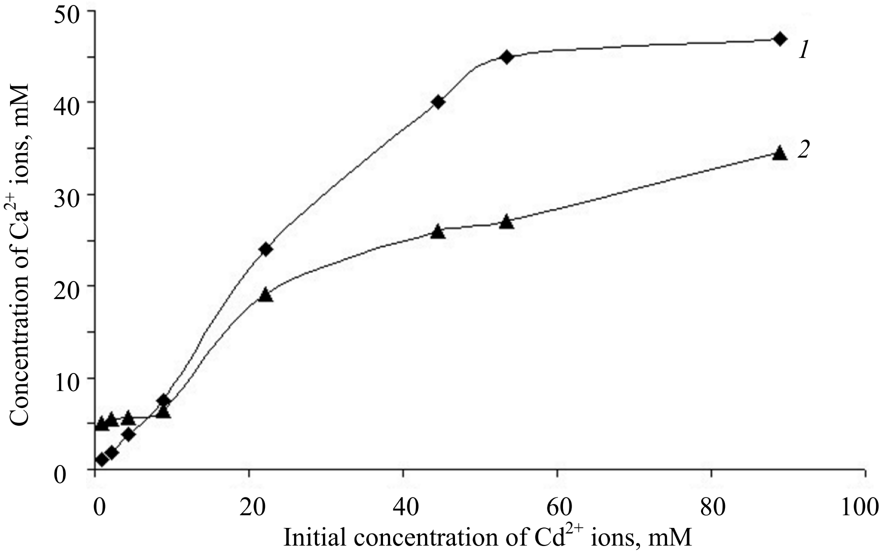

Fig. 6. Plot of the concentration of Ca^{2+} ions in the filtrate versus initial concentration of Cd^{2+} ions after sorption by (*1*) sorbent **I** and (*2*) sorbent **II**.

seen that the sorption capacity of $CaCO_3$ is considerably lower as compared to the examined silicate sorbents (Fig. 1); Langmuir equation parameters: $k = 0.833\pm0.16$ L/mol, $A_m = 3.6\times10^{-2}$ mmol/g). Therefore, the main contribution to sorption of Cd^{2+} ions from solution is provided by calcium silicate hydrate. However, cadmium silicate hydrate formed by reaction of cadmium chloride with calcium silicate hydrate is X-ray amorphous, so that it cannot be detected by XRD analysis in the spent sorbent.

While studying the mechanism of sorption with sorbent **II**, we examined the dependence of the sorption capacity of the initial borogypsum on the concentration of Cd^{2+} ions (Fig. 5). The sorption capacity of borogypsum is much lower than that of calcium silicate hydrate obtained therefrom (Langmuir parameters for Cd^{2+} sorption with borogypsum: $k = 0.046\pm0.008$ L/mmol, $A_m = 0.43\pm0.08$ mmol/g). Sorption of cadmium ions with borogypsum may be determined by the presence therein of minor impurities of such minerals as calcite, wollastonite, etc., which were not removed upon treatment of datolite concentrate with sulfuric acid.

Figure 6 illustrates variation of the concentration of Ca^{2+} in the filtrate obtained after separation of the sorbent versus initial concentration of Cd^{2+}. The concentration of Ca^{2+} in solution in control experiments with sorbents **I** and **II** was 0.05 and 4.8 mM, respectively. In both cases, the concentration of Ca^{2+} increased in parallel with the initial concentration of Cd^{2+}, which indicated Ca/Cd cation exchange in calcium carbonate and calcium silicate hydrate constituting the examined sorbents.

CONCLUSIONS

Materials based on calcium silicate hydrate of both synthetic and anthropogenic origins may be recommended for use as efficient sorbents for extraction of Cd^{2+} ions from aqueous solution. The examined sorbents are characterized by insignificant difference in their sorption capacities. The Cd^{2+} sorption process is described by the Langmuir equation. The maximum sorption capacity of the synthetic silicate sorbent is 1.76±0.352 mmol/g, and that of the anthropogenic material, 1.7±0.34 mmol/g.

There are no considerable differences in the sorption kinetics for the examined sorbents, and the sorption equilibrium is achieved in 1 min after the process started. The sorption mechanism involves Ca/Cd cation exchange in calcium silicate hydrate and calcium carbonate that are components of the sorbents.

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