



BIOSORPTION OF THORIUM FROM AQUEOUS SOLUTIONS BY *Moringa oleifera* BARK: EQUILIBRIUM AND KINETIC STUDIES

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AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration between all authors. Author SWAR carried out all the experimental work. Author AAJ calculated and inter-pretend the data gathered from the experimental work. While author BMM designed the study and managed the literature survey. All authors read and approved the final manuscript.

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ABSTRACT

In this study, a biosorbent was successfully applied to remove thorium metal Th(IV) from aqueous solutions. *Moringa oleifera* bark was fractionated into 60-mesh particles to perform characterization and extraction experiments. The adsorption kinetics for Th(IV) followed a pseudo second-order model, and small difference between the experimental and calculated Q_{eq} values [4.38 and 3.32 mg/g for $Q_{eq}(exp.)$ and $Q_{eq}(cal.)$, respectively] was observed. The maximum capacity (Q_{max}) value calculated using the modified Langmuir equation 5.46 mg/g.

Keywords: Biosorption; Freundlich isotherm; kinetic studies; Langmuir isotherm; *Moringa oleifera*; thorium.

1. INTRODUCTION

Thorium is a widely distributed element making up about 15 ppm of the earth's crust. It occurs in nature together with uranium and other rare earth elements [1]. The world consumption of thorium in 1970 has been estimated to be about 270 tonnes, 50% is used as thorium nitrate for gas-mantels, which was widely used for fixed gas-lighting systems. However, an increasing amount of 40% of the production is being used for metallurgical purposes [1]. Recently, it has been reported that the estimated world thorium resources is 6.355 million tonnes. India, Brazil, Australia and USA are the main resource countries [2]. Thorium is radioactive element and emits α -particles with

energy of 3.98 MeV and its half-life is 1.389×10^{10} years [3].

Contamination of water by heavy metals has been a major concern for researchers and government involved with the pollution control, mainly by toxic heavy metals, harmful contaminants due to their ability of retaining and accumulating in the human body. Some metals are essential elements and used in the biological metabolism, however other such as mercury, lead, cadmium and radioactive elements are considered toxic even at trace levels [4].

Biosorption of heavy metals from aqueous solutions is a relatively new process that is proven very promising in the removal of contaminants from aqueous

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effluents. Adsorbed materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from waste water streams [5]. Moreover, the process has other advantages such as no need for any pretreatment of material, high efficiency and the possibility of recovery of metal adsorbed [6]. Many studies have used seeds, leaves and bark of plant for removal heavy metals from aqueous solutions; they used such as jatropha tree, castor tree and neem tree [7-9]. *Moringa oleifera* is a drought tolerant cosmopolitan tropical tree and it has various pharmacological uses and analgesic effects [10]. The powdered bark of *Moringa oleifera* tree has many properties that have been used for various aspects of water treatment such as total dissolved solid and antibacterial [11] it has also biosorption behaviour for the removal of toxic metals from wastewater. *Moringa oleifera* was used for removal many heavy metals including lead, nickel and zinc [12-14]. Recent studies have shown that Th(IV) can be removed from aqueous solutions and wastewater using a new biosorbents such as reduced graphene oxide [15], a novel nanoporous ZnO [16], deoiled karanja seed cake [17] and banana peels nanosorbent [18].

No previous study has used *Moringa oleifera* to remove thorium from aqueous solutions. In the present study, *Moringa oleifera* bark will be used for removing Th(IV) from aqueous solution. Biosorption efficiency of *Moringa oleifera* bark to remove Th(IV) from wastewater will be investigated by measuring the efficiency of the removal % of thorium from artificial wastewater by varying content. Time contact, pH, adsorbent dosage and effect of pretreatment in a batch process series of experiment will be also studied.

2. MATERIALS AND METHODS

2.1 Preparation of the Biosorbent

Samples of *M. oleifera* bark were collected from Tripoli city (Wadi Al-Rabeea, Libya) in July 2016. These samples were air dried and ground to get fine powder. The powder was washed twice with deionized water and dried at 60°C for 24 h, then boiled in double distilled water by changing the water repeatedly until water becomes colorless. The washed and boiled bark was oven dried at 80°C for 24 h and stored in desiccator to prevent moisture adsorption before its use. This treated *M. oleifera* bark powder is called as MOB.

