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Original Article

Comparative study on the performance of natural and synthesized adsorbents onto uranium (VI) sorption

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ABSTRACT

The aim of this study is to compare the performance of natural and synthesized material to adsorb uranium. Synthesized Silico-Alumino-Phosphate (SAPO) material is compared to raw and chemically activated Algerian Aleppo pine sawdust (Raw-AAPS and CA-AAPS). The uranium sorption parameters, isotherms modelling, kinetic modelling and decontamination factor results, showed that adsorbents used are effective for the removal of uranium (VI) ions and the performance of the adsorbents follows the order: SAPO > CA-AAPS> Raw-AAPS.

The natural material presents less sorption capacity comparatively to the synthesized adsorbent, but it is economically favored because of its abundance in nature and its low cost.

1. Introduction

Uranium is the most common radionuclide present in aqueous solution, generated from nuclear industry [1-3]. It is known for its hazardous effect onto environment and human health [4]. In this respect, uranium (VI) is removed using a great number of natural and synthetic adsorbents [3-8]. It is well understood that using natural abundant adsorbents for such applications is more profitable. Furthermore, the adsorbent is most favoured, when it presents an important adsorption capacity [9]. Algerian Aleppo pine sawdust is one possible material considered as good adsorbent due to its abundance in nature (The Aleppo pine trees occupies an area of 800,000 ha, representing about 37% of the wooded areas of northern Algeria), and its low-cost and renewable source (agricultural waste). Moreover, several studies highlighted its heavy metals removal efficiency [7, 9-11]. It is well known that cellulosic waste materials can be used as cost effective adsorbent [9]. These materials exhibit higher adsorption capacities when they are chemically modified [7, 9]. A comparison between modified and unmodified sawdust indicated that the maximum adsorption is obtained with base treatment of sawdust by increasing the number of binding sites [12]. In our previous work a synthesized silico-Alumino-Phosphate material was used as sorbent of uranium (VI) and the sorption results showed that the SAPO material is very effective uranium uptake [5,6].

The aim of this work is to compare the performance of natural (Raw Algerian Aleppo pine sawdust and chemically activated Algerian Aleppo pine sawdust) with the synthesized SAPO adsorbent to uptake uranium (VI). Comparison study is investigated on the experimental sorption parameters conditions, the equilibrium, kinetic isotherms, thermodynamic study, nature of the process and the adsorption capacities.

2. Materials and Methods

2.1. Natural adsorbent preparation

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The natural adsorbent used in this study is Algerian sawdust from Aleppo pine (AAPS). The Aleppo pine tree covers practically all regions of Algeria (east, west, north and south). Its geographical distribution in Algeria isshown in Fig. 1.

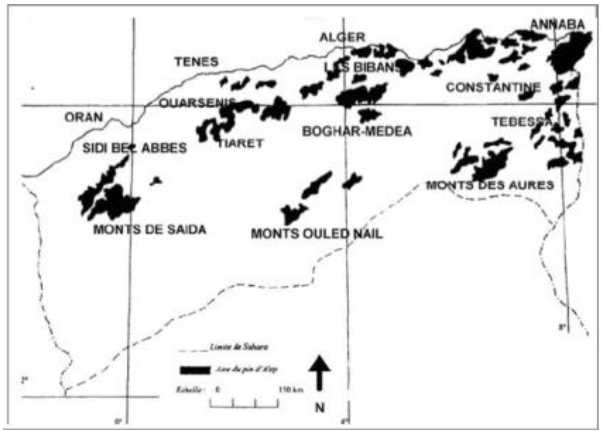

Fig 1. Geographical distribution of the Aleppo Pine in Algeria [13].

AAPS obtained from Algerian timber is firstly purified through several rinsing with distilled water and then dried at 50 °C for 48h. Subsequently, it is crushed, sieved and the collected different grain sizes are stored in desiccators. The purpose of this pre-treatment is to obtain the first adsorbent called raw Algerian Aleppo pine sawdust (Raw-AAPS).

