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# Equilibrium, isotherms and kinetic studies of uranium sorption onto $\text{AlPO}_4\text{-5}$ and SAPO-5 materials

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**Abstract.** The present work deals with the investigation of the use of the elaborated aluminophosphate ( $\text{AlPO}_4\text{-5}$ ) and silico-aluminophosphate (SAPO-5) materials, in uranium sorption from aqueous solution and real effluents obtained from Nuclear Research Center of Draria, Algiers, Algeria. The surface charge and acidic–basic character of  $\text{AlPO}_4\text{-5}$  and SAPO-5 is investigated by the determination of point of zero charge. Batch adsorption experimental studies are carried out to evaluate the influence of initial uranium concentration, final solution pH, contact time, solid-to-liquid ratio and temperature. A maximum adsorption capacity of 61.96 and 74.10 mg/g was obtained for  $\text{AlPO}_4\text{-5}$  and SAPO-5 respectively, at pH 7 with an adsorbent ratio of 0.1/150 g/ml and an equilibrium time of 120 min. Kinetic models (pseudo-first order, pseudo-second order and Weber–Morris) are applied to find the mechanism for the removal of uranium ions, experimental data are analyzed by equilibrium models (Langmuir, Freundlich, Dubinin–Radushkevich and Temkin). Modeling sorption results show that uranium sorption is a chemical and endothermic process. The results showed that  $\text{AlPO}_4\text{-5}$  and SAPO-5 are effective materials for the removal of uranium (VI) ions.

**Keywords.** Equilibrium, Modeling, Kinetic, Adsorption, Uranium,  $\text{AlPO}_4\text{-5}$ , SAPO-5.

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## 1. Introduction

Environmental pollution due to uranium has largely been as result of development of the nuclear industry [1]. Uranium is the most hazardous long-lived radionuclide in the environment [2]. For both human health security and environment protection, the removal of uranium is necessary [3–5]. Many processes have been used for this purpose such as precipitation, ion exchange, polymeric membrane, solvent extraction, and sorption. Sorption is one of the promising technologies for the removal of toxic heavy metals [6–8]. In this respect, many adsorbents are used such as zeolites and their derivatives [9–16]. Among all these materials, porous zeolite-like aluminophosphate ( $\text{AlPO}_n$ ) molecular sieves have the best technological impact due to their catalytic and effective sorptive properties [17]. Synthesis of new materials is made by isomorphic substitution of  $\text{Al}^{3+}$  and/or  $\text{P}^{5+}$  by Si (IV), creating a negative charge in the framework of silico-aluminophosphate (SAPO) materials, which considerably influences their sorption capacity [18,19]. The channel diameter of aluminophosphates-five materials ( $7.3 \text{ \AA}$ ) is larger than the diameter of the hydrated uranyl ( $6.5 \text{ \AA}$ ) which allowed a possible sorption of uranium by  $\text{AlPO}_4$ -5 and SAPO-5 materials [20,21]. The aim of this work is to improve the sorption of uranium (VI) onto the elaborated  $\text{AlPO}_4$ -5 and SAPO-5, by investigating the experimental sorption parameters such as uranium concentration, pH, solid-to-liquid ratio and temperature. In order to understand the nature of the uranium sorption process, equilibrium and kinetic models are used. Finally, the experimental results are applied to the real effluents from Nuclear Research Center of Draria, Algiers, Algeria.

## 2. Experiments

### 2.1. $\text{AlPO}_4$ -5 and SAPO-5 elaboration

According to the literature and our previous work,  $\text{AlPO}_4$ -5 and SAPO-5 are synthesized by hydrothermal crystallization in fluorhydric acid medium [18,22]. The molar gel's composition for SAPO-5 and  $\text{AlPO}_4$ -5 respectively are  $0.8\text{Al}_2\text{O}_3$ ,  $1\text{P}_2\text{O}_5$ , 1.4 R,  $0.2\text{SiO}_2$ ,  $50\text{H}_2\text{O}$  and  $1\text{Al}_2\text{O}_3$ ,  $1\text{P}_2\text{O}_5$ , 1.4 R,  $50\text{H}_2\text{O}$ , where R is the structuring agent. The gels are introduced into autoclaves and heated at

473 K under autogenic pressure for 24 h. The crystallization is stopped by cooled water. The powders obtained are separated by filtration, washed with distilled water and dried at 353 K overnight. The obtained powders are calcined at 823 K for 6 h.

### 2.2. Point of zero charge (PZC) of $\text{AlPO}_4$ -5 and SAPO-5

The determination of point of zero charge (PZC) is done to investigate the surface charge and acidic-basic character of  $\text{AlPO}_4$ -5 and SAPO-5 adsorbents. For that  $\text{KNO}_3$  (0.01 M) solution is prepared and its initial pH is adjusted between 2 to 11 by adding  $\text{NaOH}$  (0.1 M) or  $\text{HNO}_3$  (0.1 M). Then 10 mL of  $\text{KNO}_3$  and 0.1 g adsorbent are interacted in test tubes. The samples are kept at  $25 \text{ }^\circ\text{C}$  for 24 h and the final pH of solutions is measured. The  $\text{pH}_{\text{PZC}}$  point of  $\text{AlPO}_4$ -5 and SAPO-5 is estimated from the plot of  $\text{pH}_{\text{final}} - \text{pH}_{\text{initial}}$  versus  $\text{pH}_{\text{initial}}$  of suspensions.

