Adsorption of uranium and thorium on new adsorbent prepared from Moroccan oil shale impregnated with phosphoric acid

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Abstract

Attention has been focused recently on the production of new adsorbents from Moroccan oil shale of Tarfaya (layer R3) by chemical activation with phosphoric acid and its application in wastewaters treatment. The optimal conditions for the preparation were searched and the tests of adsorption of uranium and thorium ions were affected. The best product was obtained by used of the ratio of activated agent/precursor equal 3 and activation of the mixture in air at 250°C during two hours after prepocessing at 120°C in air. Under these conditions the maximal adsorption capacity of methylene blue and specific area (S_{BET}) of the new adsorbent were 526 mg/g and 630 m^2/g, respectively. A batch mode experiment was used to explore the performances of this adsorbent for the removal of the U and Th from aqueous solutions prepared from $UO_2(NO_3)_2.6H_2O$ and $Th(NO_3)_4.5H_2O$. The adsorption parameters for the two radioelements were determined by application of the Langmuir, Freundlich and Elovich models.

***Keywords*:** oil shale – activation – phosphoric acid – adsorption – methylene blue –radionuclide – isotherms

Introduction

To satisfy the increasing number of directives referring to the control of environmental radioactivity and its health aspects, numerous treatments of radioactive waste have been developed [1]. Considering the potential risks presented by radionuclides for humans and the environment [2-5], it is necessary to envisage the problem for all nuclear activities. A number of processes for the treatment by natural and synthetic materials [6-8] has been reported, the principal ones being based on the elimination of specific species such as U, Th and Ra by

organic, inorganic, or composite (polymer and metallic oxides) adsorbents [9-12]. In this context, the utilization of Moroccan oil shale of Tarfaya (layer R3) as a raw material for production of a new adsorbents and the adsorption capacity for radionuclides U and Th, by these products have been studied. The precursor was obtained by elimination of the carbonates in the native rock by 6N HCl. The obtained powder (R3H) was mixed with **30** N phosphoric acid and treated in different conditions [13]. The change of microtexture between the precursor and the obtained adsorbents was examined by different analytical methods. The best adsorbents obtained were applied for the removal of the U and Th from aqueous solutions. The curves of kinetics and isotherms adsorption were presented and the adsorption parameters for the two radioelements were determined by application of the Langmuir, Freundlich and Elovich models.

Materials and methods

Preparation of the precursor

The raw material used in this work is Moroccan oil shale of Tarfaya (layer R3). This material is composed from the organic matter chemically linked to the mineral matter essentially formed by calcite, dolomite, silicate and clays (table 1) [13-15].

Table 1: Mineralogical composition of the Tarfaya oil shale

Constituent	Calcite	Dolomite	Clays and others	Organic matter	Silicate	Pyrite
Wt. (%)	63.7	3.5	10	15.9	6.5	<1

The naturally oil shale was crushed and ground to 100-200 μm and the resulting product was attacked with 6N HCl. This attack was continued until there was no more CO_2 release. After filtration, the residue was washed by distilled water to eliminate excess acid. The product obtained, referred to as R3H, was used as the precursor for preparing the new adsorbents. Elemental analysis of this precursor (Table 2) shows the presence of C, O, H, S, Si, Fe, Al and other elements [13].

Table 2: Chemical composition of the precursor R3H

Element	C	H	Si	O	S	Al	Fe	N
Atomic %	34.38	46.06	8.6	5.28	2.05	1.35	1.15	0.9

Activation of the precursor and characterization of the product

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The precursor R3H, a particle size of 80-100µm in diameter, was mixed with the phosphoric acid at 80%, with a weight ratio H_3PO_4/precursor = 3. The choice of the activating agent and the weight ratio was dictated by results obtained after many studies trials in the laboratory and according to our previous studies [13-15]. The activation experiments were performed under various conditions to obtain the optimal condition for activation.

The mixture was heated in furnace under various atmosphere gases (nitrogen or air) at different temperatures (250-450°C) after preprocessing at 120°C in oven under air [13]. Thermally treated product, referred by P, was washed with distilled water in a Soxhlet extractor, to eliminate excess acid and soluble matter then dried at 110°C.

Before used in adsorption tests the adsorbent was sieved, more 95% of the final particles had an average diameter than of 100 µm.

The general procedure of the activation process for this study is described below an dis schematically outlined in figure 1.

