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SORPTION OF URANIUM BY IMMOBILIZED *WATER HYACINTH* ROOTS

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ABSTRACT

Sorption of uranium by *water hyacinth* roots, calcium alginate in gel and dry forms, and immobilized *water hyacinth* roots by calcium alginate gel and dry forms were investigated. The sorption of uranium was examined as a function of pH, initial concentration, and weight of sorbents, solution volume, and temperature to study the effect of immobilization on the sorption. Kinetics and sorption isotherms were also discussed. When studying concentration, weight, and volume impact, calcium alginate in gel form showed the highest sorption percentage followed by immobilized *water hyacinth* roots in gel form. On the other hand, *water hyacinth* roots immobilized in calcium alginate in dry form showed higher sorption percentage than that of calcium alginate dry form when studying pH, concentration, and time effect.

KEYWORDS: Immobilized *water hyacinth* roots, Sorption, Uranium, Calcium alginate, Kinetics, Sorption isotherms.

INTRODUCTION

The use of freely-suspended biomass for the uptake of heavy metal ions is plagued with problems, including the need for separation of the suspended biomass from the aqueous medium, and the possible clogging of pipelines and filters. In general, the biomass is not mechanically strong and has a wide size distribution, which can lead to problems including channelling in column operation (Lu, and Wilkins, 1996). Immobilization of the biomass overcomes many of these problems. So many studies were directed towards the immobilization of biomaterials, for example: fungi (Khoo, and Ting 2001), *Trichoderma harzianum* (Akhtar, et.al 2009), and *Prottheca zopfii* (Suzuki, et al 1998) were immobilized successfully. Among the various immobilization methods, encapsulation is one of the most commonly used methods. For the immobilization matrix to be suitable for practical use in bio-sorption, it must be mechanically strong and chemically stable to withstand the real conditions.

Polyacrylamide was the first polymer used for cell entrapment, and was found to be toxic to both microorganisms and humans due to the generation of free radicals during the polymerization process (Grainger, and Lynch, 1984). Natural polysaccharides such as alginates, carrageenan and agarose are commonly used in cell immobilization and encapsulation (Rome, and de Gadd, 1991). Alginates, in particular, have received considerable attention due to the ease of laboratory preparation, and have been very widely used in cell immobilization for bio-sorption studies (Chen, et al 1997).

Alginic acid or alginate, the salt of alginic acid, is the common name given to a family of linear polysaccharides containing 1,4- linked -d-mannuronic (M) and R-L-guluronic (G) acid residues arranged randomly along the chain. The salts of alginic acid or alginate with monovalent ions (alkali metals and ammonium) are soluble, whereas those with divalent or polyvalent metal ions (except Mg^{2+}) and the acid itself are insoluble and form gel (Percival, and McDowell, 1967). In the presence of calcium or other divalent cations, alginate gel adopt a structure of cross-linked chains known as the “egg-box” model (Torres, et al 2005) where each divalent metal ion binds to two carboxyl groups as adjacent alginate molecules (Rees, and Welsh, (1977).

A schematic representation of the alginate’s structure “egg-box junction” is given in Figure 1. It should be noted that this particular structure of the alginates leaves free carboxylic functional groups in the H-form, which may interact with metal ions (Grant, et al. 1973).

Some advantages of alginate beads are the biodegradability, hydrophilicity, the presence of carboxyl groups and natural origin. The presence of carboxyl groups in the alginate structure enhances the adsorption of many metal ions compared with other adsorbents (Kacar, et al. 2002). The Calcium alginate is used as gel form and dry form, the advantages of using dry alginate beads instead of the gel type are ease of handling and storage, greater precision during weighing and greater stiffness.

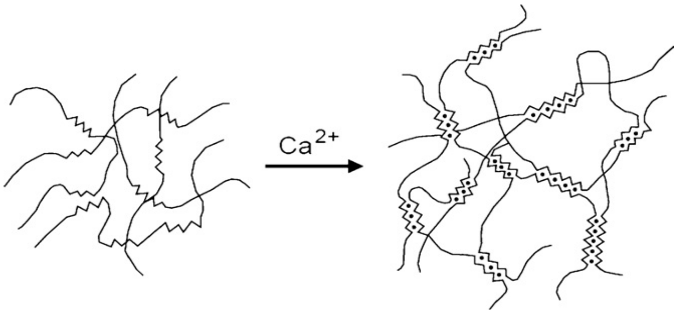

Figure 1: Schematic representation of the Calcium-induced gelation of alginate in accordance with the "egg-box" structure (Christensen, et al. 1990).

To investigate the ability of *water hyacinth* roots as bio-sorbent to remove uranium from aqueous solution, *water hyacinth* roots immobilized in calcium alginate gel and dry form were compared to calcium alginate in gel and dry form, under various experimental conditions such as concentration of uranium, contact time, solution volume, ionic strength, and weight of roots. The sorption isotherm has been analysed in terms of Langmuir Freundlich, Timken and Dubinin-Radushkevich (D-R) equations. The first order and second orders kinetics models were discussed.

MATERIAL AND METHODS

Water hyacinth roots preparation

Water hyacinth roots collected from the River Nile at Cairo city, Egypt, were cleaned thoroughly to remove dirt and the unhealthy parts, rinsed in double distilled water, dried at 80 °C overnight. Roots were then boiled using double distilled water to remove any soluble compounds, filtered, dried at 80 °C, and ground by a gate mortar (Retch).

Preparation of calcium alginate and calcium alginate immobilized roots

1 gm sodium alginate was mixed with 20 mL of water to make slurry, completed to 50 ml and stirred for 24 h then dropped into 200 ml $Ca\ Cl_2$ solution 0.2 M (ice bath) and kept in the refrigerator for 24 h. Finally, it was, removed from the Ca_2Cl_2 solution, washed with double distilled H_2O to remove Ca_2Cl_2, and used directly in case of gel form, or air dried for 72 h before using in dry form. In case of immobilized *water hyacinth* roots, 1 gm *water hyacinth* roots was mixed with 1 gm sodium alginate while following the previous procedure. In all cases, the produced quantity was divided into ten equal portions and 2.9, 0.12, 3.00, 0.24 gm

were used from calcium alginate gel and dry, water hyacinth roots immobilized in calcium alginate gel and dry forms respectively.

Preparation of uranium stock solution

A 1000 µg mL^{-1} stock uranium solution was prepared by dissolving $UO_2\ (NO_3)_2.6H_2O$ (Merk) in drops of concentrated nitric acid (Merck). The resulting solution was made up to 1 liter using double distilled water then diluted to have the desired concentration. The pH was adjusted to the desired value using 1 mol L^{-1} CH_3COONa and 1 mol L^{-1} HNO_3 solutions. All the chemicals used were of analytical reagent (AR) grade.

Methods and Instrumentation

All glassware used in the experiment were cleaned with detergent, thoroughly rinsed with tap water, soaked in 7 % HCl solution and finally rinsed double distilled water. The sorption of uranium on roots was studied by batch technique; a known weight was equilibrated with 20 ml of the uranium solution of known concentration in a stoppered Pyrex glass flask at 25 °C in a shaker water bath (GFL- 1083 model) at speed of 100 rpm for a known period of time. After sorption, the sorbent were separated by filtration, and then the residual uranium in the filtrate was determined using the Arsenazo III method (Marczenko1986) using a UNICAM UV/Vis spectrometer UV4. Sorption yield (%) was calculated as follow:

$$\text{Sorption yield (\%)} = \frac{(U_i - U_e)}{U_i} X100 \quad (1)$$

U_i and U_e are concentrations of uranium in the initial and equilibrium solution, respectively.

All experiments were conducted in duplicate. Controls were simultaneously carried out to ensure that the sorption was done by *water hyacinth* roots and not on the wall of the container or precipitation. The pH of the solutions was measured using a digital pH meter model HI 8519 (Hanna).

The sorption experiments were carried out with uranium solution in presence of one of the following sorbents:

1- *Water hyacinth* roots (WHR).

2- Calcium alginate gel form (CaAGF).

3- Calcium alginate dry form (CaADF).

4- *Water hyacinth* roots immobilized in Ca alginate gel form (WHRCaAGF).

5- *Water hyacinth* roots immobilized in Ca alginate dry form (WHRCaADF).

