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SYNTHESIS AND PROPERTIES
OF INORGANIC COMPOUNDS

# Effect of the Conditions of the Synthesis of Calcium Silicates on the Kinetics of Microbiological Treatment of Aqueous Media

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**Abstract**—The formation of calcium silicates under ordinary conditions (20°C) and under the conditions of autoclave treatment of the reaction mixture (220°C) was investigated. The composition and morphology of synthetic calcium silicates were studied, and so was their capacity to sorb the microorganisms *Escherichia coli* and *Bacillus subtilis.* It was determined that the sorption capacity of the studied samples is highest (to 79.4%) in the case of the sorption of the bacteria *Escherichia coli.* The efficiency of the sorption of *Bacillus subtilis* is lower (to 45.5%) than that of *Escherichia coli.* The kinetic parameters of the studied process were found using the equation of the kinetics of topochemical reactions. It was shown that the experimental results of studying the kinetics differ with only minimum deviations from the values calculated from the proposed equation throughout the studied time range. The obtained results are of certain scientific and practical interest in developing promising environmentally safe materials for microbiological treatment of aqueous media.

**Keywords:** immobilization of microorganisms, sorption, kinetics

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## INTRODUCTION

Natural and synthetic silicates of various compositions and structures, and also materials based on them are actively studied to apply them in processes of removal of various pollutants (heavy metals, long-lived radionuclides, pesticides, dyes, phenols, inorganic anions) from environmental objects. The interactions of silicates with various microorganisms, including pathogenic and opportunistic ones, are investigated, which extends the application ranges of these compounds toward, e.g., intestinal adsorbents with sorption–detoxification properties and also water treatment agents [1–6].

It was explored [7] whether or not one can use construction pit sand, finely porous granulated technical silica gel, and a zeolite-containing rock (composition: 12% clinoptilolite, 2% feldspar, 17.5% quartz, 28.5% cristobalite, 18.1% calcite, 20.3% smectite, and 3.9% mica) to sorb the bacteria *Escherichia coli* in an aqueous medium. It was determined that the zeolite-containing rock and the silica gel have a high capacity to sorb *E. coli* cells and can be recommended for further testing to clean polluted aqueous media as sorbents of pathogenic and opportunistic microorganisms.

The adsorption of *Escherichia coli* and *Streptococcus suis* on montmorillonite and kaolinite was studied as a function of the pH (in the range 4.0–9.0) and ionic strength of a solution (1–100 mM KCl and $CaCl_2$) [8]. In was found that the studied minerals adsorb more *S. suis* than *E. coli*, and that the adsorption capacity of montmorillonite is higher than that of kaolinite.

It was suggested [9] to create a standard series of small-scale automated water iron removal and disinfection plants, in which zeolites modified with silver ions are proposed to be used at the second stage of water treatment for fine purification and disinfection. The studies made on the microorganisms *E. coli* demonstrated that zeolite modified with silver ions can be included in the system of water treatment for drinking and household uses as an element of fine purification and disinfection of water.

Of certain interest are silicates of various compositions and structures (including alkaline-earth metal silicates), and also materials based on them [10]. For example, national and international publications present data on the sorption characteristics of calcium and barium silicates.

The capacity to sorb heavy metal ions were investigated for such compounds as xonotlite $Ca_6[Si_6O_{17}](OH)_2$, wollastonite $Ca_6Si_6O_{18}$, and 11 Å tobermorite $Ca_{10}[Si_{12}O_{31}](OH)_6{\cdot}8H_2O$ [11–14]. Sorbents based on amorphous barium silicates and aluminosilicates $BaSiO_3$ and $BaAl_2Si_2O_8$ were analyzed [15, 16]. There are almost no literature data on the sorption of microorganisms by synthetic calcium and barium silicates, although it is logical to assume that these products should have high capacity to also sorb microbial populations.

Significant advantages of synthetic analogs of these compounds over natural substances are their stable and controllable composition, and also the possibility to obtain a material with given properties.

