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S. K. Milonjić[a]; M. R. Bošković[a]; T. S. Ćeranić[b]
[a] THE BORIS KIDRIČ INSTITUTE OF NUCLEAR SCIENCES, BELGRADE, YUGOSLAVIA [b] FACULTY OF SCIENCE, UNIVERSITY OF BELGRADE, BELGRADE, YUGOSLAVIA

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Adsorption of Uranium(VI) and Zirconium(IV) from Acid Solutions on Silica Gel

S. K. MILONJIĆ and M. R. BOŠKOVIĆ
THE BORIS KIDRIČ INSTITUTE OF NUCLEAR SCIENCES
P.O. BOX 522, 11001 BELGRADE, YUGOSLAVIA

T. S. ĆERANIĆ
FACULTY OF SCIENCE
UNIVERSITY OF BELGRADE
P.O. BOX 550, 11001 BELGRADE, YUGOSLAVIA

Abstract

Adsorption of uranium(VI) and zirconium(IV) from aqueous solutions on silica gel was investigated by the batch equilibration method. The influence of shaking time and concentrations of nitric acid (i.e., pH of solution) and metal ions in solution were studied. Adsorption of uranium(VI) and zirconium(IV) increases with an increase of pH (decrease of nitric acid concentration) and ion concentrations. The adsorption mechanism of uranium(VI) and zirconium(IV) from aqueous solutions on silica gel is proposed. It is shown that zirconium(IV) and uranium(VI) can be separated if the concentration of nitric acid in solution is higher than 0.01 mol/dm^3.

INTRODUCTION

Among inorganic oxides, which generally withstand high temperature and radiation doses, silica (SiO_2) finds many applications in nuclear technology. Sorption properties of silica gel arise from the presence of surface hydroxyl groups whose dissociation depends on the pH. General and theoretical aspects of sorbents, based on silica gel in radiochemistry, have been covered in a book (*1*). The property of silica gel to adsorb on its surface polyvalent ions, which easily hydrolyze from acidic solutions, is of particular significance. A typical representative of that group of elements is zirconium.

An exhaustive literature survey on the sorption behavior of uranium, including inorganic and chelating sorbents, has been published (*2*). A number of papers have been devoted to the study of the influence of certain conditions on uranium and zirconium sorption by silica gel (*3–5*). In spite of numerous studies on this problem, there seems to be no conclusive quantitative explanation either for the adsorption mechanism of uranium(VI) and zirconium(IV) or for the higher selectivity of silica toward zirconium(IV).

The aim of the present paper is to investigate the adsorption of uranium(VI) and zirconium(IV) from nitric acid solutions on silica gel as a function of shaking time and concentrations of nitric acid (pH of solution) and metal ions in order to clarify the adsorption mechanism of these ions on silica gel.

EXPERIMENTAL

Silica gel (a commercial product of Kemika, Zagreb, Yugoslavia) for chromatographic use, as a 0.2–0.5 mm fraction, was used as an adsorbent. The specific surface area of the fraction, as determined by a Ströhlein area meter using the single point nitrogen adsorption method, was found to be 292 ± 3 m^2/g. The amorphous structure of the material was established by the x-ray method, using a Siemens Kristalloflex 4 instrument with CuK_α radiation.

Uranium solutions were prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ (Kemika, Zagreb, Yugoslavia, p.a. quality). Zirconium solutions were prepared from zirconyl oxychloride ($ZrOCl_2 \cdot 8H_2O$) made in our laboratory from zirconium basic carbonate (Magnesium Electronic Inc.: Batch C 163-T 3). Details on zirconyl oxychloride preparation are given elsewhere (*6*). Solutions, fresh for each experiment, were prepared by using doubly distilled water and nitric acid (Unis, Goražde, Yugoslavia, p.a. quality).

In all experiments, 0.250 g of the silica gel was equilibrated with 25 cm^3 of aqueous solutions containing uranium(VI) or zirconium(IV) in stoppered plastic vials. The vials were agitated by using a mechanical shaker in thermostated air at 22 ± 2°C.

Concentrations of uranium and zirconium in solutions were determined spectrophotometrically by using ammonium thioglycolate at a wavelength of 380 nm (*7*) and alizarin S at 520 nm (*8*, *9*), respectively. The difference in the metal ion solution concentrations before and after equilibration gave the adsorbed ion amount on silica gel. The pH of the solutions before and after adsorption was recorded.