The chemical activated Aleppo pine sawdust denoted CA-AAPS used in this comparative study is prepared by adding an amount of AAPS into a solution of activation agent and stirring the mixture at a rate of 200 rpm for 60 min. The solution is then filtered and the obtained cake is washed several times with distilled water to remove the excess of activation agent until neutral pH. The obtained (CA-AAPS) adsorbent is dried at 50 °C overnight.

The nomenclature used to denote the adsorbents used in this comparative study are given in Table 1.

Table 1: Nomenclature used to denote the studied adsorbents.

Adsorbent	**Nomenclature**
Raw Algerian Aleppo pine sawdust	Raw- AAPS
Algerian Aleppo pine sawdust Activated chemically	CA-AAPS
Silico-Alumino-Phosphate material	SAPO

2.1. SAPO adsorbent preparation

According to the literature and our previous work [6, 7, 14], SAPO was synthesized through hydrothermal method using an initial solution of silico-Alumino–Phosphate gel and structuring agent (R) with the molar composition of: 0.8 Al_2O_3, 1P_2O_5, 1.4 R, 0.2 SiO_2, 50 H_2O. Thus, the synthesis gel was transferred to a Teflon-lined stainless steel autoclave, heated for 24 h in an oven at a temperature of 100 °C, and finally cooled down with fresh water to stop crystallization. The wet solid recovered after the hydrothermal treatment, was filtered and thoroughly rinsed with demineralized water, dried at 80 °C overnight, and calcined at 550 °C for 6 h.

2.2. PZC of natural and synthesized adsorbents

The acidic-basic character and the surface charge of both natural (Raw-AAPS), the activated natural (CA-AAPS) and the synthesized SAPO adsorbents are investigated by the determination of the point of zero charge (PZC). Accordingly, KNO_3 (0.01M) solution is prepared and its initial pH is adjusted between 2 to 11 by adding HNO_3(0.1M) or NaOH (0.1M). Then, 0.1 g of each adsorbent is contacted in test tubes with 10 mL of KNO_3. The samples are kept at 25 ºC for 24 h and the final pH of solutions is measured. The pH_{Pzc} point of Raw-AAPS, CA-AAPS and SAPO is evaluated from the plot of $pH_{final}- pH_{initial}$ vs. $pH_{initial}$ of suspensions.

2.3. Adsorption experiments

Uranyl nitrate (UO2 (NO3)2) used for the preparation of U(VI) aqueous solutions is declared in the framework of IAEA guarantees. The uptake conditions of uranyl ion onto natural and synthesized adsorbents are optimized. Subsequently, the effect of initial uranium concentration, contact time, pH, solid to liquid ratio and temperature is highlighted. These parameters are studied by the batch method, where a mass m (g) of the adsorbent is contacted in polyethylene flasks with a volume V (mL) of uranium solution at different initial concentrations and maintained under stirring. The solids are then separated from the liquid by filtration. The residual uranium in the collected filtrates is analysed using a UV-spectrometer following Arsenazo–III method [15].

The sorption and the equilibrium uranium adsorption capacity q_e(mg/g) are calculated respectively from the following expressions:

$$Adsorption_{uptake} = \frac{C_i - C_{eq}}{C_i}.100 \qquad (1)$$

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

where C_i and C_{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 the adsorbent (g).

3. Result and Discussion

3.1. *Mineral elements analysis* of natural and synthesized *adsorbent*

Table 2 lists the mass percentage of the elements (sodium, magnesium, aluminium, potassium, calcium, zinc, copper, iron, manganese, etc.) present in natural and synthesized adsorbent, determined with XRF analysis.

Table 2: Elemental analysis of Algerian Aleppo pine sawdust.

Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Ti**	**Fe**	**Cu**	**Zn**
(%) AAPS	0.03	0.14	0.03	0.06	0.01	0.03	0.05	0.01	0.43	0.005	0.015	0.002	0.004
(%) SAPO	-	-	48.9	7.5	43.6	-	-	-	-	-	-	-	-

From these values, it can be concluded that the content of Aleppo pine sawdust consists mainly of trace elements less than 0.1 wt.%. However, magnesium and calcium have mass percentage ranging between 0.1 and 0.5 %.

The mass percentage greater than 5% for the elements contained in the synthesized adsorbent SAPO indicates that aluminium, silicon and phosphorous are major elements contained in this adsorbent.

3.2. *Optimization of chemical activation parameters*

In general, higher adsorption capacities are obtained when plant wastes are chemically activated compared to those unmodified [12]. Hence activated Aleppo Pine sawdust is used in this study. Activation parameters for Aleppo pine sawdust are optimized by varying only one parameter at a time. The adsorption tests are carried out on a solution of uranyl nitrate at 150 mg/L. The particle size fraction of the used Aleppo pine sawdust is in the range 180-630 µm.

Table 3 summarizes the activation conditions of Aleppo Pine sawdust. These results show that 20 g of Algerian Aleppo sawdust is activated by 1000 ml of NaOH (1M) during 60 minutes.

3.3. *Characteristic and chemical composition of natural adsorbent*

Sawdust or wood waste contains mainly cellulose (45–50%), lignin (23–30%), hemicellulose (20–30%), and different extractives (acids, soluble sugar, resins, waxes, oil, etc.) (1.5–5%) [12, 16].

These main components (Cellulose, lignin, and hemicelluloses) are complex polymers made of glucose molecules ordered in long chains (galactose, arabinose, xylose, etc.). Therefore, phenols, hydroxyls, and carboxyls are functional characteristic groups of these polymers (Fig. 2).

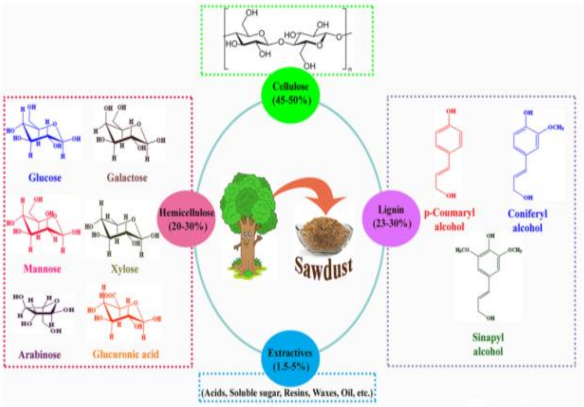

Fig 2. Sawdust and its structure [12] (with the permission of the journal Editor from the authors).

Table 3: Chemical activation conditions of Algerian Aleppo pine sawdust.

	Activation		**S/L ratio (g/L)**	**Concentration (mole/L)**
	Agent	**Time (min)**		
Range of variation	HCl NaOH	0-240	10-50	0.5-3
Optimal conditions	NaOH	60	20	1

The chemical composition of the natural studied adsorbent (sawdust) is determined according to the standard protocols of Technical Association of the Pulp and Paper Industry norms (TAPPI) [7].

The characteristic of the Aleppo pine sawdust become from Algerian trees, as the carboxylic concentration, the percentage of ash, total lignin and extractives of the Raw Algerian Aleppo pine sawdust and chemical activated adsorbent composition is given in Table 4.

Table 4: Properties and chemical composition of the natural adsorbent.

Adsorbent	**Raw -AAPS**	**CA-AAPS**
Average diameter (µm)	644	644
Density (g/ml)	0.150	0.167
Dry matter Ms (%)	92.31	96.08
[COO-] mmol/g	1.80	2.25
Ash (%)	1.23	1.79
Total lignin (%)	27.16	29.87
Extractives (%)	1.87	0.37

As seen in the Table 4, the proportions of carboxylic group, ash and lignin increased, while the extractives decreased during the modification with NaOH. This may be explained by the conversion of methyl esters which are the major constituents in cellulose, hemicelluloses and lignin to carboxylate ligands as shown in the equation below [9]:

$$RCOOR' + H_2O \quad OH^- \rightarrow RCOO^- + R'OH \qquad (3)$$

The results obtained for lignin seems to be encouraging and beneficial, since documented research has demonstrated that heavy metals are much more adsorbed by lignin [10].

