The Kinetics of Adsorption Binding of \( \text{Ba}^{2+} \) Ions by Trimethylsilylated Silica

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It was established that incomplete substitution of free silanols of fumed silica surface on (CH\(_3\))\(_3\)Si-groups leads to an increase in the ability of modified SiO\(_2\) to adsorb Ba\(^{2+}\) cations from an electrolyte solution. Silica with 48.3% of trimethylsilyl (TMS) groups adsorbs 1.8 mmol·g\(^{-1}\) of Ba\(^{2+}\) cations from 0.01 M BaCl\(_2\) solution, that in 3 times more than the adsorption of these cations by unmodified silica.

It was found that the adsorption of cations by basic and modified silica is well described by the pseudo-second order Lagergren equation. The high adsorption activity of silica with chemisorbed TMS-groups is due to the formation of local regions with relatively large values of negative and positive electrostatic potentials in the vicinity of grafted TMS-groups.

**Keywords:** silica, silanols, chemosorption, trimethylsilyl groups, adsorption binding of ions.

Introduction

Aerodispersed amorphous silica, obtained by combustion of silicon-containing substances (SiCl\(_4\), CH\(_3\)SiCl\(_3\)) in air-hydrogen flame at 1100-1350°C, are used as adsorbents in medicine, biology, chromatography, carriers of active substances in catalysis, polymer fillers, thickening of liquids environments, etc. [1-5]. Fumed silica acquire new useful properties as a result of the chemical modification of their surface, in particular, due to incomplete substitution of their silanols (hydroxyls) on TMS (CH\(_3\))\(_3\)Si-groups. The investigation of the effect of grafted (CH\(_3\))\(_3\)Si-groups on the physicochemical properties of aerodispersed silica revealed that the change of the chemical state of the oxide material surface in such way increases its adsorption properties. Modified silica with 37.2% of grafted TMS-groups binds a large amount of water – up to 5 g of H\(_2\)O per 1 g of SiO\(_2\) [6]. The silica surface becomes especially active, i.e. adsorbs nonpolar molecules of methane and hydrogen when a hydration degree \( h = 0.05 \) (0.005 g of H\(_2\)O per 1 g of SiO\(_2\)). It was also found that the organosilica acquires lyophilic properties as a result of the substitution of 30-50% of silanols on the TMS-groups [7]. In the aqueous medium, the interparticle interaction decreases and the interaction of the particles’ surface with the molecules of the aqueous medium increases. Modified silica suspensions have higher equilibrium viscosity compared to that of basic silica, moreover SiO\(_2\) particles do not lose the ability to thicken the dispersed medium even when their fractal structure is destroyed by ultrasonic field.

At present, the search for materials that are capable to adsorb the heavy metal ions is being used to solve environmental problems. Since the new properties of trimethylsilylated silica are due to a change in the distribution of the electrostatic potential on its surface, it can be expected that chemical modification of the surface also increases SiO\(_2\) activity as regards adsorption binding of metal ions in aqueous media.

The purpose of this work is to investigate the effect of incomplete trimethylsilylation of the silica surface on its ability to adsorb Ba\(^{2+}\) ions from the aqueous medium, as well as to study the kinetics of the binding of these ions of the basic and modified SiO\(_2\).

I. Objects and methods

An aerodispersed product A-300, obtained by combustion of SiCl\(_4\) vapor in a hydrogen-air flame at 1100-1350°C in industrial conditions, was as the basic silica for chemisorption of (CH\(_3\))\(_3\)Si-groups on its surface [9, 10]. The specific surface of silica was 302 m\(^2\)·g\(^{-1}\), the
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concentration of free silanol groups on its surface – 0.8 mmol·g\textsuperscript{-1}.

The trimethylethoxysilane (CH\textsubscript{3})\textsubscript{3}SiOC\textsubscript{2}H\textsubscript{5} (TMES) (Sigma-Aldrich, USA) was used as the precursor for silica modification. The chemical grafting of (CH\textsubscript{3})\textsubscript{3}Si-groups was carried out as a result of contacting a modifier vapour with SiO\textsubscript{2} surface at 150-160\textdegree C. Small amount of acetic acid (as a catalyst) was added to the reactor to reduce the temperature of the chemosorption process.

