Studies on Thorium Adsorption Characteristics upon Activated Titanium Hydroxide Prepared from Rosetta Ilmenite Concentrate

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Abstract

The titanium hydroxide prepared from Rosetta ilmenite concentrate has been applied for Th (IV) adsorption from its acid aqueous solutions. The prepared hydroxide is first characterized by both Fourier transform infrared (FT-IR) spectrum and thermogravimetric analysis. The relevant factors affecting the adsorption process have been studied. The obtained equilibrium data fits well with the Langmuir isotherm rather than Freundlich isotherm, while the adsorption kinetic data follow the pseudo-second order model. The different thermodynamic parameters have also been calculated and indicate that the adsorption process is spontaneous.

Keywords: Thorium; Titanium hydroxide; Ilmenite; Adsorption

Introduction

The environmental behavior of both lanthanides and actinides has indeed aroused a great interest in terms of the radioactive waste disposal [1-3]. To assess the radionuclides behavior, the different radionuclide phenomena such as sorption, migration and diffusion in natural minerals and oxides are of paramount importance. The fate and transport of the radionuclides in the environment is generally controlled by sorption reactions, complexation, colloid formation, etc. [4-6]. Thorium is only stable at its tetravalent state in solution, and is usually used as a chemical analogue of other tetravalent actinides such as Np (IV), U (IV), and Pu (IV) which are difficult to be studied in the tetravalent form. Thorium is a chemical, toxic, heavy and radioactive metal that is found in the nature and vastly spread in the earth's crust, It has been widely used in nuclear fuel industry, alloy, and laboratory investigations. Thorium has been extensively used in a variety of applications since the last century. These applications have produced various gaseous, liquid and solid wastes containing isotopes of uranium and thorium and their daughter products. The direct toxicity of thorium is low due to its stability at ambient temperature [7]. Thorium is long-lived radionuclides with a suite of radioactive daughter products which can pose a human health and ecosystems risk. It is reported that when thorium nitrate enters living organisms it is mainly localized in liver, spleen and marrow and it precipitates in a hydroxide form [8]. Therefore, the removal and recovery of thorium ions from contaminated water is an urgent and essential work.

Various methods including chemical precipitation, solvent extraction, ion exchange and adsorption are effective methods to remove thorium ions from aqueous solutions. Among these methods, adsorption is an efficient and convenient method because it is a cost effective treatment, easy operation besides no chemical reagents are needed and no sludge produced. In this respect, numerous adsorbents have actually been used for the removal of thorium from the aqueous solution, such as natural and modified clays, carbon materials, biosorbents, molecular sieves, various resins and other specific materials [9-11].

In this regard, it is of greater interest to refer to the work of Shigetomi et al. who has studied the extraction of U (VI) from sea water by its adsorption on gel particles containing titanium hydroxide. From the studied factors, it is found that the U (VI) adsorption tended to increase with the increase of shaking time, while temperature has no effect [12-16].

From the above givings, the aim of the present study is to investigate the influence of the various relevant parameters on thorium (IV) adsorption by activated titanium hydroxide. The latter has been prepared from Rosetta ilmenite by HCl dissolution followed by TOPO extraction of Ti [17,18]. After determination of the optimum conditions for maximum adsorption, the nature of the adsorption process with respect to the equilibrium isotherms as well as to the thermodynamic aspects have been evaluated. Finally, desorption of the adsorbed Th (IV) has been studied by both hydrochloric and nitric acid at different molarities.

Experimental

Material

A sample of East Rosetta beach ilmenite concentrate was used in the present work to prepare the working titanium hydroxide adsorbent. The beach ilmenite sample was first grinded to -200 mesh size then leached with HCl under the following parameters: HCl concentration of 12M with solid/liquid ratio of 1/8 at 80°C for 1.5 hr and finally about 10% Fe powder has been added [17,18]. The leach liquor was subjected to liquid/liquid extraction using TOPO followed by 0.25M HCl stripping after being filtered. For about 2 hr some seed nuclei of Ti $(OH)_4$ were added gradually and shaked with the stripping solution to prepare the titanium hydroxide and the hydrolysis reaction can be represents as follow:

$$TiCl_4 + 4H_2O \rightarrow Ti\,(OH)_4 + 4HCl$$
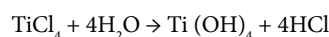
The hydrolyzed precipitate of titanium hydrate was filtered, washed and dried. Activation of the prepared titanium hydroxide was necessary for the removal of any adsorbed impurities. Thus, it was mixed with 5M NaOH for 4-6 hours with stirring followed by separation and washing by double distilled water. The product was subjected to acid washing

using 5M HNO_3 for 4-6 hours with stirring followed by separation and washing using centrifugation at 500 rpm for 25 minutes. Finally, the treated product was dried at 80˚C for 4 hours [19].