### 2.3. Adsorption experiments

In order to optimize uranyl ion removal conditions, the effect of contact time, initial uranium concentration, pH, solid-to-liquid ratio and temperature are studied. Batch adsorption is performed in polyethylene flasks by agitating a mass  $m$  (g) of the adsorbent with a volume  $V$  (mL) of solution at different initial concentrations of uranium. The residual concentration of the uranium left in the supernatant phase is determined using a UV-spectrometer following Arsenazo-III method [21,23].

The adsorption uptake and the equilibrium metal uptake capacity  $q_e$  (mg/g) are respectively calculated from the following expressions

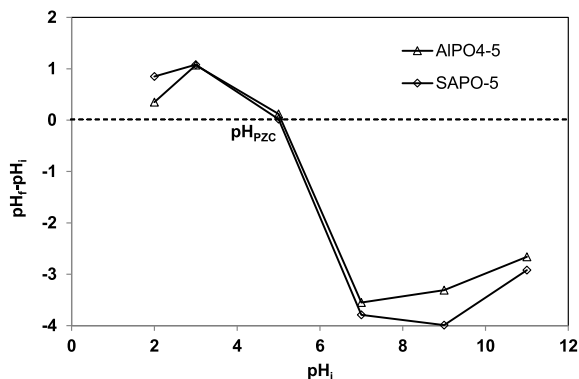
$$\text{Adsorption uptake} = \frac{C_i - C_{\text{eq}}}{C_i} 100 \quad (1)$$

$$q_e = V \frac{C_i - C_{\text{eq}}}{m} \quad (2)$$

where  $C_i$  and  $C_{\text{eq}}$  are the initial and equilibrium concentrations of uranium ion (mg/L).  $V$  is the volume of the solution (L) and  $m$  is the mass of adsorbent (g).

### 2.4. Error analysis

The inherent bias resulting from the linearization of the isotherm and kinetic models are highlighted.



**Figure 1.** Point of zero charge (PZC) of  $\text{AlPO}_4\text{-5}$  and SAPO-5.

**Table 1.** Error functions

Error	Function
Root mean square	$\text{RMSE} = \sqrt{\frac{1}{n-2} \sum_1^n (q_i - q_{ie})^2}$
Chi-squared	$\chi^2 = \sum_{i=1}^n \frac{(q_i - q_{ie})^2}{q_{ie}}$
Average relative error	$\text{ARE} = \frac{100}{n} \sum_{i=1}^n \left  \frac{q_i - q_{ie}}{q_i} \right $
Sum of the absolute errors	$\text{SAE} = \sum_{i=1}^n  q_i - q_{ie} $

Four different error functions (Table 1), RMSE,  $\chi^2$ , ARE and SAE, are employed to estimate the fitting quality [23].

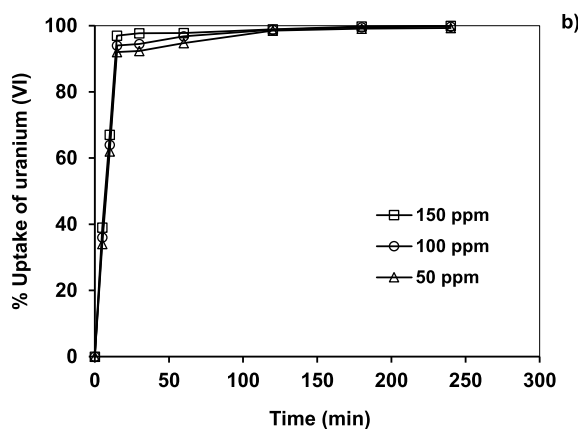
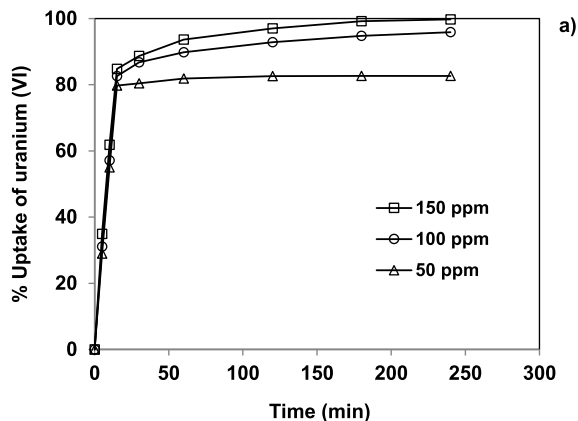
The lower values obtained with these error functions favored the isotherm or the kinetic model used in this study.

### 3. Results and discussion

#### 3.1. Point of zero charge (PZC)

The plot of  $\text{pH}_{\text{final}} - \text{pH}_{\text{initial}}$  versus  $\text{pH}_{\text{initial}}$  for  $\text{AlPO}_4\text{-5}$  and SAPO-5 suspension is shown in the Figure 1. It is interesting to note that the PZC is determined at  $\text{pH}_{\text{final}} - \text{pH}_{\text{initial}}$  equal to zero and the charge is positive below and negative above the PZC. In the PZC region the pH variation is negligible and lies within  $\pm 0.2$  pH unit.

The PZC for  $\text{AlPO}_4\text{-5}$  and SAPO-5 used in the present study is found to be 5.00. For pH less than



**Figure 2.** Effect of the initial uranium concentration and contact time on adsorption onto (a)  $\text{AlPO}_4\text{-5}$  and (b) SAPO-5. pH 7, S/L 0.1/150 g/mL,  $T$  20 °C.

$\text{pH}_{\text{pzc}} = 5$  the surface of both materials is generally positively charged and conversely if greater than 5.