Previously, we made a comparative study of the capacity of amorphous and crystalline calcium silicates produced from aqueous solutions under ordinary conditions and under autoclave synthesis conditions to sorb test cultures of the microorganisms *Escherichia coli* and *Bacillus subtilis* and associations of freshwater bacteria. The results of the study showed the advisability of further investigations [17].

The purpose of this work was to study the capacity of synthetic calcium silicates to sorb the microorganism *Escherichia coli* and *Bacillus subtilis* under various conditions of their formation.

## EXPERIMENTAL

Calcium silicates were synthesized under ordinary conditions ($t = 20°C$, sample 1) and under the conditions of autoclave treatment of the reaction mixture ($t = 220°C$, sample 2).

The specific surface area of the samples was determined by low-temperature nitrogen adsorption with a Sorbtometr-M device (Russia).

The X-ray powder diffraction patterns were recorded with a Bruker D8 ADVANCE diffractometer (Germany) ($CuK_\alpha$ radiation) and were analyzed using the EVA search software with the Powder Diffraction File database (Soorya N. Kabekkodu, 2007).

The morphology of the samples was studied with a Hitachi S5500 ultrahigh-resolution scanning electron microscope (Japan) with a Thermo Scientific energy-dispersive X-ray analysis accessory.

The sorption characteristics of the obtained samples were investigated using test cultures of microorganisms stored at the Museum of Cultures, Zhirmunskii Scientific Center for Marine Biology, Russian Academy of Sciences, Vladivostok, Russia: *Escherichia coli* ATCC 15034 and *Bacillus subtilis* BKM B501. The bacterial strains were grown on tryptose soy agar for 24 h at 28°C. The bacterial colonies were suspended in a 0.05 M NaCl solution to obtain a suspension with an optical density of $OD_{670} = 0.300$.

The binding of microorganisms to the sorbent was detected by turbidimetry from the change in the cell concentration in the aqueous medium with a Shimadzu UV-1280 spectrophotometer. For this purpose, 0.5 $cm^3$ of the studied sample was mixed with 20 mL of the bacterial suspension with $OD_{670} = 0.300$. The mixture was placed on a shaker for a certain time (30, 60, 90, and 120 min) at room temperature and then centrifugated at 4000 rpm for 15 min: the optical density of the supernatant was measured. The cell concentration in the suspension after the centrifugation was estimated with the spectrophotometer according to preliminarily plotted calibration curves. The number of adsorbed cells was calculated from the equation

$$I = \frac{C_0 - C_1}{C_0} \times 100\%,$$

where $C_0$ and $C_1$ are the concentrations of bacterial cells before and after the interaction with the samples, respectively, cells/mL. All the experimental data are presented as the averages of the results of three independent experiments.

## RESULTS AND DISCUSSION

### *Characteristics of Sorbents Based on Calcium Silicates*

According to the X-ray powder diffraction data, sample 1 with a specific surface area of 105.9 $m^2/g$ contains an amorphous phase and calcite $CaCO_3$. $CaCO_3$ forms in the multicomponent system $CaCl_2$–$Na_2SiO_3$–$H_2O$ under ordinary conditions by the carbonation of calcium hydroxide, which, in turn, forms by the interaction of amorphous calcium silicate with carbon dioxide dissolved in water.

Sample 2 with a specific surface area of 146.4 $m^2/g$ contains an amorphous phase and phases of monoclinic wollastonite $CaSiO_3$, calcium hydrosilicate $Ca_{1.5}SiO_{3.5}\cdot xH_2O/1.5CaO\cdot SiO_2\cdot xH_2O$, and 9 Å tobermorite $Ca_4(Si_6O_{15})(OH)_2\cdot 5H_2O$ (Table 1).

