



Elimination of thorium ion by an adsorbent prepared from Moroccan oil shale of Timahdit activated by phosphoric acid

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ABSTRACT

Attention has been focused recently on the production of adsorbents from Moroccan oil shale of 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 2 and activation of the mixture in air at 300°C during two hours after preprocessing at 120°C in air. Under these conditions the maximal adsorption capacity of methylene blue and specific area (S_{BET}) of the prepared adsorbent were 502 mg/g and 354 m²/g, respectively. A batch mode experiment was used to explore the performances of this adsorbent for the removal of the Th from aqueous solutions prepared from $Th(NO_3)_4 \cdot 5H_2O$. The adsorption parameters for the radioelement ion were determined by application of the Langmuir, Freundlich and Elovich models.

Keywords: oil shale, activation, phosphoric acid, adsorption, methylene blue, radionuclide.

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 Timahdit (layer Y) as a raw material for production of a new adsorbents and the adsorption capacity for Th ion, by these products have been studied. The precursor, referred YH, obtained by elimination of the carbonates in the native rock, was mixed with phosphoric acid and treated in different conditions [13]. The change of microtexture between the precursor and the resulting adsorbents was examined by different analytical methods. The best adsorbent was applied for the removal of the Th ion from aqueous solutions. The curves of kinetics and isotherms adsorption were presented and the adsorption parameters for the radioelement were determined by application of the Langmuir, Freundlich and Elovich models.

EXPERIMENTAL SECTION

Preparation of the precursor

The raw material used in this work is Moroccan oil shale of Timahdit (layer Y). 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].

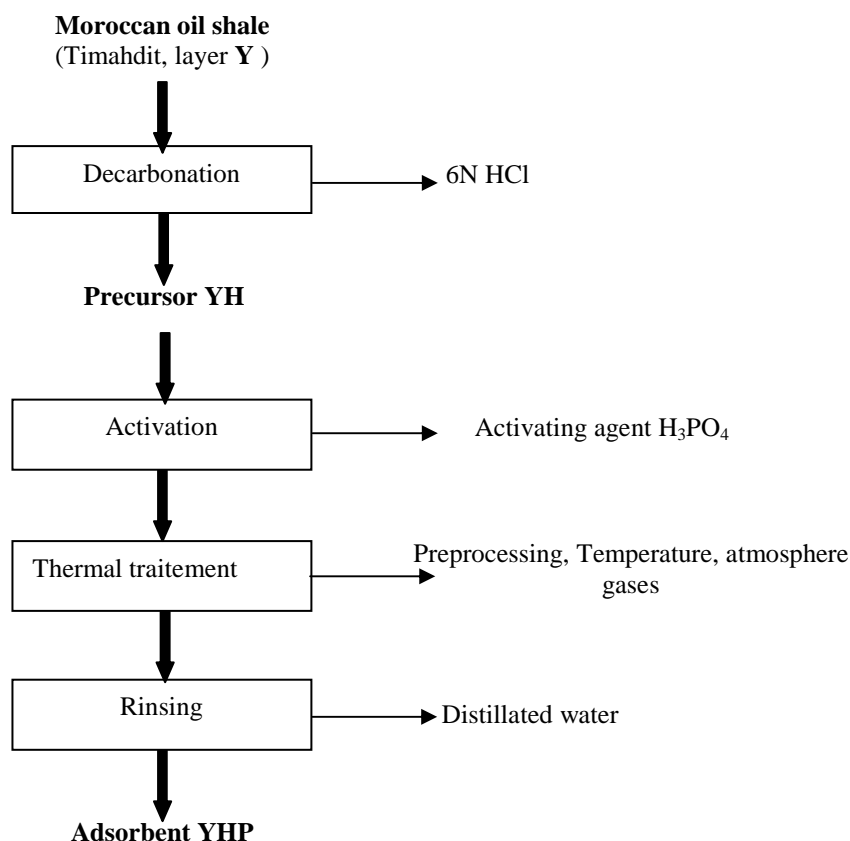
Table 1: Mineralogical composition of the Timahdit oil shale

Constituent	Calcite	Dolomite	Clays	Silicate	Organic matter
Wt. (%)	15.16	12.33	26.87	21.75	23.89

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 YH, was used as the precursor for preparing the adsorbents. Elemental analysis of this precursor (Table 2) shows the presence of C, O, H, S, Si, Mg and other minorities' elements [13].

