



Thermodynamic studies and adsorption behavior of uranium recovery by silica gel

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Abstract

The adsorption of uranium (VI) from aqueous solutions by silica gel has been studied in a batch process. The parameters that affect the uranium (VI) adsorption, such as contact time, initial uranium (VI) concentration, and temperature, have been investigated and optimized. Equilibrium isotherm studies were used to evaluate the maximum adsorption capacity of silica gel and experimental results showed this to be 62.11 mg/g. The Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) models have been applied. The correlated data with Freundlich model show that the adsorption nature is physical (the adsorption energy $E_{ads} = 3.78$ kJ/mol). Thermodynamic parameters ($\Delta H^{\circ} = -14.9$ kJ/mol, $\Delta S^{\circ} = -5.1$ J/mol.K, ΔG° (298.15 K) = -13.4 kJ/mol) showed the exothermic adsorption and the feasibility of the process.

Keywords: *Uranium recovery; Silica gel; Adsorption*

1. Introduction

The recovery, concentration, and purification of uranium for its industrial use and potential environmental hazards are of great importance. Because of the expected shortage of uranium in the near future, further research is to be directed to the recovery of uranium from nonconventional resources such as seawater, industrial wastewaters, industrial phosphoric acid, and other waste sources in relation to the pollution of the natural environment [1, 2].

Therefore, many processes have been proposed for uranium (VI) removal from industrial wastewaters and radioactive wastes. Chemical precipitation, ion exchange, solvent extraction and adsorption are the most commonly used methods; each has its merits and limitation in application.

Adsorption of uranium (VI) by various solids is important from purification, environmental and radioactive waste disposal points of view [3, 4]. Contributions in this regard have been made by many researchers, who have utilized a number of materials, such as activated charcoal [5], olivine rock [6], coir pith [7], smectites [8], kaolinite [9], bentonite [10,11], montmorillonite [12–14], biomass [15,16], goethite [17], and polymeric materials [18]. The silica gel has been chosen for its chemical, radiation, and thermal stability. In fact, the silica gel can be considered as the most

effective and economic process. The purpose of this work is to study the feasibility of uranium (VI) adsorption by silica gel. The uranium (VI) adsorption was analyzed as function of the following parameters: contact time, initial uranium concentration, and temperature. Equilibrium adsorption isotherms are analyzed to obtain the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) constants. Full kinetic and thermodynamic investigations are also undertaken.

2. Chemicals

The specification of silica gel adsorbent is given in Table 1. All aqueous solutions were prepared with deionized water and aqueous solutions of U (VI) were prepared by concentrated uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) solution. The pH of the solutions was adjusted to 5.0 by 1M NaOH.

Table 1. Characterization of silica gel

Appearance	Particle size mm)(Real density g.cm^{-3})(Bulk density g.cm^{-3})(Average pore size (μm)	Specific area $\text{m}^2.\text{g}^{-1}$)(
white	0.25–1.5	1.86	0.45	4	578

3. Theory

3.1. Distribution coefficients

Distribution coefficient values of U (VI), in uranyl nitrate solutions, were determined by batch experiments. 100 cm^3 of aqueous solution and 5 g of silica gel were equilibrated with shaking for 15 minutes and remained for 5 hours. The adsorption temperatures were adjusted over the range of $298.15\text{--}338.15 \pm 2$ K. In the preliminary experiments, it was confirmed that the adsorption equilibrium has reached around 5 hours. The experiment time was sufficient to attain the equilibrium. The distribution ratio of uranium, between silica gel and aqueous solution, is defined as:

$$K_d = \frac{\text{mg of adsorbed uranium corresponding to 1 g of silica gel}}{\text{mg of uranium remaining in 1 cm}^3 \text{ of aqueous solution}} \quad (1)$$

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m} \quad (2)$$

Where C_0 (mg/l) and C_e (mg/l) are initial and equilibrium concentrations, respectively, V/m is the ratio volume of uranium solution to silica gel mass.