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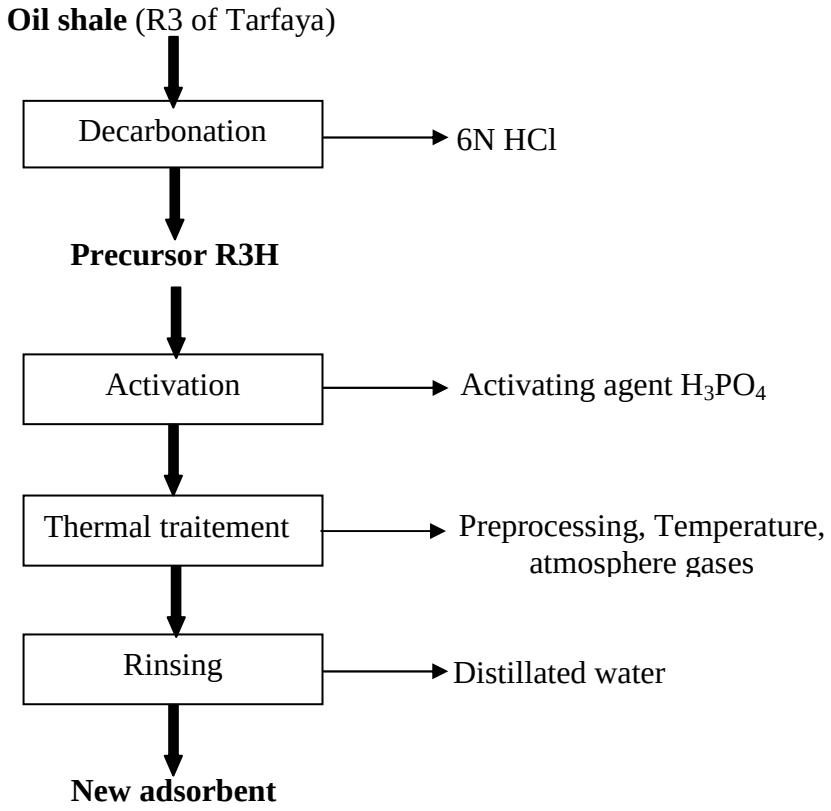


Figure 1: Flow diagram for activation process

The performance of a new adsorbent was evaluated by determination of the maximum adsorption capacity of methylene blue, the specific area (S_{BET}) and the surface functions.

Adsorption test of U and Th

To evaluate the applicability of adsorbent for waste water treatment, adsorption tests were performed using U Th ions as adsorbate. The synthetics waste water containing U and Th were prepared from $UO_2(NO_3)_2.6H_2O$ (Merck) and $Th(NO_3)_4.5H_2O$ (Merck), 1-2 days before the experiments. The concentration of U and Th remaining in solution before and after adsorption was measured photometrically with UV-Visible PERKIN ELMER spectrophotometer, the colour reaction is obtained by Arsenazo III. This reagent is frequently used for the determination of Th, U and other elements [13].

Effect of pH on adsorption test

The effect of pH in water on U and Th adsorption was studied by performing equilibrium sorption tests at different initial pH. Batch sorption experiments were performed at room temperature. Fixed amounts (30 mg) of a new adsorbent were added to aqueous solutions (100 ml) containing 10 µg/ml of radionuclide (U or Th) in 150 ml Erlenmeyer's flasks. The pH was adjusted either with 0.1 N HCl or 0.1 N NaOH as required. The mixture was shaking using a mechanical shaker for 20 hours. When the equilibrium was reached, the mixture was separated and the residual concentration of U or Th was measured by spectrophotometer.

2.5.1. Adsorption kinetics

Two important physicochemical aspects for the evaluation of the parameter of sorption process as a unit operation are the kinetics and the equilibrium time of sorption. Kinetics of sorption, describing the solute uptake rate which in turn governs the residence time of sorption reaction, is on of the important characteristics defining the efficiency of sorption.

For kinetic studies, 150 mg/l of adsorbent was added to 500 ml of aqueous solutions containing 4.92 µg/ml of U or 5.22 µg/ml of Th. After adjustment of pH to approximately 7, the mixture was shaken at room temperature. The concentration of radioelement in the aqueous solutions was measured.