The thermogravimetric analysis (Fig. 1) demonstrated that the synthesized samples contain to 20% water, which is released in the temperature range of 20 to 700°C. The water content is maximum in sample 1 obtained under ordinary conditions (20°C). The thermogravimetric curves of samples 1 and 2 at temperatures of 816 and 822°C, respectively, showed exothermic events, which represent the transition of amorphous hydrated forms of calcium silicates to the crystalline phase of wollastonite. This was confirmed by the X-ray powder diffraction analysis of nonvolatile residues in the calcination of the samples to the above temperatures. The exothermic event is most pronounced for the sample synthesized under ordinary conditions.

The scanning electron microscopy showed differences in morphology between the obtained samples (Fig. 2). Under the conditions of autoclave treatment of the reaction mixture at 220°C, agglomerates of particles 1 to 40 μm in size with developed porous surface, including finely divided nanosized needle-like particles. The sample produced in the multicomponent system $CaCl_2$–$Na_2SiO_3$–$H_2O$ under ordinary conditions (20°C) also comprises agglomerates of finely

**Table 1.** Phase composition and specific surface area of the products of synthesis in various systems under various conditions (samples after drying at 85°C)

| Sample | System and conditions of synthesis | Phase composition | Specific surface area, $m^2/g$ |
|---|---|---|---|
| 1 | $CaCl_2$–$Na_2SiO_3$–$H_2O$, 20°C | Amorphous phase, calcite $CaCO_3$ | 105.9 |
| 2 | $CaSO_4 \cdot 2H_2O$–$SiO_2 \cdot nH_2O$–KOH–$H_2O$, 220°C (autoclave) | Amorphous phase; monoclinic wollastonite $CaSiO_3$ (PDF-2, 00-027-0088) with unit cell parameters $a$ = 15.42600 Å, $b$ = 7.32000 Å, and $c$ = 7.06600 Å, $\alpha$ = 90.000°, $\beta$ = 95.400°, $\gamma$ = 90.000°; calcium hydrosilicate $Ca_{1.5}SiO_{3.5} \cdot xH_2O/1.5CaO \cdot SiO_2 \cdot xH_2O$ (PDF-2, 00-033-0306); and 9 Å tobermorite $Ca_4(Si_6O_{15})(OH)_2 \cdot 5H_2O$ (PDF-2, 01-089-6459) with unit cell parameters $a$ = 6.73500 Å, $b$ = 7.38500 Å, $c$ = 22.48700 Å, $\alpha$ = 90.000°, $\beta$ = 90.000°, $\gamma$ = 123.250° | 146.4 |

divided porous particles 1 to several tens of microns in size. There are no needle-like particles.

### *Kinetics of the Sorption of Microorganisms by Calcium Silicates*

Table 2 and Fig. 3 present the data on the kinetics of the sorption of microorganisms by calcium silicates. These data show that there are common features in the sorption of the studied bacteria by samples 1 and 2. The sorption capacity increases with increasing time of contact of microorganisms with the studied samples. Of the two studied microorganisms, the sorption capacity of both samples is highest in the case of the sorption of the bacteria *Escherichia coli*. In as little as 30 min, the sorption efficiencies of samples 1 and 2 are 76.1 and 79.4%, respectively. The capacity to sorb *Escherichia coli* is highest for sample 2, which is a material consisting of several crystalline phases of calcium silicates and having a large specific surface area. The efficiencies of the sorption of *Bacillus subtilis* by samples 1 and 2 are lower than those of *Escherichia coli* and, in 30 min, are 45.5 and 43.3%, respectively.

The obtained kinetic data were analyzed using the kinetic equation proposed previously [18]:

$$\alpha_\tau = \alpha_m k\tau\left[\frac{1}{(1+k\tau)}\right], \tag{1}$$

where $k$ is a constant ($\text{time}^{-1}$), $\alpha_\tau$ is the conversion at time $\tau$, $\alpha_m$ is the maximum conversion, $\tau$ is the reaction time.