4. Results and discussion

4.1. Adsorption isotherms

The obtained experimental data of the adsorption isotherms of U (VI) from uranyl nitrate solutions on silica gel at different temperatures are given in Table 2. These results show the efficiency of silica gel for the adsorption of uranium in a wide range of concentrations.

The distribution of U (VI) between the solid-liquid interface at equilibrium has been applied to different adsorption isotherms. The Langmuir isotherm was applied by plotting C_{aq}/C_s vs. C_{aq} , where C_{aq} and C_s are the concentrations of uranium in solution and on silica gel at equilibrium. The plots yield straight lines, as shown in Fig. 1, indicating that the adsorption isotherms of U (VI) follow Langmuir isotherm. According to the Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at this site. From the slope and intercept of the plots, the Langmuir parameters ($C_{s, max}$ and b) for U (VI) are listed in Table 3 for different temperatures. The Langmuir parameters can be used to predict the affinity between the adsorbate and adsorbent using the dimensionless separation factor R_L [19–21]:

$$R_L = 1 / (1 + bC_0) \quad (3)$$

The values of R_L for adsorption of uranium (VI) by silica gel are shown in Fig. 2. They indicate that adsorption of uranium (VI) is more favorable at higher initial uranium (VI) concentrations than at lower ones. Freundlich isotherm was applied by drawing a plot of $\log C_s$ vs. $\log C_{aq}$. The Freundlich model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces. The adsorption of U (VI) followed the Freundlich isotherm over the entire investigated concentration range. These plots are shown in Fig. 3. From the slope and intercept of the plots, the Freundlich parameters (K_F and $1/n$, where K_F and n represent relative adsorption capacity of the adsorbent (mg/g) and adsorption intensity, respectively) for adsorption of uranium (VI) were listed in Table 4 for different temperatures. The slopes of the Freundlich isotherm for all cases are less than 1, indicating a concentration-dependent adsorption of uranium on silica gel. The adsorption data were tested for another isotherm expression such as Dubinin-Radushkevich (D-R) [22]. The Dubinin-Radushkevich isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential. The D-R equation is:

$$C_s = [C_s]_m e^{-B\varepsilon^2} \quad (4)$$

Where $[C_s]_m$ is the maximum amount of uranium that can be adsorbed into the silica gel, i.e., adsorption capacity, B is a negative constant related to the energy, and ε (Polanyi potential) = $RT \ln(1 + 1/C_{aq})$, where R is the gas constant in $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, T

is the absolute temperature in Kelvin, and C_{aq} is the concentration of uranium in solution at equilibrium. The D-R can be linearized as:

$$\ln C_s = \ln[C_s]_m - B\varepsilon^2 \quad (5)$$

Table 2. Experimental isotherm data for adsorption of U (VI) by silica gel at different temperatures

Metal ion	Initial Concentration		C_{aq} , (mg/ml)			C_s , (mg/g)			K_d , (ml/g)		
	g/l)(mol/l)(298 K	318 K	338 K	298 K	318 K	338 K	298 K	318 K	338 K
U(VI)	3.490	1.47×10^{-2}	0.617	0.715	1.072	57.46	55.70	48.56	93.12	77.6	45.3
	1.745	7.33×10^{-3}	0.094	0.181	0.280	33.02	31.28	29.40	351.28	172.8	105.0
	0.873	3.66×10^{-3}	0.026	0.041	0.060	16.93	16.64	16.30	651.54	405.8	271.6
	0.436	1.83×10^{-3}	0.002	0.007	0.018	8.68	8.58	8.39	3944.12	1225.7	466.1

Table 3. Langmuir parameters of uranium (VI) adsorbed into silica gel from uranyl nitrate solutions in pH=5 at different temperatures

Temperature K)($C_{s,max}$, mg/g silica gel)(b , ml/g silica gel)(
298.15	62.11	17.89
318.15	61.34	9.41
338.15	54.65	6.53

