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# Adsorption of Thorium(IV) and Uranium(VI) onto Azraq Humic Acid, Jordan

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**Abstract:** Humic Acid (HA) is an important constituent of soil organic matter that was the subject of several environmental studies. In this work, the adsorption isotherms of Thorium (IV) and Uranium(VI) onto Azraq Humic acid (AZHA) were studied at different temperature and pH values. The results indicate that Thorium(IV) has higher adsorptivity than Uranium(VI). The increasing of pH resulted in higher adsorptivity of Thorium(IV) and Uranium(VI). In contrast to transition metals and lanthanides, such as Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Gd(III), Ce(III) and Yb(III), the adsorption was entropy driven, while the adsorption of actinides on HA was found to be exothermic and so enthalpy driven. This leads to the hypothesis that Thorium(IV) and Uranium(IV) are encapsulated in the interior of HA helix with their water of hydration because the interior is full with water. However, transition metals and lanthanides are adsorbed on the exterior of HA helix.

**Keywords:** Humic acid; Adsorption; Thorium(IV) and Uranium(VI) metal ions; Adsorption isotherms; Enthalpy; Entropy.

## Introduction

Azraq Oasis is located in the eastern desert of Jordan 100 km east of Amman and has a total area of about 26 km$^2$, where there is a plenty of plants, water, animal and bird life and warm weather. These are the best conditions for the formation and the development of humic acid (HA) [1, 2]. For this reason, Azraq Oasis is considered as a national park and a natural laboratory. It is a laboratory for studying soils, aquifers, erosion, bird migration and planting. It is also a laboratory for studying birds and the distinctive human culture of the Bedouins. Also, there is a potential pollution from the increasing traffic on the highways passing through Azraq to Iraq and Saudi Arabia. This is why Azraq is an important place to be studied [3].

Humic substances (HA's), the major organic constituents of soil and sediments, are widely distributed over the earth's surface, occurring in almost all terrestrial and aquatic environments. It arises from the chemical and biological degradation of plant and animal residues and from synthetic activities of microorganisms. The products so formed tend to associate into complex chemical structures that are more stable than the starting materials. Important characteristics of humic substances are: their ability to interact with metal ions, hydrous oxides, clay minerals and organic compounds such as alkanes, fatty acids, dialkylphthalates, pesticides, … etc.

HA's are amorphous, dark-colored, acidic, predominantly aromatic, hydrophilic, chemically complex and polyelectrolyte-like materials that range in molecular masses from a few hundreds to several thousands of Dalton's [4]. HA exists in soil and aquatic systems in either dissolved or particulate (solid) state.

The complexation of dissolved HA from Azraq with metal ions ($pH > 4$) has been studied extensively [5]. However, previous studies on adsorption of metal ions on solid HA ($pH < 4$)

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are restricted to few measurements of % metal uptake by HA. Recently, the adsorption isotherms of transition and Lanthanide metals ions: Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Gd(III), Ce(III) and Yb(III) on solid AZHA (at pH < 4) were studied in order to achieve better understanding of interaction of metal ions with HA. In addition, the effect of environmental factors such as pH, temperature and ionic strength on adsorption capacity of HA have been studied [6, 7]. One of the important results drawn from these works was about the nature of interaction between transition metals, Lanthanides and HA surface. The results indicate that there is a significant covalent (specific adsorption) interaction in addition to electrostatic (nonspecific adsorption) interaction between transition metals and HA surface. Thorium and uranium metals have different chemistry and higher oxidation states (IV and VI), respectively than transition metals(II) and lanthanides(III). The present work's aims are:

1. Studying the adsorption isotherms of Uranium(VI) and Thorium(IV) metal ions on solid AZHA at pH =1.0, 2.0 and 3.0 at 25 $^{o}$ C, 35$^{o}$ C and 45$^{o}$ C to give a better understanding of the nature of adsorption of metal ions on HA.
2. Comparing the chemistry of transition metals and lanthanides interaction with HA with that of uranium and thorium.

## Experimental

### Materials and methods

All reagents used in this study were of analytical grade. $Th(NO3)_4.5H_2O$ is from Riedel DeHaën Chemical company Inc., $UO_2(NO_3)_2.6H_2O$ and $NaClO_4$ are from Merck, EDTA and PAR (4-(2-Pyridyl azo)resorcinol(I)) indicator are from Park, Sodium fluoride from RiedelDeHaën, Triethanolamine from Peking's Reagent, Sulphosalicylic acid and 35% Hydrochloric acid from Analatical Rasayan. Arsenazo(III) indicator from BDH Chemicals Ltd. Sartorius PP-25 pH meter model was used for pH measurements. The analytical balance used is from Shimadzu and its type is AW120, its readability: 0.1 mg. Shaking of samples was done using Memmert shaker equipped with a thermostat. UV-VIS spectrophotometer from Spectroscan model 80DV with software UV Win5 v5.0.5. Centrifuge model ALC PK130 was used.