RESULTS AND DISCUSSION

Effect of pH

Sorption was investigated at pH range 1–5. The different sorbents were equilibrated in 20 ml of 100 µg. ml^{-1} solution of uranium and shaken for 2 hours at 25 °C. Figure 2 shows the effect of pH of solution on sorption of uranium.

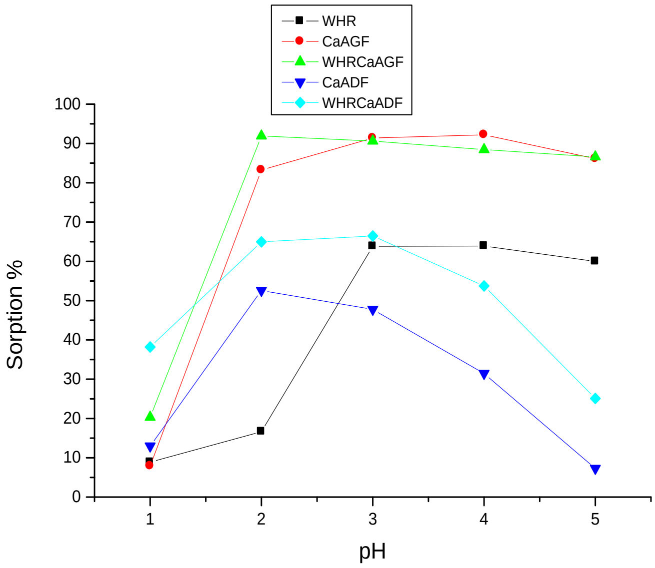

Figure 2: Sorption of uranium on WHR (0.1g), CaAGF (2.9g), CaADF (0.12g), WHRCaAGF (3g), and WHRCaADF (0.24g) as function of pH.

All investigated sorbents showed similar pattern of uranium sorption with increasing the pH. Sorption increased by increasing the pH to reach a maximum followed by drop at higher pH. Sorption of uranium by WHR increased from 8.87 % (pH 1) to reach a maximum of 63.89% at pH 3 followed by drop to 59.97 % at pH 5. For CaAGF, sorption increased from (7.9%) (pH 1) to a maximum of 92.21% at pH 4 and decrease to 86.1 % at pH 5.

For CaADF, sorption increased from 12.98% (pH 1) to a maximum of 52.6% at pH 2 followed by gradual decrease to reach 7.82% at pH 5.

In case of WHRCaAGF, sorption increased from 20.3% (pH)1 to a maximum of 91.89% at pH 2 followed by slight decrease by increasing the pH to reach 86.5 % at pH 5.However, for WHRCaADF, sorption increased from 38.2% (pH 1) to a maximum of 66.45% at pH 3, and gradually decreased to reach 25 % at pH 5.

Based on the above results, it is clear that sorption of uranium by any sorbent change by changing the pH of the solution. The studied sorbents showed different behaviors which could be attributed the change in proton concentration modifying the redox potential of sorbates and sorbents, provoke dissolution of the sorbent material and modify chemical speciation of sorbates as well as surface charge of sorbents which change the ability to absorb uranium [Volesky, (2003).

WHRCaAGF performed much better than free biomass (*water hyacinth* roots) due to the fact that alginate itself is a good sorbent [Akhtar, et.al (2009)].

On the other side, CaADF and WHRCaADF showed lower percentage of sorption than that of gel form. This may be attributed to formation of uranium complexes with acetate group that become larger than uranyl ion to penetrate into the pores of CaADF and WHRCaADF as a result of shrinkage of the voids, the pores diameters, and channels within the dried beads. WHRCaADF has sorption percent more than CaADF in all the studied pH range. As a result of shrinkage or immobilization of *water hyacinth* roots in calcium alginate beads the dense outer-layer in the beads causes different "screening effect", hence shielding the *water hyacinth* roots and/or calcium alginate that were embedded in the matrix from uranyl ions, thus, resulting in a lower specific uranium uptake than free *water hyacinth* roots and/or calcium alginate gel form.

Effect of the initial concentration

As pH 3 showed the maximum sorption of uranium by WHR, it was chosen as the working pH for all the sorbents. Therefore, the effect of concentration, temperature, etc. were studied at this pH.

Sorption was investigated within concentration range of 20–200 $\mu g.ml^{-1}$. All the sorbents were equilibrated in 20 ml of pH 3 solution and shaken for 2 hours at 25 °C. Figure 3 shows the effect of initial concentration of uranium on sorption percentage.

The initial concentration provides an important driving force to overcome all mass transfer resistance of uranium between the aqueous and solid phases [Cem, and Sute, (2009)].

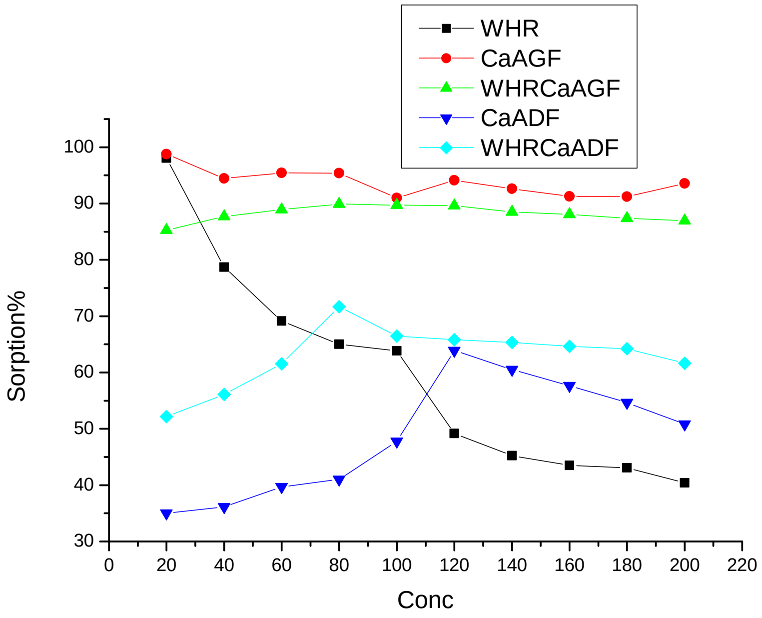

Figure 3: Sorption of uranium on WHR (0.1g), CaAGF(2.9g), CaADF (0.12g), WHRCaAGF (3g) and WHRCaADF (0.2g) as function of concentration.

The obtained results indicate a different influence of initial uranium concentration on the sorption percent over the investigated range (20–200 µg.ml^{-1}).

In the case of WHR, the sorption decrease by increasing the concentration. The maximum sorption was reached at 20 µg.ml^{-1} (98%) while at 200 µg ml^{-1} sorption dropped to 40.4%. Sorption was more efficient in diluted solutions. In the case of CaAGF, over the range from 20-80 µg.ml^{-1}, sorption increased from 74 % to the maximum of 95%, and thereafter it slightly decrease by decreasing the concentration to reach 90% at 200 µg.ml^{-1}.

In the case of CaADF, the sorption almost doubled from 35 %at 20 µg.ml^{-1} to 64% at 120 µg.ml^{-1} followed by slight declination to reach 51% at 200 µg.ml^{-1}.

In the case of WHRCaAGF, the sorption was less sensitive to increasing the concentration where the fluctuation in sorption was about 1% over at the studied range. In the case of WHRCaADF, the sorption increased from 52% to reach a maximum of 72% at 80 µg ml^{-1} followed by declining to 62% at 200 µg.ml^{-1}.

Figure 4 presents the quantities of uranium uptake in mg of uranium using the investigated sorbents.

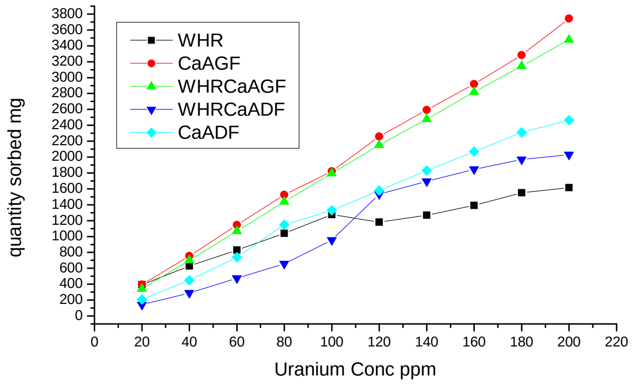

Figure 4: Quantity of uranium sorbed by WHR (0.1g), CaAGF(2.9g), CaADF (0.12g), WHRCaAGF (3g) and WHRCaADF (0.2g) as function of concentration.