Adsorption procedure

Several Th (IV) adsorption experiments were carried out by shaking different sample portions (10 mg) of the prepared activated $Ti(OH)_4$ with 10 ml sample volumes of $Th(NO_3)_4$ solution. The pH values were adjusted to the desired values by the addition of 0.1 mol/l HCl and/or NaOH. The beakers were shaken for 30 min. at room temperature to get complete equilibration. The adsorbent was separated by filtration and the concentration of Th (IV) in solution was determined with UV-Vis spectrophotometer using Thorin as reagent [20,21]. The adsorption capacity (qe) and removal efficiency were obtained using the Eqs. (1) and (2):

$$q_e \left(\mu\_mol / g \right) = \left(\frac{C_o - C_e}{m} \right) V \qquad (1)$$

Removal efficiency (%) =

$$= \frac{(C_o - C_e)V}{C_o V} \times 100 = 1 - \left(\frac{C_o}{C_e} \right) \times 100 \qquad (2)$$

Where C_o and C_e are the Th (IV) ions concentration in the solution initially and at equilibrium (μ_mol/l), respectively, V is the volume of the solution (l), m is the weight of adsorbent (g) and q_e is the amount of Th (IV) adsorbed on Ti $(OH)_4$ at equilibrium (μ_mol/g).

The adsorption experiments were studied in detail under varying operating conditions, such as the pH value of Th (IV) solutions (1-8), contact time (15-120 min), adsorbent dosage (2-20 mg), the initial Th (IV) concentration (100-600 ppm) and temperature (298-333˚K). Furthermore, the pseudo-first-order and pseudo-second-order to describe the adsorption process. The Langmuir, Freundlich and Frendlsh isotherm models were applied to describe the adsorption equilibrium at room temperature. The thermodynamic constants ($\Delta H˚$, $\Delta S˚$ and $\Delta G˚$) of the adsorption process were also evaluated. All the experiments have been carried out in duplicate and the averaged values were taken with the standard deviation.

Results and Discussion

Characterization of activated Ti $(OH)_4$

Fourier transform infrared FTIR spectra of Ti $(OH)_4$ before and after thorium adsorption: The FTIR spectra of $Ti(OH)_4$ A and B (Figure 1) showed some typical peaks before and after the sorption process respectively. In the spectrum A, peaks at 340 and 1103 cm^{-1} reflect presence of OH group, while the peak appeared at 1624 cm^{-1} is likely attributed to the H-O-H bending vibrations [22], while these peaks at 412-779 cm^{-1} are guidance for Ti-O stretching and Ti-O-Ti bridging stretching modes [16]. Such surface hydroxylation supports the photocatalytic activity of the Ti $(OH)_4$ crystals where it provides high capacity for the adsorption processes.

On the other hand, some changes were observed after Th (IV) sorption onto the Ti $(OH)_4$ adsorbent where; a new peak of Th- Ti $(OH)_4$ complex appeared at 2098 cm^{-1}, broading of the previous peak at 3340 cm^{-1} to cover the range from 3448 to 3309 cm^{-1} and shifting of the peak at 1103 to 1041 cm^{-1}. These changes are interpreted as feedback for the formation of Th-Ti $(OH)_4$ complex.

An endothermic peak was observed at about 100°C in the DTA curve for prepared adsorbent, this peak is attributed to the dehydroxyl group of titanium hydroxide [23], which prove that the obtained product is back to of titanium hydroxide (Figure 2).

Specific surface areas of the produced Ti $(OH)_4$: The specific surface area of both the raw material (ilmenite) and the adsorbent before and after activation were measured using automatic surface area and pore analyzer (Table 1). The specific surface area of the raw material was 0.5 m^2/g, while that of the prepared adsorbent was 172.8 m^2/g; which was about 350 times higher than that of raw material. This result matches with the high specific surface area of amorphous titanium gel with resembles the main component of the prepared adsorbent.

Thorium adsorption behavior onto Ti $(OH)_4$ adsorbent

Effect of ph: Testing of the pH effect on the sorption process was carried out using 10 mil of thorium solution (50 mg/l), 0.1gm sorbent, Temperature 25˚C, shaking time 30 min. and variable pH in the range of 1-8.

The results (Figure 3) showed that the maximum thorium adsorption at pH 3 where at alight acidic medium a complex formation between Th (IV) ions and the sorbent active sits are encouraged. On the other hand, at lower pH then 3 the active sits become more protonated and their ability to link with Th (IV) ions negatively affected hence
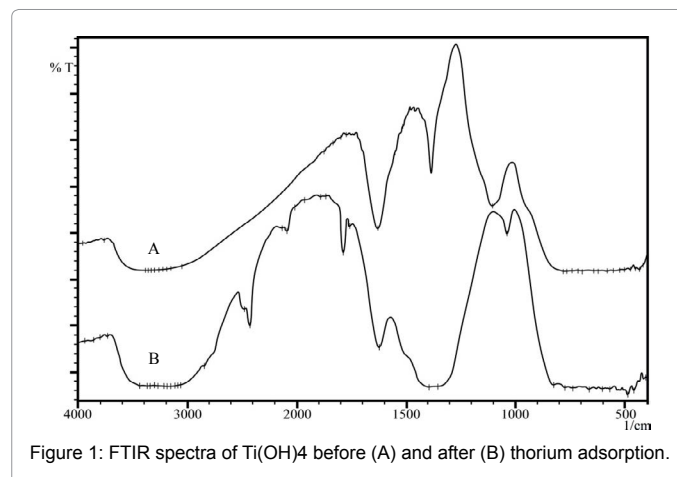

