Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(9):4386-4392

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

A comparative study on the removal of thorium ions from artificially enriched radioactive waters using Moroccan clays and oil shales

Ouasif Hicham[1*], Yousfi Samia[1], Bouamrani Mouna Latifa[1], El Kouali Mohammed[1], Benmokhtar Said[2], Talbi Mohammed[1]

[1]*Laboratoire de Chimie Analytique Physico-Chimie des Matériaux, Département de Chimie, Faculté des Sciences Ben M'Sik, Casablanca, Maroc.*
[2]*Laboratoire de Recherche de Chimie-Physique Générale des Matériaux, Département de Chimie, Faculté des Sciences Ben M'Sik, Casablanca, Maroc.*

ABSTRACT

The adsorption behaviour of thorium from aqueous solutions by natural adsorbents (clays and oil shales) has been investigated by a batch technique. The natural samples were characterized by X-ray powder diffraction and X-ray fluorescence. The thorium adsorption on natural adsorbents was studied as a function of shaking time (adsorption kinetics). The adsorption data from experiments were fitted with Langmuir (forms I, II and III), Freundlich, Elovich and Temkin isotherms. The equilibrium process was described by the Langmuir model very well. Comparison of the oil schales adsorption capacity and the clays adsorption capacity indicated that the oil schales had a higher selectivity for thorium removal.

Keywords: Sorption, Thorium, Clays, Oil Shales, Isotherms.

INTRODUCTION

The content of radioelements and their distribution in rocks, soil and surface waters is still a current research topic of great importance. Thorium, one of the most studied radioelements, is a heavy element that could exist in natural samples.

The presence of radionuclides in wastes is a major environmental concern. Removing radioactive ions from wastewater is an important issue in liquid waste treatment because these ions are hazardous with respect to the environment and human health given both their high toxicity even at low concentrations and their half-life time (long half live times). The occurrence of these pollutants in water is directly related to industrial activities such as mining, nuclear power generation plants, nuclear weapon production and various laboratory activities [1].

The adsorption of toxic ions from aqueous solutions onto clay minerals is a very important issue in different areas of science. The treatment of radioactive liquid waste is aimed at both decontamination and volume reduction (so as to simplify its storage). The sorption of heavy and radioactive metal ions from effluents proved to be very efficient, numerous sorbents being used for the removal of uranium and thorium from the wastewaters, such as: natural and modified clays [2-3], microorganisms [4], activated carbon [5], different types of cellulosic materials [6], zeolites [7-8] etc.

One of the most effective methods in the treating of radioactive wastewaters is based on adsorption processes. In recent years, inorganic adsorbents have emerged as an increasingly substituting or/and additional means for

conventional organic adsorbents, particularly in low radioactive wastewaters. Among natural inorganic exchangers, clays play an important role.

Clays are sedimentary rocks which constitute a major component of the earth's crust. In fact more or less hydrated aluminosilicates have a structure of very great specific surface associated very particular physicochemical characteristics.

Oil shales are present in the form of a mixture of two matters [9]; an organic matter which originates in the matter presents initially in the plants and the micro-organisms, and a mineral matter which comes from the minerals which constitute vegetable fabrics and minerals deposited by sedimentation.

The objective of this work was to investigate the ability of natural clays for thorium removal from aqueous solution and compare it with the removal ability of natural oil shales.

EXPERIMENTAL SECTION

2.1. Products preparation

Clays (commentate of Gdana, town of Ouled Said, province of Settat) and oil shales (sleep M, layer of Timahdit) were chosen for this study.

Natural clays abbreviated NC and natural oil shales abbreviated NOS.

The samples of clay minerals were ground and dry-sieved to obtain different sized particles. Prior to their application, the clays and oil shales were sieved and the particle fractions of 0.063 and 0.08 mm were selected for the adsorption experiments, without any further purification or pre-treatment.

2.2. Characterization methods

2.2.1 X-Ray Fluorescence Spectroscopy (XRFS)

The chemical analysis was carried out using a spectrometer of x-ray fluorescence (XRF, Axios; PANalytical) with dispersion wavelength using sequential spectrometer with a measurement channel based on a single goniometer covering the full range of measurement. The sample is prepared in the form of pastille and then carried at the temperature of 1000°C in an induction furnace.

2.2.2. X-Ray powder diffraction (XRD)

X-ray diffraction patterns were obtained with a Philips X'Pert PRO powder diffractometer using copper anticathode λ(Cu) = 1.5418A°) in the area of $2\theta = 10°$ with $2\theta = 55°$.