The absolute quantity of uranium sorbed by the different sorbents increased by increasing the initial uranium concentration. For WHR, CaAGF, CaADF, WHRCaAGF, and WHRCaADF uranium uptake increased from 392, 295, 208, 341, and 140 µg at 20 µg ml^{-1} to 1616, 3613, 2465, 3477, and 2032 µg at 200 µg ml^{-1} respectively.

Effect of sorbent weight

The effect of sorbent weight was investigated under the same experimental settings where, different sorbents were equilibrated in 20 ml of pH 3 solutions (100 µg ml^{-1}) and shaken at 25 °C. Figure 5 shows the effect of weight on uranium sorption.

The sorption increased by increasing the weight of the different sorbents. In the cases of WHR, CaADF, and WHRCaADF the increase was nearly linear. On the other side, for CaAGF, and WHRCaAGF the increase started as nearly linear before reaction slowed down. This could be explained as a consequence of a partial aggregation of biomass at higher biomass weights, which results in decreasing the effective surface area for the bio-sorption.

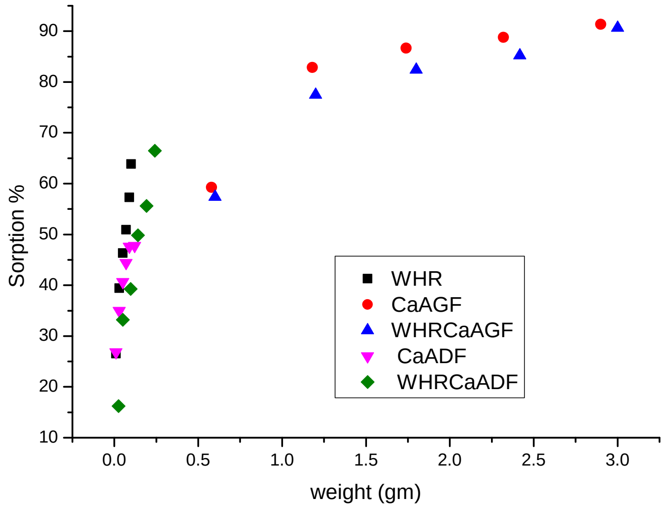

Figure 5: Sorption of uranium on WHR (0.01-0.1g), CaAGF (0.58-2.9g), CaADF (0.01-0.129g), WHRCaAGF (0.6-3g) and WHRCaADF (0.025-0.24) as a function of weight.

Effect of contact time

The sorption was investigated at different contact time ranged from 5-240 min, equilibrated in 20 ml of pH 3 solution (100 µg ml^{-1}) and shaken at 25 °C. Figure 6 shows the effect of contact time on uranium sorption.

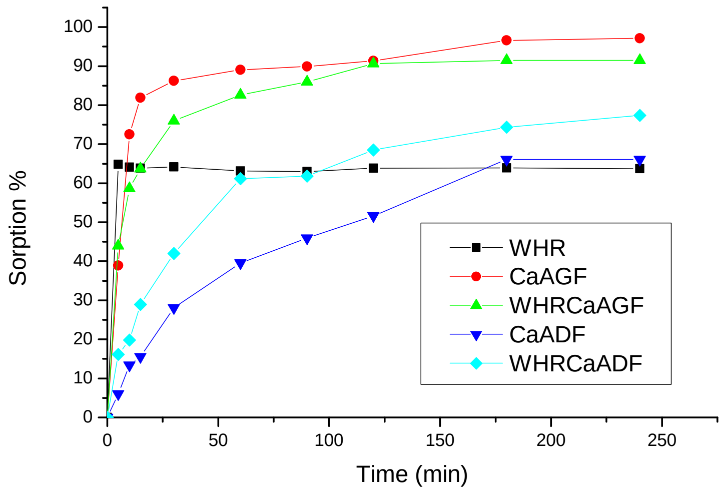

Figure 6: Sorption of uranium on WHR (0.1g), CaAGF (2.9g), CaADF (0.12g), WHRCaAGF (3gm) and WHRCaADF (0.24) as function of time.

Sorption of uranium from solution by WHR was very rapid reaching equilibrium in 5 min. On the other hand, CaADF and WHRCaAGF reach equilibrium in 180 min, while WHRCaADF and CaAGF continued over 240 min.

Although the immobilization of biomass presents several advantages, one inherent setback is the increase in the mass transfer resistance posed by the immobilization matrix. The resistance is related to factors such as the immobilization matrix characteristic and pore size of the sorbent. This problem is aggravated if the polymer matrix possesses fine pores or a small surface area [Khoo, and Ting (2001)]. This is in agreement with the present work.

Freely-suspended WHR removed about 65% of the initial metal concentration within 5 min while CaAGF, WHRCaAGF, CaADF, and WHRCaADF needed longer time as a result of immobilization; 10, 15, 90, and 180 min respectively to achieve the same percentage of removal.

CaADF, WHRCaADF, CaAGF, and WHRCaAGF are porous, where the pore diameters in the CaAGF, and WHRCaAGF beads are larger than those in the CaADF, WHRCaADF as result of shrinkage, thus, providing a lower mass transfer resistance in the former. So the CaAGF, and WHRCAGF beads manifested a faster metal uptake than the CaADF and WHRCaADF beads.

Effect of solution volume

The effect of solution volumes on sorption was investigated at volume range of 20-50 ml, pH 3 and concentration of 2000 µg. The different sorbents were equilibrated and shaken for 2 hours at 25 °C. Figure 7 shows the effect of solution volume on uranium sorption.

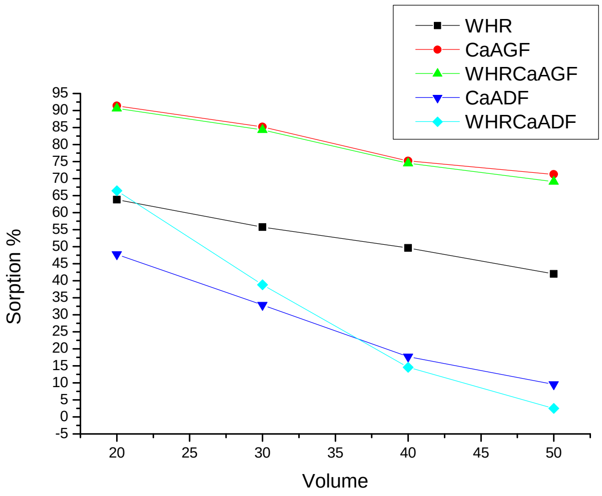

Figure 7: Sorption of uranium on WHR (0.1g), CaAGF (2.9g), CaADF (0.12g), WHRCaAGF (3gm) and WHRCaADF (0.24) as function of solution volume.

Increasing solution volume affected the sorption yield negatively. This could be attributed to reducing the interaction between sorbent and solute at high volumes.

The WHRCaADF was the most influenced by changing the volume of solution where the sorption dropped from 67% at 20 ml to 2.52% at 50 ml.

Effect of Temperature

The effect of solution temperature on sorption was investigated at temperature range of 25 – 60 °Cat contact time 120 min. Different sorbents were equilibrated in 20 ml solution (100 µg. ml^{-1}) and shaken at the investigated temperature. Figure 8 shows the effect of temperature on uranium sorption.