Table 4. Freundlich parameters of uranium (VI) adsorbed into silica gel from uranyl nitrate solutions in pH=5 at different temperatures

Temperature K)($1/n$	K_F , (mg/g Silica gel)
298.15	0.3437	67.93
318.15	0.4056	62.83
338.15	0.4269	48.05

Table 5. Dubinin-Radushkevich (D-R) parameters of U (VI) adsorbed into silica gel from uranyl nitrate solutions at different temperatures

Metal ion	Temperature, K)(B , mol^2/kJ^2 ($[C_s]_m$, (mmol/g silica gel)	R^2	E_{ads} , kJ/mol)(
U(VI)	298	-0.036	0.235	0.9634	3.78
	318	-0.0484	0.201	0.8918	3.21
	338	-0.0608	0.174	0.8801	2.87

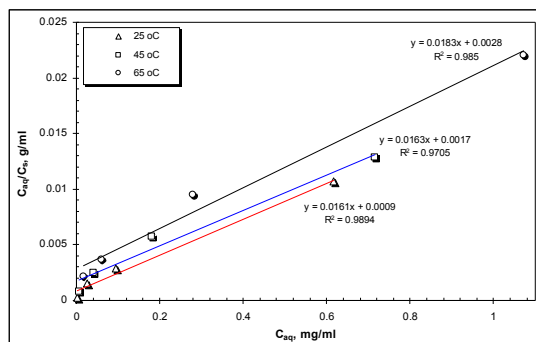


Fig. 1. Langmuir isotherms of U (VI) adsorbed into silica gel from uranyl nitrate solutions at different temperatures

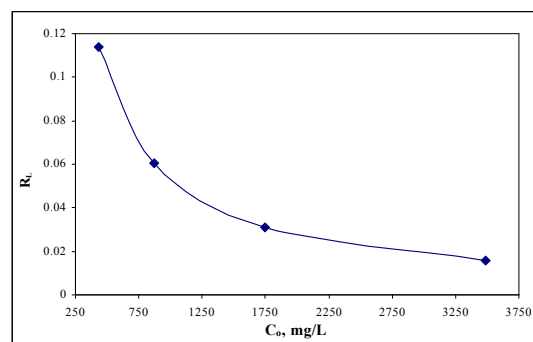


Fig. 2. Separation factor R_L of uranium (VI) adsorbed by silica gel.

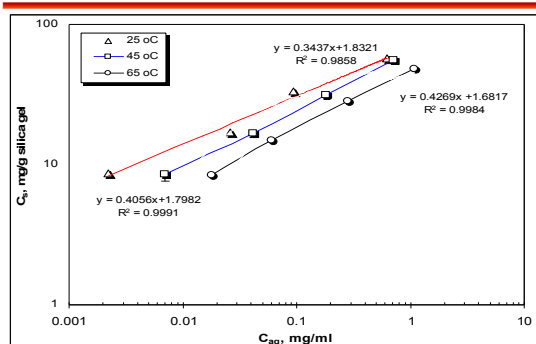


Fig. 3. Freundlich isotherms of U (VI) adsorbed into silica gel from uranyl nitrate solutions at different temperatures

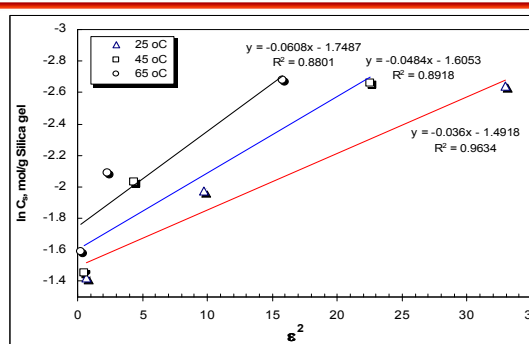


Fig. 4. Dubinin-Radshkevich (D-R) isotherms of U (VI) adsorbed into silica gel from uranyl nitrate solutions at different temperatures