### Preparation of stock solutions

Stock solutions 2500 ppm of the two metal ions were prepared by dissolving specific amounts of the nitrate salt of $UO_2$(II) and Th(IV) in 0.1 M $NaClO_4$and then adjusted to the desired pH. The stock solutions were used to prepare solutions with different concentrations. The dilution is achieved by using 0.1 M $NaClO_4$ and 0.1 M $HClO_4$ solutions with different pH 1.0, 2.0 and 3.0 (to keep the ionic strength and the pH constant for all the different concentrations prepared).

### Adsorption experiments

Batch adsorption was carried out using pyrex glass flasks. An accurate mass of batch adsorption was prepared using pyrex glass flasks. An accurate mass of 0.05 g of Azraq Humic acid (AZHA) measured to the nearest 0.1 mg was shaken with 50.0 mL of metal ion solution at different concentrations, in a thermostatted shaker for 24 h (which had been found sufficient to ensure equilibrium) at 25.0, 35.0 and 45.0 $^{o}$C and at pH = 3.0, 2.0 and 1.0. A 15 mL amount of the solution was centrifuged at 4000 rpm to separate solid humic from the solution then the supernated solution was taken and analyzed by spectrophotometer. A calibration curve was determined using standard samples prepared from metal nitrate in 0.1 M $NaClO_4$ prior to measurements. Then, the adsorption isotherms were obtained.

### Spectrophotometric determination of Thorium(IV) ions

The spectrophotometric determination of thorium(IV) ions in the aqueous solution was carried out as follows: Transfer of 1.00 mL of Arsenazo(III) indicator to a 20.0 mL of 9.0 M hydrochloric acid solution and add 1.00 mL of the aqueous test solution. Dilute the volume to 50.0 mL by addition of water. Absorption measurement was carried out using a (1.0 cm) quartz cell within one hour of sample preparation at a wavelength of 630 nm [8].

### Spectrophotometric determination of Uranium(VI) ions

The spectrophotometric determination of Uranium(VI) ions in aqueous solution was carried out as follows: Transfer of 2.00 mL of PAR indicator to a solution containing 5.00 mL of the complexing solution, 5.00 mL of the buffer solution and 4 mL of the aqueous test solution in 50.0 mL volumetric flask and diluting to 50.0 mL by water. Absorption measurement was carried out using a (1.0 cm) quartz cell within one hour of sample preparation at a wavelength of 530 nm [9].

## Results and discussion

### Rate of metal ion sorption by Humic Acid

The rate of metal ions uptake by AZHA was determined at different times (0.25, 0.5, 1.0, 2.0, 4.0, 6.0, 12.0, 18.0 and 24.0 h), with three concentrations (10, 25 and 50 ppm) at different pH and temperature values.

The percentage of metal ion loading by AZHA expressed as percentage uptake was calculated (Eq.1), where:

$\%$ Metal uptake = $C_i - C_e / C_i * 100$

$C_i$: Initial metal concentration (ppm).

$C_e$: The residual concentration of metal ion in solution at equilibrium in (ppm).

The results of these experiments are shown in Tables (1-2) and for example in Fig. 1.