2.5.2. Adsorption isotherms

The batchwise adsorption method was applied to obtain the adsorption isotherms. Different amounts (100, 200, 300, 400 and 500 mg/l) of adsorbent were added to aqueous solution (100 ml) containing 20 µg/ml of U or 28 µg/ml of Th in 150 ml flasks and agitated for 20 hours at room temperature. Afterwards, the residual concentrations of the radioelements were measured. Results were obtained by application of Langmuir, Freundlich and Elovich models [16] according to these formulas:

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$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{b_1 Q_0} \times \frac{1}{C_e} \quad (4)$$

$$\log\ q_e = \log\ K_f + n \log\ C_e \quad (5)$$

$$Ln\ \frac{q_e}{C_e} = Ln\ b_2 Q_0 - \frac{q_e}{Q_0} \quad (6)$$

Where

q_e : Adsorption capacity (*mg/g* or *mol/g*)

Q_0 : maximal adsorption capacity (*mg/g* or *mol/g*)

C_e : Residuum concentration (*mg/l* or *mol/l*)

b_1 : Thermodynamique adsorption constant (*l/mg* or *l/mol*)

b_2 : constant equal to fractional K_{ads}/K_{des} (K_{ads} and K_{des} were the sorption and desorption progress respectively)

K_f and n : Freundlich constants related to the adsorption capacity and adsorption intensity respectively.

Results and discussion

Properties of a new adsorbent

To found the best properties of the prepared adsorbent, numerous experimental were carried at different conditions of preparation with the change of activation temperature, time in furnace, nature of atmosphere gases and conditions of preprocessing [17-18]. The best properties of a new adsorbent were obtained by activation a mixture *R3H/H_3PO_4* at low temperature (250°C) in furnace during 2 hours in oxidant atmosphere (air) after preprocessing at 120°C in oven under air. The product obtained in these conditions was referred to as **P_{15}**. The maximum adsorption capacity of methylene blue, the specific area (S_{BET}), the total surfaces acidity and the *electronic microsonde* data for this adsorbent (P_{15}) compared to those of precursor R3H were presented in table 3 and 4.

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Table 3: The electron microprobe values of adsorbent P15 and precursor R3H

	Electron microprobe (% atomic)				
	C	O	Si	S	P
R3H	60.00	18.68	16.98	4.34	0.00
P_{15}	63.50	24.80	5.83	0.75	2.40

Table 4: Characteristics values of the prepared adsorbent P15 and precursor R3H

	Functional groups in surface (meq/g)			Total surface acidity (meq/g)	Methylene blue capacity (mgg^{-1})	S_{BET} (m^2g^{-1})
	Carboxylic	lactone	hydroxyl			
R3H	0.48	0.20	0.00	0.68	68	12
P_{15}	0.58	0.34	0.47	1.39	526	630

The results mentioned in tables 3 and 4 shows the improvement of the textural and structural properties of the product P_{15} compared to the precursor R3H. The values regrouped in table 3 revealed the increase of amount of carbon and oxygen due to carbonization of the precursor and the formation of the carbon skeleton. The presence of phosphor element suggested the incorporation of this element in structure of the adsorbent and the formation of the bonds C-O-P. The new adsorbent has the important values of surface area and methylene blue adsorption capacity of respectively 630 m^2/g and 526 mg/g. On the other hand; we note the increase in the functions surface groups values and total acidity.

The microtexture of the products P_{15} and the precursor R3H has been observed by scanning electron microscope (Figure 2) which shows significant morphology differences among the samples. The figure shows the development of porosity in P_{15} compared to R3H. These observations account for the values obtained in adsorption tests and surface area values.