3.4. Surface charge of natural and synthesized adsorbents

The plot of pH_{final}– $pH_{initial}$ vs. $pH_{initial}$ for the studied adsorbents (raw-AAPS, CA-AAPS and SAPO) suspensions is shown in the Fig. 3. From this plot, the PZC is determined at pH_{final}– $pH_{initial}$ equal to zero. In this region, the pH variation is negligible and lies within ± 0.2 pH unit. Furthermore, the surface charge is positive below the PZC and negative above it.

The PZC value of raw-AAPS and CA-AAPS is equal to 5.5 and 5.73, respectively. For SAPO used in the present study is found to be 5.00. Whereas, the surface of the adsorbents is generally positively charged for pH less than PZC, and conversely if greater than it.

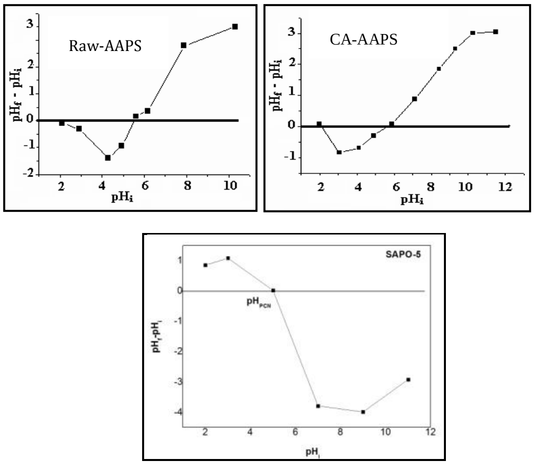

Fig 3. Point of zero charge of natural and synthesized adsorbents.

3.5. Optimisation of the adsorption parameters

Based on our previous works [5, 7], and the results of uranium sorption onto chemical activated sawdust a comparative parametric study is investigated and results are summarized in Table 5.

The effect of the initial uranium concentration, contact time, pH, solid to liquid ratio and temperature on the adsorption of uranium (VI) onto Raw- AAPS, CA-AAPS and SAPO are studied and the optimal parameters favouring the uranium sorption are presented in Table 5. By comparing the optimal parameters, we conclude that uranium sorption onto natural and synthesized adsorbent depends on the initial uranium concentration, contact time, pH, S/L ratio and temperature. Close optimal values are obtained for uranium concentration and contact time for all used adsorbents. A great difference in solid liquid ratio values is observed for the natural and synthesized adsorbents. An amount of 0.66 g is sufficient for uranium removal using synthesized SAPO, while 25 g of natural adsorbent is used in 1000 mL of uranium solution. We can also observe that uranium sorption onto SAPO is favoured at high temperature while onto natural adsorbent is disfavoured.

The experimental maximum adsorption capacities obtained are 18.52, 31.04 and 74 mg/g for Raw-AAPS, CA-AAPS and SAPO, respectively. The different values of the adsorption capacities are due to the difference in the constituents of the natural and synthesized adsorbents.

In the case of the synthesized SAPO adsorbent, hydroxyl groups (–OH) bounded to P-OH, Al-OH, Si-OH and SiOHAl–, are responsible its strong acidity. The later favour the sorption of positively charged uranyl ion [5].This adsorption of the uranium (VI) bearing species on silanol group has been predicted according to the following reactions [17]:

$>SiOH+UO_2^{2+} \rightarrow [>SiO\text{-}UO_2]^{+} + H^{+}$ (4)

$>SiOH+UO_2^{2+} + H_2O \rightarrow [>SiO\text{-}UO_2OH] + 2H^{+}$ (5)

$>SiOH+UO_2^{2+}+2H_2O \rightarrow [>SiO\text{-}UO_2(OH)_2]^{-} +3H^{+}$ (6)

It is also noticed that at optimal pH condition of 7 for the SAPO material, the surface charge is negative since the pH 7 is above the PZC determined at section 3.4, which favour the adsorption of positively charged uranyl ions UO_2^{2+}.