2.2 Chemicals and Instruments

All reagents used were of AR grade. Deionized double distilled water was used throughout the

experimental studies. Stock solution (1000 mg/L) was prepared by dissolving $\text{Th}(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$. Working thorium solutions were prepared just before used by appropriate dilutions of stock solution. Reagent grade HCl, NaOH and buffer solutions (E. Merck) were used to adjust the solution pH. A pH meter (JENWAY) was used for pH measurements. The pH meter was calibrated using buffer standard solutions of pH 4.0, 7.0 and 10. Thorium content was analyzed spectrophotometry (6505 UV/Vis Spectrophotometer, JENWAY).

2.3 Experimental Procedure

Adsorption operations were carried out by batch method using continuous shaking at room temperature and different optimized parameters [pH (from 1 to 8), contact time (from 5 to 120 min), initial concentrations (from 10 to 100 mg/L of Th(IV)) and effect of foreign ions] were studied. The effects of contact time, initial pH and initial thorium concentration were investigated by varying any one of the process parameters and keeping the other parameters constant.

For kinetic studies of thorium adsorption, amount of MOB (0.2 g) was suspended in 20 ml of an aqueous solution containing 50 mg/L of Th(IV) (from $\text{Th}(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$). The pH of each solution was adjusted to the chosen pH (pH = 4.0). The mixture was shaken, and then the remaining thorium in solution was checked by taking aliquots at the considered time (5 to 120 minutes). Thorium content was analyzed spectrophotometry (6505 UV/Vis Spectrophotometer, JENWAY) at 665 nm, following a procedure adapted by Savvin using arsenaza III [19]. Adsorption isotherm experiments were carried out at different pH values (1–8). Different concentrations of Th(IV) were prepared (10 –100 mg/L), a volume of 20 ml of thorium solution was then mixed with 0.3 g of biomass and shaking for 120 min until reach to the equilibrium. Th(IV) content in supernatant solution was filtered through a filter paper (Whatman 42) and then analyzed spectrophotometry.

The amount of Th(IV) adsorbed (Q_{eq}) in mg/g at equilibrium was computed by using the following Equation (1):

$$Q_{eq} = \frac{(C_o - C_e)V}{1000m} \quad (1)$$

where C_o and C_e are the Th(IV) concentrations in mg/L initially and at equilibrium, respectively, V is the volume of Th(IV) solutions in ml, and m is the weight of sorbent in grams.

3. RESULTS AND DISCUSSION

3.1 Characteristics of the Biosorbent (MOB)

Elemental analysis of MOB has been reported [13], compositions of MOB were $44.8 \pm 1.50\%$ carbon, $5.9 \pm 0.18\%$ hydrogen, $0.8 \pm 0.01\%$ nitrogen, $0.9 \pm 0.01\%$ sulphur and $47.6 \pm 1.82\%$ oxygen. Sulphur groups may be given MOB qualifies it as a potential biosorbent. Description of biosorbent surface and structure lead to understanding the metal binding mechanism onto biomass.

3.2 X-ray Diffraction

XRD pattern of the MOB shown in (Fig. 1a) illustrates the presence of a significant amount of amorphous material due to lignin and tannin in the sample. However, (Fig. 1b) showed that another beak appeared at around 45 which may indicate to Th-O binding.

3.3 FT-IR Spectroscopy

From the FTIR spectra of MOB (Fig. 2), many functional groups have been appeared, indicating the complex nature of MOB biosorbent. A strong band at 3342 cm^{-1} indicated the presence of hydroxyl groups. A peak at 2912 cm^{-1} is due to the C-H stretching frequency and the peak at 1630 cm^{-1} is due to C=O stretching mode of the primary and secondary amides

(NH_2CO). The peaks at 1507 cm^{-1} and 1371 cm^{-1} are indicative of the N-H stretching of the primary and secondary amides, and the presence of amide (III) or sulfamide band, respectively. Bands at 1328 cm^{-1} and 1242 cm^{-1} indicate presence of carboxylic acids [20]. Weak bands at 1442 cm^{-1} and 1507 cm^{-1} are attributed to aromatic C=C and two sharp peaks at 1743 cm^{-1} and 1630 cm^{-1} characteristic of carbonyl group stretching were also observed. The strong C-O band at 1043 cm^{-1} confirms the lignin structure of the MOB [21]. These results indicated that the biosorption of Th(IV) might be occurred at hydroxyl, carboxyl, and carbonyl functional groups present on the surface of MOB.