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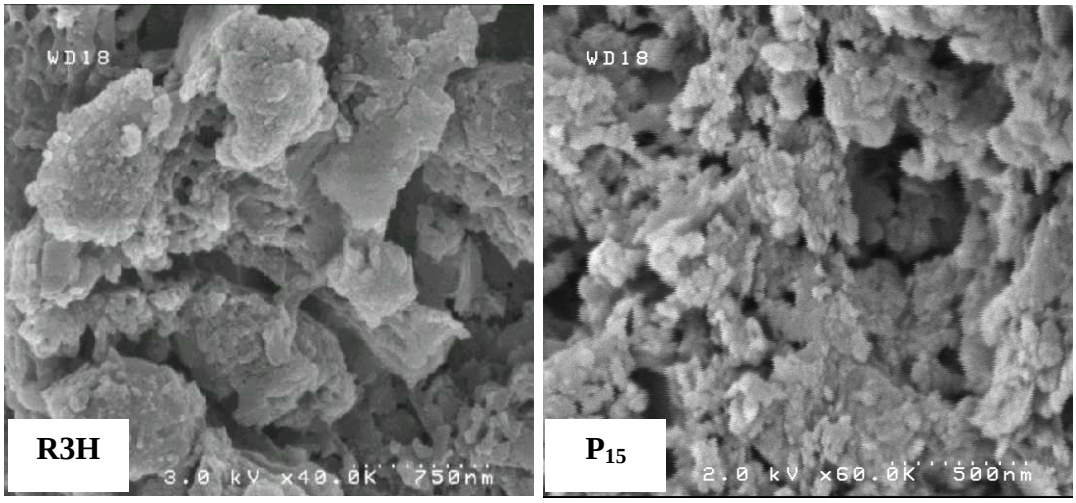


Figure 2: SEM of precursor R3H and prepared adsorbent **P_{15}**

Adsorption tests

Solutions pH influence

Figure 3 shows the pH of U and Th solution influence on adsorption in P_{15}. The sorption of UO_2^{2+} increase with increasing pH, the maximum of adsorption of this ion (75.5%) was reached of pH to approximately 7. This indicates the important effect of the solution pH on adsorption of ion UO_2^{2+}. However, the sorption of Th^{4+} is very important of pH from 4 to 10.8, the rate of adsorption is close to 100%.

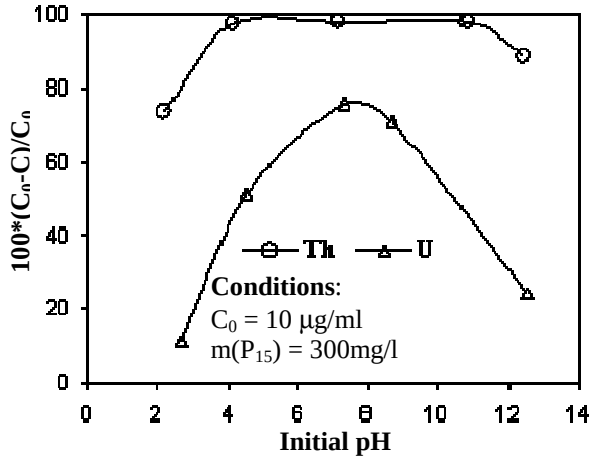


Figure 3: solution pH influence on the UO_2^{2+} and Th^{4+} adsorption by P_{15}

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Kinetics of adsorption

To evaluate the adsorption characteristics of the produced adsorbent 5P15) for radionuclide ions, the change of adsorption rate with time for UO_2^{2+} and Th^{4+} has been investigated. Figure 4 shows the results of the kinetics adsorption of UO_2^{2+} and Th^{4+} by the adsorbent P_{15} compared to this of the precursor R3H. The adsorption rate of two ions on P15 rises rapidly at initial stage of adsorption reaching about 63 and 81% for UO_2^{2+} and Th^{4+} respectively, after 30 min. No appreciable increase in adsorption rate was observed beyond this time and equilibrium adsorption was essentially reached within 120 min. the curves of adsorption on R3H shows that the rate adsorption in equilibrium, of two ions UO_2^{2+} and Th^{4+}, is about 15 and 28% respectively.