2.3. Preparation of Th(IV) stock solution

Stock solution of Th(IV) was prepared (1000mgL^{-1}) by dissolving the desired quantity of $Th(NO_3)_4.5H_2O$, in distilled water. The test solutions were prepared by diluting the stock solution to the desired Th(IV) concentrations.

2.4. Analysis of Th(IV) concentration

The total Th(IV) concentration of the aqueous solution was determined spectrophotometrically, using Arsenazo III as complexing agent [10] at 620nm. All the spectrophotometrical analyses have been done by using an UVmini-1240 spectrophotometer.

The spectrophotometric determination of Thorium (IV) ion in the aqueous solution was carried out as follows: Transfer 2 ml of Arsenazo (III) indicator to a 3 ml of 0.1 M Hydrochloric acid solution, and add 10 ml of the aqueous Thorium (IV) test solution. Dilute the volume to 25.0 ml by addition of water.

2.5. Adsorption experiments

In the adsorption kinetic experiments, in a 100ml conical flask, a weighed samples was mixed with 50 ml Th(IV) solution of known concentration at T = 298 K. The adsorbents and standard aqueous solutions were shaken for various mixing time. The shaking rate was the same for all the experiments (stirring rate 300 rpm). Filter-separating of solid phase from liquid was followed by centrifuging at 3000 rpm for 10 min and thorium concentration was determined as mentioned above.

Removal efficiency of Thorium (IV) (P %) was defined as:

P (%) = 100 × (C_0 – Ce)/C_0

where C_0 (mg L^{-1}) and Ce (mg L^{-1}) are the liquid-phase concentrations of Th (IV) at initial and equilibrium, respectively.

In the determination of equilibrium adsorption isotherm, the amount of Th (IV) adsorption at equilibrium, qe (mg g^{-1}), was calculated by:

qe = (C_0 – Ce) V/w

where V (L) is the volume of the solution, w (g) the mass of dry adsorbent used.

The adsorption data from experiments were fitted with:

Freundlich isotherm

Freundlich isotherm [11] is used for modelling the adsorption on heterogeneous surfaces. This isotherm can be explained by the following equation:

$$q_e = K_F C_e^n$$

Where, K_F and n are constants indicating adsorption capacity and adsorption intensity, respectively. The constants were obtained from the plots of the linearized equations:

$$\log q_e = \log K_F + n \log C_e$$

Langmuir isotherm

Langmuir isotherm [12] can be defined according to the following formulas:

$$\frac{q_e}{q_m} = \theta = \frac{K_L.C_e}{1 + K_L.C_e}$$

Where q_m (mg g^{-1}) is the maximum adsorption capacity corresponding to complete monolayer coverage and K_L (L mg^{-1}) is the Langmuir constant relating to adsorption energy [13]. Development of this equation leads to linear forms of Langmuir isotherm. Among, the three forms are presented in the **table 1** [12].

Table 1: The three forms of Langmuir isotherm

LANGMUIR I	$\frac{1}{q_e} = (\frac{1}{q_m}) + (\frac{1}{K_L.C_e.q_m})$	**1/qe *vs* 1/Ce**
LANGMUIR II	$\frac{C_e}{q_e} = C_e \frac{1}{q_m} + \frac{1}{q_m.K_L}$	**Ce/qe *vs* Ce**
LANGMUIR III	$q_e = -\frac{1}{K_L}\frac{q_e}{C_e} + q_m$	**qe *vs* qe/Ce**

Elovich isotherm

Elovich model [14] is based on an expansion kinetics assuming that the adsorption sites increases exponentially with the adsorption, which implies a multi-layer adsorption. When it is used, it is expressed by the equation [15]:

$$\frac{q_e}{q_m} = \theta = K_E.C_E.\exp(-\frac{q_e}{q_m})$$

K_E is the Elovich constante (L.mg^{-1}), the linearization of Elovich model conduct to:

$$\ln\frac{q_e}{C_e} = -\frac{q_e}{q_m} + \ln(K_E.q_m)$$

Temkin isotherm

The Temkin model [16] assumes that when the gas absorption, heat of adsorption due to interactions with the adsorbate decreases linearly with the recovery rate. It is an application of the Gibbs adsorption where the surface is considered energetically homogeneous [17]. Several authors [15, 18-19] propose to use this model in the liquid phase, tracing qe based LnCe:

$$\frac{q_e}{q_{\max}} = \theta = (\frac{RT}{\Delta Q})\ln(K_T.C_e)$$

Where R = 8.314 $J.mol^{-1}.K^{-1}$, T, absolute temperature (K), ΔQ, energy change of adsorption ($J.mol^{-1}$), K_T, Temkin constant ($L.mg^{-1}$).