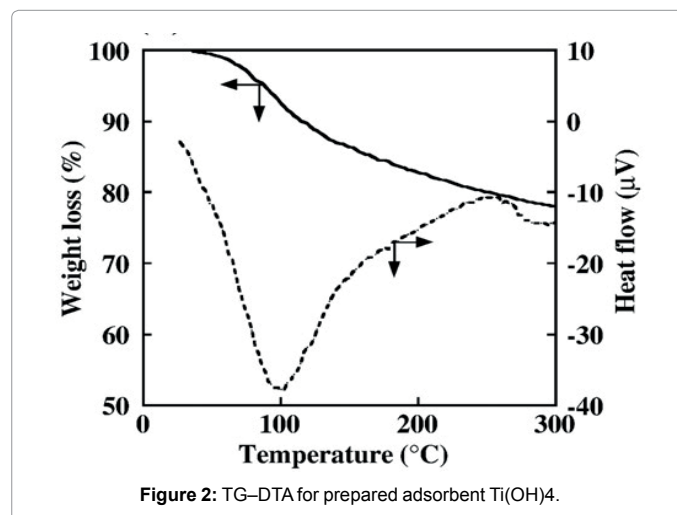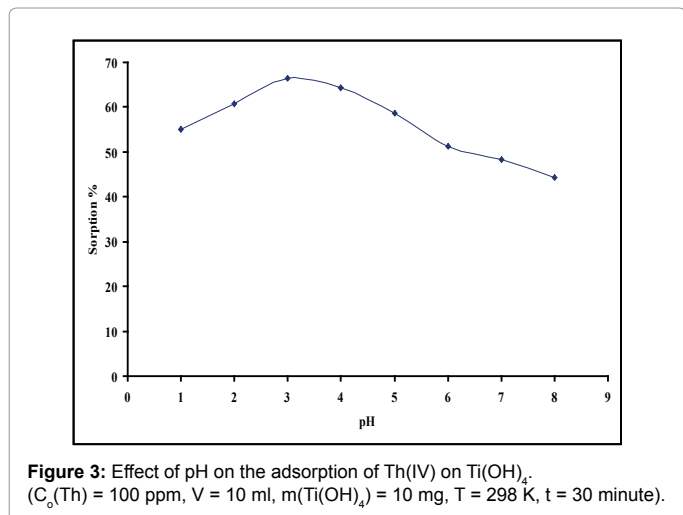Figure 1: FTIR spectra of Ti(OH)4 before (A) and after (B) thorium adsorption.

Figure 2: TG–DTA for prepared adsorbent Ti(OH)4.

Type	S_{BET} (m²/g)	V_t (cm³/g)
Ilmenite	0.5	0.091
Ti(OH)$_4$ Before activation	121.13	0.349
Ti(OH)$_4$ after activation	172.8	0.517

S_{BET}: specific surface area and V_t: total pore volume
Table 1: Specific surface areas of raw material and the prepared adsorbent.

Figure 3: Effect of pH on the adsorption of Th(IV) on Ti(OH)$_4$.
(C$_o$(Th) = 100 ppm, V = 10 ml, m(Ti(OH)$_4$) = 10 mg, T = 298 K, t = 30 minute).

Figure 4: Effect of contact time on the adsorption of Th(IV) on Ti(OH)$_4$.
(C$_o$(Th) = 100 ppm, V = 10 mL, m(Ti(OH)$_4$) = 10 mg, T = 298 K, pH = 3).

Figure 5: The results fitted by the pseudo-first order kinetic model.

Figure 6: The pseudo-second order kinetic model.

the sorption decreased. However, the increasing of pH value beyond 3; hydrolysis precipitation starts due to the formation of complexes in aqueous solution. The hydrolysis of thorium ions results in decline of adsorption capacity of Th (VI) [24,25].

Effect of contact time: Under the conditions of 0.1 g adsorbent amount, pH 3, temperature, 25°C and 50mg/l thorium and the contact time varied from 15-120 min, the effect of contact time on to the sorption process was examined. The conducted results (Figure 4) pointed to that at 45 min. the maximum sorption was achieved.