The results obtained are the mean values of at least two independent experimental runs. The overall adsorption measurement error is estimated to be not greater than ±3%.

RESULTS AND DISCUSSION

Preliminary experiments were carried out to establish the time required for the adsorption of uranium(VI) and zirconium(IV) from nitric acid solutions (various concentrations) on silica gel to reach equilibrium. The rate of U(VI) adsorption was very rapid, and equilibrium was usually approached within 5 min. On the contrary, the adsorption of zirconium(IV) proceeded slowly and attained equilibrium after about 24 h. The results obtained are in agreement with the results of Ahrland et al. (*3*). Therefore, 2 and 24 h equilibration times were employed, respectively, in all the uranium(VI) and zirconium(IV) adsorption measurements.

The aqueous solution pH is an important variable which controls the adsorption of metal ions by the oxide/aqueous solution interface. Therefore, the effect of pH (i.e., nitric acid concentration) on the adsorption of uranium(VI) and zirconium(IV) on silica gel was examined. The results are given in term of percent adsorption (%), which was estimated from

$$\%\ \text{adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where C_0 and C_e are the initial and the equilibrium metal ions concentrations, respectively.

The adsorption of uranium(VI) from nitric acid solutions with different pH values in the 2–5 range on silica gel was examined. The results are shown in Fig. 1. The percent adsorption increases with an increase in aqueous solution pH. It increases sharply between pH 3.2 and 4.2, reaching a maximum value (98%) in the vicinity of pH 4.7. This may be explained by a mechanism involving prior hydrolysis of uranium(VI) to give a hydrolysis product. Data on the hydrolysis tend to support this mechanism. The concentration of the hydrolyzed uranium(VI) species depends on the uranium(VI) concentration and the solution pH. The distribution of various hydrolyzed uranium(VI) species as a function of pH at a total uranium concentration of 4.0×10^{-4} mol/dm^3 is presented in Fig. 2. The percentage of uranium(VI) hydrolysis products was calculated from the following stability constants (*10–12*):

$$UO_2^{2+} + H_2O \rightleftarrows UO_2(OH)^+ + H^+,\ \log K_{11} = -5.8 \qquad (2)$$

$$2UO_2^{2+} + 2H_2O \rightleftarrows (UO_2)_2(OH)_2^{2+} + 2H^+,\ \log K_{22} = -5.92 \qquad (3)$$

$$3UO_2^{2+} + 5H_2O \rightleftarrows (UO_2)_3(OH)_5^+ + 5H^+,\ \log K_{35} = -15.63 \qquad (4)$$

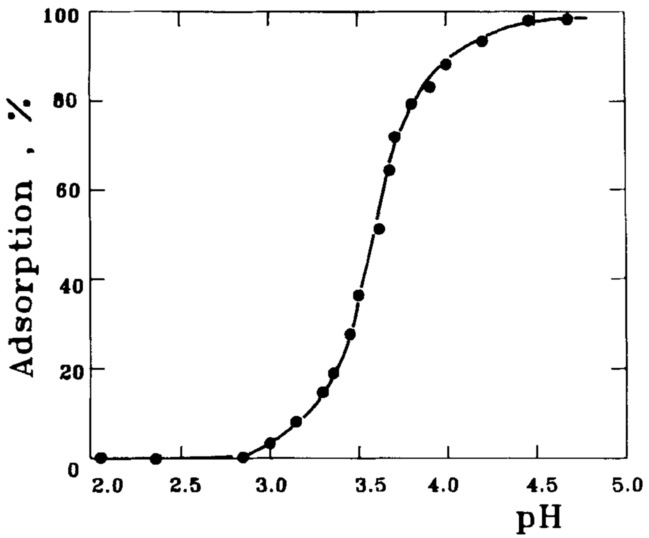

FIG. 1. Percentage of aqueous uranium(VI) adsorption on silica gel. $[U]_{init} = 2.0 \times 10^{-4}$ mol/dm^3.