A comparison between raw and chemical activated sawdust indicates that adsorption capacity increases when the sawdust is modified with NaOH (Table 5). This behaviour could be due to an increasing of the binding sites number of the sawdust surface giving rise to a better exchangeability and consequently an improving of the uranium sorption [9, 12]. The active ion exchange compounds in natural sawdust adsorbent consist mainly of cellulose, hemicelluloses, lignin. These compounds contain methyl esters groups, which do not bind uranium ions significantly. Nevertheless, these methyl esters are modified to carboxylate ligands by treating the sawdust with NaOH (Table 4). Thus, these ligands contribute to increasing the uranium binding ability of the sawdust [18].

Table 5: Optimal uranium sorption parameters onto natural and synthesized adsorbents.

Parameters	**Adsorbent**	**[U] (mg/L)**	**Contact time t(min)**	**Initial pH solution**	**Solid to liquid ratio (g/L)**	**Temperature T(K)**
Range of variation	Raw-AAPS	50-150	0-240	2 to 10	5-90	293-323
	CA-AAPS	50-150	0-240	2 to 10	5-90	293- 323
	SAPO	50-150	0-240	2 to 10	0.33-10	293- 323
Optimal parameters	Raw-AAPS	150	20	5.0	25.00	293
	CA-AAPS	150	20	5.5	23.00	293
	SAPO	150	30	7.0	0.66	323
q_{max}(mg/g)	Raw-AAPS	18.52	-	-	-	-
	CA-AAPS	31.04	-	-	-	-
	SAPO	74.00	-	-	-	-

The probable principal mechanisms are guessed hydrogen bonding as well as ion exchange. Therefore, the mechanisms of uranium onto the sawdust can occur on the below equations:

Ion exchange:

$2R\text{-}COH + UO_2^{2+} \rightarrow (R\text{-}CO)_2UO_2 + 2H^{+}$ (7

$R\text{-}COH +UO_2OH^{+} \rightarrow R\text{-}COUO_2OH + H^{+}$ (8

Hydrogen bonding:

$2R\text{-}COH+UO_2(OH)_2 \rightarrow (R\text{-}COH)_2UO_2(OH)_2$ (9

In order to compare the performance of adsorbents used in this study toward uranium ions, the sorption capacities order is:

$q_tSAPO > q_tCA\text{-}AAPS > q_tRaw\text{-}AAPS$

3.6. Kinetic characteristics of uranium ions sorption

The experimental data for natural and synthesized adsorbents are evaluated using kinetic models (pseudo-first order, pseudo-second order and Weber & Morris) presented in Table 6.

The rate constants and the equilibrium capacities are calculated using the slope and the intercept of the first and second order models plotting [19]. The fitting quality is estimated by the error functions showed in Table 6 (RMSE, χ^2, SAE and ARE). The lower values obtained from these error functions calculation is used to select the appropriate kinetic model [20].

The kinetic parameters of uranium ions uptake onto Raw AAPS, CA-AAPS and SAPO adsorbents are shown in Table 7.