3.4 Effect of pH in Th(IV) Biosorption

Effect of pH in Th(IV) adsorption was examined. A series of experiments were carried out using 50 mg/L of Th(IV) and 0.3 g dose of biomass in aqueous solutions, with varying pH from 1 to 8 (Fig. 3) shows the equilibrium biosorption removal of Th(IV) on biosorbent increased with further increase in pH (by $\text{pH} = 4$), and then decreased slightly with a further increase of pH. The main factors influencing the pH on biosorption process were Th(IV) species and surface functional groups on the adsorbents. The adsorption decreased when pH was ($\text{pH} < 2$) due to increase the acidity by increasing the H^+ ions in the solution. The adsorption also decreased when pH was higher than 4, which might be attributed to the coordination of OH^- anions with the metal ion.

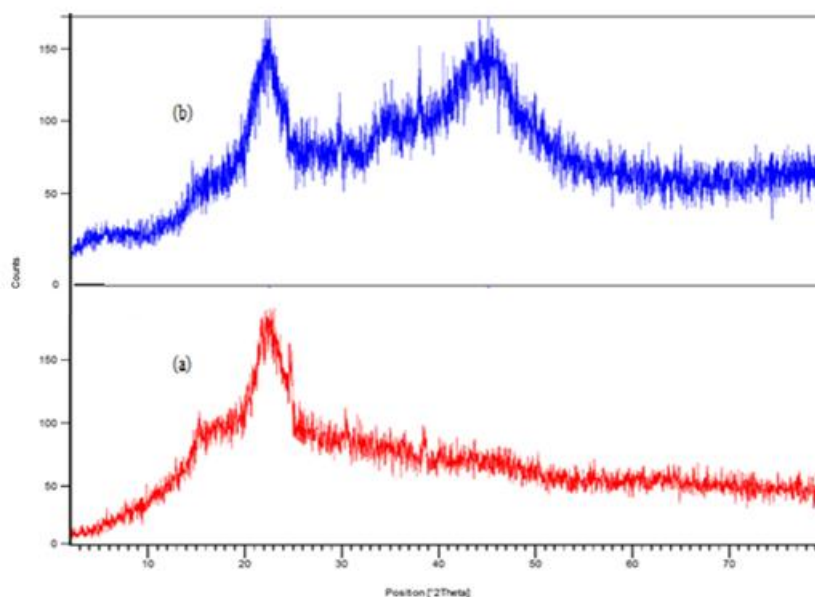


Fig. 1. (a) XRD of MOB (Native material). (b) XRD of MOB loaded with Th(IV)