The distribution diagram of various hydrolyzed uranium(VI) species shows that, at a uranium(VI) concentration of 4.0×10^{-4} mol/dm^3, the hydrolysis of uranyl ions in aqueous solution starts at pH 3.2. However, it should be emphasized that the hydrolysis of uranyl ions in aqueous silica suspension can occur even when it does not take place in solutions without oxide, i.e., at lower pH values. It was recently shown (*6*) that alkaline earth cations hydrolyze more easily in electrolytic solutions containing inorganic oxide than in solutions without oxide. James and Healy (*13*) also reported that precipitation of Co^{2+} takes place at lower pH values in an SiO_2 aqueous suspension.

By comparing the adsorption results with the distribution diagram of the uranium(VI) ion species as a function of pH (Fig. 2), it can be concluded that uranium(VI) sorption in the region of pH < 2.8 [i.e., the region where uranium(VI) exists as uranyl ion] on silica gel is negligible. Similar shapes of the adsorption and the $(UO_2)_3(OH)_5^+$ species curves are also evident. The results presented indicate that uranium(VI) is adsorbed on silica gel in the form of a hydrolytic species. This is in agreement with the results of other authors (*5*, *13–15*) who concluded that uranium(VI) was adsorbed as a hydrolytic species [$(UO_2)_3(OH)_5^+$] on hydrous thorium oxide, γ-alumina, hematite, and magnetite.

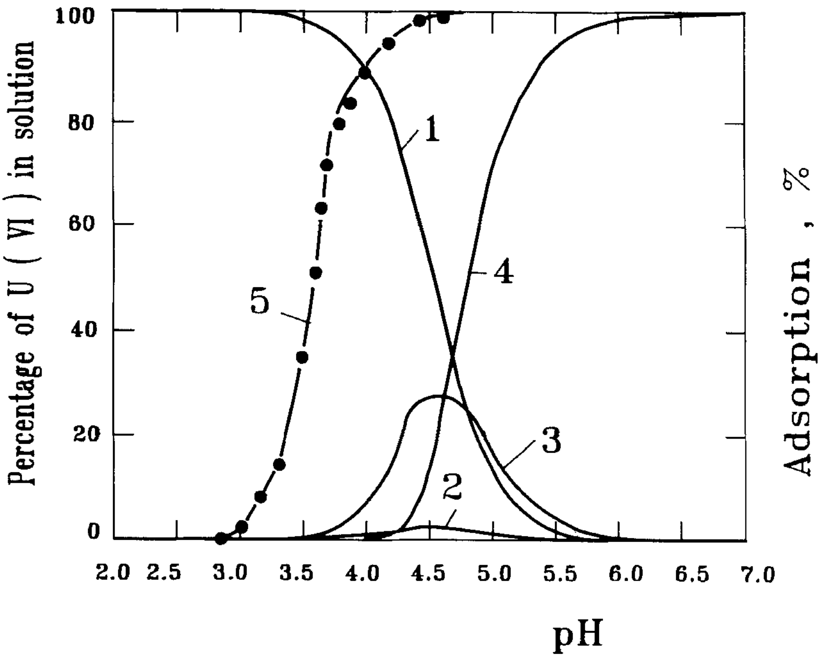

FIG. 2. Comparison of the pH dependence of adsorption of uranium(VI) on silica gel with the percentage of uranium(VI) hydrolysis products. $[U(VI)]_{tot} = 2.0 \times 10^{-4}$ mol/dm^3. (1) UO_2^{2+}, (2) $UO_2(OH)^+$, (3) $(UO_2)_2(OH)_2^{2+}$, (4) $(UO_2)_3(OH)_5^+$, (5) adsorption curve.

Most published papers on the adsorption of inorganic ions from solutions on silica gel explain the adsorption as an ion-exchange reaction between the inorganic ions and the hydrogen ions of the silanol groups. Figure 3 presents typical data for U(VI) adsorption at different pH values plotted as the log distribution coefficient, K_d, versus pH. The distribution coefficient was computed from the relation

$$K_d = \frac{C_0 - C_e}{C_e} \cdot \frac{V}{W} \tag{5}$$

where V is the volume of solution and W is the amount of silica gel. The distribution coefficient can also be determined from the ratio of ion equilibrium concentrations on adsorbent ($\overline{C}_e$) to those in solution (C_e), $K_d = \overline{C}_e/C_e$. The slope of log K_d vs pH (Fig. 3) is close to 1, which indicates that U(VI) is adsorbed as a positive monovalent ion species.