The adsorbent mass was 20-30 mg and the BaCl\textsubscript{2} volume solution was 10 ml at measuring the adsorption value \(A_{eq}\) at adsorption-desorption equilibrium. The duration of interaction of the adsorbent with the electrolyte solution was 180 min. The initial concentration of Ba\textsuperscript{2+} ions in the solutions varied from 0.0025 to 0.1 mol·l\textsuperscript{-1}. The pH value of the electrolyte was ~ 7.0 at those concentrations.

The BaCl\textsubscript{2} solution concentration was 0.01 mol·l\textsuperscript{-1} and the sorption duration varied from 1 to 180 min at studies of kinetics of Ba\textsuperscript{2+} ion binding.

The number of silanols and TMS-groups on SiO\textsubscript{2} surface was controlled by IR-spectroscopy using the Specord M-80 spectrometer (Carl Zeiss, Yena, Germany). The degree of SiO\textsubscript{2} modification \(\theta\) (in percentages) was determined by the ratio of the optical density of the absorption band of free silanol groups 3750 cm\textsuperscript{-1} in the spectrum of modified and basic silica using the formula:

\[
\theta = 100 \left(1 - \frac{D}{D_0}\right),
\]

where \(D_0\) and \(D\) – the area of the absorption band 3750 cm\textsuperscript{-1} in initial and modified SiO\textsubscript{2}, respectively.

The hydrophilicity of basic and modified silica was determined by P. Rebinder’s method. For this purpose, the specific heat of wetting of the material surface by polar and nonpolar solvents was measured [7] and the hydrophilicity coefficient \(\beta\) was calculated analytically by the formula:

\[
\beta = \frac{Q_w}{Q_d},
\]

where \(Q_w\) and \(Q_d\) – heat of wetting of surface by water and decane, respectively. The heat of wetting of materials was measured using differential calorimeter DAC1.1A (EPSE, Chernogolovka). Calibration of the device was carried out by the thermal effect of KCl dissolving in an aqueous medium (18.6 ± 0.012 kJ·mol) at 20\textdegree C.

The adsorption ability of trimethylsilylated and basic silicas for binding of Ba\textsuperscript{2+} ions was determined by a method that involves mixing the material with the electrolyte solution of the appropriate concentration, keeping the mixture in a static mode at 20\textdegree C for 4 hours, and removing of the adsorbent from the solution by centrifugation. The equilibrium concentration of cations in the overprecipitate solution \(C_{eq}\) (mmol·l\textsuperscript{-1}) was determined by the method of complexometric titration [10, 11]. For this purpose, an ammonium buffer mixture NH\textsubscript{4}Cl + NH\textsubscript{4}OH and a few drops of 5% alcohol solution of eriochrome black T were added to the solution, then titration was performed by sodium edetate solution. The adsorption value \(A\) (mmol·g\textsuperscript{-1}) was calculated by the formula:

\[
A = \frac{(C_{in} - C_{res})V}{m},
\]

where \(C_{in}\) and \(C_{res}\) – concentration of ions in the initial and residual solution, respectively; \(m\) – adsorbent mass, \(V\) – solution volume.

The distribution coefficient \(K_d\) (l·g\textsuperscript{-1}) of adsorbents was determined by the formula:

\[
K_d = \frac{A}{C_{res}}.
\]

The value of the distribution coefficient indicates the volume of solution from which 1 g of adsorbent is able to remove (bind) the entire amount of dissolved adsorbate.

II. Results and discussion

Complete substitution of silanols of pyrogenic silica surface on TMS-groups is used to obtain an organophilic product that is not wetted by water [5]. Experimental standards of modified silica containing 27.2, 37.2, and 48.3% of chemosorbed (CH\textsubscript{3})\textsubscript{3}Si-groups are denoted as M30, M40, and M50, respectively (Table 1).