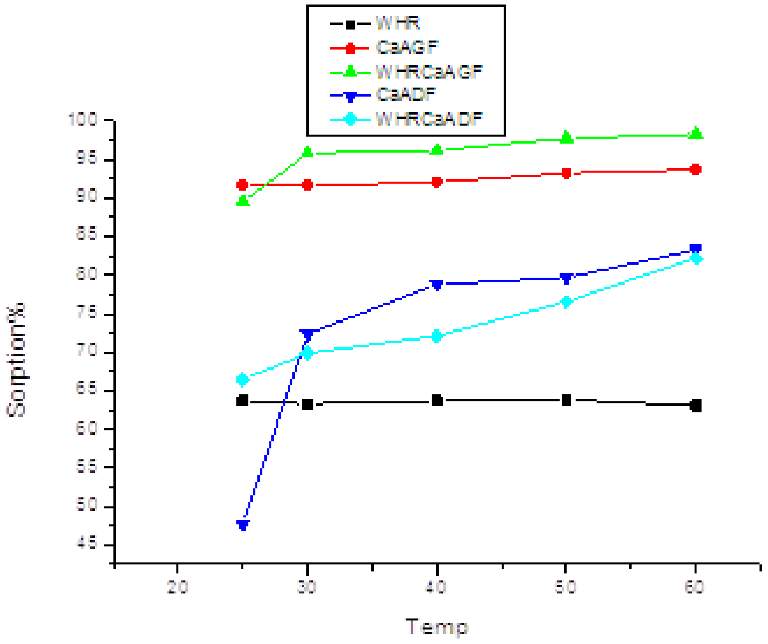

Figure 8: Sorption of uranium on WHR (0.1g), CaAGF (2.9g), CaADF (0.12g), WHRCaAGF (3gm) and WHRCaADF (0.24) as function of solution temperature.

Temperature did not affect the sorption of uranium by WHR where the sorption at 25 ˚C was 64% and 63%at 60˚C is. CaAGF showed almost same behavior where the sorption changed from 91.7% at 25 ˚C to 93.72 % to at 60˚C. WHRCaAGF was slightly affected by temperature where the sorption changed from 89% at 25 ˚C to 98% at 60˚C is. On the other hand the temperature had an obvious effect on CaADF and WHRCaADF, where sorption increased from 48% and 66% to 83% and 82% by increasing temperature from 25 to 60˚C respectively.

Based on the results presented in Figure 8, it is noted that the ability of sorption of uranium changed at different temperatures where at 25 ˚C the sequence was:

CaAGF > WHRCaAGF > WHRCaADF > WHR > CaADF

While at 30 to 60 ˚C was:

WHRCaAGF > CaAGF > CaADF > WHRCaADF > WHR

Sorption of uranium was more favored by WHRCaAGF than CaAGF and also by CaADF than WHRCaADF and WHR by increasing the temperature more than 25 ˚C. This may be related to the increase in the volume of the beds as a result of swelling especially in the case of CaADF, and WHRCaADF. This swelling consequently increased the external surface area of the sorbents, the pores diameters, and channels inside the sorbents, which then increased the ability of the sorbents to absorb uranium.

Sorption isotherm

Sorption isotherm data for WHR, CaAGF, WHRCaAGF, CaADF, and WHRCaADF uranium were indicated in Figure 9 to 14. In every Figure a, b, c, d, e, and f represent Langmuir linear isotherm, Langmuir nonlinear isotherm, Freundlich linear isotherm, Freundlich nonlinear isotherm, Timken isotherm, and D-R isotherm respectively.

The Langmuir model is expressed by the following equation:

$$U_{eq}/y = \left(\frac{1}{a}\right) + \left(\frac{b}{a}\right).\ U_{eq} \qquad (2)$$

Where U_{eq} is the concentration of solute in the solution phase at equilibrium (g L^{-1}), y is the amount of solute sorbed per unit weight of sorbent (mg g^{-1}), b and a are Langmuir constants: b is represented as the ratio of sorption and desorption rate coefficient (L g^{-1}), and

$$a = b.Q_{ms} \qquad (3)$$

Q_{ms} is the maximum sorption capacity (mg g^{-1}). At low concentrations the Langmuir equation is reduced to a linear relationship, while the maximum sorption capacity, Q_{ms}, is attained at concentrations corresponding to monolayer coverage.

The Freundlich model is applied to describe heterogeneous system characterized by a heterogeneous factor of 1/n. The logarithmic form of the Freundlich equation is:

$$\text{Log}\, y = \text{Log}\, K + \frac{1}{n}\text{Log}\, U_{eq} \qquad (4)$$

The graphical relation between Log y and Log U_{eq}, gives a straight line with a slope equals to 1/n and the intercept = log *K*.

Dubinin-Radushkevich (D-R) isotherm model equation is used in order to understand the sorption type. The linearized (D-R) isotherm equation is written as:

$$\text{Ln}\, X = \text{Ln}\, X_m - KE^2 \qquad (5)$$

$$E = RT\, \text{Ln}\, (1 + 1/C_e) \qquad (6)$$

Where X is the amount of metal adsorbed per unit mass of adsorbent (mol g^{-1}), X_m is the theoretical adsorption capacity. C_e is the equilibrium concentration of uranium (mol L^{-1}). R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and *T* is the absolute temperature in Kelvin.

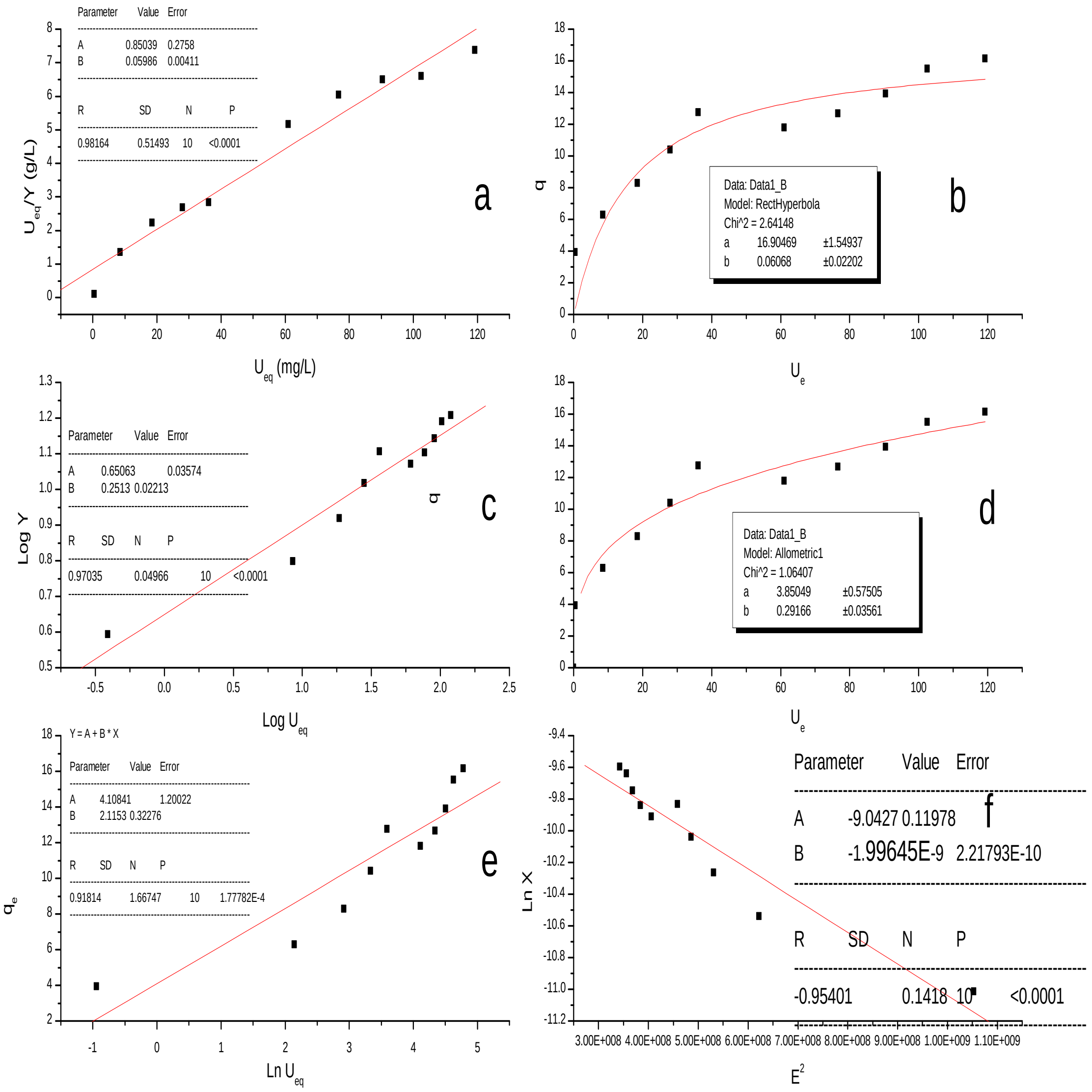

Figure 9: Sorption isotherms of WHR.