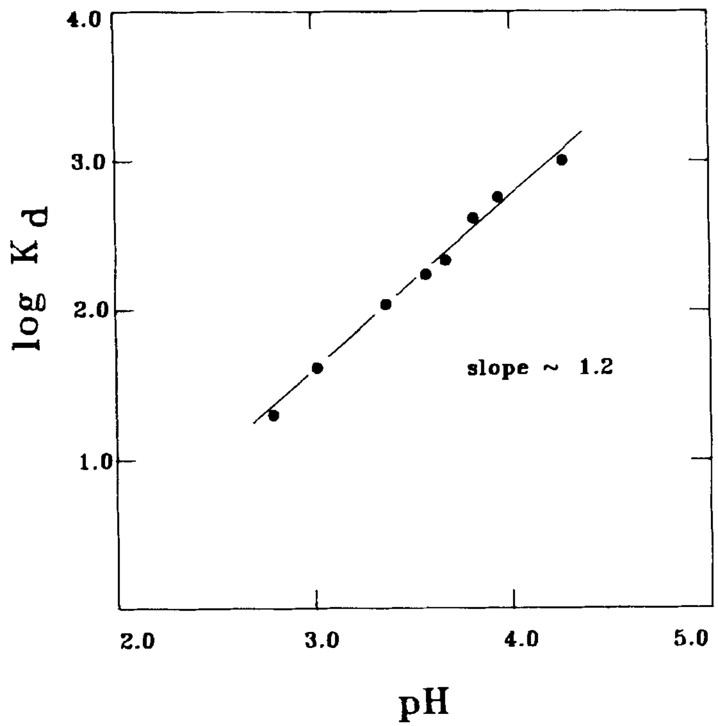

FIG. 3. Log K_d vs pH plot at constant [U]. $[U]_{init} = 4.0 \times 10^{-4}$ mol/dm^3.

Since U(VI) undergoes hydrolysis in the pH range studied, the adsorption of U(VI) on silica gel may be represented as

$$\geq SiOH + (UO_2)_3(OH)_5^+ \rightleftarrows \geq SiO(UO_2)_3(OH)_5 + H^+ \tag{6}$$

Neglecting activity coefficients, the mass law expression of Reaction (6) becomes

$$K = \frac{[\geq SiO(UO_2)_3(OH)_5][H^+]}{[\geq SiOH][(UO_2)_3(OH)_5^+]} \tag{7}$$

where K is the equilibrium constant. By using logarithms, Eq. (7) becomes

$$\log K_d = \log K + \log [\geq SiOH] + pH \tag{8}$$

where

$$K_d = [\geq SiO(UO_2)_3(OH)_5]/[(UO_2)_3(OH)_5^+]$$

Equation (8) shows a linear relationship between log K_d and pH. This relationship, first observed by Kurbatov et al. (*16*, *17*) on metal oxides, is only valid if $C = \log K + \log [\geq SiOH]$ is independent of pH.

Adsorption of zirconium(IV) on silica gel was studied as a function of nitric acid (0.01–4.0 mol/dm^3) concentration in solution. The results are given in term of percent adsorption (Fig. 4). The adsorption decreases between 0.01 and 1.0 mol/dm^3 nitric acid concentrations and attains a constant value for higher HNO_3 concentrations.

The results obtained, as presented in Figs. 1 and 4, indicate that zirconium (IV) can be separated from uranium(VI) if the concentration of nitric acid in solution is higher than 0.01 mol/dm^3.

Since the point of zero charge of silica is pH_{pzc} 2.5–3.0 (*18*), the silica surface is expected to be positively charged at pH < pH_{pzc} and negatively charged at pH > pH_{pzc}. Therefore, cations adsorption will be favored at