The kinetics of Th (IV) adsorption were studied based on the Pseudo-first-order (Figure 5) and pseudo-second-order (Figure 6) models according to their equations below and the calculated parameters are shown in Table 2.
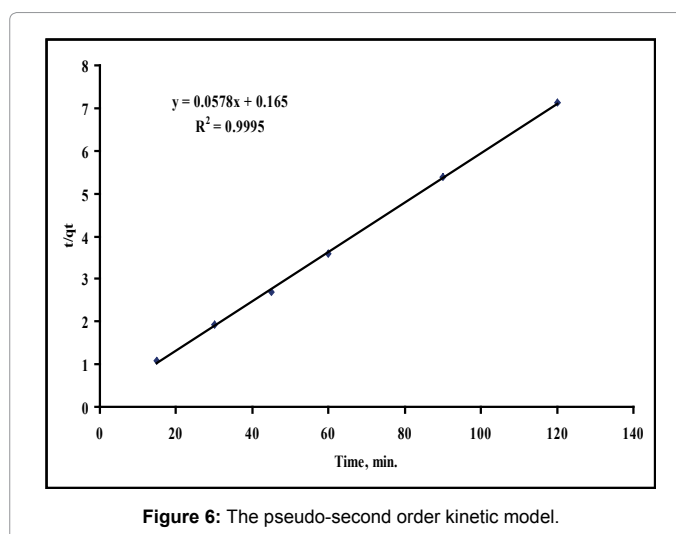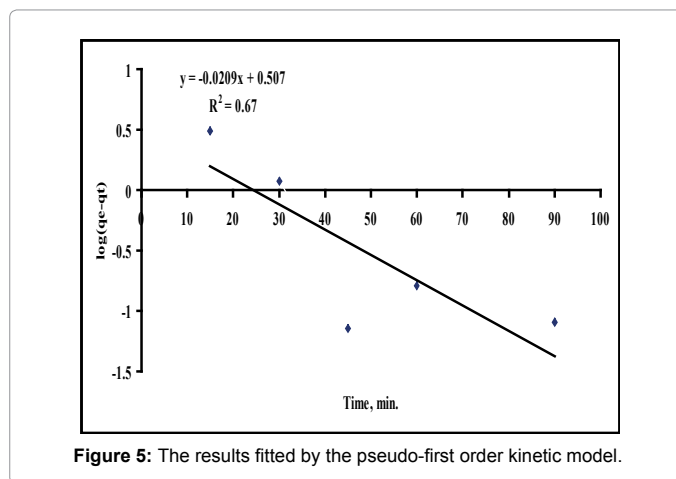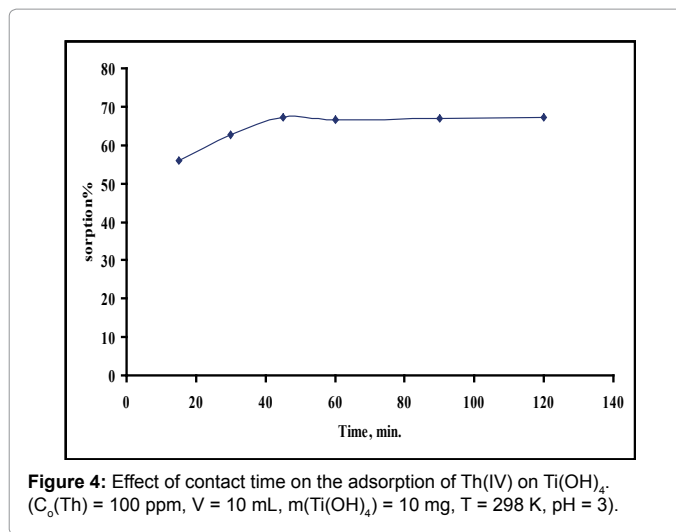
$$\ln(q_e - q_t) = \ln q_e - K_{1t} \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e t} \qquad (4)$$

where t is the contact time (min), q_t and q_e are the amount of Th (IV) ions adsorbed at time t and at equilibrium (μmol/g) respectively and k_1 and k_2 are the rate constants for pseudo-first-order kinetic (min⁻¹) and pseudo-second-order kinetic [26,27] (g/μmol min) respectively.

As shown in Table 2, referring to q_e, q_t and r^2 values, it is found that the studied adsorbing process follows the Pseudo-second order model suggesting the adsorption is a rate-limiting step involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate.

Effect of adsorbent dose: The efficiency of Ti (OH)$_4$ was evaluated at different adsorbent doses under the conditions of constant initial Th (IV) concentration (100 ppm), contact time (45min), pH 3, temperature (25°C), with varying adsorbent doses (0.025-0.2 gm). The results (Figure 7) showed continuous increasing of Th (IV) adsorption with increasing of the adsorbent dose till 0.1 gm while the higher adsorbent dose didn't effect on increasing of Th (IV) uptake. Increase in thorium removal with adsorbent dose till 0.1 gm could be attributed to the increase in the surface area and the availability of more adsorption sites. On the

Sorbent	Kinetic data						
	Pseudo first order			Pseudo second order			
	k_1	q_e	r^2	k_2	q_t	q_e	r^2
$Ti(OH)_4$	0.04813	3.214	0.67	0.02	16.8	**17.3**	0.9995