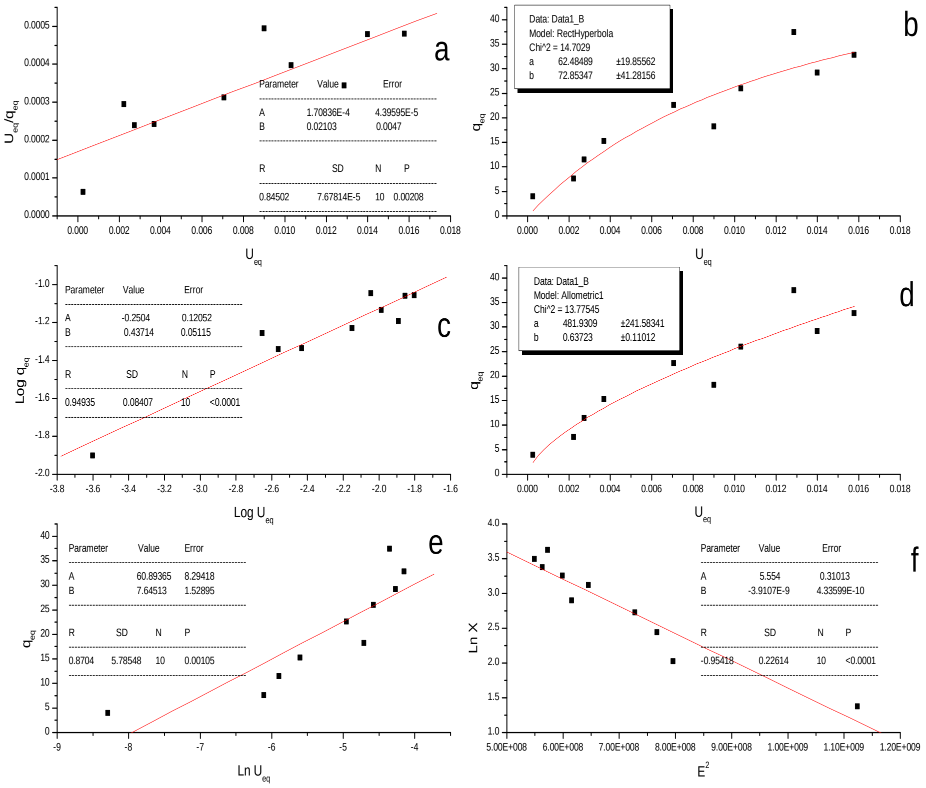

Figure 10: Sorption isotherms of CaAGF.

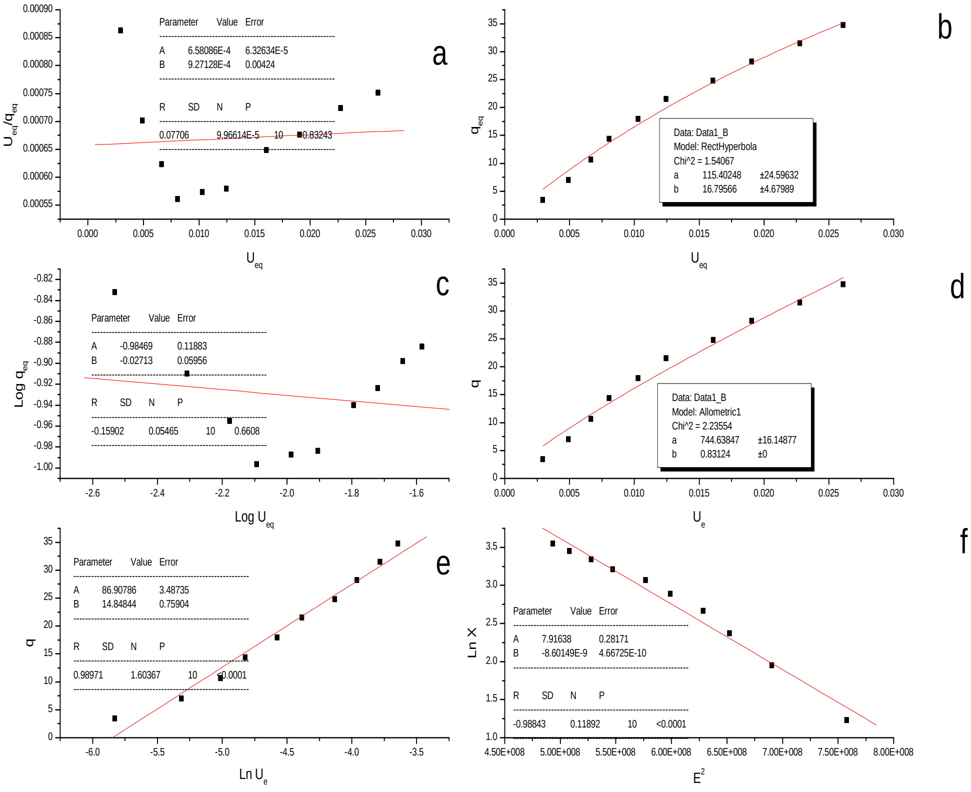

Figure 11: Sorption isotherms of WHRCaAGF.

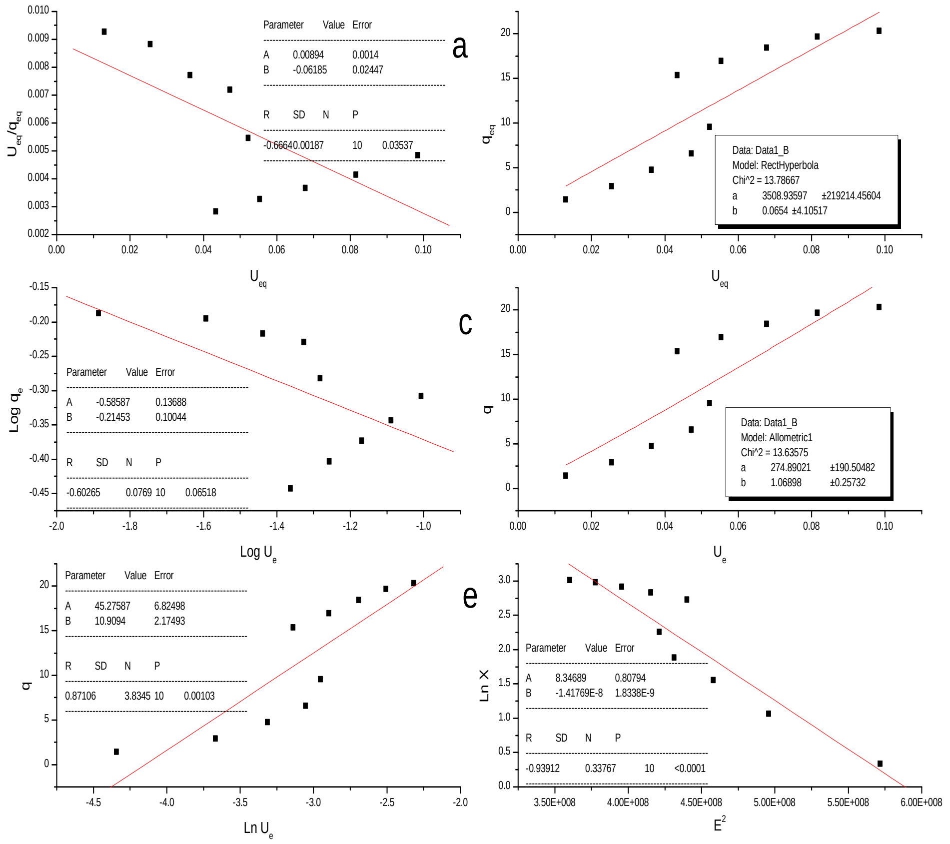

Figure 12: Sorption isotherms of CaADF.