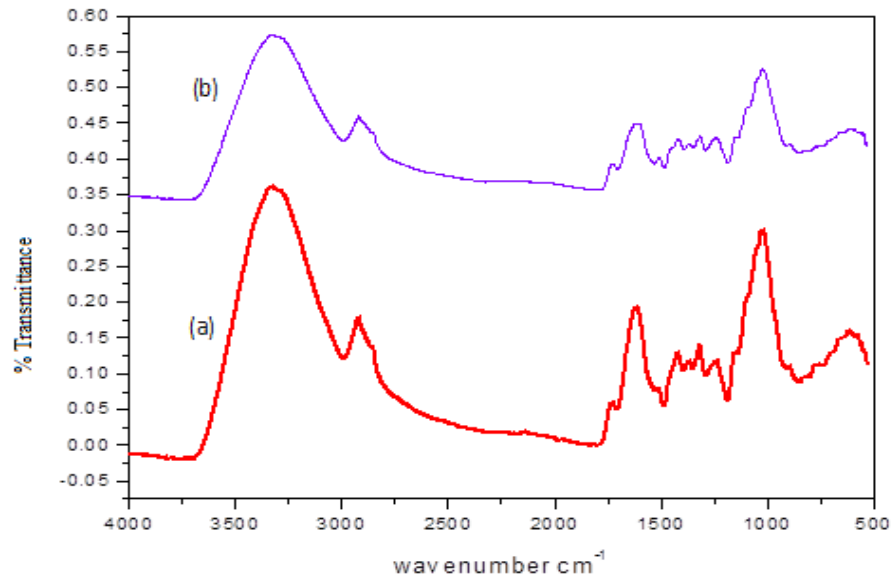


Fig. 2. FT-IR spectra of: (a) MOB; (b) Th(IV)-loaded MOB

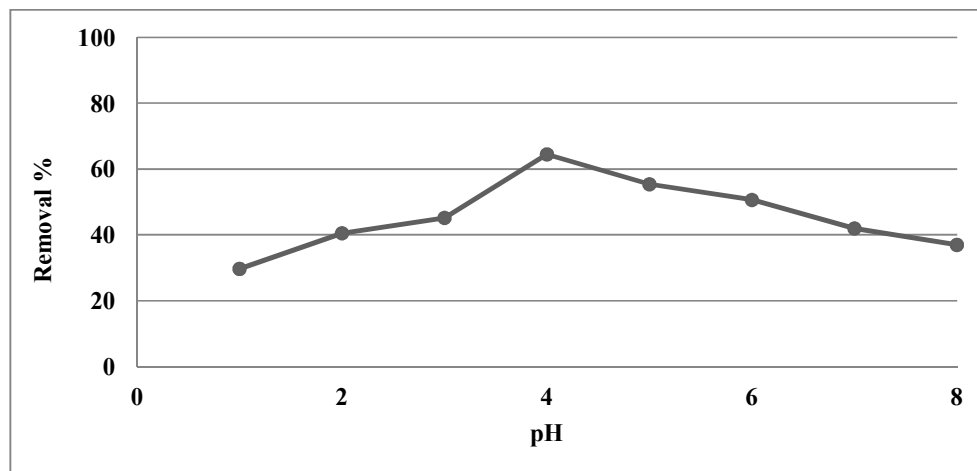


Fig. 3. Effect of pH on the biosorption of Th (IV) onto MOB

3.5 Effect of Biosorbent Dose

The influence of biosorbent dose on the percentage removal of Th(IV) was also examined by carrying out concurrent experiments with biomass concentrations from 0.05 to 0.6 g, although the total volume (20 ml), initial concentration of the metal solution (50 ppm), contact time (60 min.) and the pH value was kept constant (pH = 4). The amount of Th(IV) adsorbed had increased with an increase in the biosorbent dosage from 0.05 to 0.6 g. This result could be explained by the fact that for optimum biosorption, extra sites must be available for biosorption reaction,

whereas by increasing the MOB amount, a number of sites available for biosorption site had increased. The maximum biosorption percentage reached 61.3% for Th(IV) while MOB amount reached 0.3 g or over. Herein, the biosorption system reached to the equilibrium between the amount of MOB and the concentration of Th(IV) in the solution, as shown in Fig. 4. Therefore, the optimum biomass amount was taken as 0.3 g for conducting further batch experiments. A similar trend was reported for biosorption of Pb(II) using chemically modified *Moringa oleifera* tree leaves [12].