Table 6: Errors, kinetic, isotherms models functions and plotting

Isotherm	**Functional form**	**Plotting**
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	*Log (q_e-q_t) vs t*
Pseudo-second order	$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{h} \qquad where\, h = k_2 \cdot q_e^2$	t/q_t *vs t*
Weber &Morris	$q_t = k_{id} \cdot t^{0.5} + C$	q_t *vs* $t^{0.5}$
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b q_{\max}}$	C_e/q_e *vs* C_e
Freundlich	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$	$\ln q_e$ vs $\ln C_e$
Dubinin-Radushkevich	$\ln q_e = \ln q_{\max} - K\varepsilon^2$	$\ln q_e$ vs ε^2
Temkin	$q_e = B_T \ln K_T + B_T \ln C_e$	q_e vs $\ln C_e$
Root mean square	$RMSE = \sqrt{\frac{1}{n-2} \sum_1^n (q_i - q_{ie})^2}$	-
Chi-squared	$\chi^2 = \sum_{i=1}^{n} \frac{(q_i - q_{ie})^2}{q_{ie}}$	-
Average relative error	$ARE = \frac{100}{n} \sum_{i=1}^{n} \left\lvert \frac{q_i - q_{ie}}{q_i} \right\rvert$	-
Sum of the absolute errors	$SAE = \sum_{i=1}^{n} \lvert q_i - q_{ie} \rvert_i$	-

Table 7: Kinetics parameters of uranium (VI) adsorption by natural and synthesized adsorbents

Kinetic model	**Pseudo-first order**			**Pseudo-second order**		
	Raw-AAPS	**CA-AAPS**	**SAPO**	**Raw-AAPS**	**CA-AAPS**	**SAPO**
k_1 (min^{-1})	0.085	0.053	0.026	-	-	-
k_2 (g/mg.min)	-	-	-	0.030	0.011	0.092
q_e(mg/g)	7.80	1.40	1.29	13.30	14.5	74.07
$q_{e,exp}$(mg/g)	13.07	15.31	74.10	13.07	15.31	74.10
R^2	0.94	0.70	0.79	0.99	1.00	1.00
RMSE	5.30	15.83	2.71	0.70	0.16	0.42
χ^2	7.89	890.37	39.96	0.33	0.013	0.48
SAE	14.53	75.58	15.41	2.69	0.74	1.98
ARE	34.5	91.70	71.26	3.96	0.61	1.28

Table 8: Intraparticle diffusion parameters for uranium (VI) adsorption onto natural and synthesized adsorbents

	Raw-AAPS	**CA-AAPS**	**SAPO**
K_{id1} (mg.g^{-1}min$^{0.5}$)	1.52	2.38	1.44
C_1	4.59	12.50	67.00
R^2	0.98	0.99	0.99
K_{id2} (mg.g^{-1}min$^{0.5}$)	0.004	0.099	0.020
C_2	13.03	14.0	73.00
R^2	0.92	0.97	0.90

	Raw-AAPS	**CA-AAPS**	**SAPO**
K_{id1} (mg.g^{-1}min$^{0.5}$)	1.52	2.38	1.44
C_1	4.59	12.50	67.00
R^2	0.98	0.99	0.99
K_{id2} (mg.g^{-1}min$^{0.5}$)	0.004	0.099	0.020
C_2	13.03	14.0	73.00
R^2	0.92	0.97	0.90

The quasi similar calculated and experimental adsorption capacity values for the studied adsorbents (Raw AAPS, CA-AAPS and SAPO) and the less error function values reported in Table 7 indicate that the uranium (VI) sorption onto these adsorbents fits well the pseudo-second order kinetics. Additionally, these results suggest that uranium (VI) adsorption is controlled by chemisorption process [21-22]. In order to compare the performance of absorbents used in this study, the results show that the order of adsorption capacities values is:

$$q_t \text{ Raw-AAPS} < q_t \text{ CA-AAPS} < q_t \text{ SAPO}$$

In order to identify the diffusion mechanism of uranium (VI) sorption onto Raw-AAPS, CA-AAPS and SAPO adsorbents, the kinetic results are also analysed by intraparticle diffusion model (Table 8).

Table 8 show the values of the calculated intraparticle diffusion constants k_{id1} and $k_{id2,}$ and the correlation coefficients R^2. These results highlight larger diffusion rate in the first stage (k_{id1}) compared to the second one (k_{id2}) for all the studied adsorbents. In fact, a fast external surface sorption of uranium (VI) via film diffusion is firstly observed. When the external surface reaches saturation, uranium (VI) enters the internal pores of these adsorbents [23].