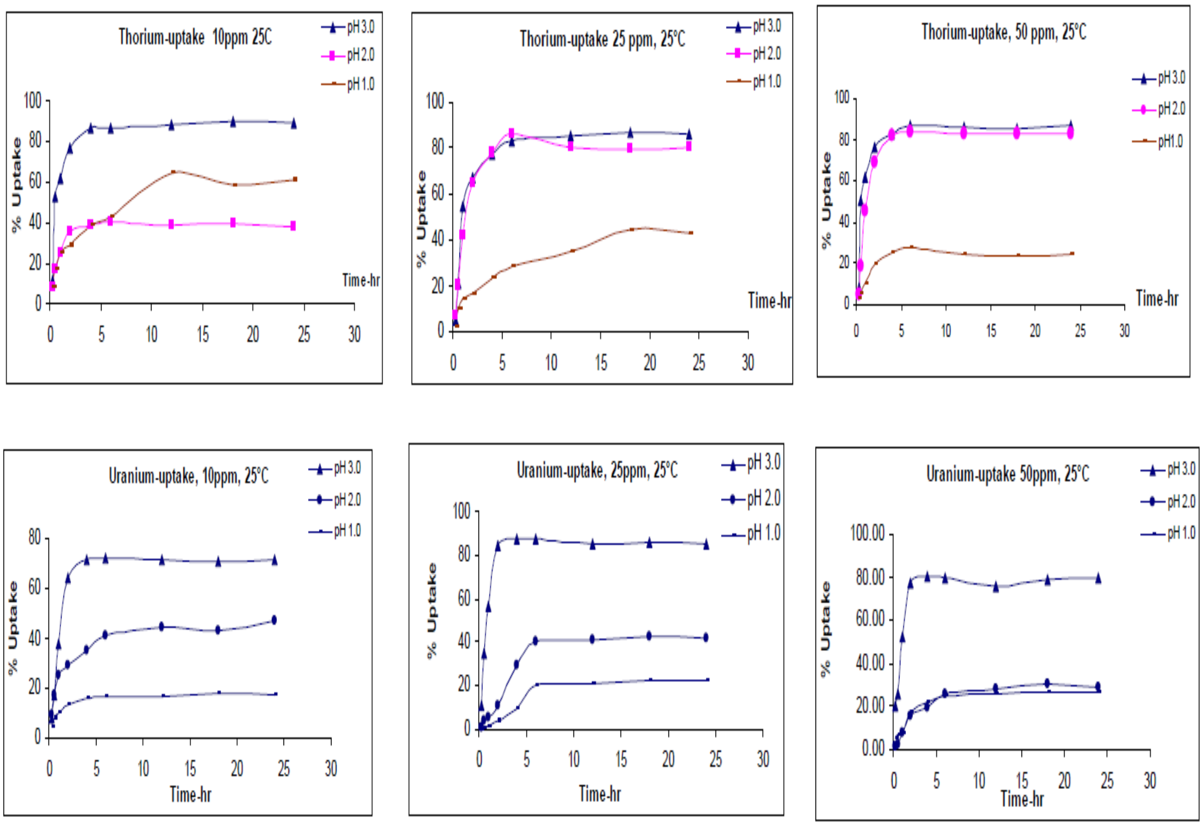


FIG. 1: Thorium(IV) and Uranium(VI) % uptake by HA at pH 1.0, 2.0 and 3.0, at T= 25°C and initial metal concentration of 10ppm.

As shown in Fig. 1 and Tables 1-2, there is an increase in the rate of adsorption as the pH increases. This is due to the deprotonation of carboxyl sites in the humic acid (HA), which causes humic acid strands to disaggregate due to the repulsion of negative charges and increases the number of sites on HA available for interaction with positively charged metals ions.

TABLE 1. Thorium(IV) uptake by HA at pH 1.0, 2.0 and 3.0, from an initial concentration of 10, 25 and 50 ppm and T= 25 °C.

| Time (hr) | Conc. of 10 (ppm) at pH 1.0 | Conc. of 25 (ppm) at pH 1.0 | Conc. of 50 (ppm) at pH 1.0 | Conc. of 10 (ppm) at pH 2.0 | Conc. of 25 (ppm) at pH 2.0 | Conc. of 50 (ppm) at pH 2.0 | Conc. of 10 (ppm) at pH 3.0 | Conc. of 25 (ppm) at pH 3.0 | Conc. of 50 (ppm) at pH 3.0 |
|---|---|---|---|---|---|---|---|---|---|
| 0.25 | 8.0 | 1.8 | 3.3 | 8.0 | 7.60 | 5.2 | 11.2 | 5.2 | 8.3 |
| 0.50 | 17.0 | 10.5 | 6.0 | 17.0 | 20.1 | 18.6 | 53.3 | 21.2 | 50.8 |
| 1 | 25.8 | 14.8 | 10.7 | 25.8 | 42.4 | 45.5 | 62.0 | 55.0 | 62.0 |
| 2 | 28.8 | 16.5 | 19.6 | 35.3 | 65.2 | 69.2 | 76.5 | 67.0 | 76.1 |
| 4 | 39.2 | 23.2 | 25.6 | 39.2 | 78.4 | 81.9 | 87.1 | 77.6 | 83.2 |
| 6 | 42.9 | 28.4 | 27.3 | 40.3 | 86.0 | 83.3 | 86.7 | 82.9 | 87.4 |
| 12 | 64.7 | 34.8 | 24.7 | 38.8 | 80.0 | 83.1 | 88.6 | 85.1 | 86.3 |
| 18 | 59.0 | 44.4 | 23.4 | 39.7 | 79.5 | 83.3 | 90.3 | 86.9 | 85.5 |
| 24 | 61.0 | 42.8 | 24.1 | 37.7 | 80.2 | 83.1 | 89.3 | 86.0 | 87.0 |

TABLE 2. Uranium(VI) uptake by HA at pH 1.0, 2.0 and 3.0, from an initial concentration of 10, 25 and 50 ppm and T= 25 °C.

| Time (hr) | Conc. of 10 (ppm) at pH 1.0 | Conc. of 25 (ppm) at pH 1.0 | Conc. of 50 (ppm) at pH 1.0 | Conc. of 10 (ppm) at pH 2.0 | Conc. of 25 (ppm) at pH 2.0 | Conc. of 50 (ppm) at pH 2.0 | Conc. of 10 (ppm) at pH 3.0 | Conc. of 25 (ppm) at pH 3.0 | Conc. of 50 (ppm) at pH 3.0 |
|---|---|---|---|---|---|---|---|---|---|
| 0.25 | 4.6 | 0.0 | 5.4 | 9.0 | 0.8 | 1.4 | 8.0 | 10.8 | 20.3 |
| 0.50 | 7.9 | 0.4 | 7.3 | 17.0 | 3.6 | 2.6 | 17.0 | 35.0 | 25.5 |
| 1 | 10.1 | 1.6 | 8.0 | 25.0 | 5.2 | 7.8 | 37.5 | 56.6 | 52.7 |
| 2 | 28.8 | 4.0 | 17.3 | 29.0 | 10.8 | 15.8 | 64.3 | 84.4 | 77.3 |
| 4 | 13.3 | 9.2 | 21.5 | 35.0 | 29.2 | 19.8 | 71.6 | 87.3 | 80.8 |
| 6 | 15.8 | 20.4 | 24.6 | 41.0 | 40.4 | 26.0 | 72.1 | 87.8 | 79.3 |
| 12 | 16.5 | 21.2 | 26.1 | 44.0 | 40.8 | 28.4 | 71.2 | 85.4 | 76.2 |
| 18 | 17.6 | 22.4 | 26.4 | 43.0 | 42.8 | 30.2 | 70.9 | 86.2 | 79.2 |
| 24 | 17.2 | 22.8 | 26.9 | 47.0 | 42.0 | 29.2 | 71.4 | 85.3 | 80.0 |