#### 3.2. Optimization of the adsorption parameters

##### 3.2.1. Effect of the initial uranium concentration and contact time

Figure 2a and b illustrate the effect of the initial uranium concentration and contact time on the adsorption onto  $\text{AlPO}_4\text{-5}$  and SAPO-5, respectively. Uranium (VI) adsorption uptake for both  $\text{AlPO}_4\text{-5}$  and SAPO-5 increases with initial ion concentration. This is a result of an increase in the driving force, which corresponds to the solution concentration. Also, notice that the amount of uranium ion sorbed increases

rapidly with time in the early stages for both  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$ , while the increase is more gradual afterward until equilibrium is reached (120 min). The initial fast sorption could be due to the fact that initially all active sites on the surface of  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$  adsorbents are vacant and the uranium concentration gradient is high. As time elapses the extent of uranium sorption decreases significantly because active sites as well as concentration gradient decreases [24]. The maximum sorption is reached at a contact time of 120 min and the equilibrium values at this time are used in all subsequent measurements.

The uptake of uranium (VI) is larger for  $\text{SAPO-5}$  than for  $\text{AlPO}_4\text{-5}$ , this behavior may be explained by the silico-aluminophosphate framework negative charge [19,22], which could favor the adsorption of positively charged uranyl ion species  $\text{UO}_2^{2+}$  through important electrostatic interactions in contrast to the neutral framework of  $\text{AlPO}_4\text{-5}$  [22]. The difference in adsorption capacity of  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$  behavior is also due to the acidity originated by the difference in their constituents. The acidity of  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$  molecular sieves is assigned to both weak Lewis and strong Brønsted acid sites. The weak acidity of  $\text{AlPO}_4\text{-5}$  is related to hydroxyl groups ( $-\text{OH}$ ) bound to the defect sites, i.e.  $\text{P-OH}$  and  $\text{Al-OH}$  while weak acidity of  $\text{SAPO-5}$  is related to hydroxyl groups ( $-\text{OH}$ ) bound to  $\text{P-OH}$ ,  $\text{Al-OH}$  and  $\text{Si-OH}$  (Figure 3) and notice that the bridging hydroxyl groups, i.e.  $-\text{SiOHAl}-$ , are responsible for the strong acidity of  $\text{SAPO-5}$  [25,26].

### 3.2.2. Effect of pH

The pH effect on the removal efficiency of uranium is studied in the range from 2 to 11, using a solution of 50 mg/L of U (VI) at 293 K for 120 min. The influence of the pH on uranium removal is shown in Figure 4.

The results display a strong dependence of uranium (VI) adsorption on solution pH. The uptake of uranium (VI) by adsorption increases with pH up to the value  $\text{pH} = 7$ , then decreases up to  $\text{pH} = 11$ . The same trend is observed for both  $\text{SAPO-5}$  and  $\text{AlPO}_4\text{-5}$  with a larger percentage U (VI) removal observed for  $\text{SAPO-5}$  at all pH values used in this study.

The observed behavior can be explained by the presence of different mononuclear and polynuclear U (VI) hydrolysis products in the form  $[(\text{UO}_2)_p(\text{OH})_q]^{(2p-q)+}$  at different pH values [27].

At lower pH, there is a high concentration of  $\text{H}^+$  ion, which competes with uranyl ion for the binding sites on the surface of sorbent, resulting in a decreased adsorption of uranium (VI) ions. Along with the increase of pH,  $\text{H}^+$  ions leave the surface of  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$  making the sites available to the uranium (VI) ions. We can also notice that above  $\text{PZC} = 5$ , determined in Section 3.1, the  $\text{SAPO-5}$  and  $\text{AlPO}_4\text{-5}$  surface charge is negative, favoring the adsorption of positively charged uranyl ions  $\text{UO}_2^{2+}$ . Moreover, at pH values higher than 7.0, the decrease of adsorption uptake results from the formation of dissolved hydroxide and carbonate complex [28].

### 3.2.3. Effect of solid-to-liquid ratio

Here, we investigate the evolution of the removal uptake of uranium ion onto  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$  aluminophosphate molecular sieves as a function of solid-to-liquid ratio. This effect is highlighted by using 0.1 g of adsorbents mixed with different volumes (10, 30, 40, 100, 150, 200, 250 and 300 mL) of 50 mg/L uranium (VI) solution during 120 min.