Table 1

<table>
<thead>
<tr>
<th>Standard</th>
<th>Substitution degree of silanols on TMS-groups for explored standards</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-300</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>M30</td>
<td>27.2</td>
<td>1.6</td>
</tr>
<tr>
<td>M40</td>
<td>37.2</td>
<td>1.5</td>
</tr>
<tr>
<td>M50</td>
<td>48.3</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The modified silica retains its hydrophilicity when replacing almost half of the SiO\textsubscript{2} particles’ silanols on TMS-groups (standard M50). The hydrophilicity coefficient of this standard decreases from 2.0 to 1.4 compared with the basis silica A-300. The extrapolation of \(\beta = f(\theta)\) dependence to the value \(\beta = 1.0\) allows to determine that complete non-wetting of the silica surface takes place at ~ 80% substitution of silanols on TMS-groups.

The adsorption indices of Ba\textsuperscript{2+} ions from 0.01 M BaCl\textsubscript{2} solution by explored standards of basic and modified silica are given in Table 2. The results of the studies confirm that the adsorption of Ba\textsuperscript{2+} ions increases with increasing of number of grafted TMS-groups.

The standard M50 adsorbs 1.8 mmol·g\textsuperscript{-1} of Ba\textsuperscript{2+} cations, that in three times exceeds the adsorption rate of these ions by the unmodified standard A-300. Characteristically, the modification of silica also improves the distribution coefficient of the adsorbent. In particular, 1 g of the standard M50 is capable of
removing all $\text{Ba}^{2+}$ cations from 0.46 l of 0.01 M $\text{BaCl}_2$ solution, while the same amount of basic adsorbent is able to bind all cations only with 0.07 l of this solution.

The isotherms of adsorption of $\text{Ba}^{2+}$ cations by basic and modified silica (Fig. 1) are typical for the case of Langmuir’s monomolecular adsorption [12].

For the practical use of adsorbents, information is needed about their maximum sorption capacity in the state of equilibrium and on the kinetics of the process itself. The adsorption results within the framework of the appropriate kinetic model allow to predict the results of adsorption processes and ensure their maximum efficiency.

The common kinetic models of adsorption processes are the absorption (diffusion) model and the Elovich kinematic model [13-16]. In the last two decades, researchers have used the Lagergren equation of the pseudo-first or pseudo-second order for an analytical description of the kinetics of adsorption processes [15-19].

Analyzing graphic dependences $A_t = f(t)$ (Fig. 2), it can be found that the adsorption value is different for each standard during first minutes of contacting the materials with the electrolyte solution. The smallest value is characteristic for basic silica – 66 mg·g$^{-1}$. When the number of grafted TMS-groups increases, the initial value increases to 1.2 mg·g$^{-1}$ for A-300, 1.7 mg·g$^{-1}$ for M30, and 1.8 mg·g$^{-1}$ for M50.

Table 2

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>Electrolyte</th>
<th>Adsorption, mmol·g$^{-1}$</th>
<th>Distribution coefficient, l·g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-300</td>
<td>$\text{Ba}^{2+}$</td>
<td>0.01 M $\text{BaCl}_2$</td>
<td>0.59 ± 0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>M30</td>
<td>$\text{Ba}^{2+}$</td>
<td>0.01 M $\text{BaCl}_2$</td>
<td>1.2 ± 0.17</td>
<td>0.24</td>
</tr>
<tr>
<td>M40</td>
<td>$\text{Ba}^{2+}$</td>
<td>0.01 M $\text{BaCl}_2$</td>
<td>1.7 ± 0.35</td>
<td>0.45</td>
</tr>
<tr>
<td>M50</td>
<td>$\text{Ba}^{2+}$</td>
<td>0.01 M $\text{BaCl}_2$</td>
<td>1.8 ± 0.06</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Nonlinear equation</th>
<th>Linear equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elovich</td>
<td>$\frac{dA_t}{dt} = a e^{-bt}$</td>
<td>$A_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t)$</td>
</tr>
<tr>
<td>Absorption binding</td>
<td>$-$</td>
<td>$A_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t)$</td>
</tr>
<tr>
<td>Pseudo-first order</td>
<td>$\frac{dA_t}{dt} = K_2 (A_{eq} - A_t)$</td>
<td>$\lg(A_{eq} - A_t) = \lg A_{eq} - \frac{K_2}{2.303} t$</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>$\frac{dA_t}{dt} = K_3 (A_{eq} - A_t)^2$</td>
<td>$\frac{t}{A_t} = \frac{1}{K_3 A_{eq}^2} + \frac{t}{A_{eq}}$</td>
</tr>
</tbody>
</table>