## Adsorption isotherms

The adsorption isotherms were determined for Thorium(IV) and Uranium(VI) at different pH values (1.0, 2.0 and 3.0) and temperatures (25 $^{o}$C, 35 $^{o}$C and 45 $^{o}$C). The adsorption isotherms results were analyzed by using the following linearized Langmuir [10] and Freundlich isotherm [11] equations:

Langmuir isotherm:

$$c/q = 1/(qm\ K_L) + (1/qm)\ c \quad (1)$$

Freundlich isotherm:

$$\mathrm{Log}\ q = \log K_F + (1/n) \log c \quad (2)$$

Therefore, a plot of c/q versus c gives a straight line of slope (1/qm) and intercept 1/(qm $K_L$), and a plot of log q versus log c gives a straight line with a slope 1/n and intercept log $K_F$ as shown in Tables (3-4) and Figures(2-3) for example. Where $K_L$ parameter is related to the strength of the adsorbed ion– adsorbent binding (i.e. Thorium(IV) ions–HA), qm is the saturation adsorption capacity, $K_F$ is a parameter related to the adsorption capacity and n is a measure of adsorption intensity [12, 13].

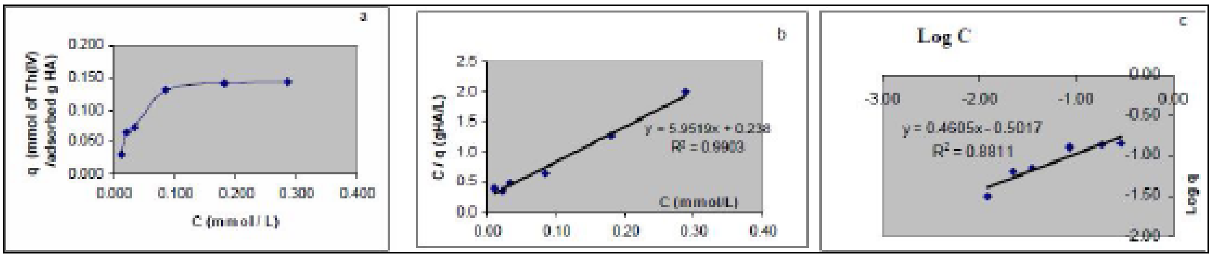


FIG. 2: Plots of (a) adsorption isotherm of Thorium(IV), (b) linearized Langmuir, (c) linearized Freundlich at pH = 1.0 and T= 25 °C.

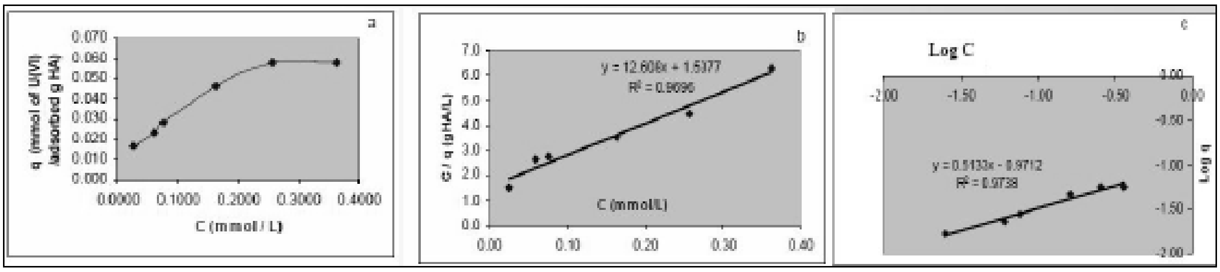


FIG. 3: Plots of (a) adsorption isotherm of Uranium(VI), (b) linearized Langmuir, (c) linearized Freundlich at pH = 1.0 and T = 25 °C.