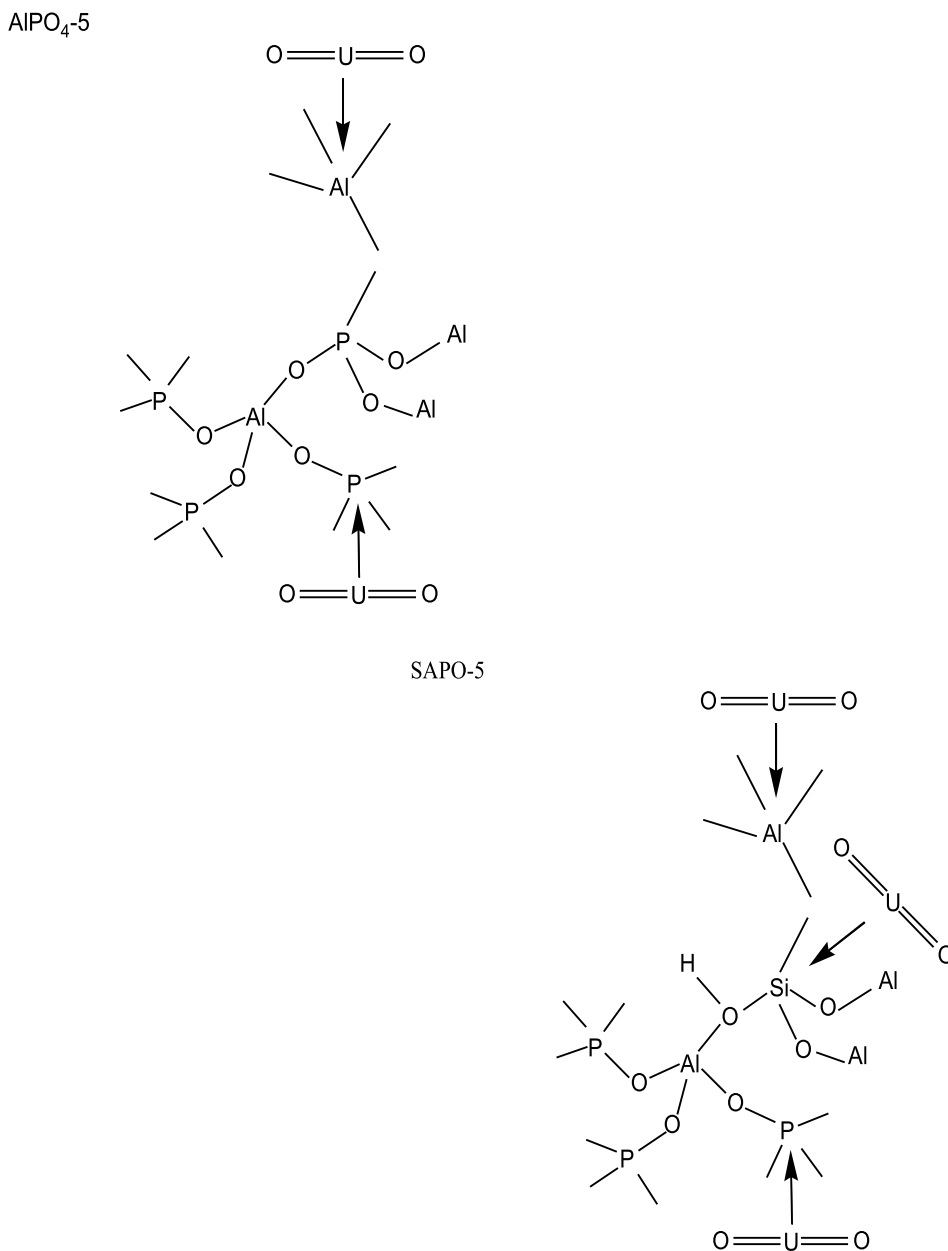
The results presented in Figure 5 shows that the uptake of uranium into both adsorbents increase with the solid-to-liquid ratio up to 0.1/150 g/mL. Note that the percentage of uranium uptake is 82 and 98% for  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$  respectively. This is due to the presence of larger adsorption sites on the surface of the adsorbents. Further increase of solid-to-liquid ratio did not increase adsorption much. This behavior can be explained by the saturation of the active sites present in  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$  surfaces by the uranyl ions.

### 3.2.4. Effect of Temperature

The effect of temperature on the adsorption of uranium (VI) is studied by varying the temperature from 293 to 323 K with the other parameters kept constant at their optimum values. The obtained results are reported in Figure 6. It can be observed that the uptake of uranium onto  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$  increases with increasing temperature, indicating that the process is endothermic for both adsorbents used in this study.

## 3.3. Adsorption kinetics

In order to understand the kinetic characteristics of uranium ions adsorption onto  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$



**Figure 3.** Schematic representation for uranium adsorption onto acidic sites of AIPO<sub>4</sub>-5 and SAPO-5.

sorbents, three well-known kinetic models namely; pseudo-first order, pseudo-second order and Weber and Morris (Table 2) are tested to evaluate the experimental data for both adsorbents.

The slope and the intercept of the plotting of first order (Figure 7) and second order models (Figure 8) are used to calculate the rate constants and the

equilibrium capacities [29], the results are shown in Table 3.

The observed linear regression coefficients close to 1, the calculated values of the adsorption capacity for AIPO<sub>4</sub>-5 and SAPO-5 close to the experimental values and less error function values reported in Table 3 indicate that the adsorption of uranium (VI) on

**Table 2.** Kinetic and isotherms models functions and plotting

Isotherm	Functional form	Plotting
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}}$	$C_e/q_e$ versus $C_e$
Freundlich	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$	$\ln q_e$ versus $\ln C_e$
Dubinin–Radushkevich	$\ln q_e = \ln q_{\max} - K\varepsilon^2$	$\ln q_e$ versus $\varepsilon^2$
Temkin	$q_e = B_T \ln K_T + B_T \ln C_e$	$q_e$ versus $\ln C_e$
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	$\log(q_e - q_t)$ versus $t$
Pseudo-second order	$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{h}$ avec $h = k_2 \cdot q_e^2$	$t/q_t$ versus $t$
Weber and Morris	$q_t = k_{id} \cdot t^{0.5} + C$	$q_t$ versus $t^{0.5}$