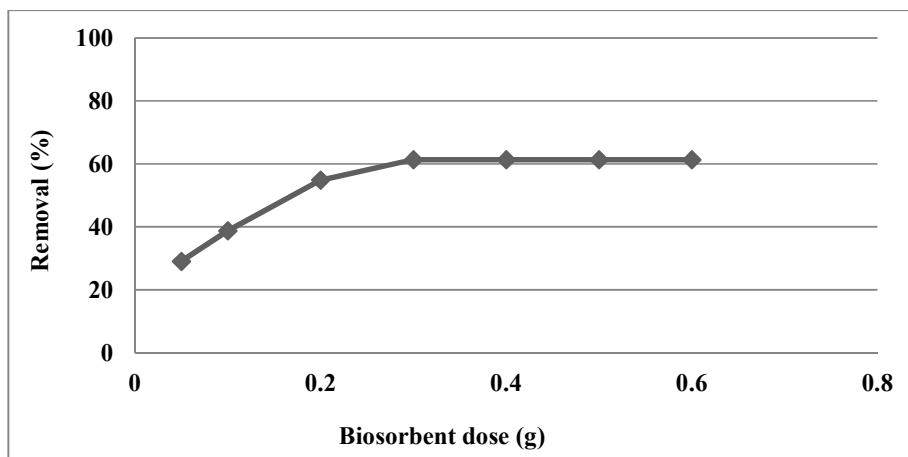


Fig. 4. Effect of biosorbent dose on the biosorption of Th (IV) onto MOB

3.6 Effect of Contact Time

The effect of period of contact time between the adsorbent and adsorbate on the removal of Th(IV) ion was determined by keeping pH (pH = 4), dose of biomass (0.3 g), total volume (20 ml) and the initial concentration of Th(IV) constant (50 ppm), the rate of Th(IV) removal by MOB with contact time was calculated. The rate of uptake of Th(IV) ion was quite rapid within 10 min by MOB, slowing down between 10 - 20 min, this could be due to two different sorption processes, a fast ion exchange process followed by chemisorption. Results shown (Fig. 5), the biosorption capacity of Th(IV) was illustrated to increase from 1.93 to 3.06 mg/g.

The Adsorption Removal efficiency (AR), at time t, is calculated from the Equation (2):

$$AR\% = \frac{(C_0 - C_e)}{C_0} 100 \quad (2)$$

where; C_0 = the initial concentration (mg/L) and C_e = the equilibrium concentration (mg/L).

3.7 Biosorption Isotherm

Biosorption isotherm for the Th(IV) removal was studied using an initial concentrations of Th(IV) between 10 and 100 mg/L at room temperature keeping the other conditions constant, the pH (pH = 4), dose of MOB (0.3 g), the total volume (20 ml) and the contact time (60 min.). The biosorption equilibrium data have been conveniently represented by biosorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent Q_{eq} and the solute concentration for the solution at equilibrium C_e .

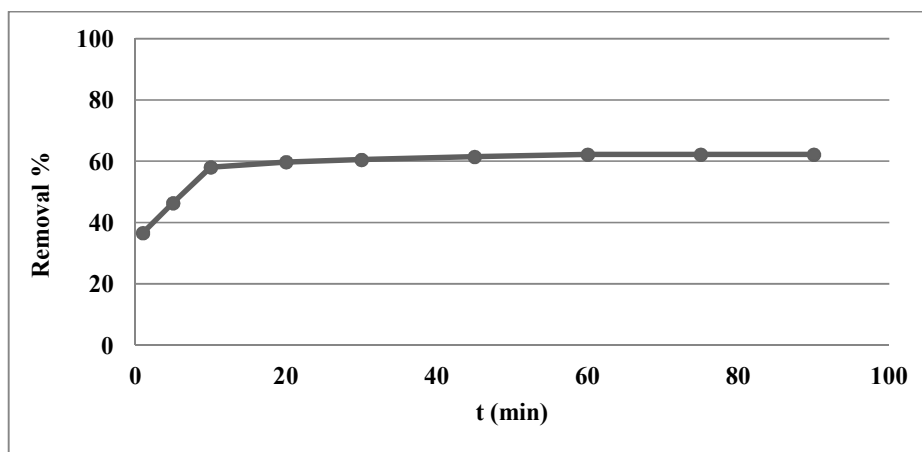


Fig. 5. Effect of contact time on the biosorption of Th (IV) onto MOB

There are many theoretical models to describe the adsorption process of heavy metal ions including Langmuir and Freundlich. It is expected that the adsorption of Th(IV) on MOB should correlate with Langmuir isotherm since it is possible for more than one layer of the metals ions to accumulate on the adsorbent's surface. From the findings this assertion is not supported.

Langmuir isotherm is valid for monolayer sorption onto surfaces and assumes that all of the sorption sites have equal adsorbate affinity [22], which is given by Equation (3):

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where; C_e (mg/L) is the equilibrium solute concentration in mg/L, Q_{eq} (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent in mg/g and K_L is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption.

The maximum adsorption % of Th(IV) ions was 61.3%, which is low when compared with adsorption efficiency of other biosorbent, for example, the adsorption efficiency of *Moringa oleifera* bark for removal Ni(II) is about 98% [13] and biosorption of Pb(II) ions from aqueous solution using *Moringa oleifera* pods is about 84% [23]. Results in the present study showed that the biosorption of thorium ions was dependent on experimental parameters, such as contact time, initial concentration, and pH of Th(IV) solution.