Table 2: Kinetic data of thorium adsorption.
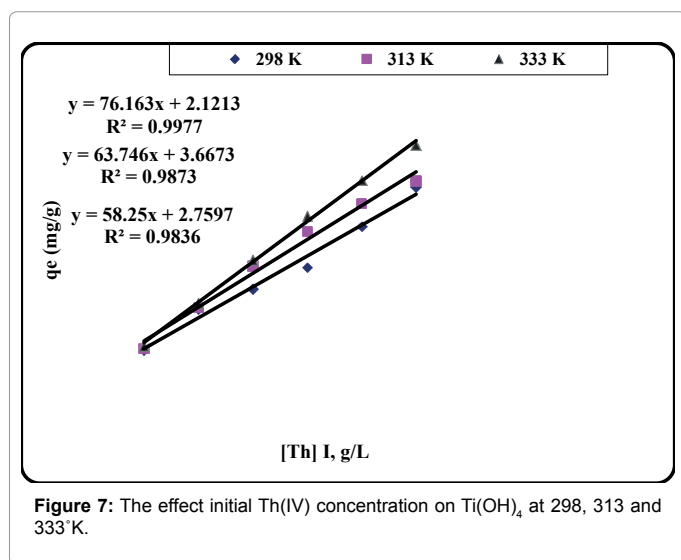
Figure 7: The effect initial Th(IV) concentration on $Ti(OH)_4$ at 298, 313 and 333°K.

Figure 8: Effect of adsorbent dose on Th(IV) removal.

Fitting Parameters						
Langmuir				Freundlich		
$T (°C)$	r^2	K_l	q_{max}	r^2	n	K_f
25	0.979	23.12	42.55	0.9527	2.5	1.708
40	0.997	39.9	43.86	0.9814	1.681	1.327
60	0.989	69.5	50.51	0.9858	1.613	1.451

Table 3: Fitting parameters of adsorption model isotherms.
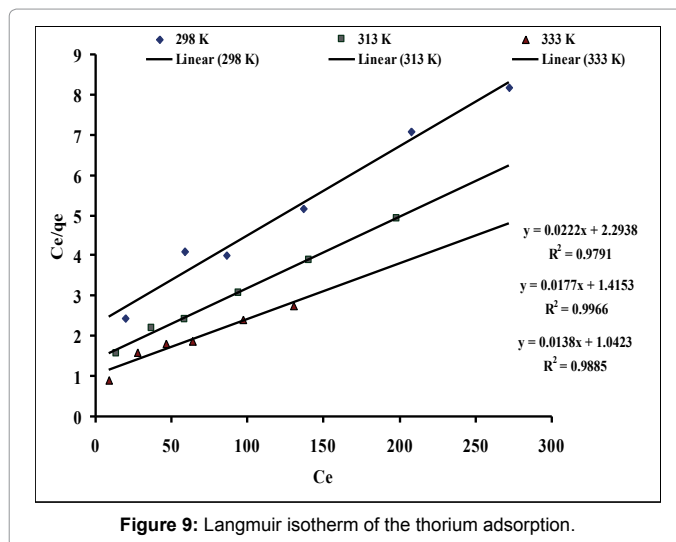
Figure 9: Langmuir isotherm of the thorium adsorption.

other hand, stability of Th (IV) removal with adsorbent dose greater than 0.1 gm is due to the increase of the dose with the same constant concentration of Th (IV) on the medium.

Effect of initial thorium concentration

Adsorption isotherm: The effect of the initial thorium concentration on the adsorption capacity of the Ti $(OH)_4$ were studied using a range of initial thorium concentrations, 0.1 to 0.6 g/l. The results are shown in Figure 8. It is clear that the adsorption capacity of thorium increased with increasing the initial thorium concentration in the aqueous solution, this is because more mass of thorium is put into the system with increasing the initial thorium concentration in the aqueous solution, but the same amount of adsorbent.

Studying the adsorption isotherm of Th (IV) onto the Ti $(OH)_4$ was carried out at three different temperature 25, 40, and 60°C (Figure 8), with other experimental condition include pH 3, contact time 45 min., adsorbent dose 0.1 gm and 20 ml of variable Th (IV) concentration, the achievable data were applied in to both Langmuir and Freundlich equations (Table 3).