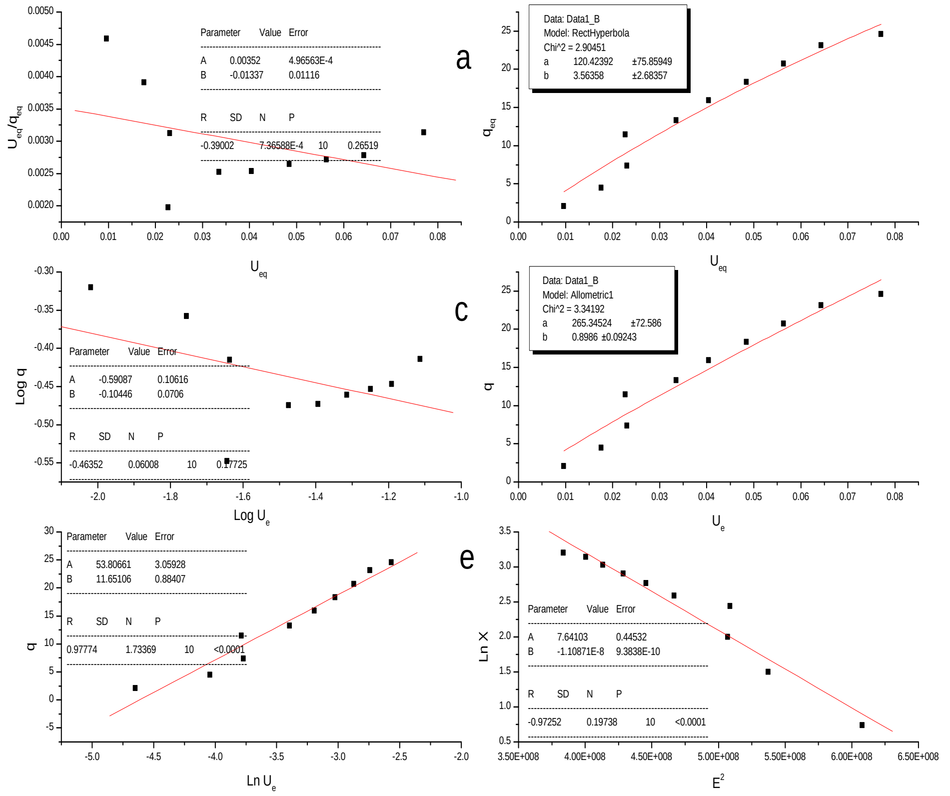

Figure 13: Sorption isotherms of WHRCaADF.

By comparing the isotherms of every sorbent we can conclude that:

- WHR fits Langmuir isotherm more than Freundlich, Temkin and D-R isotherm as shown in Figure 9.
- CaAGF fits Freundlich isotherm more than Langmuir, Temkin and D-R isotherm as shown in Figure 10.
- WHRCaAGF fits Langmuir isotherm more than Freundlich, Temkin and D-R isotherm as shown in Figure 11.
- CaADF fits D-R isotherm more than Langmuir, Freundlich and Temkin isotherm as shown in Figure 12.
- WHRCaADF fits D-R isotherm more than Langmuir, Freundlich and Temkin isotherm as shown in Figure 13.

This is in agreement with [Cem, and Sute, (2009)], where bio-sorption of uranium by Ca alginate (dry form) provided a good fit for Langmuir better than freundlich and did not fit Dubinin-Radushkevich isotherm.

WHR, CaAGF, and CaADF showed scattered experimental points around the curves of isotherms where the results of WHRCaAGF, and WHRCaADF are well fitted to sorption isotherms.

The isotherms results of WHR, and CaADF appeared as two separated groups which may indicate the presence of two mechanisms or functional groups. Both processes may different in activation energy and the nature of sites. In case of CaADF, there are two curves each of them with different slope and intercept i.e. different activation energy (D-R isotherm).

b is the constant related to the free energy of the adsorption (in case Langmuir isotherm)

$$b= a\ e\text{-}\Delta G/RT \qquad (7)$$

It reflects the sorbent-sorbate affinity. Higher b value is indicative of more favorable sorption. The b values for WHR, CaAGF, WHRCaAGF, CaADF, and WHRCaADF, are 0.06068, 72.8, 16.79, 0.0654, and 3.56, respectively.

The b results revealed similar affinity of both WHR and CaADF. CaAGF, WHRCaAGF and WHRCaADF have higher affinity than the freely WHR, and CaADF. It may indicate that the uranium is more stabilized by CaAGF, WHRCaAGF and WHRCaADF, thus resulting in a higher affinity matrix.

Maximum sorption capacity calculated from Langmuir isotherm was 16.9 mg/g for WHR, 62.48 mg/g for CaAGF, 115.4 mg/g for WHRCaAGF and 120 mg/g for WHRCaADF. CaADF represented the highest sorption capacity of 3508.93 mg/g.

It should be considered that 1gm from CaADF is obtained from drying of 23.986 g CaAGF, while 1gm from WHRCaADF is obtained from drying of 12.40 g from WHRCaAGF. Therefore, 23.9 g from CaAGF can sorb 1498.65 mg which produce 1g dried material and can absorb 3508.9 mg from uranium. 12.4 g of WHRCaAGF can sorb 1431 mg and when dried to 1 g (WHRCaADF) can absorb 120.4 mg uranium.

Sorption kinetics

The sorption kinetics first order linear form of WHR, CaAGF, WHRCaAGF, CaADF, WHRCaADF are shown in Figures 14 to 18where a, b, c, and d represent first order linear, first order nonlinear, second order linear, and second order nonlinear respectively. Figure 14 (a) is empty as the first order linear form was not applicable to WHR.

Two sorption kinetic models were used in order to quantify the changes in the sorption with time and also to evaluate the kinetic parameters, namely a first – order kinetic equation and a pseudo- second order kinetic equation.

The first order nonlinear equation form:

$$q = q_e(1 - k_1^t) \qquad (8)$$

And the second order nonlinear equation form:

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \qquad (9)$$

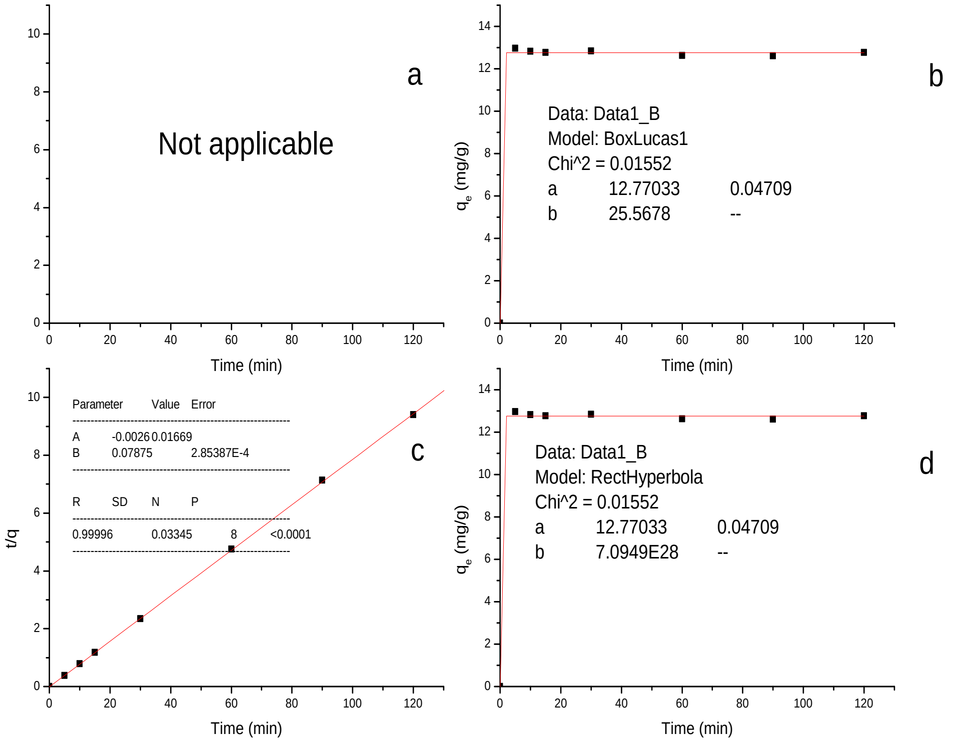

Figure 14: Sorption kinetics of WHR.