Freundlich isotherm [24] is an empirical relationship established upon sorption onto a heterogeneous assumption that different sites with several adsorption energies are involved, which is given by Equation (4):

$$Q_e = K_F C_e^{1/n} \quad (4)$$

where; K_F (mg/g) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption, respectively.

Freundlich isotherm model is used for homogenous systems in which the heat of sorption decreases in magnitude with an increasing extent of sorption [24]. Freundlich isotherm model describes the ratio of the amount of solute that is adsorbed onto a given mass of

adsorbent to the concentration of solute in the solution.

Langmuir equation represents adsorption process very well, the correlation coefficient, R^2 was, however, higher the Langmuir isotherm than the Freundlich isotherm and was closer to unity indicating a very good mathematical fit. Consequently, among the two isotherm models used, the Langmuir model offers the best correlation factors. By comparing the correlation coefficients (Table 1) parameters determined by these two isotherms, Langmuir isotherm model is better fit than Freundlich isotherm.

3.8 Biosorption Kinetic

The kinetics of the MOB and Th(IV) metal ion interaction was tested with two kinetic models including pseudo-first order and pseudo-second-order models. The pseudo first-order kinetic model equation is written as [25]:

$$\frac{dQ_e}{dt} = K_1 (Q_e - Q_t) \quad (5)$$

where; Q_t and Q_e are the amount adsorbed at time t and at equilibrium and k_1 is the rate constant of the pseudo first-order sorption process. On integration under the boundary conditions of $t = 0$ and $t = t$ and $Q_t = 0$ to $Q_t = Q_t$, gives a linear expression:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (6)$$

where; Q_t (mg/g) is the amount of the metal ion biosorbed at time t . The value of k_1 can be obtained from the slope of the plot of $\log(Q_e - Q_t)$ versus t .

The pseudo second -order kinetic equation [26] is expressed in Equation (7):

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (7)$$

In Equation (7) Q_e^2 is the maximum adsorption capacity (mg/g) and k_2 (g/mg min) is the adsorption rate constant of pseudo second-order. From the plot of t/Q_t against t , Q_e and k_2 can be evaluated. The initial sorption rate h_0 (mg/g min) is defined as [27]:

$$h_0 = K_2 Q_e^2 \quad (8)$$

Table 1. Adsorption isotherm constants for adsorption of Th(IV) onto MOB adsorbent

Langmuir isotherm			Freundlich isotherm		
Q_{max} (mg/g)	K_L	R^2	K_F (mg/g)	n	R^2
5.46	0.01284	0.993	0.0253	0.691	0.983

Plotting t/Q_t versus “t” at different adsorbate concentrations provided the second-order sorption rate constant (k_2) and Q_e values from slopes and intercepts.

The pseudo first-order data do not fall on straight line indicating that this model is not appropriate (Fig. 6). The experimental and calculated q_e values, pseudo first-order rate constant and coefficient of determination (R^2) values are given in Table 2. The theoretic values ($Q_{e,cal}$) are far lower than the corresponding experimental data, $Q_{e,exp}$ implying that the biosorption process does not follow fully the pseudo first-order biosorption rate expansion.

The dependence of t/Q_t versus t gives an excellent straight line relation for Th(IV) biosorption onto MOB (Fig. 7), and the R^2 value is close to 1 (Table 2), confirming the applicability of the pseudo second-order equation. In addition, there is only little

difference between the $Q_{eq, exp.}$ and $Q_{eq, cal.}$ (Table 2), reinforcing the applicability of this model.

As a result compared to the pseudo first-order and second-order kinetics models, a good correlation coefficient was obtained for pseudo second-order kinetic model, which indicate the Th(IV) biosorption onto MOB follows pseudo second-order rate expression.

The lower correlation factors obtained for pseudo first-order model (0.896) as compared with that obtained for the pseudo second-order model (0.999) for the biosorption of Th(IV) ions, implies that the pseudo first-order model is less conducive for explaining the kinetics of the biosorption of the metal. Therefore, the option exercised in favour of the pseudo second-order model better represented the sorption kinetics and thus supported the assumption behind the model.