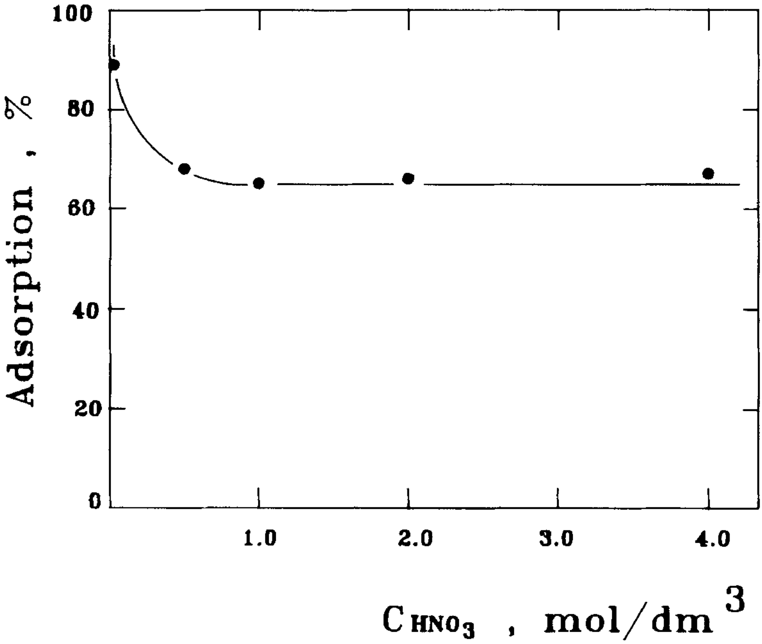

FIG. 4. Percentage of aqueous zirconium(IV) adsorption on silica gel. $[Zr]_{init} = 1.3 \times 10^{-3}$ mol/dm^3.

pH values greater than pH_{pzc} while anions adsorption will be favored at pH values lower than pH_{pzc}.

It is well known from the literature that the Zr(IV) ion hydrolyzes easily. As a function of the nitric acid concentration, the following ion species can exist in solution: Zr^{4+}, $Zr(OH)^{3+}$, $Zr(OH)_2^{2+}$, $Zr(OH)_3^+$, $Zr(OH)_4$, and $Zr(OH)_5^-$ (*10*, *19*). Only the constant K_{11} of the hydrolytic reaction

$$Zr^{4+} + H_2O \rightleftarrows Zr(OH)^{3+} + H^+ \tag{9}$$

has been determined accurately. Based on literature data (*19*) on the stability constant values of the hydrolytic species $Zr(OH)^{3+}$, $Zr(OH)_2^{2+}$, $Zr(OH)_3^+$, and $Zr(OH)_4$ ($pK_{11} = -0.05$, $pK_{12} = 0.28$, $pK_{13} = 0.43$, and $pK_{14} = 0.80$), the distribution of these ion species was calculated as a function of the HNO_3 concentration (Fig. 5). It can be seen from Fig. 5 that Zr(IV) in nitric acid solutions of the concentration range studied is present in the form of different hydrolytic species. A similarity between the adsorption and the $Zr(OH)_4$ species curve is also evident.

The fact that the adsorption of zirconium(IV) on silica gel takes place in a solution with a pH much below the pH_{pzc} of SiO_2 indicates the formation

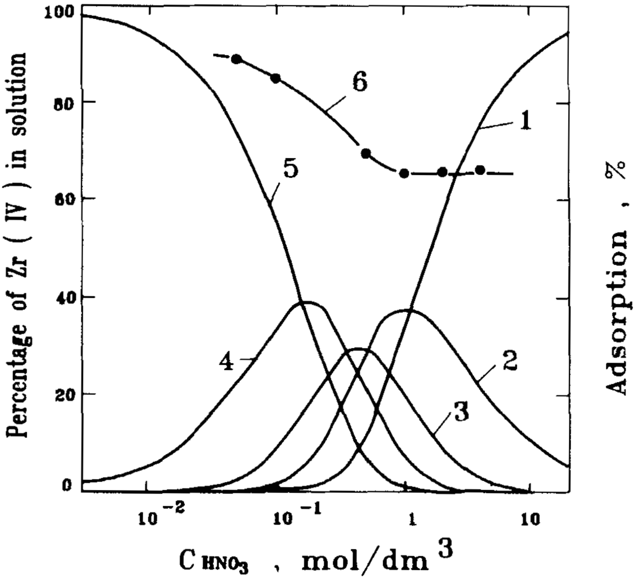

FIG. 5. Comparison of the pH dependence of adsorption of zirconium(IV) on silica gel with the percentage of zirconium(IV) hydrolysis products. $[Zr(IV)]_{tot} = 1.3 \times 10^{-3}$ mol/dm^3. (1) Zr^{4+}, (2) $Zr(OH)^{3+}$, (3) $Zr(OH)_2^{2+}$, (4) $Zr(OH)_3^+$, (5) $Zr(OH)_4$, (6) adsorption curve.

of bonds between the adsorbed species and the silica gel surface oxygen groups or precipitation of $Zr(OH)_4$ on the silica surface. As can be seen from Fig. 6, the slope of log K_d vs pH is close to zero, which suggests that Zr(IV) is adsorbed as $Zr(OH)_4$.