$A_t$, $A_{eq}$ – adsorption value at the time $t$ and the state of adsorption-desorption equilibrium, respectively [mg·g$^{-1}$]; $a$ – initial value of adsorption [mg·g$^{-1}$·min$^{-1}$];

$b$ – binding degree of adsorbent due to chemisorption [g·mg$^{-1}$]; $K_1$ – the constant of diffusion insertion of the adsorbive [mg·g$^{-1}$·min$^{-0.5}$]; $K_0$ – mass fraction of the boundary layer [mg·g$^{-1}$]; $K_2$ – coefficient [min$^{-1}$]; $K_3$ – coefficient [g·mg$^{-1}$·min$^{-1}$].
adsorption of Ba\(^{2+}\) ions also increases for samples M30, M40, and M50 and is 106, 129, and 148 mg·g\(^{-1}\), respectively.

The curves of the kinetic process for A-300, M30 and M40 standards exhibit slight deviations from the parabolic dependence in the direction of \(A_t\) values decreasing in the time interval of 20-40 min. This indicates on instability of the adsorption-desorption equilibrium in the system oxide material-electrolyte solution in this time period.

For the search analytic equations describing the kinetic process of Ba\(^{2+}\) ions binding by basic and modified silica, known mathematical models were used (Table 3).

The adequacy of the equation of the kinetic model of adsorption with experimental data was estimated by the correlation coefficient \(R^2\) [20-21]. In particular, Table 4 shows the adsorption equations of Ba\(^{2+}\) ions for experimental adsorbents in the approximation of the Elovich model and their corresponding correlation coefficients \(R^2\).

The adequacy of the analytic equations to the experimental values of adsorption is also illustrated by Fig. 3. The correlation coefficient \(R^2\) of the Elovich equation for adsorption of cations by basic silica is 0.196. The growth of the number of grafted TMS-groups on the surface of adsorbents improves the accuracy of analytic equations. For example, \(R^2\) value increases for standards M30 and M40, i.e. equal to 0.774 and 0.876, respectively. The constant magnitude of the inclination angle of the linear dependences \(A_t = f(\ln t)\) for standards A-300, M30 and M40 indicates the invariability of the

### Table 4

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Process duration, min</th>
<th>Adsorption equation</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-300</td>
<td>1-180</td>
<td>(A_t = 3.75 \ln t + 86.86)</td>
<td>0.196</td>
</tr>
<tr>
<td>M30</td>
<td>1-140</td>
<td>(A_t = 6.96 \ln t + 104.98)</td>
<td>0.774</td>
</tr>
<tr>
<td>M40</td>
<td>1-180</td>
<td>(A_t = 17.66 \ln t + 118)</td>
<td>0.876</td>
</tr>
<tr>
<td>M50</td>
<td>1-10, 10-180</td>
<td>(A_t = 29.61 \ln t + 147.7)</td>
<td>0.959</td>
</tr>
</tbody>
</table>

Fig. 3. The linear dependences of adsorption of Ba\(^{2+}\) ions by basic silica A-300 (a) and modified silica M30 (b), M40 (c) and M50 (d) in Elovich model approximation.
The adsorption equation for Ba\(^{2+}\) ions by modified silica M50 in the approximation of absorption and the pseudo-first order models and their correlation coefficients \(R^2\)

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Adsorption equation and correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption model</td>
<td>First stage</td>
</tr>
<tr>
<td></td>
<td>(A_1 = 30.3t^2 + 123.6)</td>
</tr>
<tr>
<td>Pseudo-first order model</td>
<td>(\lg(A_{eq} - A_t) = -0.7t + 2.0)</td>
</tr>
</tbody>
</table>

Table 5

The adsorption equation for Ba\(^{2+}\) ions by adsorbents M50 in the approximation of the pseudo-second order model and their correlation coefficients \(R^2\)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption equation</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-300</td>
<td>(\frac{t}{A_t} = 0.009t + 0.016)</td>
<td>0.996</td>
</tr>
<tr>
<td>M30</td>
<td>(\frac{t}{A_t} = 0.007t + 0.020)</td>
<td>0.996</td>
</tr>
<tr>
<td>M40</td>
<td>(\frac{t}{A_t} = 0.005t + 0.014)</td>
<td>0.999</td>
</tr>
<tr>
<td>M50</td>
<td>(\frac{t}{A_t} = 0.004t + 0.012)</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table 6