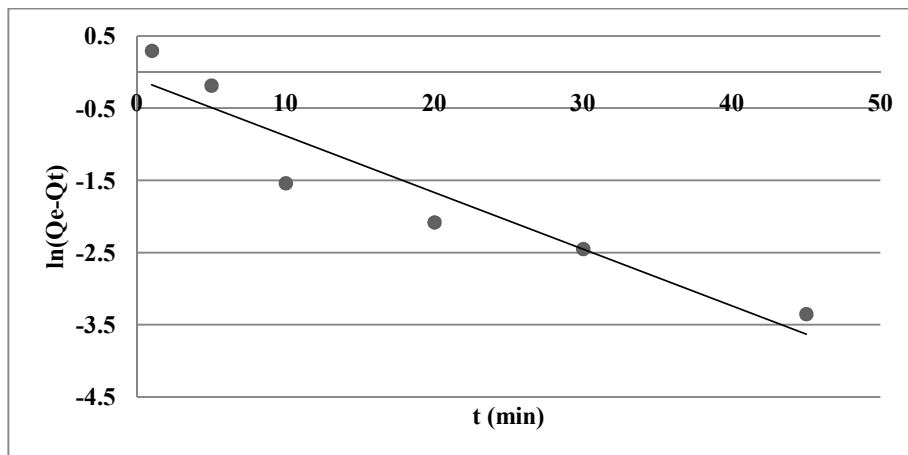


Fig. 6. Pseudo first-order plot for biosorption of Th(IV) onto MOB

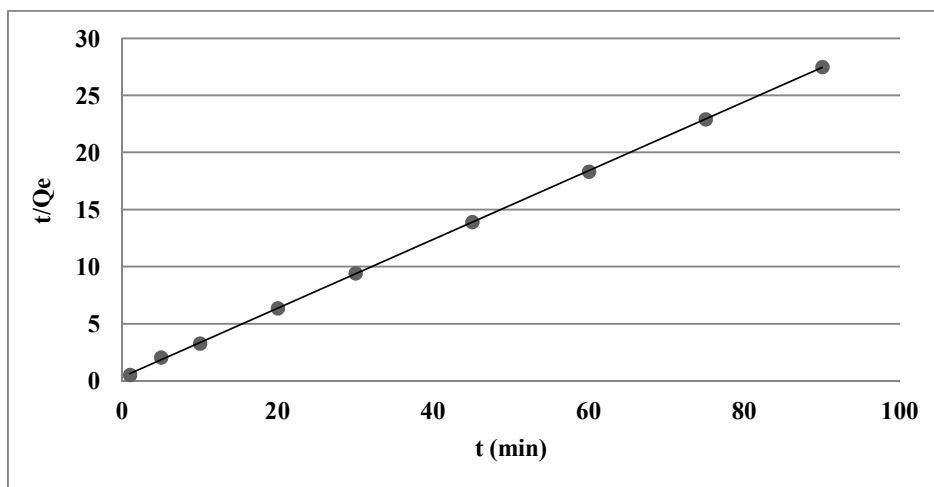


Fig. 7. Pseudo second-order plot for biosorption of Th(IV) onto MOB

Table 2. Kinetic parameters obtained by studying Th(IV) adsorption onto the MOB

Pseudo first-order		$Q_{eq} (exp.) (mg/g)$	Pseudo second-order	
$K_1 (min^{-1})$	7.85×10^{-2}	4.38	$K_2 (min^{-1})$	26.5×10^{-2}
$Q_{eq}(cal.) (mg/g)$	0.905		$Q_{eq}(cal.) (mg/g)$	3.32
R^2	0.896		R^2	0.999

3.9 Desorption Study

Desorption of thorium from Th(IV)-loaded biomass was treated by HCl as desorption agent. HCl acid is usually as a strong desorption agent to remove metals from metal-loaded biosorbent. The reason for this aspect is due to increasing the acidity and increasing the H^+ ions in the solution, which release the loaded Th(IV) from MOB. Similar results were previously reported [28]. The adsorbed Th(IV) ion onto MOB, was desorbed with different hydrochloric acid concentrations (0.25, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 M). A selected weight (0.10 g) of MOB containing Th(IV) was stirred with 10 ml aliquots of HCl concentration for 60min and then filtered and washed by double distilled water three times. Concentrations of Th(IV) in solutions were analysed.