**Table 3.** Kinetic parameters of uranium (VI) adsorption by AlPO<sub>4</sub>-5 and SAPO-5 materials

Kinetic model	Pseudo-first order		Pseudo-second order	
	AlPO <sub>4</sub> -5	SAPO-5	AlPO <sub>4</sub> -5	SAPO-5
$k_1$ (min <sup>-1</sup> )	0.028	0.026	—	—
$k_2$ (g/mg·min)	—	—	0.098	0.092
$q_e$ (mg/g)	1.37	1.29	53.79	74.07
$q_{e,\text{exp}}$ (mg/g)	61.96	74.10	61.96	74.10
$R^2$	0.82	0.79	0.99	1.00
RMSE	2.40	2.71	0.42	0.42
$X^2$	26.63	39.96	0.63	0.48
SAE	13.42	15.41	2.44	1.98
ARE	64.93	71.26	1.62	1.28

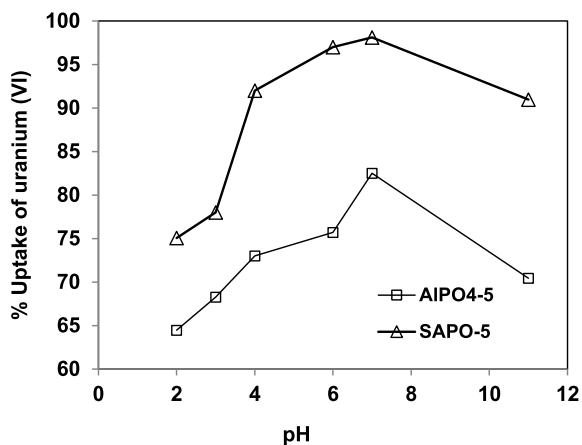
AlPO<sub>4</sub>-5 and SAPO-5 fits well the pseudo-second order kinetics. These results suggest that uranium (VI) adsorption appears to be controlled by chemisorption process [30,31].

To identify the diffusion mechanism, the kinetic results are then analyzed by using the intraparticle diffusion model expressed by Weber and Morris equation:

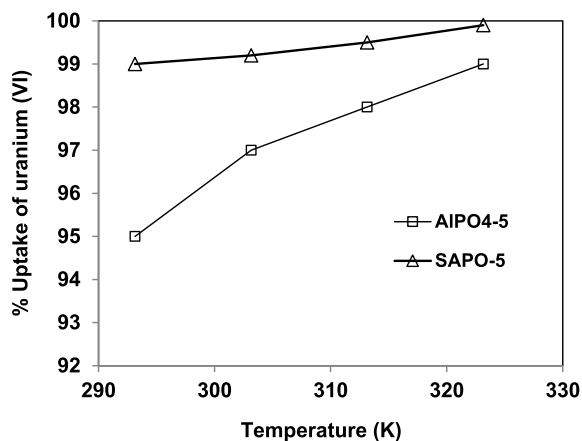
$$q_t = k_{id} \cdot t^{0.5} + C \quad (3)$$

where  $q_t$  is the adsorption capacity (mg/g) at time  $t$  and  $k_{id}$  is the intraparticle diffusion rate constant (mg/g·min). The values of the intercept  $C$  provide an indication of the thickness of the boundary layer. If the rate controlling step is intraparticle diffusion,

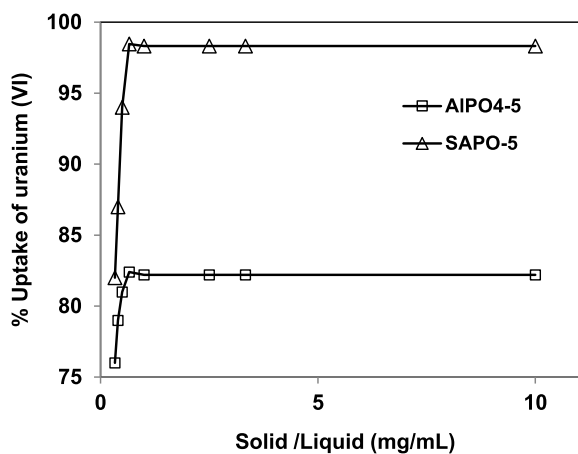
a plot of  $q_t$  versus  $t^{0.5}$  should yield a straight line passing through the origin. The plot of  $q_t$  versus  $t^{0.5}$  is shown in Figure 9, where two straight lines with two different slopes are observed for SAPO-5 and AlPO<sub>4</sub>-5. It is clearly shown that the intraparticle diffusion is not applicable to the entire time scale of the adsorption [32]. The first straight line corresponds to the external surface's fast adsorption. The second straight line is the gradual adsorption stage. A similar two-stage kinetics has been reported earlier [11]. The calculated intraparticle diffusion constants  $k_{id1}$  and  $k_{id2}$ ,  $C$  and the obtained correlation coefficients  $R^2$  are presented in Table 4. As expected, the diffusion rate  $k_{id1}$  in the first stage is larger than in the second ( $k_{id2}$ ). Indeed, uranium (VI) is adsorbed



**Figure 4.** Effect of pH on the uptake percentage of uranium ion onto  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$ .  $t$  120 min,  $S/L$  0.1/150 g/mL,  $T$  20 °C,  $[U]$  50 mg/L.