RESULTS AND DISCUSSION

3.1. Samples characterization

3.1.1. X-Ray Fluorescence Spectroscopy (XRFS)

The composition confirmed by X-ray fluorescence data (Table 2) showing the presence of SiO_2, CaO, Al_2O_3, MgO and Fe_2O_3 as major elements in NC and NOS.

Table 2: Chemical compositions of various samples by X-ray fluorescence (mass %)

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	P_2O_5	Na_2O	TiO_2	SO_3	LOI (Loss on ignition)	Total
NC	42,62	15,76	4,96	10,48	4,39	2,93	2,96	0,57	0,65	0,26	14,23	99,81
NOS	21,81	5,76	2,3	21,71	3,28	0,73	0,92	0,17	0,2	3,31	39,70	99,89

3.1.2. X-Ray powder diffraction (XRD)

The X-ray diffractogram (**Fig.1**) of the powder produced from the natural samples NC and NOS shows that it is composed essentially of carbonates (calcite and dolomite) and silicates. Moreover, we also note the presence, in the X-ray diffractogram of NC, of the characteristic peaks of Illite and kaolinite.

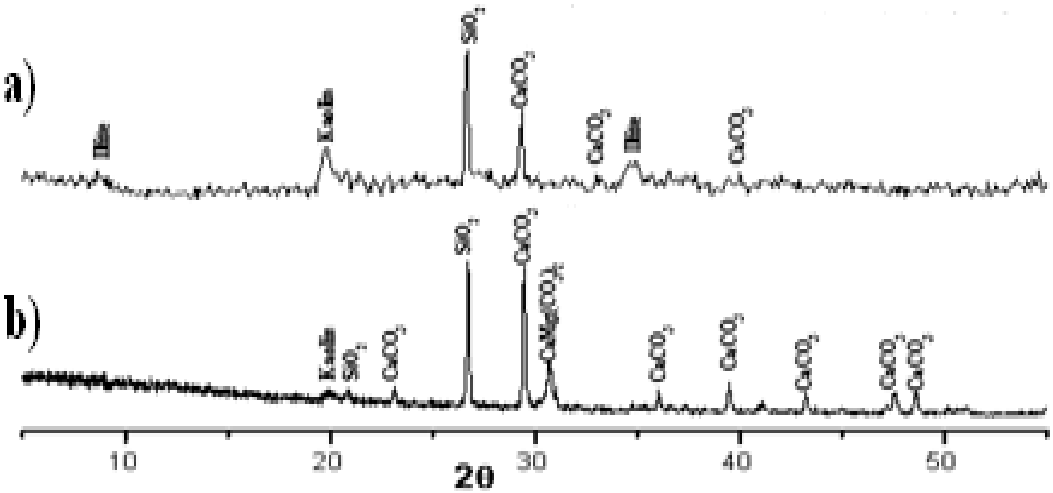

Fig.1: X-ray diffraction patterns of various samples: a) clays and b) oil shales

3.2. Adsorption study

3.2.1. Adsorption kinetics

The sorption of Th(IV) ions has been investigated onto the various adsorbents as a function of shaking time in the range of 0–410 min. The results are given in **Fig.2**. One can see that the adsorption is rapid in the first minutes of contact time and remained constant after equilibrium time. The nature of the samples had a marked effect in Th(IV) removal, leading to the oil shales having higher adsorption capacity than the clays.

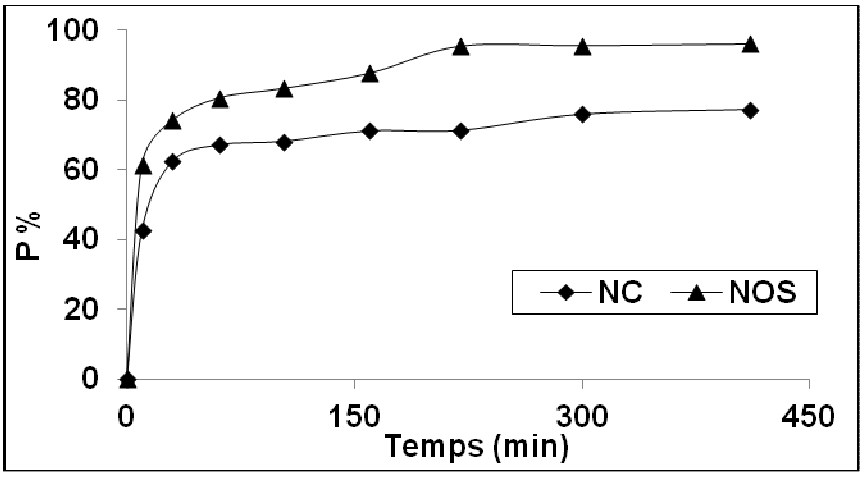

Fig.2: Adsorption kinetics of Th(IV) onto clays and oil shales

3.2.2. Adsorption isotherm

An adsorption isotherm describes the relationship between the amount of adsorbate which is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium [20]. The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems.