From the results of this study, more than 70% (0.10 g of MOB containing $0.5 \mu g$ of Th(IV) with 10 ml of HCl) desorption of Th(IV) happened at 0.25 M of HCl, however, the complete desorption (> 94%) was performed with 3.0 M of HCl (Fig. 8). In Fig. 8 shows that with the increasing of hydrochloric acid concentration, rate of desorption increased, the maximum percentage recovery of Th(IV) was 94.4% with 3.0 M HCl solution, and then with 4.0 M HCl the rate of desorption becomes stable. The results of desorption are an indication that most of Th(IV) held

on MOB surface might be through strong chemisorption or ion-exchange type of binding. Therefore, recovery of the adsorbed Th(IV) and recurrent usability of the biosorbent is feasible with the application of MOB as a biosorbent in the practical applications of treatment of industrial effluent.

3.10 Effect of the Foreign Ions on Th(IV) Adsorption

As an application well water from Wadi Al-Rabeea area, Tripoli (pH 7.5, $Na^+ = 45.5$, $K^+ = 2.8$, $Mg^{+2} = 27.7$, $Ca^{+2} = 56$, $Cl^- = 73.5$ and $SO_4^{-2} = 100$ mg/L) spiked with Th(IV) (50 mg/L) was used. The results here show that more than 89% of Th(IV) was adsorbed on the biomass and there was no limited effect on adsorption of Th(IV) from foreign ions in water. Acetate ions were used as a buffer solution and no effect on biosorption was noticed. On the other hand, the Th(IV) adsorption experiments were carried out in the presence of some heavy metals (Cd, Pb and U) with higher concentration than Th(IV) (50 mg/L of Th(IV) and 250 mg/L of heavy metal ions) for the study of foreign ions effect. Cd(II) and Pb(II) ions appeared slightly decrease, the Th(IV) sorption (about 15%), whereas U(IV) ions appeared high decrease, the Th(IV) sorption (30% decrease).

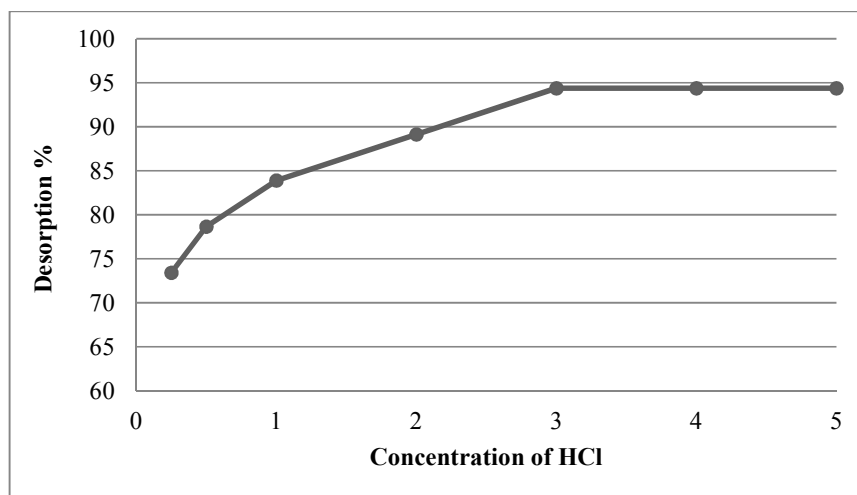


Fig. 8. Desorption Th(IV) (0.10 g of MOB containing $0.5 \mu g$ of Th(IV) with 10 ml of HCl)

4. CONCLUSION

The results of the study revealed that MOB wastes could be converted into an innovative low -cost biosorbent with good biosorption capacity. The optimised parameters in this study were the pH = 4, the dose of biomass (0.3 g), the initial concentration (50 ppm) and the total volume (20 ml). The biosorption of Th(IV) by MOB from aqueous solution was found to be greatly dependent on solution pH. The studies of adsorption isotherms suggests that Langmuir isotherm better explained the experimental data of Th(IV) biosorption by MOB than Freundlich isotherm with correlation coefficients greater than 0.99. The values of the maximum adsorption capacity Q_{max} calculated from Langmuir model were also closer to the experimental value of Q_e than that of other models. A pseudo second- order model was more suitable than a pseudo first-order model with correlation coefficients greater than 0.99. For foreign ions effects were studied in the current study, the slightly effect has been showed by Cd and Pb, however more effected showed by U(IV).

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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