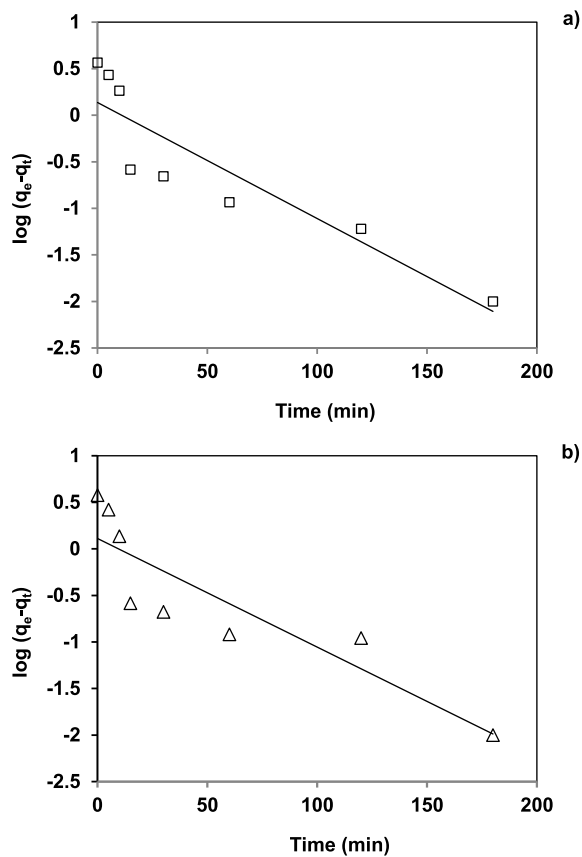
**Figure 6.** Effect of temperature on the removal of U (VI) by  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$ .



**Figure 5.** Effect of solid-to-liquid ratio on the removal of U (VI) by  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO-5}$ .  $t$  120 min,  $T$  20 °C, pH 7,  $[U]$  50 mg/L.

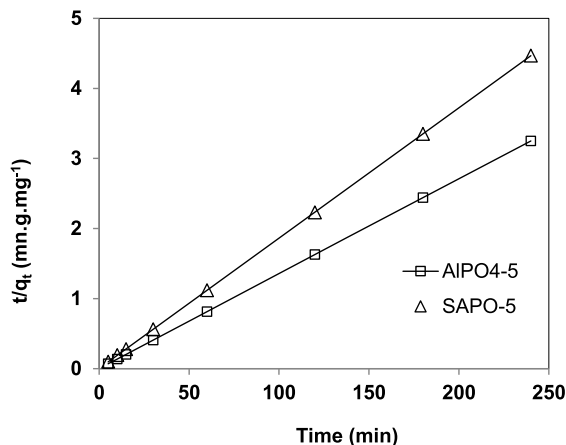
quickly by the external surface via film diffusion. When the external surface reaches saturation, the uranium (VI) enters the internal pores of the studied materials [3].

The value of the intercept  $C$  provides information related to the thickness of the boundary layer. Larger values of the intercept obtained for  $\text{SAPO-5}$  suggest that the surface diffusion has a larger role as the rate-limiting step [30].

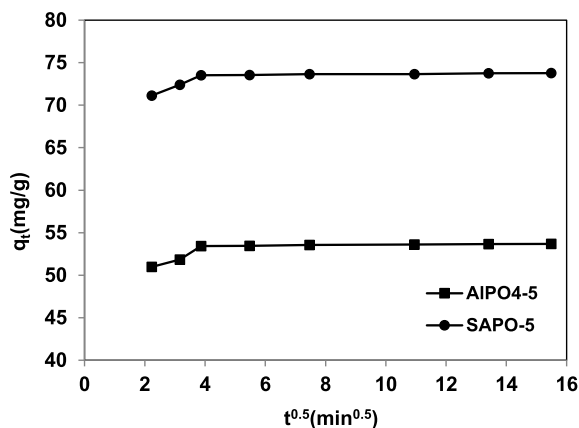


**Figure 7.** Pseudo-first order plots for the adsorption of uranium (VI) by (a)  $\text{AlPO}_4\text{-5}$  and (b)  $\text{SAPO-5}$ .





**Figure 8.** Pseudo-second order plots for the adsorption of uranium (VI) by AlPO<sub>4</sub>-5 and SAPO-5.



**Figure 9.** Intraparticle diffusion plots for the uranium adsorption onto AlPO<sub>4</sub>-5 and SAPO-5.

### 3.4. Equilibrium modeling

The study of equilibrium isotherms is fundamental in supplying the essential information required for the design of a sorption process. Our sorption results are subjected to different sorption isotherms, namely the Langmuir, Freundlich, Dubinin–Radushkevich and Temkin models, which assume a linearized form given in Table 2.

The constants for isotherms, correlation coefficients and error values of Langmuir, Freundlich, D–R and Temkin models are given in Table 5.

**Table 4.** Intraparticle diffusion rate constants for uranium (VI) adsorption onto AlPO<sub>4</sub>-5 and SAPO-5 materials

	AlPO <sub>4</sub> -5	SAPO-5
$K_{id1}$ (mg·g <sup>-1</sup> ·min <sup>0.5</sup> )	1.46	1.44
$C_1$	47	67
$R^2$	0.94	0.99
$K_{id2}$ (mg·g <sup>-1</sup> ·min <sup>0.5</sup> )	0.021	0.020
$C_2$	53	73
$R^2$	0.92	0.90

The obtained equilibrium values for uranium (VI) uptake with the Langmuir model are 76.92 and 52.63 mg/g for SAPO-5 and AlPO<sub>4</sub>-5 respectively. These values are close to the experimental adsorption capacity of the adsorbents.

The essential characteristics of the Langmuir isotherm can be explained in terms of a dimensionless constant separation factor  $R_L$  defined by:

$$R_L = \frac{1}{1 + bC_i} \quad (4)$$

The values of  $R_L$  indicate the type of isotherm: irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ) [32,33].