Based on the k_{id1} results, we noticed that the external surface adsorption of uranium (VI) is faster in the following order: CA-AAPS > Raw-AAPS > SAPO.

3.7. Equilibrium modelling

Uranium ions sorption onto Raw-AAPS, CA-AAPS and SAPO results are subjected to the Langmuir, Freundlich, Dubinin–Radushkevich and Temkin models, their functional form and plotting are given in Table 6.

Table 9 show the obtained parameters values for these models. The equilibrium values for uranium (VI) sorption obtained with the Langmuir model are 19.95; 48.66 and 76.92 mg/g for Raw-AAPS, CA-AAPS and SAPO, respectively. These values are close to the experimental adsorption capacities of the adsorbents.

Nevertheless, the Freundlich model fits better SAPO data with a high correlation coefficient R^2 = 0.99 and lower error function values. Furthermore, the calculated Freundlich constant (n) values are 3.38, 1.57 and 1.31 for Raw-AAPS, CA-AAPS and SAPO respectively. The constant (n) value should be in the range of 1–10 for a favourable adsorption [24-26]. This shows the effectiveness of the studied adsorbents for UO_2^{2+} removal from aqueous solutions.

The analysis of the equilibrium data of the considered adsorbents using the D-R model shows a large deviation from linearity. This is highlighted by the registered low R^2 coefficient and the high error function values (Table 9). However, the experimental data o these adsorbents are in good agreement with the Temkin model. Indeed, this model shows high correlation coefficient and acceptable error functions values.

Table 9: Model constants and error function values for adsorption of uranium by natural and synthesized adsorbents

Model	**Langmuir**			**Freundlich**			**D-R**			**Temkin**		
	Raw-AAPS	**CA-AAPS**	**SAPO**	**Raw-AAPS**	**CA-AAPS**	**SAPO**	**Raw-AAPS**	**CA-AAPS**	**SAPO**	**Raw-AAPS**	**CA-AAPS**	**SAPO**
q^{exp}(mg/g)	18.52	31.04	74.10									
q_{max}(mg/g)	19.95	48.66	76.92									
b (L/g)	0.11	0.059	0.04									
R_L	< 1	< 1	< 1									
K_f(mg/g)				4.88	3.78	3.28						
n				3.38	1.57	1.31						
q_{max}(mg/g)							16.76	23.23	27.54			
$K.10^6$ (mol^2/kJ^2)							6.42	1.93	-2.61			
K_T										1.47	0.65	0.53
B_T										3.74	10.30	13.22
R^2	0.99	0.98	0.95	0.99	0.94	0.99	0.83	0.79	0.83	0.90	0.98	0.98
RMSE	0.95	1.29	0.85	0.95	3.82	1.06	15.75	8.83	13.76	1.46	1.55	4.29
X^2	0.49	0.06	0.20	0.49	3.08	0.21	44.16	20.92	34.38	1.02	1.58	4.25
SAE	6.41	7.05	4.76	6.41	18.32	5.26	68.46	53.34	66.34	9.78	9.31	19.23
ARE	5.66	6.04	4.09	5.66	12.61	3.51	90.71	39.96	84.47	7.99	10.38	15.97

3.8. Thermodynamic study

The thermodynamic parameters are calculated from the slope and the intercepts of ln K_d vs 1/T using the following equations:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (10)$$

$$K_d = \left(C_i - C_{eq}\right)\cdot\left(\frac{V}{C_{eq}.m}\right) \qquad (11)$$

where K_d is the distribution coefficient (mL/g), C_i and C_{eq} are the initial and equilibrium concentrations (mg/L), V is the volume of uranium solution (mL) and m is the amount of adsorbent (g).