Table 2: Chemical composition of the precursor YH

Element	C	O	Si	S	Mg	P
Atomic %	50.00	35.60	8.12	1.87	0.95	0.07

**Figure 1: Flow diagram for activation process****Activation of the precursor and characterization of the product**

The precursor YH, a particle size of 80-100 μm in diameter, was mixed with the phosphoric acid at 80%, with a weight ratio $\text{H}_3\text{PO}_4/\text{precursor} = 2$. 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 oxidant atmosphere gaze (air) at different temperatures bitewing 250 and 450°C, after preprocessing at 120°C in oven under air [13]. Thermally treated product, referred by YHP, was washed with distilled water in a Soxhlet extractor, to eliminate excess acid (H_3PO_4) and soluble matter then dried at 110°C.

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

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

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

Adsorption test of thorium ion (Th^{4+})

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

Effect of pH on adsorption test

The effect of pH in water on 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 prepared adsorbent (YHP) were added to aqueous solutions (100 ml) containing 10 mg/mL of radionuclide (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 Th was measured by spectrophotometer.

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, 75 mg of adsorbent (YH or YHP) was added to 400 ml of aqueous solutions containing 10 mg/L 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 in different time.

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 mg/L of Th ion in 150 ml flasks and agitated for 20 hours at room temperature. Afterwards, the residual concentrations of the radioelement were measured. Results were obtained by application of Langmuir, Freundlich and Elovich models [16] according to these formulas:

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

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

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

Where

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

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

C_e : Residuuum 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 prepared adsorbent

The best adsorbent, referred by **YHP**, was obtained by activation a mixture YH/H_3PO_4 at low temperature (300°C) in furnace during 2 hours in air after preprocessing at 120°C in oven under air. The maximum adsorption capacity of methylene blue, the specific area (S_{BET}), the total surfaces acidity and the Electron Spectroscopy for Chemical Analysis (ESCA) data for this adsorbent (YHP) compared to those of precursor YH were presented in table 3 and 4.

Table 3: The ESCA values of the precursor YH and the adsorbent YHP

Element	ESCA (% atomic)	
	YH	YHP300/2h
C(1s)	42.29	51.17
In(3d)	0	0.12
N(1s)	1.32	0.6
Ca(2p)	0.28	0
P(2p)	0.46	2.45
O(1s)	42.1	34.5
Si(2p)	8.83	10.85
Al(2p)	2.62	0.35

Table 4: Characteristics values of the prepared adsorbent YHP and precursor YH

	Methylene blue capacity (mgg ⁻¹)	S_{BET} (m ² g ⁻¹)
YH	84	24
YHP	502	354

The results mentioned in tables 3 and 4 shows the improvement of the textural and structural properties of the product YHP compared to the precursor YH. 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 value of surface area is around of 350 m²/g and the methylene blue adsorption capacity is greater than 500 mg/g. The micro-texture of the products YHP and the precursor YH 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 YHP compared to YH. These observations account for the values obtained in adsorption tests and surface area values.