The calculated  $R_L$  constant values shown in Table 6 lie between 0 and 1 for all uranium concentration values used in this study. This indicates that both AlPO<sub>4</sub>-5 and SAPO-5 favor uranium (VI) uptake. Similar results have been reported by Jain *et al.* [29], for the removal of Ni(II) from aqueous solution.

The Freundlich model is shown to fit better the SAPO-5 data values with a high correlation coefficient  $R^2 = 0.99$  and lower error function values. The Freundlich constant  $n$  values should be in the range of 1–10 in order for that adsorption to be favorable [2, 25,32]. The calculated values of  $n$  are 1.31 for SAPO-5 and 1.36 for AlPO<sub>4</sub>-5. These values show the effectiveness of the adsorbents considered in the present study for UO<sub>2</sub><sup>2+</sup> removal from aqueous solutions.

The analysis of the equilibrium data with the D–R model adsorbents shows a large deviation from linearity for both SAPO-5 and AlPO<sub>4</sub>-5. This is evidenced by the low  $R^2$  coefficient and the high error function values observed (Table 5). We conclude that the D–R model cannot be applied to the two adsorbents being considered.

**Table 5.** Model constants and correlation coefficients for adsorption of uranium by aluminophosphate molecular sieves

Model	Langmuir		Freundlich		D–R		Temkin	
	AlPO <sub>4</sub> -5	SAPO-5	AlPO <sub>4</sub> -5	SAPO-5	AlPO <sub>4</sub> -5	SAPO-5	AlPO <sub>4</sub> -5	SAPO-5
$q^{\text{exp}}$ (mg/g)	61.96	74.10						
$q_{\text{max}}$ (mg/g)	52.63	76.92						
$b$ (L/g)	0.01	0.04						
$K_f$ (mg/g)			1.14	3.28				
$n$			1.36	1.31				
$q_{\text{max}}$ (mg/g)					20.81	27.54		
$K \cdot 10^6$ (mol <sup>2</sup> /kJ <sup>2</sup> )					-27.04	-2.61		
$K_T$							0.17	0.53
$B_T$							9.84	13.22
$\Delta\theta$ (kJ/mol)							13.03	14.18
$R^2$	0.97	0.95	0.98	0.99	0.90	0.83	0.99	0.98
RMSE	0.57	0.85	1.39	1.06	10.14	13.76	0.68	4.29
$X^2$	0.09	0.20	0.47	0.21	24.07	34.38	0.26	4.25
SAE	2.64	4.76	6.52	5.26	47.13	66.34	3.37	19.23
ARE	2.42	4.09	5.40	3.51	77.80	84.47	4.68	15.97

**Table 6.**  $R_L$  values for uranium adsorption obtained from Langmuir equation

[U] <sub>0</sub> (mg/L)	40	50	100	150	200
AlPO <sub>4</sub> -5	0.66	0.61	0.43	0.34	0.28
SAPO-5	0.41	0.36	0.22	0.16	0.12

The experimental data for SAPO-5 and AlPO<sub>4</sub>-5 are in good agreement with the Temkin model, with a high correlation coefficient and acceptable error functions values.

The obtained positive value of  $B_T$  confirms the endothermicity of the process for both adsorbents.

The adsorption energy is useful for predicting whether the adsorption process is physical or chemical in nature.

The adsorption energy  $\Delta\theta$  is calculated by using the formula:

$$B_T = q_m \frac{RT}{\Delta\theta}. \quad (5)$$

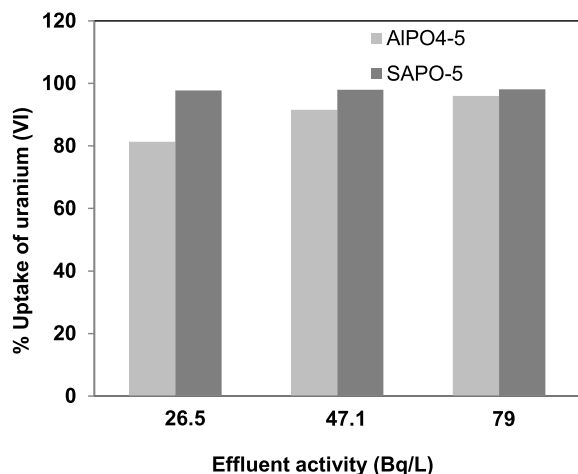
The  $\Delta\theta$  values are 14.18 and 13.03 kJ·mole<sup>-1</sup> for SAPO-5 and AlPO<sub>4</sub>-5 respectively, which are greater than 8 kJ·mole<sup>-1</sup>, indicating that the adsorption process is chemical.

The comparison of the obtained correlation coefficient  $R^2$  and error function values for both AlPO<sub>4</sub>-5 and SAPO-5 with the selected models shows that the Freundlich model is more appropriate for fitting the uranium (VI) equilibrium data of SAPO-5 while the Temkin model is better for the AlPO<sub>4</sub>-5 experimental equilibrium data.

### 3.5. Behavior of AlPO<sub>4</sub>-5 and SAPO-5 toward uranium species from real effluent

The uranium adsorption tests of the synthesized materials are performed using real effluents collected from the Nuclear Research Centre of Draria, Algiers, Algeria.