It follows from Eq. (1) that the constant $k$ can be determined both from the experimental dependences of $\alpha_\tau$ on $\tau$ by calculations from the equation

$$k = \sum \frac{\frac{\alpha_\tau}{\tau}\left(\frac{1}{\alpha_m - \alpha_\tau}\right)}{N}, \tag{2}$$

where $N$ is the number of the $\alpha_\tau$ values at the corresponding reaction times, and graphically by representing the experimental kinetic as a linear dependence of $\frac{1}{\alpha_\tau}$ on $\frac{1}{\tau}$:

$$\frac{1}{\alpha_\tau} = \frac{1}{\alpha_m} + \frac{1}{k\tau\alpha_m}, \tag{3}$$

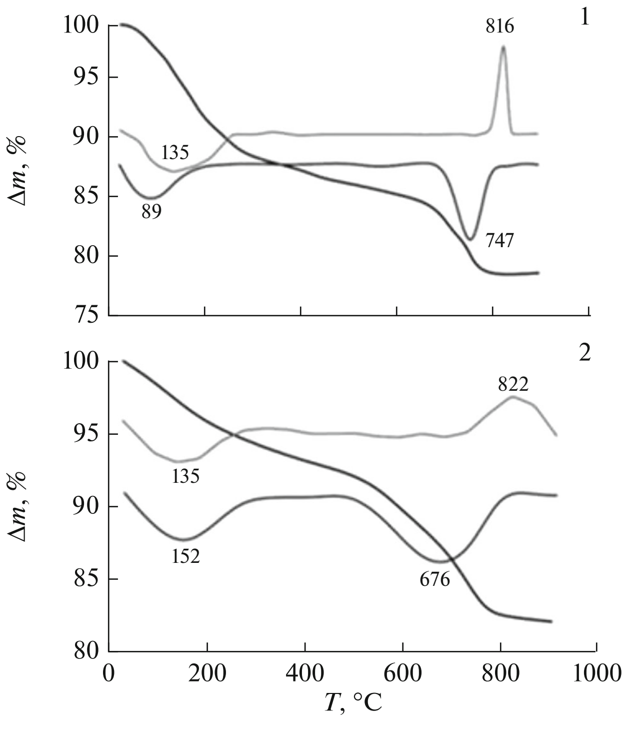

**Fig. 1.** Thermogravimetric curves of samples 1 and 2 dried at 20°C.

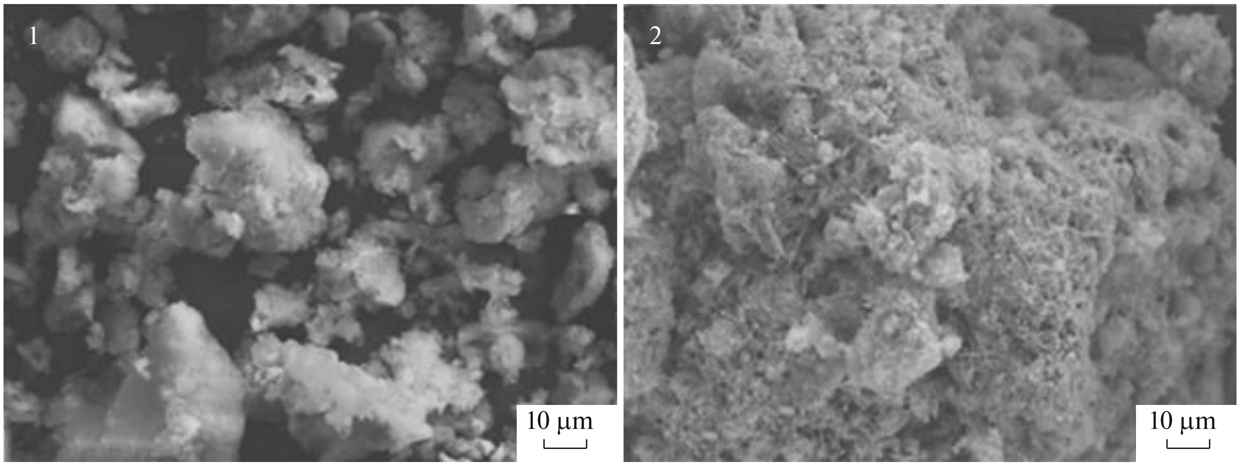

**Fig. 2.** Scanning electron microscopy images of microparticles of samples 1 and 2 after drying at 85°C.

where $1/\alpha_m$ is the ordinate as $\tau \to \infty$, and $k$ is found from the slope of the straight line or from the equation obtained by processing the experimental data by the least squares method:

$$y = a + bx, \tag{4}$$

where $a = 1/\alpha_m$, $b = 1/\alpha_m \cdot 1/k$, and $k = a/b$.