Table 10 summarizes the results of the investigated adsorption thermodynamics process of uranium (VI) onto Raw-AAPS, CA-AAPS and SAPO adsorbents. The observed positive and larger than 40 kJ/mol values of the enthalpy ΔH° indicate an endothermic process of uranium sorption. The sorbate binding to the surface occurs by chemisorption for the synthesized adsorbent [27]. Whereas, this process is exothermic for the natural adsorbents (raw-AAPS and CA-AAPS). Moreover, the positive value of entropy ΔS° registered for all the studied adsorbents reflects their affinity of to uranium uptake. The uranium removal affinity order is:

SAPO > CA-AAPS > Raw -AAPS

The thermodynamic parameter, ΔG° is calculated from the following Gibbs-Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T\cdot\Delta S^\circ \qquad (12)$$

where ΔG° is the standard Gibbs free energy. From eq (12), the data of ΔG° are obtained at different temperatures. We noticed that the values are negative for the studied adsorbents indicating a spontaneous adsorption process.

3.9. Selection of suitable adsorbent

In waste management applications, decontamination factor DF is more appropriate for selection of suitable materials as sorbent. DF is dimensionless ratio used to compare the contamination level before and after treatment. It is calculated by using the following equation:

$$K_d = \left(DF - 1\right)\cdot\frac{V}{m} \qquad (13)$$

where K_d is the distribution coefficient, DF the decontamination factor, V the volume of liquid effluent and m is the amount of adsorbent.

DF values obtained at T=293 K are 7.76; 21.80 and 50 for Raw-AAPS, CA-AAPS and SAPO, respectively. This indicates a significant decontamination effect of natural and synthesized adsorbents. By comparing these values, the order of the more suitable adsorbent for uranium removal is:

SAPO > CA-AAPS > Raw-AAPS.

This result confirms the uranium adsorption affinity order obtained in section 3.6.

Table 10: Thermodynamic parameters for uranium (VI) sorption onto natural and synthesized adsorbents

Adsorbents	**ΔH° (kJ/mol)**	**ΔS° (J/mol.K)**	**ΔG° (kJ/mol)**			
			293K	**303 K**	**313K**	**323K**
Raw-AAPS	-12.61	4.16	-15.83	15.87	-15.90	-15.95
CA-AAPS	-2.17	56.03	-18.58	-19.14	-19.50	-20.26
SAPO	47.88	242.51	-23.21	-25.63	-28.06	-30.48

4. Conclusion

In the present comparative study, the Algerian Aleppo pine sawdust and the synthesized SAPO are used as adsorbents of uranium (VI) ion from aqueous solutions. The maximum adsorption of uranium (VI) occurs at different optimal values of pH, contact time, uranium concentration, solid to liquid ratio and temperature for the studied adsorbents. The isotherms modelling, the equilibrium and kinetic studies indicate that adsorption capacities are in the following order:

q_t(Raw-AAPS) < q_t(CA-AAPS) < q_t(SAPO)

The experimental kinetics data of natural (Raw-AAPS, CA-AAPS) and synthesized (SAPO) are in accordance with the pseudo-second order model. This indicates that the adsorption of uranium (VI) is dominated by chemisorption which is confirmed by modelling results. Based on the obtained thermodynamic parameters and decontamination factor values, the uranium removal affinity order is: SAPO > CA-AAPS > Raw -AAPS.

The thermodynamic study shows that uranium sorption onto synthesized adsorbent is spontaneous and endothermic, while the process is spontaneous and exothermic onto natural Algerian Alepo pine sawdust.

The comparison study showed that the studied natural and synthesized materials are effective for the removal of uranium (VI) ion. The natural Algerian Aleppo Pine Sawdust material presents less adsorption capacity comparatively to the synthesized material SAPO. Nevertheless, the natural Algerian Aleppo Pine (CA-AAPS) is cost-effective adsorbent for a large removal of uranium from an effluent.

Conflict of Interest: The authors declare that they have no conflict of interest

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