If $\ln C_s$ is plotted against ε^2 , a straight line should be resulted. The D-R plots of $\ln C_s$ vs. ε^2 for U (VI) at different temperatures are given in Figure 4. The linear plots indicate that the D-R isotherm expression is followed for U (VI) adsorption. This isotherm yields the values of B and $[C_s]_m$ and the mean adsorption energy change, i.e., E, for a mole of adsorbed uranium into silica gel as [20]:

$$E = \frac{1}{\sqrt{-2B}} \quad (6)$$

Parameters of D-R equation evaluated for U (VI) adsorption at different studied temperatures are presented in Table 5. The values of E obtained through regression and the slopes of the D-R plots are similar. The maximum adsorption capacities, calculated from the D-R equation, are in that range of 0.174–0.235 mmol U (VI)/g silica gel and the mean free energies are in the range of 2.87–3.78 kJ/mol, which is not within the energy range of ion-exchange reactions, 8–16 kJ.mol⁻¹ [21]. Thus, type of uranium adsorption on silica gel is a physical adsorption. The correlation coefficient values of Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) models indicated that Freundlich model is the most suitable ($R^2 = 0.97$).

4.5. Distribution coefficients and thermodynamic parameters

Figure 5 shows the temperature dependence of the distribution coefficients of U (VI) adsorbed from uranyl nitrate solutions into silica gel as a function of uranium (VI) concentration in the aqueous phase. The distribution coefficients of U (VI) decrease with an increase in initial concentration and this behavior is identical to conventional solid–liquid adsorption. Also, in Fig. 5. can be seen that temperature has no significant influence on K_d in the case of U(VI) and K_d decreases as temperature increases. Nitric acid concentration in the silica gel will remain constant. Thus, the measured K_d values for uranium adsorbed from nitric acid solutions can be assumed to be proportional to the corresponding equilibrium

constant values. So, the Van't Hoff equation [22] in the form given below can be utilized to calculate the enthalpy changes associated with the adsorption of uranium:

$$\log K_d = \frac{-\Delta H^\circ}{2.303R} \frac{1}{T} + \frac{\Delta S^\circ}{2.303R} \quad (7)$$

Where K_d is the distribution coefficient (ml/g), ΔS° is standard entropy, ΔH° is standard enthalpy and T is the absolute temperature (K). The standard free energy values were calculated from:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

Where ΔG° is the standard free energy. As it is seen in Table 6, enthalpy values for all the different adsorption conditions are negative. Decrease in the value of ΔG° with increase in temperature shows that the reaction performs easier at lower temperature. The values of ΔS° for adsorption of U (VI) are also given in Table 6. Marcus and Kolarik [23] concluded that the negative sign of the entropy term (ΔS°) for adsorption of U (VI) ion, was due to the association of a few molecules of uranyl ion and silica gel adsorbent to form a single complex. The magnitude and sign of the enthalpy change (ΔH) associated with the adsorption process will consist of (1) enthalpy change for dehydration (ΔH_d) which can be expected to be positive because energy is required to break the ion–water and water–water bonding of the hydrated uranium, and (2) enthalpy change for associating (ΔH_a) which will make ΔH more negative due to the formation of a single collection [24]. The negative ΔH_{ads} value obtained for the adsorption of uranium indicates that association seems to be more significant than dehydration in adsorption process.