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. In order to investigate the sorption isotherm, four equilibrium models (Langmuir (forms I, II and III), Freundlich, Elovich and Temkin) were analysed. The isotherms for all systems were given in **Fig.3**. They were classified as the L curves of Giles' classification [21-22], in which the solution has such a high affinity for the solute that in dilute solutions it is, completely, adsorbed resulting in a vertical initial part of the isotherm.

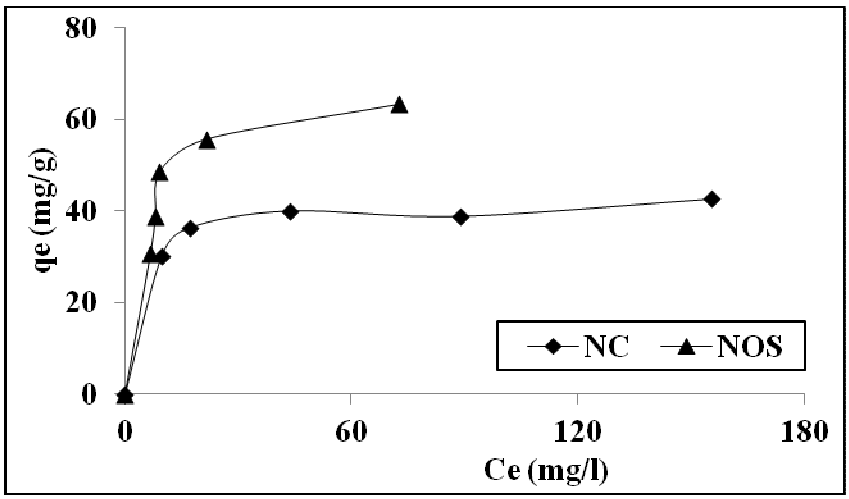

Fig.3: Adsorption isotherms of Th(IV) onto clays and oil shales

The experimental data of Th(IV) adsorption were regressively analyzed with Freundlich, Langmuir, Elovich and Temkin isotherms models:

Freundlich isotherm

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules, and is not restricted to the formation of a monolayer.

The values of K_F and n can be obtained from the slope and intercept of the plot of log(qe) against logCe. The Freundlich models constants for adsorption of Th(IV) onto clays and oil shales and R^2 are tabulated in **Table 3**.

Table 3: The Freundlich models constants and correlation coefficients for adsorption of Th(IV) onto clays and oil shales

Adsorbents	K_F (L g^{-1})	n	R^2
NC	25.29	0.105	0.801
NOS	23.27	0.251	0.734

Langmuir isotherm

The Langmuir isotherm model is based on the assumption that there is a finite number of active sites which are homogeneously distributed over the surface of the adsorbent These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between adsorbed molecules [12].

The Langmuir models constants for adsorption of Th(IV) onto clays and oil shales and R^2 are tabulated in **Table 4**.

Table 4: The Langmuir models constants and correlation coefficients for adsorption of Th(IV) onto clays and oil shales

Adsorbents	Langmuir (I)			Langmuir (II)			Langmuir (III)		
	q_m (mg.g^{-1})	K_L (L.mg^{-1})	R^2	q_m (mg.g^{-1})	K_L (L.mg^{-1})	R^2	q_m (mg.g^{-1})	K_L (L.mg^{-1})	R^2
NC	42.74	0.258	0.934	43.10	0.220	0.995	42.66	0.268	0.802
NOS	71.43	0.129	0.823	68.49	0.170	0.996	67.49	0.181	0.838

Elovich isotherm

In the Elovich isotherm, the plot of Ln(qe/Ce) according to qe achieves the constants qm and K_E. The results are grouped in **table 5.**

Table 5: The Elovich model constants and correlation coefficients for adsorption of Th(IV) onto clays and oil shales

Adsorbents	K_E (L.mg^{-1})	qm (mg.g^{-1})	R^2
NC	2.095	5.30	0.776
NOS	1.275	21.55	0.638