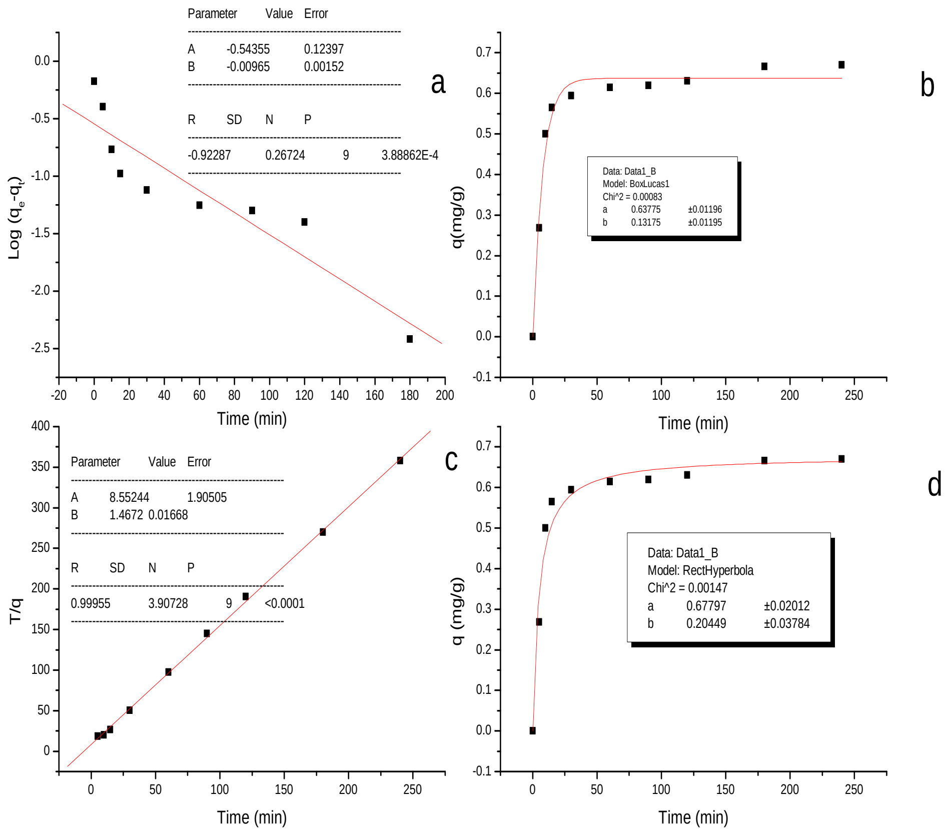

Figure 15: Sorption kinetics of CaAGF.

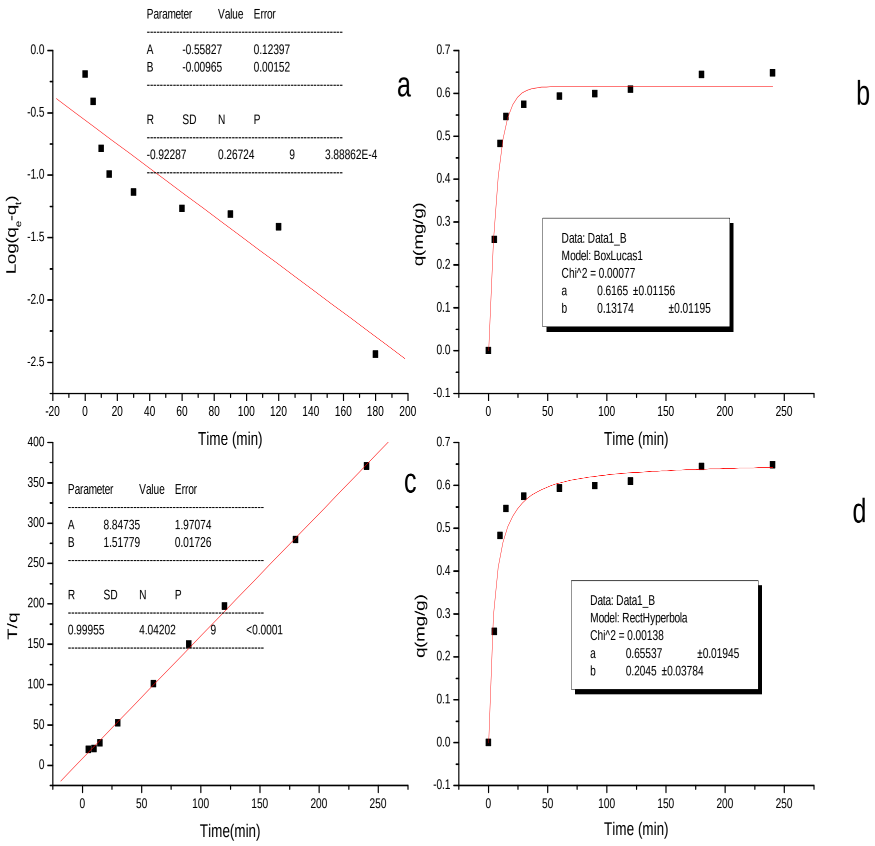

Figure 16: Sorption kinetics of WHRCaAGF.

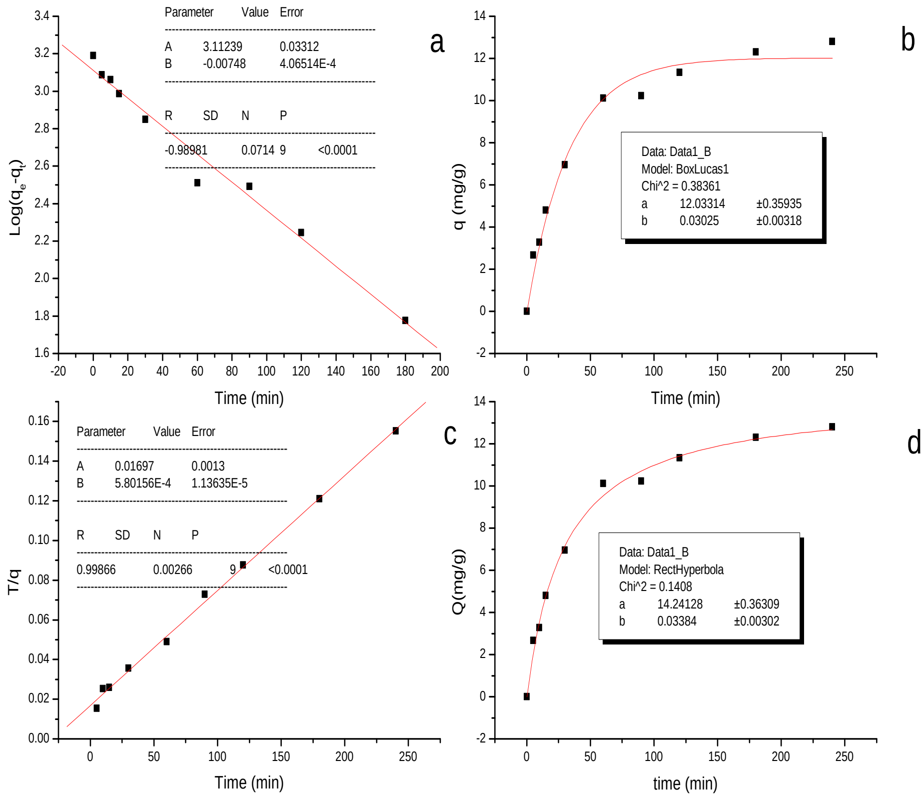

Figure 17: Sorption kinetics of CaADF.