Table 6. Thermodynamic parameters and their standard deviation of U (VI) adsorbed into silica gel from uranyl nitrate solutions

C_0 , (mol/dm ³)	ΔH° , kJ/mol)(ΔS° , J/K.mol)(ΔG° , (kJ/mol)		
			298 K	318 K	338 K
1.47×10^{-2}	-14.9	-5.1	-13.4	13.3-	-13.2
7.33×10^{-3}	-18.6	-15.8	-13.9	-13.6	-13.3
3.66×10^{-3}	-23.3	-26.4	-15.4	-14.9	-14.4
1.83×10^{-3}	26.6-	-35.3	-16.1	-15.4	-14.7

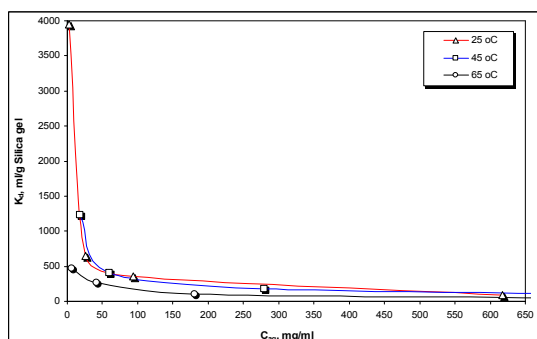


Fig. 5. Effect of temperature on the distribution coefficients of U (VI) adsorbed into silica gel from uranyl nitrate solutions

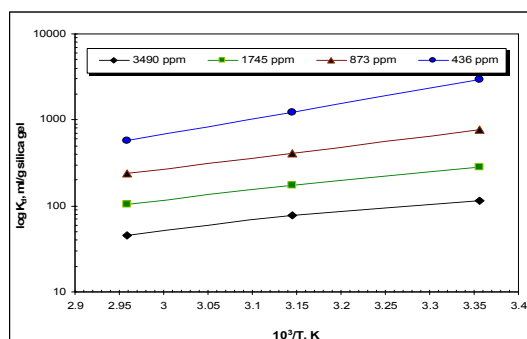


Fig. 6. Variation of $\log K_d$ with $1/T$ for the adsorption of U (VI) by silica gel from uranyl nitrate solutions.

Negative values of ΔG^0 indicate the spontaneous nature of U (VI) adsorption. The experiments were carried out at 298, 318 and 338K for different concentrations (1.83×10^{-3} , 3.66×10^{-3} , 7.33×10^{-3} and 1.47×10^{-2} mol.dm⁻³). The distribution coefficient (K_d) values decreased with temperature indicating the exothermic nature of adsorption of uranium by silica gel.

5. Conclusions

According to the results obtained in the study of the adsorption of uranium (VI) by silica gel, we can conclude that

- The silica gel has been used for adsorption uranium(VI) from aqueous solutions over concentration range 300–3500 mg/L, contact time 5 min, pH 5.0 ± 0.1 , and amount of adsorbent 5 g. These concentration ranges could be extending the maining of the uranium absorption in lower and upper of given concentration limit by extrapolation of results in Figures of 3-6.
- The temperature was found to have an inverse effect on adsorption of uranium (VI).
- The maximum removal of uranium (VI) was observed at pH 5.0 ± 0.1 at initial concentration of 43.6–349 mg/L and an amount of silica gel equal to 5 g.
- The dimensionless separation factor R_L has shown that silica gel can be used for removal of uranium (VI) from aqueous solutions.
- The experimental results have been analyzed by the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) adsorption isotherms. The main energy of adsorption $E_{ads} = 3.78$ kJ mol⁻¹ was calculated from the Dubinin–Radushkevich adsorption isotherm, which implies that uranium (VI) was mainly adsorbed physically by silica gel; this low adsorption-energy value indicates that the adsorption reaction is diffusion controlled. In the next our research ("Kinetic studies of uranium adsorption from aqueous solutions by silica gel") to understand the significance of the diffusion mechanisms and to accurately estimate the diffusivities inside the adsorbent particles, a model for uranium (VI) adsorption by silica gel was applied.
- The thermodynamic parameters ΔH^0 ; ΔS^0 and ΔG^0 values of uranium(VI) adsorption by silica gel show a exothermic adsorption, indicating that the process of uranium adsorption decreased with increasing of temperature and favored at low temperatures. The negative entropy value was due to the association of a few molecules of uranyl ion and silica gel adsorbent to form a single complex.

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