Temkin isotherm

The plot of the Temkin isotherm allow us to determine B_T (B_T=qm.R.T/ΔQ), then introducing a value of qm (eg after the application of Langmuir) to calculate the variation of adsorption energy ΔQ as presented in the following **table 6.**

Table 6: The Temkin model constants and correlation coefficients for adsorption of Th(IV) onto clays and oil shales

Adsorbents	K_T (L.mg^{-1})	ΔQ (kJ.mol^{-1})	R^2
NC	49.741	28.117	0.823
NOS	3.603	14.294	0.813

From **Tables 3**, **4**, **5** and **6**, The correlation coefficients (R^2) for Langmuir (Langmuir (II)) isotherms were 0,995 and 0.996 for NC, and NOS, respectively, indicate that the adsorption of Th(IV) onto clays and oil shales follows the Langmuir model better than the Freundlich (R^2 = 0,801 and 0.734 for NC, and NOS, respectively), Temkin (R^2 = 0,823 and 0.813 for NC, and NOS, respectively) and Elovich (R^2 = 0,776 and 0.638 for NC, and NOS, respectively) models; this shows that the isotherm data type L are best described by the Langmuir model **[**23**].**

Comparison of the oil shales and the clays (**Table 4**) indicated that the oil shales had a higher adsorption capacity for Th(IV) removal.

CONCLUSION

The experimental data of the adsorption studies on thorium using Moroccan clays and oil shales was described well by Langmuir isotherm model; this indicates that the adsorption of thorium from aqueous solutions could be either monolayer.

The adsorption capacity of the adsorbent, obtained from the Langmuir model, was up to 43.10 mg/g and 68.49 mg/g for NC and NOS, respectively.

The adsorption kinetic indicates that the oil shales had a higher adsorption capacity for Th(IV) more than clays.

REFERENCES

[1] AK Kaygun; S Akyil. *J. Hazard. Mater.*, **2007**, 147, 357–362.
[2] E Popovici; D Humelnicu; C Hristodor. *Rev. Chim. Bucharest.*, **2006**, 57, 675–678.

[3] D Humelnicu; E Popovici; C Mita; E Dvininov. *J. Radioanal. Nucl. Chem.*, **2009**, 279, 131–136.
[4] T Tsuruta; J Biosci. *Bioeng.*, **2002**, 94, 23–28.
[5] HH Someda; RR Sheha. *Radiochemistry*., **2008**, 50, 56–63.
[6] D Bontea; C Mita; D Humelnicu. *J. Radioanal. Nucl. Chem*., **2006**, 268, 305–311.
[7] S Akyil, MAA Aslani; M Eral. *J. Radioanal. Nucl. Chem*., **2003**, 256, 45–51.
[8] OS Aytas; S Akyil; M Eral. *J. Radioanal. Nucl. Chem*., **2004**, 260, 119–125.
[9] O Bekri, M Ziyad. Abstract presented at Oil Shale Symposium, Lexington, Kentucky, U.S.A, **1991**.
[10] SB Savvin. *Talanta.*, **1961**, 8, 673–685.
[11] H Freundlich. *Synthesis and catalysis.*, **1909**, 4
[12] I Langmuir. *J. American Chemical Society*., **1918**, 40, 1361–1403.
[13] W Songkasiri; DT Reed; BE Radiochim. *Acta Physicochim*., **2002**, 90, 785–789.
[14] SY Elovich; OG Larinov. Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk, **1962**, 2, 209-216.
[15] O Hamdaoui; E Naffrechoux. *J. Hazard. Mater.*, **2007**, 147, 381-394.
[16] MJ Temkin; V Pyzhev. *Acta Physicochim*., **1940**, 12, 217-256,
[17] J Toth. *Acta Chim. Acad. Sci. Hung.,* **1971**, 32-39.
[18] O Hamdaoui. *J. Hazard. Mater*., **2006**, B135, 264-273.
[19] F Gimbert; NM Crini; F Renault; PM Badot; G Crini. *J. Hazard. Mater*., **2008**, 157, 34-46.
[20] N Roostaei; FH Tezel. *J. Env. Man*., **2004**, 70, 157-164.
[21] CH Giles; D Smith; A Huitson. *J. Colloid. Inter. Sci*., **1974**, 47, 755-765.
[22] G Limousin. JP Gaudet; L Charlet; S Szenknect; V Barthes; M Krimissa. *Applied Geochemistry*., **2007**, 22, 249-275.
[23] C Hinz. *Geoderma*., **2001**, 99, 225-243.