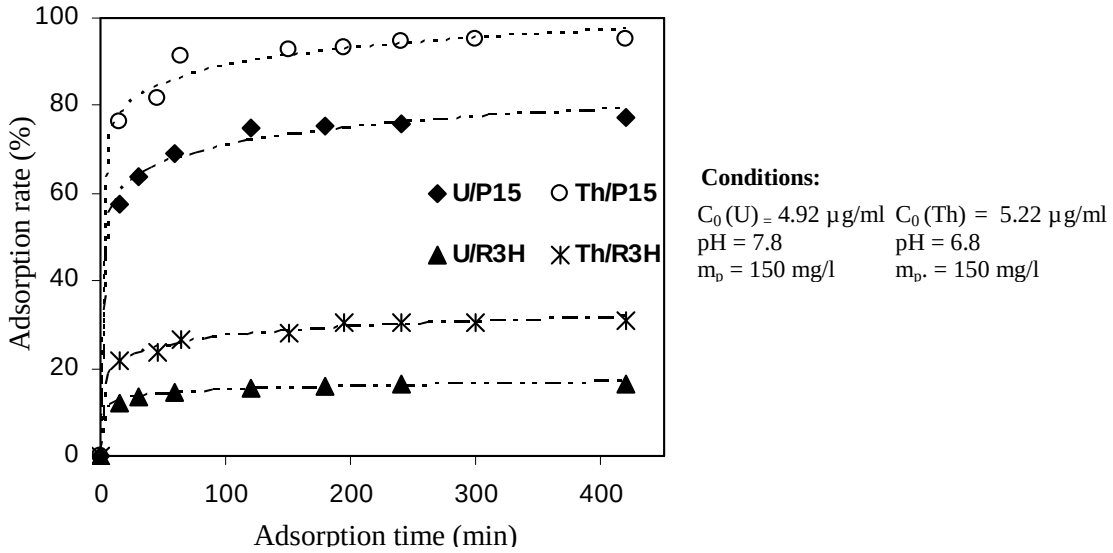


Figure 4: Kinetics adsorption of UO_2^{2+} and Th^{4+}on P_{15} and R3H

Adsorption data usually described by adsorption isotherms, such as the Langmuir, Freundlich and Elovich isotherms. These isotherms relate adsorbed specie uptake per unit weight of adsorbent Q_e to the equilibrium adsorbate concentration in the bulk fluid phase, C_e.

Figures 5-7 present the Langmuir Freundlich and Elovich isotherm plots for U and Th adsorption on P_{15}, respectively. Based on the values of the correlation coefficients (r^2) for different isotherm plots, the Langmuir and Freundlich isotherms give the good fit for data. These plots were used to calculate the isotherms parameters, of adsorption of two elements, given in table 5.