The above equation of the kinetics of topochemical reactions describes, with only minimum deviations, the sorption of metal ions by sorbents, the sorption mechanism of which is related to ion exchange; the kinetics of the reaction of production of calcium hydrosilicates; and the kinetics of the sorption of heavy metal ions by ion-exchange resins [16, 18].

Table 3 presents the parameters determined graphically after representing the experimental kinetic data as dependences of the inverse of the conversion (in this case, the degree of absorption of microorganisms) on the inverse of process time (Fig. 4).

As Table 3 shows, the proposed equation is suitable to describe the kinetics of the studied processes, which is confirmed by the corresponding correlation coefficients.

## CONCLUSIONS

A study was made of the kinetics of the sorption of the microorganisms *Escherichia coli* and *Bacillus subtilis* by synthetic calcium silicates synthesized under ordinary conditions (20°C) and under the conditions of autoclave treatment of the reaction mixture (220°C). The common features of the sorption of the studied bacteria were determined. The sorption capacity of the studied samples is highest in the case of the sorption of the bacteria *Escherichia coli*.

The obtained kinetic data were analyzed using a kinetic equation, which was previously used to analyze the kinetics of a number of topochemical reactions. It was experimentally proven that the equation highly accurately describes the studied process, which follows from the comparison of the calculated and experimental dependences.

The results of this work are of scientific and practical interest and can be used in such a promising application of calcium silicates as selective adsorption of pathogenic and opportunistic microorganisms from aqueous media, which extends the ranges of biological and medical applications of these materials.

**Table 2.** Kinetics of sorption of microorganisms by synthetic calcium silicates

| Culture of microorganisms | Time, min | Sorption efficiency, % | |
|---|---|---|---|
| | | sample 1 | sample 2 |
| *Escherichia coli* | 30 | 76.1 | 79.4 |
| | 60 | 76.3 | 81.8 |
| | 90 | 81.2 | 89.6 |
| | 120 | 80.3 | 89.3 |
| *Bacillus subtilis* | 30 | 45.5 | 43.3 |
| | 60 | 51.9 | 50.7 |
| | 90 | 63.2 | 55.2 |
| | 120 | 72.7 | 66.7 |

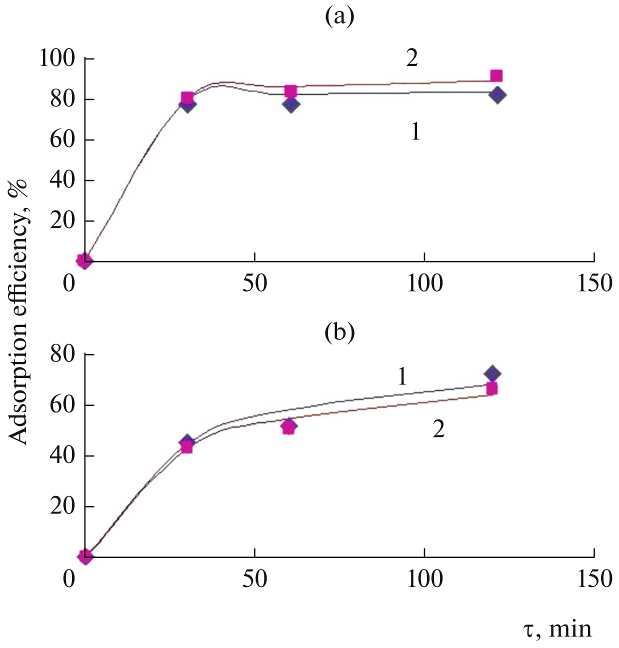

**Fig. 3.** Time dependences of the capacity of samples 1 and 2 to sorb the bacteria (a) *Escherichia coli* and (b) *Bacillus subtilis*.