TABLE 3. The $R^2$, qm, $K_L$, $K_F$ and n values obtained from Langmuir and Freundlich plots for Thorium (IV).

| T(°C) | Langmuir model | | | Freundlich model | | |
|---|---|---|---|---|---|---|
| | $R^2$ | qm (mmol/g) | $K_L$ (L/mmol) | $R^2$ | $K_F$ | n |
| pH=1.0, 25 | 0.990 | 0.168 | 25.0 | 0.984 | 0.315 | 2.172 |
| 35 | 0.969 | 0.117 | 23.3 | 0.947 | 0.168 | 2.778 |
| 45 | 0.982 | 0.108 | 20.8 | 0.881 | 0.144 | 2.904 |
| pH=2.0, 25 | 0.927 | 0.425 | 20.0 | 0.945 | 1.345 | 1.558 |
| 35 | 0.985 | 0.354 | 51.5 | 0.957 | 1.089 | 1.961 |
| 45 | 0.984 | 0.324 | 41.8 | 0.953 | 0.901 | 1.959 |
| pH=3.0, 25 | 0.927 | 0.824 | 17.8 | 0.990 | 4.933 | 1.230 |
| 35 | 0.975 | 0.896 | 17.1 | 0.999 | 5.049 | 1.240 |
| 45 | 0.924 | 0.934 | 15.1 | 0.982 | 5.244 | 1.208 |

The estimated parameters of the adsorption isotherms, calculated from the intercepts and slopes of the corresponding linear plots for Thorium(IV) and Uranium(VI) adsorption onto HA at different temperatures, together with their correlation coefficients ($R^2$), are given in Tables (3-4) at different pH values (1.0, 2.0 and 3.0). The correlation regression coefficients ($R^2$) have been determined for each isotherm. Their values are very good for Freundlich and Langmuir models. The applicability of Langmuir equation is an indication of the homogeneous sites of interaction utilized by metal ions that have almost the same heat of adsorption. The correlation regression coefficient ($R^2$) has been determined for each isotherm. In general, the Freundlich correlation coefficients are higher than the Langmuir correlation coefficients; consequently, it would appear that the Freundlich equations give a better representation of experimental isotherm data as shown in the previous Tables (3-4). This suggests that the HA contain both homogeneous and heterogeneous surfaces with more heterogeneous sites.

TABLE 4. The $R^2$, qm, $K_L$, $K_F$ and n values obtained from Langmuir and Freundlich plots for Uranium(VI).

| T(°C) | Langmuir model | | | Freundlich model | | |
|---|---|---|---|---|---|---|
| | $R^2$ | qm (mmol/g) | $K_L$ (L/mmol) | $R^2$ | $K_F$ | n |
| pH=1.0, 25 | 0.970 | 0.079 | 8.20 | 0.974 | 0.107 | 1.948 |
| 35 | 0.965 | 0.067 | 7.86 | 0.991 | 0.0844 | 2.037 |
| 45 | 0.973 | 0.066 | 7.09 | 0.930 | 0.0950 | 1.726 |
| pH=2.0, 25 | 0.870 | 0.351 | 4.83 | 0.958 | 0.664 | 1.277 |
| 35 | 0.871 | 0.331 | 3.33 | 0.980 | 0.489 | 1.255 |
| 45 | 0.942 | 0.283 | 3.26 | 0.990 | 0.381 | 1.313 |
| pH=3.0, 25 | 0.954 | 0.335 | 9.37 | 0.943 | 0.734 | 1.478 |
| 35 | 0.944 | 0.455 | 4.88 | 0.993 | 0.813 | 1.317 |
| 45 | 0.978 | 0.627 | 2.84 | 0.997 | 0.997 | 1.187 |

The estimated parameters of the adsorption isotherms, calculated from the intercepts and slopes of the corresponding linear plots for Thorium(IV) and Uranium(VI) adsorption onto HA at different temperatures, together with their correlation coefficients ($R^2$), are given in Tables (3-4) at different pH values (1.0, 2.0 and 3.0). The correlation regression coefficients ($R^2$) have been determined for each isotherm. Their values are very good for Freundlich and Langmuir models. The applicability of Langmuir equation is an indication of the homogeneous sites of interaction utilized by metal ions that have almost the same heat of adsorption. The correlation regression coefficients ($R^2$) have been determined for each isotherm. In general, the Freundlich correlation coefficients are higher than the Langmuir correlation coefficients; consequently, it would appear that the Freundlich equations give a better representation of experimental isotherm data as shown in the previous Tables (3-4). This suggests that the HA contain both homogeneous and heterogeneous surfaces with more heterogeneous sites.

Depending on the values of qm and n in Tables (3-4), the adsorption of Thorium(IV) has higher adsorptivity and is more favorable than Uranium(VI) metal ions onto AZHA at the same pH and temperature [14, 15]. This may be due to that it has larger ionic radius (small hydrated radius) and charge than Uranium(VI) in the uranyl ion ($UO_2^{2+}$) and this causes stronger electrostatic interaction.

**Comparing adsorptivity**

To compare the chemistry of transition metals, Cu(II) and Ni(II) [6] and lanthanides, Gd(III), Ce(III) [7] interaction with HA with that of Uranium and Thorium, the following trends were observed:

At pH=3.0, 25 °C

Ce > Th > Gd > Cu > U > Ni

qm = 0.951 0.824 0.798 0.451 0.455 0.336

At pH=3.0, 35 °C

Ce > Gd > Th > Cu > U > Ni

qm = 1.15 0.928 0.896 0.489 0.455 0.380

At pH=2.0, 35 °C

Ce > Gd > Th > U > Cu > Ni

qm = 1.08 0.787 0.354 0.331 0.182 0.251

At pH=2.0, 25 °C

Ce > Gd > Th > U > Ni > Cu

qm = 0.828 0.561 0.425 0.351 0.234 0.163

Table (5) shows the ionic radius for the above mentioned ions. Interestingly, the adsorptivity of metal ions (qm) on AZHA was found to be directly proportional to the ionic radius (for example, Figures (4-5)). This is due to the decrease of hydration energy (ΔHh) as the ionic radius increases [16]. Increasing the hydration energy due to the increase in the hydration shell makes it more difficult for metal ions to discharge the water of hydration and bond to HA surface.