The adsorption experimental data was subjected to analysis according to the Langmuir isotherm by plotting C_e/q_e vs. C_e (Figure 9), which gives a straight line with intercept and slope values equal to 1/bq_o and $1/q_o$, respectively. Also Freundlich isotherm was applied from the adsorption data by plotting log qe vs. log C_e giving a straight line with slope and intercept values equal to 1/n and log K_f, respectively, as
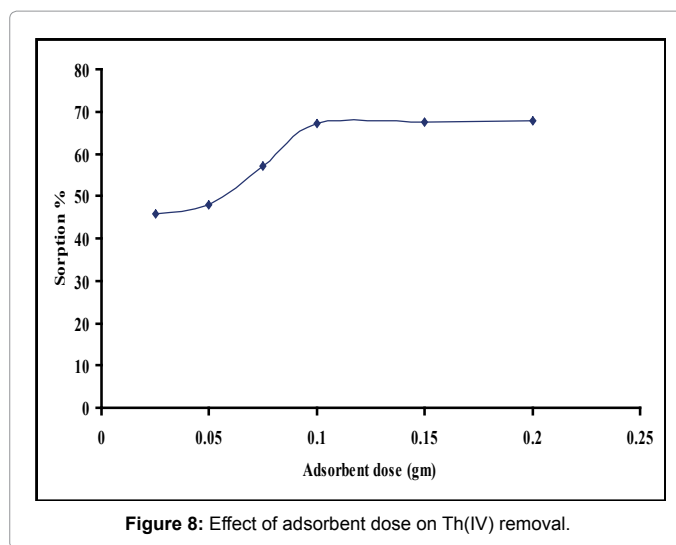
shown in Figure 10.

The calculated parameters particularly the q_{max} and r^2 indicated that the adsorption process is more fitted with Langmuir model which process the adsorption took place as mono layer on the homogenous sits of the $Ti(OH)_4$.

The parameters values presented in Table 3 show that Langmuir model best fitted to the experimental data. For the adsorption of Th (IV) were obtained through experimental data, the values of the correlation coefficient (r^2) showed that the Langmuir equation gave a better fit to the adsorption isotherm. Moreover, the calculated value of q_{max} is 42.55 mg g^{-1} from Langmuir equation was close to the experimental values
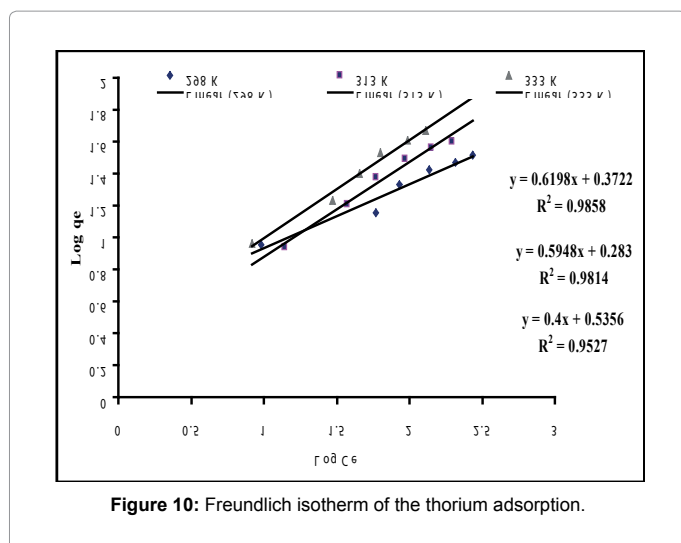
Figure 10: Freundlich isotherm of the thorium adsorption.

adsorbent	Temp. K	Thermodynamic parameters		
		ΔH° (kJ/mol)	ΔS° (KJ/mol.K)	ΔG° (kJ/mol)
Ti(OH)$_4$	298	25.38	0.111	- 7.84
	313			- 9.51
	333			-11.74

Table 4: Thermodynamic parameters for adsorption of Th(IV) on adsorbent at different temperatures.

Figure 11: Categories of adsorption isotherms (BDDT).

39.04 mg g^{-1} at room temperature. While at 40°C, the calculated value of q$_{max}$ is 43.86 mg g^{-1} was close to the experimental values 40.18 mg g^{-1}, finally at 60°C, the calculated value of q$_{max}$ is 50.51 mg g^{-1} also so close to experimental values 46.97 mg g^{-1}.

So from the obtained results and the correlation coefficient (R^2) show that the experimental data can fitted satisfying on Langmuir model.

The adsorption isotherms of Th (IV) ions on the Ti (OH)$_4$ as a function of Th (IV) concentration (pH = 3, 45 min adsorption time) are shown in Figures 9 and 10 and the Langmuir and Freundlich constants are presented in Table 3. From the obtained results, it is clear that the obtained data fit well with Langmuir model with maximum adsorption capacity of 50.5 mg g^{-1} for the Ti (OH)$_4$. Also, the higher correlation coefficients indicate that the Langmuir model fits the adsorption data better than the Freundlich model. In other words, this adsorption process took place by monolayer on the homogeneous sites of the surface of Ti (OH)$_4$.

The observed increase in the value of K$_L$ may be attributed to the increased adsorbent/metal interaction. The degree of suitability of the adsorbent towards metal ions was estimated from the values of separation factor constant (R$_L$) (equation 7) which gave indication for the possibility of the adsorption process to be proceed as follow: R$_L$ > 1.0 unsuitable; R$_L$ = 1 linear; 0 < R$_L$ < 1 suitable; R$_L$ = 0 irreversible. The values of R$_L$ lie between 0.000072 and 0.000432 which indicate the suitability of the adsorbent for Th (IV) from aqueous solution.