Fig. 4. The dependence of \(K_1\) value in the pseudo-second order equation from the contact time with the electrolyte solution for modified silica M50.
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the short-wave region of absorption bands in the infrared spectra of modified silica, associated with asymmetric oscillations of tetrahedra SiO\(_4\) (\(\nu_a\)) and deformation oscillations of siloxane bridges (\(\nu_{OSiO}\)) [22].

Simulation of the structure of a number clusters of silica surface by quantum chemistry methods revealed that there is significant change in the electrostatic potential distribution during the consistent substitution of surface silanols by the TMS-groups [23, 24]. The regions with negative potential (-60 and -113 kJ·mol\(^{-1}\)) are formed close to the silicon atom of the grafted group at the initial stages of trimethylsilylation (Fig. 5, b). An increase in the number of TMS-groups relative to a certain value is accompanied by a decrease in the negative potential region and the appearance of positive potential areas (~ 1260 and 1440 kJ·mol\(^{-1}\)) localized at the entrance to the hexagonal cavity (Fig. 5, c), which is also characteristic for fully trimethylsilylation SiO\(_2\) surface.

The results of modeling of the structure of the modified silica surface and the study of the electrostatic potential distribution allow predicting that incomplete trimethylsilylation of the SiO\(_2\) surface may also increase significantly the adsorption activity of the oxide material relative to negatively charged ions of Cl\(^-\), Br\(^-\), SO\(_4^{2-}\), CO\(_3^{2-}\), HCO\(_3^-\), etc.

**Conclusions**

It is found that the substitution of 30-50 % of free silanols of fumed silica surface on (CH\(_3\))\(_3\)Si-groups leads to an increase in the ability of modified SiO\(_2\) to adsorb Ba\(^{2+}\) cations from the electrolyte solution. In particular, modified silica with 48.3 % of TMS-groups adsorbs 1.8 mmol·g\(^{-1}\) Ba\(^{2+}\) cations from 0.01 M BaCl\(_2\) solution, that in 3 times more then the adsorption of these cations by unmodified silica.

It is show that the adsorption of Ba\(^{2+}\) ions by basic and modified silica is well described by the pseudo-second order Lagergren equation. The process of cation binding by adsorbents A-300, M30 and M40 is carried out in one stage and ends with the formation of monomolecular layer of adsorptive.

The adsorption process by modified silica M50 takes place in two stages, i.e. a monomolecular layer of the adsorptive is formed on the adsorbent surface for 10 min from the beginning of contact of trimethylsilylated silica with an electrolyte solution, and a polymolecular layer is formed over the specified time. The fraction of Ba\(^{2+}\) ions in its monomolecular layer is almost 85 % of the equilibrium amount of the bound adsorptive.
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Кінетика адсорбційного зв’язування йонів Ва\(^{2+}\) триметилсилільованими кремнеземами

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Встановлено, що неповне заміщення вільних силанолів поверхні пірогенного кремнезему на (CH\(_3\))\(_3\)Si-групи призводить до зростання спроможності модифікованого SiO\(_2\) адсорбційно зв’язувати катіони Ва\(^{2+}\) із розчину електроліту. Зокрема, кремнезем із 48,3 % триметилсилільних груп адсорбує 1,8 ммоль·г\(^{-1}\) катіонів Ва\(^{2+}\) із 0,01 М розчину BaCl\(_2\), що в 3 рази перевищує адсорбцію цих катіонів не модифікованим кремнеземом. З’ясовано, що адсорбція катіонів базовим та модифікованими кремнеземами добре описується рівнянням Лагергрена псевдодругого порядку. Висока адсорбційна активність кремнезему з хемосорбованими триметилсилільними групами обумовлена утворенням в околі прищеплених груп локальних областей із відносно великими значеннями негативного і позитивного електростатичних потенціалів.

**Ключові слова:** кремнезем, силаноли, хемосорбція, триметилсилільні групи, адсорбційне зв’язування йонів.