TABLE 5. Chemical properties of metal ions.

| Metals | Th(IV) | U(VI) | Ce(III) | Gd(III) | Cu(II) | Ni(II) |
|---|---|---|---|---|---|---|
| Coordination number | 8 | 7 | 7 | 7 | 6 | 6 |
| Ionic radius (Å) | 1.19 | 0.97 | 1.21 | 1.14 | 0.87 | 0.83 |

The adsorptivity is highest for the metal ion that has the largest radius as shown in Figures (4- 5). This can be explained by that in aqueous medium the metal ions exhibit strong hydrolysis and a distinct lowering of pH is noted when the salts of these elements are dissolved in water. The formation of aqua complex $[M(OH_2)_m]^{n+}$ takes place (where m is larger than six, perhaps eight or nine). The aqua complex, having m $H_2O$ molecules surrounding the central ion, has a definite structure and the cloud of water molecules (hydration shell) has different geometry than the rest of the water. Thus, when say $M(NO_3)_n$ salts are dissolved in water, there will be very little attraction between $[M(OH_2)_m]^{n+}$ and the solvated $NO_3^-$ ion. Unless the other ions or ligands have a strong structure-breaking influence, the sheath of water molecule will protect the metal ions from influence of other anions or ligands. When complexes are formed, the approach of a ligand will interfere with the hydration shell and the ordered geometry will break down [17]. So, metal ions with smaller radius will be surrounded by a stronger hydration shell than those with larger radius. This makes the bonding with HA more difficult, and the adsorptivity decreases. The adsorptivity (qm) values have no correlation with the charge density (charge/radius) of the metal ions. It is worthy to mention that the charge of metals ions is not the limiting factor in determining the adsorptivity of metal ions. This leads to the assumption that electrostatic interaction is not the predominant factor that determines adsorptivity.

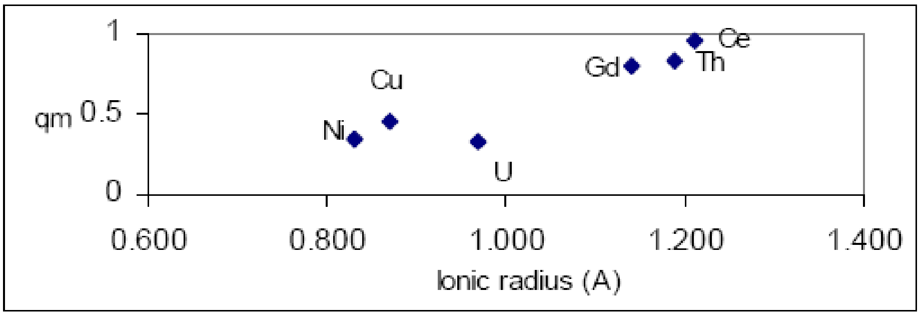


FIG. 4: The relation between qm determined from Langmuir plots and the ionic radius of metal ions at pH = 3.0 and T = 25 °C.

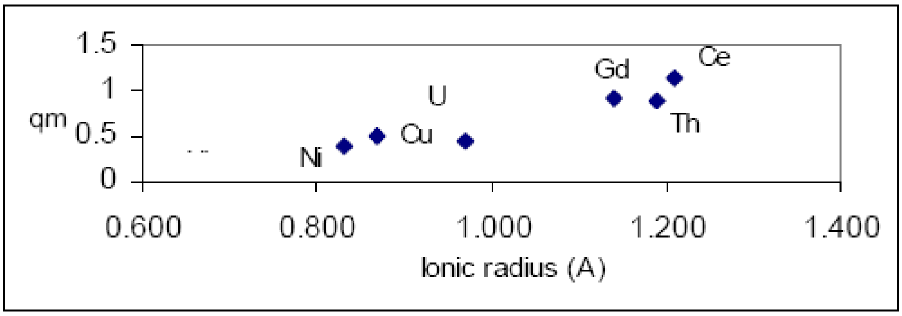
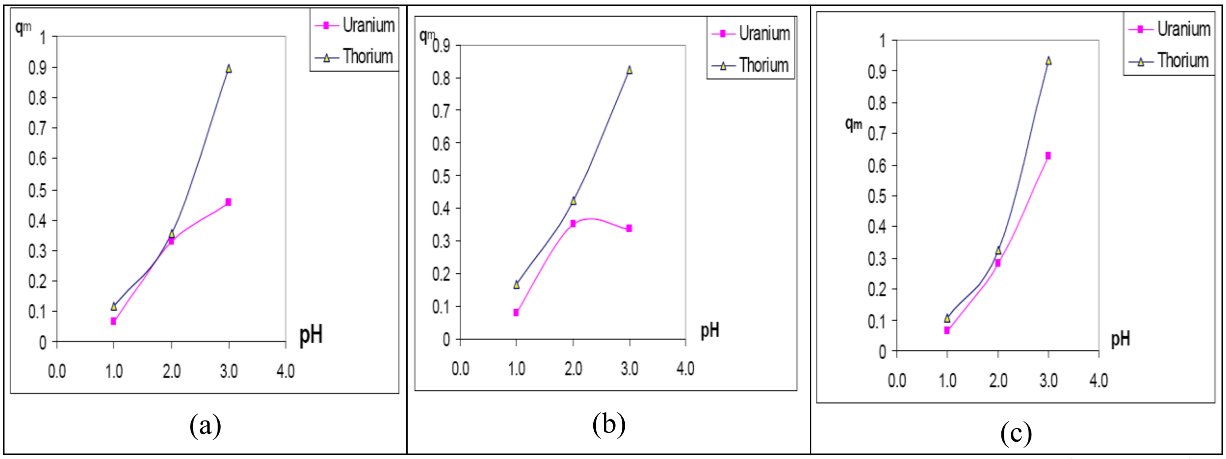