Also, the observed increase of K$_L$ values with temperature indicates that the adsorption reaction has endothermic nature. This can be confirmed by the calculation of the thermodynamic parameters.

$$\ln K_L = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (5)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (6)$$

$$R_L = \frac{1}{1 + K_L C_o} \qquad (7)$$

Other thermodynamic parameters (ΔH°, ΔS° and ΔG°) were calculated from the equations listed blew and their values were shown in Table 4. The observed increase in the negative values of ΔG° with

increasing temperature indicated that the adsorption process became more favorable at higher temperature. At all studied temperature the values of $|\Delta H^\circ| < |T\Delta S^\circ|$. This indicated that the adsorption process was dominated by entropic rather than enthalpic changes. The positive values of ΔH° indicated that the reaction was an endothermic adsorption process. The positive value of ΔS° could be explained by the increased degree of randomness.

Surface analysis of the activated titanium hydroxide showed that the sample have the parameters expected so as to be classed as mesoporous. The adsorption desorption isotherm shows the material follows a Type IV isotherm (Figure 11) and suggests the material has mesopores with a narrow pore distribution.

The Brunauer-Deming-Deming-Teller (BDDT) classification methodology categorizes the gas adsorption isotherm into five fundamental types, as illustrated in Figure 12. The first type of the adsorption isotherm is called single-molecule adsorption, and it is characterized by continuous increases in the adsorption volume till the relative pressure surpasses a certain value. This also occurs when the multi-layer adsorption fills up the micropore. Single molecule adsorption is suitable for depicting a situation in which the adsorption temperature is higher than the critical temperature of the adsorbate. The second type exhibits a slow increase in the convex curve in the first half (AB) and a sharp increase in the second half of the isotherm (BC) because of multilayered adsorption, capillary filling, and capillary condensation. Under these circumstances, no adsorption saturation point exists on the curve. This fits situations in which the adsorption temperature is lower than the critical temperature of the adsorbate. This category has what is called an anti-S-shaped adsorption isotherm. The third type of adsorption isotherm exhibits a gradual increase of the adsorption volume with the relative pressure. The surface area of the adsorption agent has the same pore allocation as the second type, and the difference only lies in the interaction between the adsorbent and the adsorbate. In the fourth type of adsorption isotherm, both the adsorption volume and the adsorption rate increase with relative pressure.

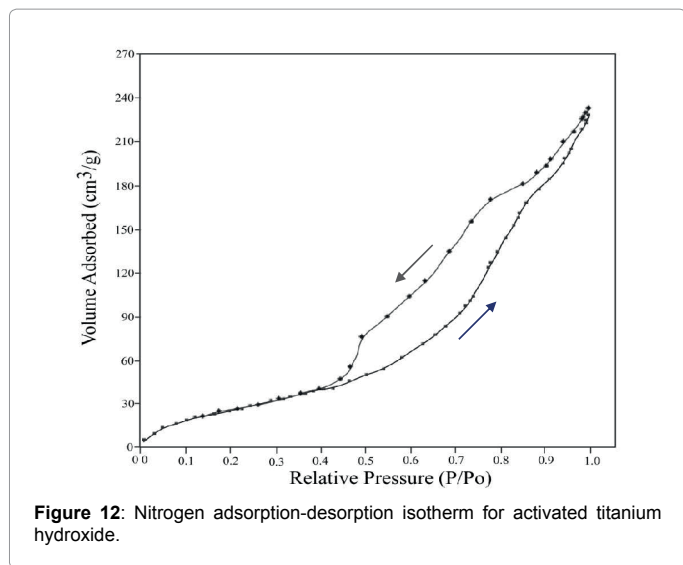**Effect of temperature:** The effect of temperature on the adsorption

Figure 12: Nitrogen adsorption-desorption isotherm for activated titanium hydroxide.
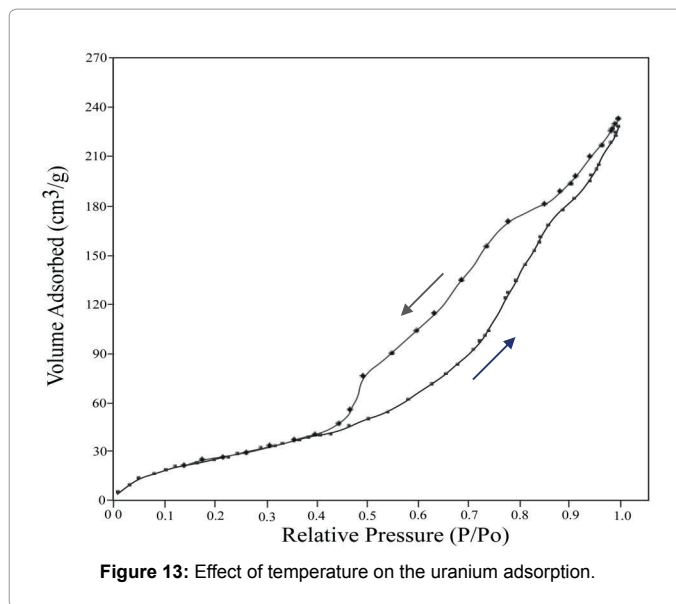

Figure 13: Effect of temperature on the uranium adsorption.

of thorium by Ti(OH)$_4$ was studied in the rang from 25 to 80˚C. The results shown in (Figure 13) revealed that adsorption capacity of thorium increased gradually with rising of the temperature from 30˚C and reached its maximum at 60˚C then remained constant after 60˚C.