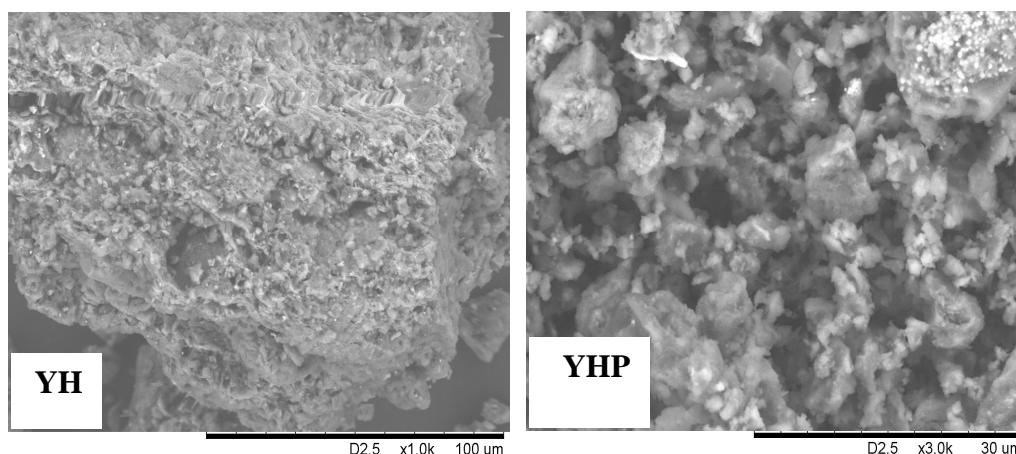


Figure 2: SEM of precursor YH and prepared adsorbent YHP

*Adsorption tests**Solutions pH influence*

Figure 3 shows the pH of Th solution influence on adsorption in YHP. The sorption of Th⁴⁺ increase with increasing pH, the maximum of adsorption of this ion (100%) was reached of pH to approximately 7. This result indicates the important effect of the solution pH on adsorption of ion Th⁴⁺.

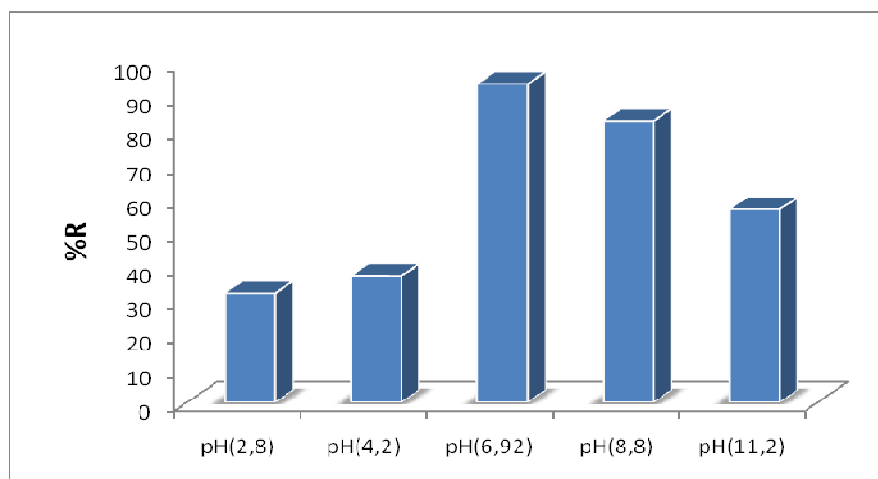


Figure 3: solution pH influence on the Th⁴⁺ adsorption by YHP

Kinetics of adsorption

To evaluate the adsorption characteristics of the produced adsorbent (YHP) for radionuclide ions, the change of adsorption rate with time for Th⁴⁺ has been investigated. Figure 4 shows the results of the kinetics adsorption of Th⁴⁺ by the adsorbent YHP compared to this of the precursor YH. The adsorption rate of Th⁴⁺ ions on YHP rises rapidly at initial stage of adsorption reaching about 70% after 30 min. No appreciable increase in adsorption rate was observed beyond this time and equilibrium adsorption was essentially reached within 120 min. The curve of adsorption on YH shows that the rate adsorption in equilibrium, of Th⁴⁺, is about 40%.