FIG. 5: The relation between qm determined from Langmuir plots and the ionic radius of metal ions at pH = 3.0 and T = 35 °C.

From Figures (4-5), the metal ion that has a large ionic radius has small hydrated radius, it will have better fitting into the hypothetical cylindrical structure of humic acid, and qm will increase.

### The effect of pH

Generally, as pH increases, adsorption increases. This is noticed by the increased values of qm with increasing pH, as we can see in Tables (3-4) and Figure (6) which represents the values of qm for Thorium(IV) and Uranium (VI) metal ions at different pH values. As the pH increases from 1.0 to 3.0, the degree of dissociation of carboxylate groups increases ($pK_a$ 4.19) and the negative charge on HA increases, which will lead to more electrostatic interaction with metal ions. Thus, it seems that there are other binding sites like carbonyl, alcohol and thiol groups which become important at this pH range, so the active sites of HA become more exposed to metal ion interaction.



(a) (b) (c)

FIG. 6: The pH dependence of qm for Thorium(IV) and Uranium(VI), pH=1.0-3.0 at T= (a) 25 °C, (b) 35 °C, (c) 45 °C.

## The effect of temperature

From Langmuir equation, $K_L$ values were calculated at different temperatures. From the data in Tables 3- 4, the relation between ln $K_L$ and 1/T was plotted at pH = 1.0 and 3.0 as shown in Figures (7- 8) below, and from the van't Hoff equation, ΔH and ΔS were calculated for Th(IV) and U(VI) as shown in Table (6).

However, from Table (6), and Figs. (7- 8), the adsorptivity process is enthalpy driven for Uranium(VI). On the other hand, the adsorptivity process is enthalpy and entropy driven for Thorium(IV). It is clear that qm values decrease with increasing temperature at pH = 1.0 and pH = 2.0.

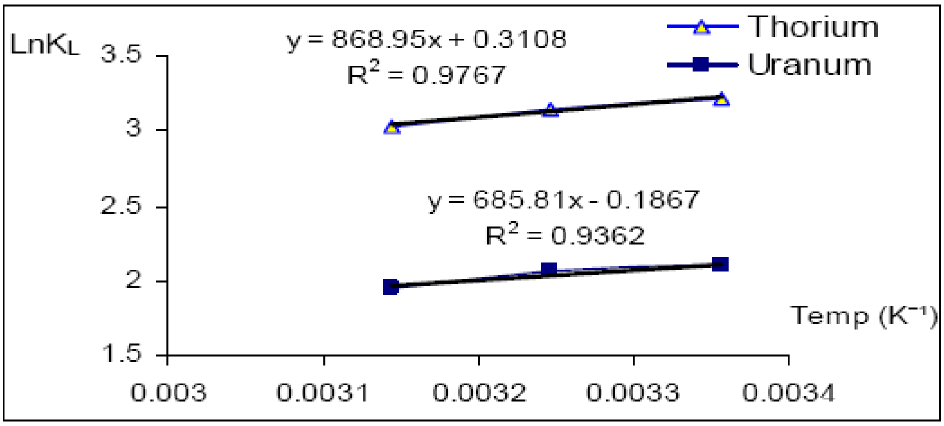


FIG. 7: The relation between ln $K_L$ and 1/T, where T = (298K, 308K and 318K) at pH = 1.0.