Experiments for uranium removal from real effluents are performed using the optimized parameters (pH = 7, contact time = 120 min and solid-to-liquid ratio of 0.1/150 (g/mL)). The percentage of adsorption of uranium (VI) ions from real effluents adsorbed onto synthesized AlPO<sub>4</sub>-5 and SAPO-5 are presented in Figure 10. The percentage of uranium adsorption for AlPO<sub>4</sub>-5 are important values which are 81.35, 91.57 and 95.98% respectively for



**Figure 10.** The uranium uptake percentage from real effluents adsorbed onto AlPO<sub>4</sub>-5 and SAPO-5.

the studied activities of 26.5, 47.1 and 79 Bq/L. Furthermore, SAPO-5 presents larger values with 97.77, 97.98 and 98.11% for the three effluents used in this study.

### 3.6. Comparison with other solid adsorbents

Performance of adsorbents is based on the maximum adsorption capacity of the adsorbent under favorable experimental conditions. Table 7 illustrates the comparison between adsorption capacities of different adsorbents in the removal of uranium [15,33–35].

By comparing these results, both AlPO<sub>4</sub>-5 and SAPO-5 seem to be very efficient and effective in eliminating uranyl ions, since the adsorption capacity values are important. Comparing the adsorption capacity obtained from synthetic solution and real effluents (Table 7), we can notice a decrease in the adsorption yield in the case of real effluents but still remains important. This behavior may be explained by the presence of the other chemical elements in the effluents [22], which can be co-adsorbed at the same time as the uranium, by occupying the active sites of the adsorbent.

### 3.7. Desorption studies

Desorption study is carried out, after performing adsorption experiments with uranium solution in the

concentration of 50, 100 and 150 mg/L, using the two adsorbents AlPO<sub>4</sub>-5 and SAPO-5. Desorption procedure is carried out using three eluting agents including HCl (0.1 M), H<sub>2</sub>SO<sub>4</sub> (0.1 M), and HNO<sub>3</sub> (0.1 M). The desorption experiments are performed by taking 0.1 g of AlPO<sub>4</sub>-5 and SAPO-5 adsorbent separately, in 50 ml each of eluting solution for 1 h. the uranyl ions desorbed into the eluting solution is separated by centrifugation and analyzed as before.

The desorption ratio is calculated according to the following equation [36]

$$\text{Desorption ratio (\%)} = \frac{\text{Amount of metal ion desorbed}}{\text{Amount of metal ion sorbed}} \times 100. \quad (6)$$

By comparing the results shown in Table 8, it was observed that a higher desorption ratio is obtained when HNO<sub>3</sub> is used for the two adsorbents (AlPO<sub>4</sub>-5 and SAPO-5). Therefore nitric acid is selected as the best desorbing agent for uranium (VI) ions.

## 4. Conclusion

In the present study, the elaborated AlPO<sub>4</sub>-5 and SAPO-5 adsorbents are used in the adsorption of uranium (VI) ion from synthetic and real effluents. The maximum adsorption of uranium (VI) occurs at pH = 7 and solid-to-liquid ratio of 0.1/150 g/mL for both AlPO<sub>4</sub>-5 and SAPO-5. The equilibrium time is reached within 120 min. Furthermore, SAPO-5 has a negative charge which permits a larger uranium adsorption compared with AlPO<sub>4</sub>-5. This behavior is due to the presence of silicon on the SAPO-5 framework giving rise to bridging hydroxyl groups, i.e. –Si OHAl, responsible for the strong acidity of SAPO-5.

The observed experimental kinetics data of the studied materials matches with the pseudo-second order model, indicating that the adsorption of uranium (VI) is dominated by chemisorption which is confirmed by modeling results.

Attempts for effective removal of uranium (VI) from real effluents with different activities obtained from Nuclear Research Center of Draria, Algeria using AlPO<sub>4</sub>-5 and SAPO-5 adsorbents are made. The uptake of uranium ions from real effluents adsorbed onto AlPO<sub>4</sub>-5 and SAPO-5 is higher than 81% and reached 98%. This study concludes that the elaborated AlPO<sub>4</sub>-5 and SAPO-5 materials are suitable adsorbent candidates for the removal of uranium.

**Table 7.** Comparison of the adsorption capacities of AlPO<sub>4</sub>-5 and SAPO-5 and various adsorbents for uranium (VI)

Adsorbent	Solution	q (mg/g)	Reference
AlPO <sub>4</sub> -5	Synthetic uranium (VI) solution at 50 mg/L	61.96	This study
	Uranyl effluent at 50 mg/L	61.01	This study
	Synthetic uranium (VI) solution at 100 mg/L	139.26	This study
	Uranyl effluent at 100 mg/L	137.35	This study
	Synthetic uranium (VI) solution at 150 mg/L	218.25	This study
	Uranyl effluent at 150 mg/L	215.95	This study
	Synthetic uranium (VI) solution at 50 mg/L	74.10	This study
	Uranyl effluent at 50 mg/L	73.32	This study
SAPO-5	Synthetic uranium (VI) solution at 100 mg/L	148.78	This study
	Uranyl effluent at 100 mg/L	146.97	This study
	Synthetic uranium (VI) solution at 150 mg/L	223.97	This study
	Uranyl effluent at 150 mg/L	220.74	This study
Carboxylate nanotube		11.73	[33]
4A		100	[34]
Synthetic NaA		6.50	[35]
Synthetic NaY		14.05	[15]

**Table 8.** The elution of adsorbed uranium ion using different types of eluting agents

Concentration of uranium (mg/L)	% recovery of adsorbed uranium					
	SAPO-5			AlPO <sub>4</sub> -5		
	HCl	H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>	HCl	H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>
50	91	89	99	89	87	98
100	90	90	98	87	88	97
150	89	91	99	88	89	98

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