The adsorption of uranium(VI) and zirconium(IV) on silica gel was also studied as a function of the concentrations of these ions and nitric acid in aqueous solutions. The uranium(VI) and the zirconium(IV) equilibrium concentrations were varied from 0.03 to 4.0 mmol/dm^3 and from 0.005 to 1.5 mmol/dm^3, respectively. The results were analyzed by Langmuir and Freundlich adsorption isotherms. It was found that the experimental data on the adsorption on silica gel of the investigated ions agrees better with the Langmuir type of adsorption isotherm:

$$\Gamma = \Gamma_m \frac{K_L \cdot C_e}{1 + K_L C_e} \qquad (10)$$

where Γ is the adsorbed concentration of metal ions on silica gel, Γ_m is the saturation capacity of silica gel, and K_L is the constant. In order to deter-

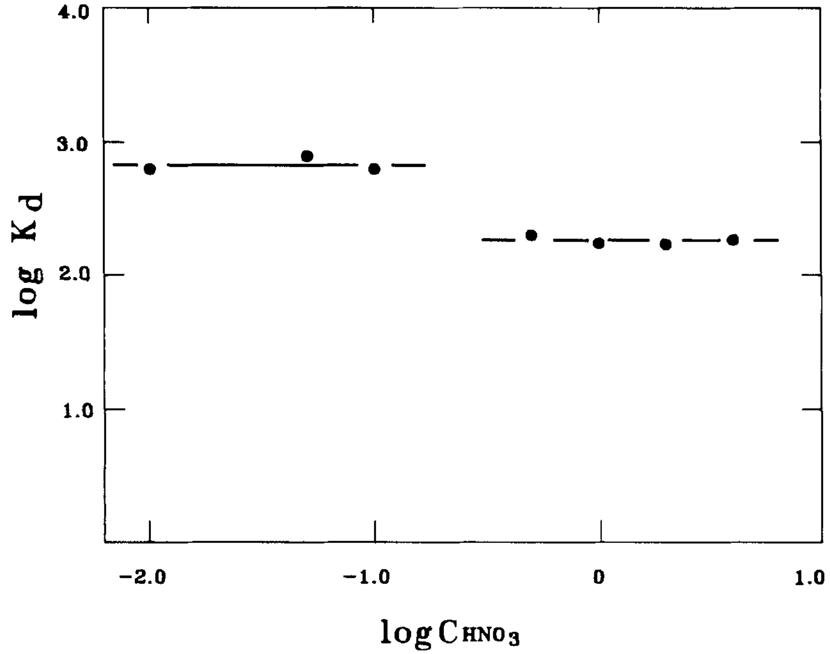

FIG. 6. Log K_d vs log C_{HNO_3} plot at constant [Zr]. $[Zr]_{init}$ = 1.3 × 10^{-3} mol/dm^3.

TABLE 1
Γ_m and K_L Values for the Adsorption of Uranium(VI) and Zirconium(IV) on Silica Gel

pH or C_{HNO_3}	Γ_m, mmol/g SiO_2	$K_L \times 10^{-3}$ dm^3/mol
	Uranium(VI)	
3.30	0.036	9.6
3.50	0.045	19.3
3.60	0.057	22.0
	Zirconium(IV)	
0.01 *M*	0.118	260
1.0 *M*	0.058	46.5

mine Γ_m and K_L, each experimental isotherm (all adsorption isotherms are similar in shape and are omitted from this article) was reduced to the linear form of the Langmuir equation:

$$1/\Gamma = 1/\Gamma_m + 1/(K_L\Gamma_m) + 1/C_e \qquad (11)$$

From the intercepts and slopes of the linear plots of $1/\Gamma$ vs $1/C_e$, the Γ_m and K_L values were obtained by using the least-squares method. The Γ_m and K_L values obtained for uranium(VI) and zirconium(IV) adsorption on silica gel are compiled in Table 1. It can be seen from the table that the Γ_m and K_L values for both metal ions increase with an increase of the solution pH, i.e., with a decrease of the nitric acid concentration.

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