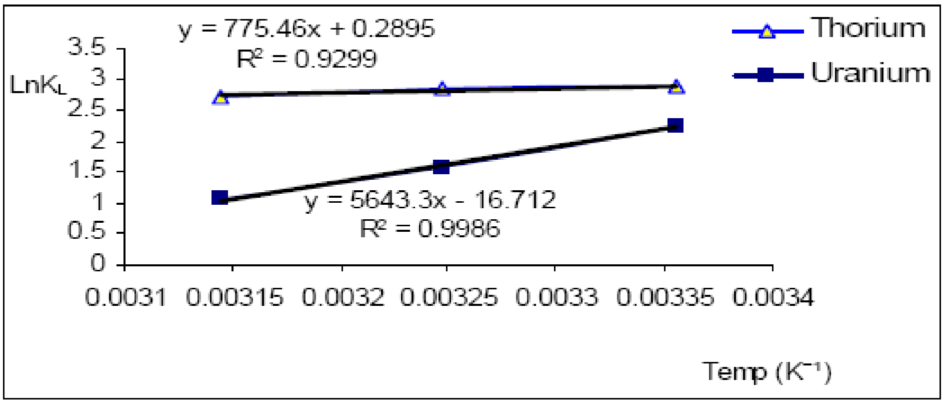


FIG. 8: The relation between ln $K_L$ and 1/T, where T = (298K, 308K and 318K) at pH 3.0.

This indicates that the interaction between metal ions with HA is exothermic. This is in contrast to that observed in the case of transition elements [6] and lanthanides [7], which have been found to have an entropy driven interaction with HA. This indicates that the discharge of water of hydration is not important in the case of actinides due to the high charge on the metal ions.

This leads to the hypothesis that Thorium(IV) and Uranium(VI) are encapsulated in the interior of HA helix with their water of hydration because the interior is full with water [18]. However, Copper(II), Nickel(II) and Gadolinium (III) are adsorbed on the exterior of HA helix as shown in Fig. 9.

TABLE 6. Enthalpy and entropy values for the adsorption of Thorium(IV) and Uranium(VI) onto AZHA.

| Metals | pH = 1.0 | | pH = 3.0 | |
|---|---|---|---|---|
| | Th(IV) | U(VI) | Th(IV) | U(VI) |
| $\Delta H$(kJmol$^{-1}$) | -7.224 | -5.701 | -6.447 | -46.918 |
| $\Delta S$(J K$^{-1}$mol$^{-1}$) | 2.584 | -1.552 | 2.407 | -138.9 |

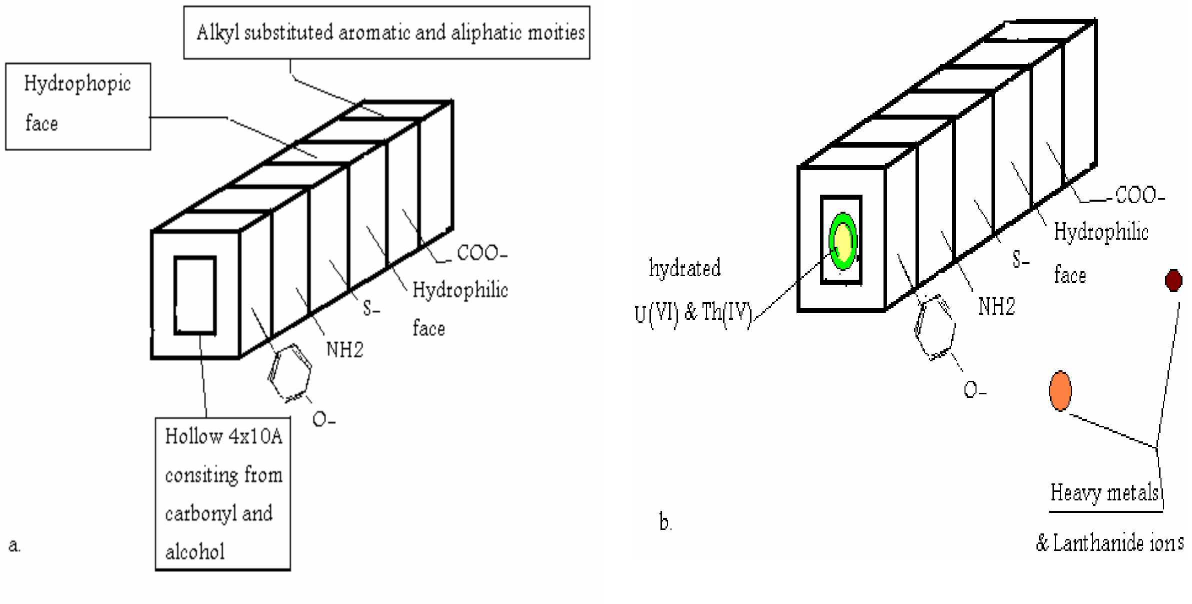


FIG. 9: Part a. Schematic view of the secondary structure of a HA strand [18]. Part b. Suggestion for loaded HA strand with different metal ions.

## Conclusion

- The adsorptivity of metal ions (transition, lanthanide and actinide) on HA is directly proportional to the ionic radius of metals ion. Large size metal ions like Cerium(II), Thorium(IV) and Uranium(VI) fit the large hollow interior (4 x 10 Å) of the rod like structure of helical strand of HA, Fig. 7 [18].
- As pH increases, the adsorptivity (qm) of metal ions increases.
- The order of adsorptivity onto AZHA for Thorium(IV) is greater than for Uranium(VI).

## References

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