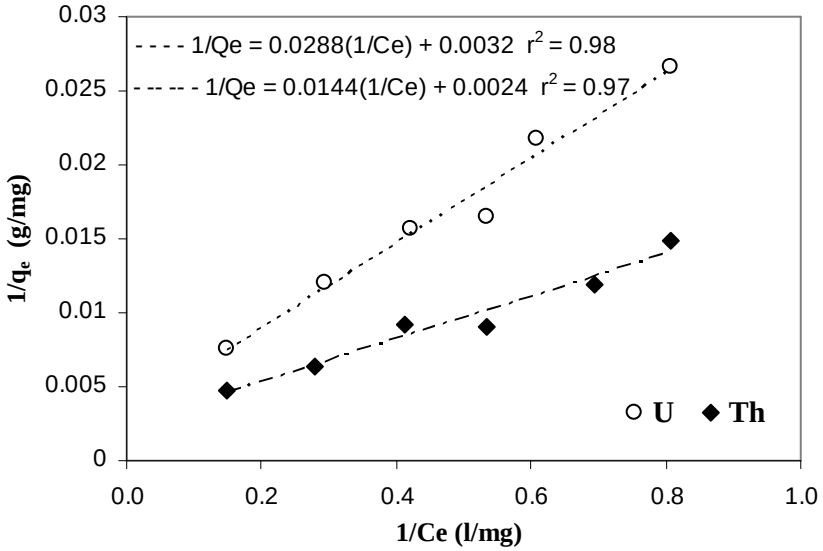


Figure 5. Langmuir isotherm plots of U and Th adsorption on P_{15}

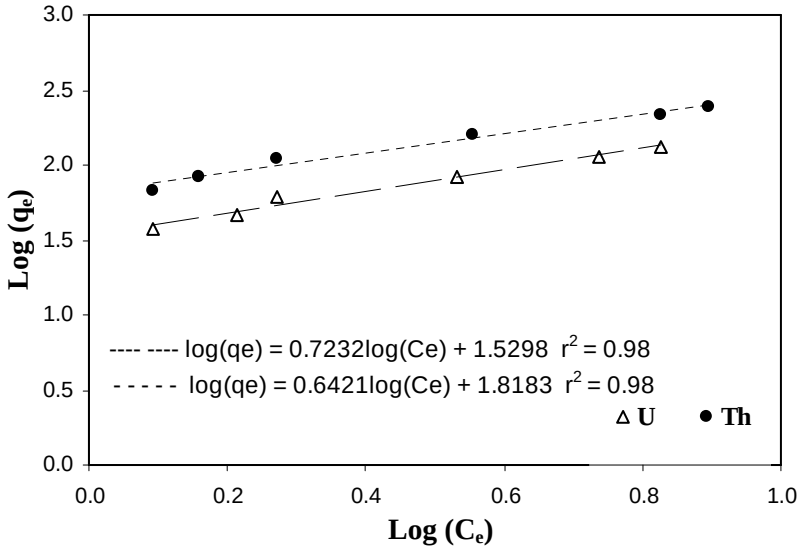


Figure 6. Freundlich isotherm plots of U and Th adsorption on P_{15}

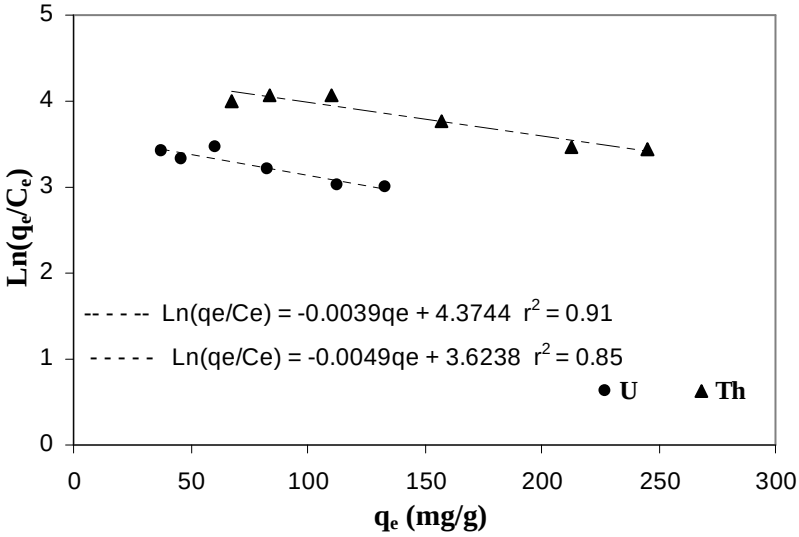


Figure 7. Elovich isotherm plots of U and Th adsorption on P_{15}

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The values of maximal adsorption capacity obtained from Langmuir and Elovich models are 334, 217 mg/g for U and 454, 204 mg/g for Th, respectively. These values are much greater compared to values of Freundlech values. Consequently, the sorption of U and Th is, essentially, achieved by formation of monolayer on the surface of the adsorbent. Differences in the extent of adsorption of U and Th are associated with chemical state of the species adsorbed and the nature of the adsorbent. First, the mobility of uranium, in the form of UO_2^{2+}, is greater than the Th^{4+} ions [8-10, 19]. Consequently, the adsorbent S_5 traps Th^{4+} rapidly and quantitatively. Second, the Th^{4+} ions are smaller than UO_2^{2+} and the sorption process depends to some extent on the nature of the forces produced by chemical interaction between the species adsorbed and the surface groups of the adsorbent [7-11, 16, 20] (e.g. oxygen and sulphur containing groups).

Table 5: Summary of isotherm parameters

	Langmuir		**Freundlich**		**Elovich**	
	Q° (mg/g)	**b_1**	**K_f**	**n**	**Q° (mg/g)**	**b_2**
U	331	0.104	34	0.735	217	0.170
Th	454	0.150	66	0.642	204	0.389

Conclusion

In this work, the Moroccan oil shale from Tarfaya, layer R3, was used as a precursor for the preparation of the new adsorbent. The oil shale was decarbonated and chemically activated with phosphoric acid. The optimization of the preparation conditions permitted the obtained the new adsorbent (P_{15}) with favourable properties of adsorption: specific area (S_{BET}) and methylene bleu capacity, respectively, equal 630 m^2g^{-1} and 526 mgg^{-1},and development of functional groups in surfaces. The results, of the lab-made adsorption of uranium and thorium ion demonstrated a high affinity of these ions facing to new adsorbent. The isotherms parameters, calculated by exploitation of Langmuir, Freundlich and Elovich isotherms, show that the adsorption of two elements was achieved by formation of monolayer on surface of adsorbent. Considering its great adsorption capacity, the abundance of the raw material in Morocco and the simplicity of the production process, the adsorbent prepared from oil shale can be used efficiently for adsorption of others radioelements and tested for the treatment of liquid radioactive waste.

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