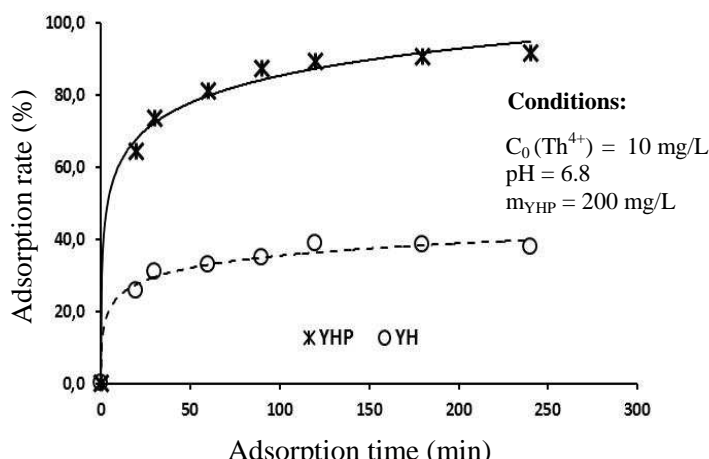


Figure 4: Kinetics adsorption of Th⁴⁺ on YHP and YH

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 Th⁴⁺ adsorption on YHP. 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.

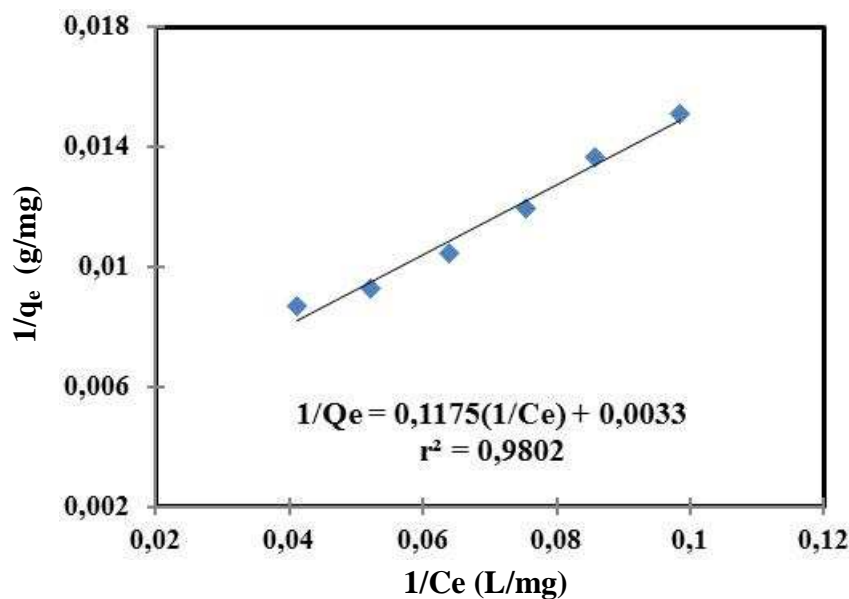


Figure 5. Langmuir isotherm plots of Th adsorption on YHP

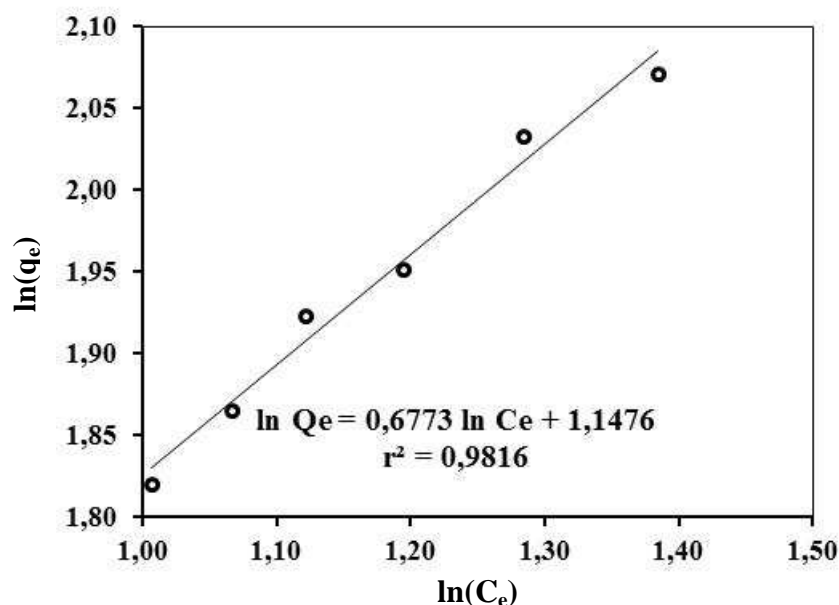


Figure 6. Freundlich isotherm plots Th adsorption on YHP

The values of maximal adsorption capacity, of the thorium ion, obtained from Langmuir and Elovich models are 303 and 454 mg/g, respectively. These values are much greater compared to values of Freundlich values (table 5). Consequently, the sorption of Th ion is, essentially, achieved by formation of monolayer on the surface of the adsorbent. The adsorption of this ion is associated with her chemical state (tetravalent) and the nature of the adsorbent. The thorium ions mobility is very low, which facilitates its trapping. In addition, its small size allows her insertion into the pores of the adsorbent YHP [8-10, 19]. Consequently, the adsorbent YHP traps Th^{4+} rapidly and quantitatively. The values accomplished were very important compared to these obtained by different studies effected on Tarfaya oil shale [21], this difference is explicated by the presence of important amount of