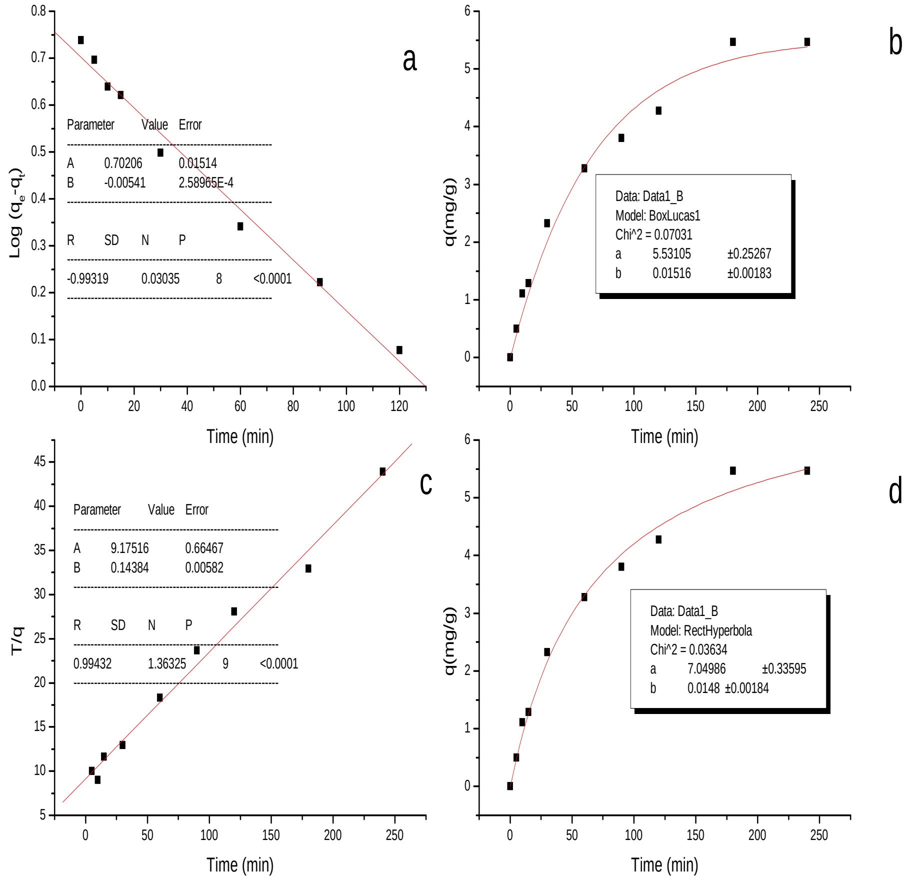

Figure 18: Sorption kinetics of WHRCaADF.

WHR, CaAGF, WHRCaAGF, CaADF, and WHRCaADF followed the second kinetic linear form, with strong linear regressions; 0.99996, 0.99955, 0.99955, 0.99866, and 0.99432 respectively. On the hand CaADF, and WHRCaADF followed the first kinetic linear form, with strong linear regressions; 0.99866, and 0.99432 respectively.

WHR, CaAGF, WHRCaAGF, CaADF, and WHRCaADF obeyed the second kinetic order non-linear better than the kinetic first order nonlinear form.

Comparing the results of the first and the second kinetic order shows that WHR, WHRCaAGF, CaADF, and WHRCaADF obey the second kinetic order better than the kinetic first order form.

Sorption thermodynamics parameters

Thermodynamic parameters determined by changing the temperature (T) from 298 to 333 K. Based on fundamental thermodynamics concept, supposing that the reaction is in an isolated system, system energy can't be gained or lost and the entropy change is the only driving force. In order to gain insight into the mechanism involved in the sorption. The variations including standard Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy change (ΔS°) for the sorption were calculated from the slope and intercept from the plots of log K_d versus 1/T, according to equation 2, 3, and 4.

$$K_d = y / M_e \quad (10)$$

$$\text{Log } K_d = \Delta S°/R - \Delta H°/RT \quad (11)$$

$$\Delta G° = \Delta H° - T\,\Delta S° \quad (12)$$

Where K_d is the distribution coefficient. ΔS° is the standard change in the entropy (kj/mol), ΔH° is the standard change in the enthalpy (kj/mol), ΔG° the standard change in Gibbs free energy (kj/mol) and T is the temperature (K) and R universal gas constant.

	ΔH (kj/mol)	**ΔS (kj/mol)**	**ΔG°(kj/mol)**				
			298K	**303K**	**313K**	**323K**	**333K**
CaAGF	7.808	0.045	-5.84	-6.07	-6.53	-6.99	-7.45
WHRCaAGF	38.986	0.151	-6.15	-6.91	-8.43	-9.94	-11.46
CaADF	35.32	0.121	-0.88	-1.48	-2.69	-3.91	-5.13
WHRCaADF	18.582	0.06791	-1.657	-1.99	-2.68	-3.36	-4.03

Results show positive ΔH° values which indicate the endothermic nature of the sorption. This fact was supported by the increase in the sorption as temperature increased. Furthermore, the negative ΔG° indicate that uranium sorption was spontaneous and thermodynamically favourable. The further decrease in ΔG° with increasing temperature implies more driving force, spontaneous sorption and more preference at higher temperature. The positive ΔS° relieved that the degree of freedom increased at the solid-liquid interface during the sorption.

The thermodynamics of CaAGF, WHRCaAGF, CaADF, WHRCaADF are shown in Figure 19. WHR not presented as it was not affected by the temperature change as shown before in Figure 8.

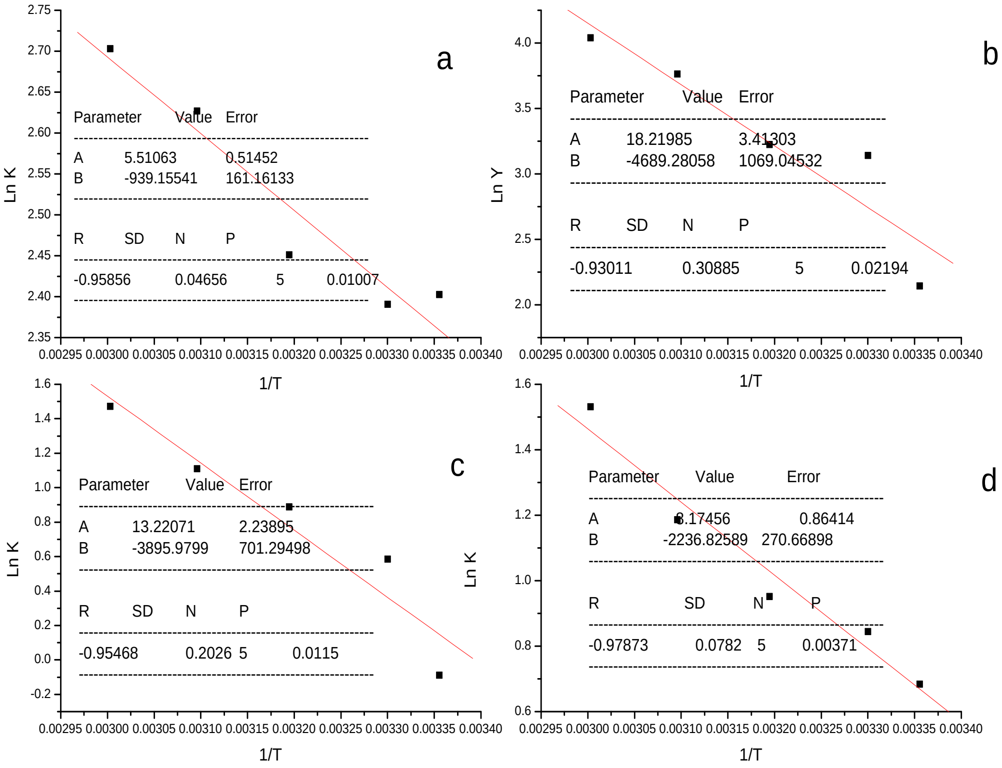

Figure 19: Influence of temperature on the thermodynamic behaviour of uranium sorption using CaAGF (a), WHRCaAGF (b), CaADF (c) and WHRCaADF(d).

CONCLUSION

W*ater hyacinth* roots were successfully immobilized by Ca alginate -in gel and dry form- and proven capabilities as uranium sorbent. Studying the effect of concentration, weight, and volume on sorption show that CaAGF provided the highest sorption followed by WHRCaAGF. WHRCaADF provided higher sorption than CaADF with pH and contact time. As a result of immobilization, the sorption of uranium became slower than that of free WHR, CaAGF, and CaADF. While WHR, CaAGF, and CaADF need 5, 10 and 90 min to sorb 65% of uranium, WHRCaAGF and WHRCaADF required 15 and 180 min. In general the sorption of uranium by the five sorbents was fast. Sorption of uranium decreased for all studied sorbents by increasing solution volume. WHRCaADF was the most influenced by changing the volume of solution where the sorption dropped from 67% at 20 ml to 2.52% at 50 ml. Temperature had an obvious effect on sorption by CaADF and WHRCaADF, where increasing temperature from 25 to 60˚C increased sorption from 48% and 66% to 83% and 82% respectively. WHRCaAGF had the highest sorption at 25˚C.

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