Elution efficiency

The pregnant adsorbent was subjected to thorium elution by using different eluents such as HCl or HNO$_3$ with different concentrations from 0.1 to 6 M. The experimental studies show that 0.1M HCl gave the best elution efficiency (Figure 14).

Application on the NMA laboratories waste water

To investigate the applicability of the prepared activated Ti (OH)$_4$ to remove Th (IV) contaminant from waste water obtained from NMA laboratories, the following experiments were occurred. This waste water was treated with activated Ti (OH)$_4$ by applying the optimum controlling factors affecting the adsorption of thorium. From the obtained data (Tables 5 and 6), it is clear that the prepared activated Ti (OH)$_4$ was efficient in thorium removal from waste effluents with efficiency exceed 99.99%. By studying the standard error of the obtained results it is clear that The accuracy (Δ) of thorium removal from waste water samples is in the ranges from ±0.0228 to ±0.143, (Table 7) which declare high accuracy and precision for the obtained results.

Conclusion

Activated Ti (OH)$_4$ was successfully prepared from ilmenite concentrate. Batch experiments showed that Th (IV) could be effectively removed by Activated Ti (OH)$_4$. The adsorption kinetics data followed the pseudo second-order kinetic model and the adsorption isotherms fitted well with the Langmuir model with maximum adsorption capacities of 42.55, 43.86, and 50.51 mg.g^{-1} at 25, 40, and 60˚C respectively. The adsorption thermodynamic parameters (ΔG˚, ΔH˚, and ΔS˚) revealed that the adsorption reaction of Th (IV) onto Activated Ti (OH)$_4$ was an endothermic and spontaneous process. Moreover, the elution of Th (IV) from pregnant Ti (OH)$_4$ was successfully done using 0.1M HCl. These results showed that activated Ti(OH)$_4$ is an efficient adsorbent to remove Th (IV) from aqueous solutions.
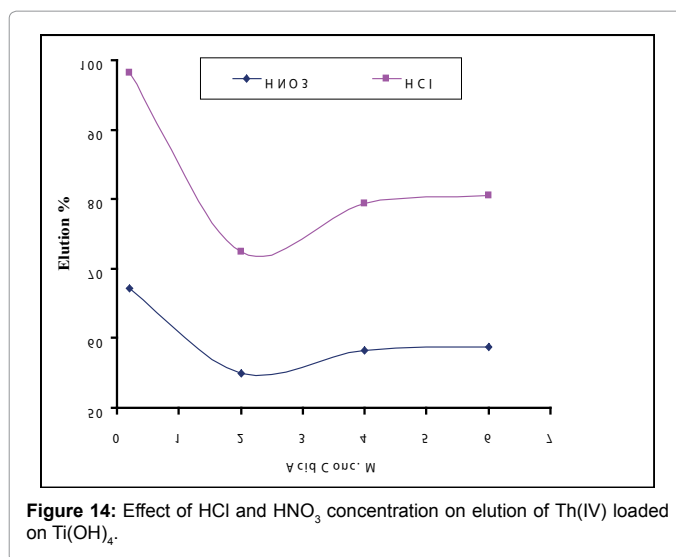

Figure 14: Effect of HCl and HNO$_3$ concentration on elution of Th(IV) loaded on Ti(OH)$_4$.

Parameter	Sample A (ppm)	Sample B (ppm)
pH	2.9	3.2
Ca^{+2}	2281	2369
Mg^{+2}	836	809
Na$^+$	52630	52489
K$^+$	612	634
Cl$^-$	82430	82271
CO$_3^{-2}$	112	99
HCO$_3^-$	1398	1456
SO$_4^-$	6292	6271
Th	63	77
Pb	7.2	9.5
Cr	11.8	13.7

Table 5: Chemical analysis of the samples.

Sample	Thorium content before adsorption (ppm)	Thorium after adsorption (ppm)
A	63	Under detection limit
B	77	Under detection limit

Table 6: Effect of activated $Ti(OH)_4$ on thorium content of the samples.

Samples No.	Thorium Content (ppm)	Arithmatic mean (X^-)	Standard deviation (S)	Standard error (S.E)	Error %	Δ
A	63.4 62.8 63.2	63.13	0.167	0.096	0.152	0.0228
B	77.3 77.1 77.9	77.4	0.418	0.241	0.312	0.143

Table 7: Statistical calculations of the samples.

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