organic matter in YH. The presence of this large quantity of organic matter favors the development of cluster surface, which produces chemical interaction forces between the adsorbent and the adsorbate [7-11, 16, 20].

Table 5: Summary of isotherm parameters of adsorption of Th ion by YHP

	Langmuir		Freundlich		Elovich	
	Q° (mg/g)	b ₁	K _f	n	Q° (mg/g)	b ₂
Th	303	0.028	3,3	0.6773	454	0.0058

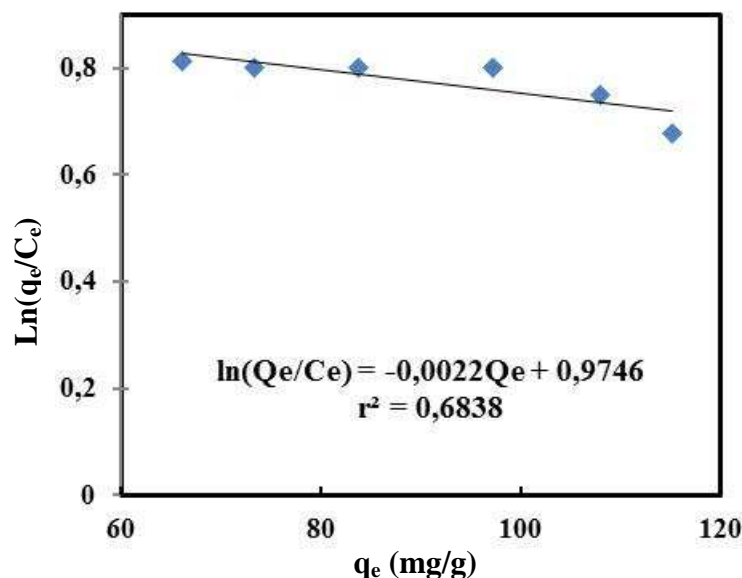


Figure 7. Elovich isotherm plots of Th adsorption on YHP

CONCLUSION

In this work, the Moroccan oil shale from Timahdit, layer Y, was used as a precursor for the preparation of the adsorbent. The oil shale was decarbonated and chemically activated with phosphoric acid. The optimization of the preparation conditions permitted the obtained the adsorbent YHP, with favourable properties of adsorption: specific area (S_{BET}) and methylene blue capacity, respectively, equal $354 \text{ m}^2\text{g}^{-1}$ and 502 mgg^{-1} . The results, of the lab-made adsorption of thorium ion demonstrated a high affinity of these ions facing to the prepared adsorbent. The isotherms parameters, calculated by exploitation of Langmuir, Freundlich and Elovich isotherms, show that the adsorption 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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