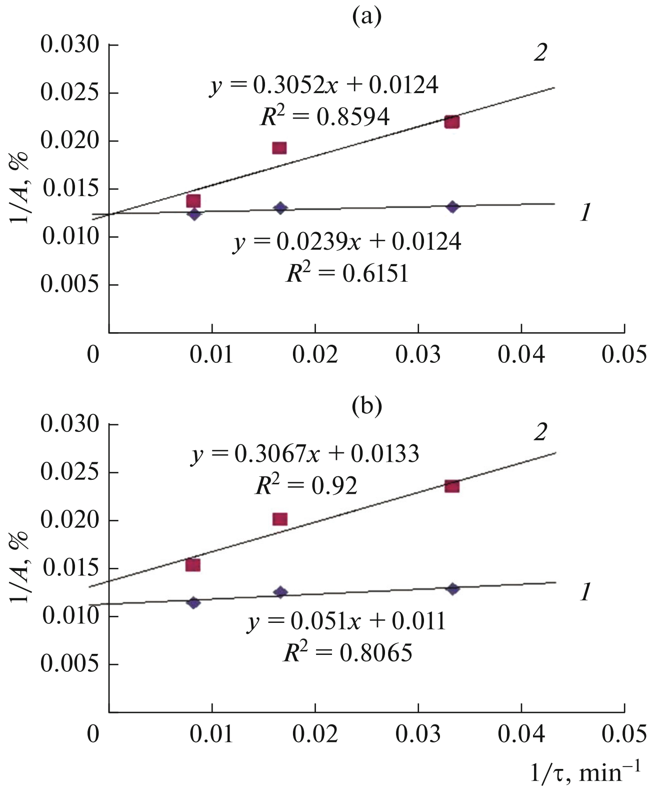

**Fig. 4.** Dependences of the inverse of the sorption capacity of samples (a) 1 and (b) 2 on the inverse of time in the sorption of the bacteria (*1*) *Escherichia coli* and (*2*) *Bacillus subtilis*.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

**Table 3.** Data on the kinetics of the sorption of bacteria by calcium silicates: Δ is the difference between the experimental and calculated conversions $A_\tau$

| Sample | Strain | τ, min | $A$, % | $y = ax + b$, ($R^2$) | $A_m$, % | $k_\tau$, min$^{-1}$ | $A_\tau$, % | Δ, % |
|---|---|---|---|---|---|---|---|---|
| 1 | *Escherichia coli* | 30 | 76.1 | $y = 0.023x + 0.012$, (0.615) | 83.33 | 0.5217 | 78.33 | 2.8 |
| | | 60 | 76.3 | | | | 80.75 | 5.5 |
| | | 120 | 80.3 | | | | 82.02 | 2.1 |
| | *Bacillus subtilis* | 30 | 45.5 | $y = 0.305x + 0.012$, (0.859) | 83.33 | 0.0393 | 45.11 | 0.9 |
| | | 60 | 51.9 | | | | 58.53 | 11.3 |
| | | 120 | 72.7 | | | | 68.77 | 5.7 |
| 2 | *Escherichia coli* | 30 | 79.4 | $y = 0.051x + 0.011$, (0.806) | 90.91 | 0.2157 | 78.74 | 0.8 |
| | | 60 | 81.8 | | | | 84.39 | 10.1 |
| | | 120 | 89.3 | | | | 87.53 | 4.4 |
| | *Bacillus subtilis* | 30 | 43.3 | $y = 0.306x + 0.013$, (0.92) | 76.92 | 0.0425 | 43.1 | 2.6 |
| | | 60 | 50.7 | | | | 55.25 | 7.1 |
| | | 120 | 66.7 | | | | 64.31 | 2.4 |

## ADDITIONAL INFORMATION

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