



## Kinetic and Thermodynamic Studies on Uranium Ions Recovery Using Magnetite- Dowex 50WX8 composite

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Batch Experiments on synthesized "Magnetite-Dowex 50WX8" composite were conducted to characterize its capability of uranium adsorption. The effect of pH, contact time, composite dose, initial uranium concentration and temperature on uranium adsorption rate was investigated to optimize the operation conditions of the synthesized composite. Thermodynamic and kinetic parameters have been studied. The maximum sorption capacity from Langmuir reached 200 mg/g at room temperature, pH 4, 25 mg of composite and 30 min. contact time. Uranium adsorption kinetics is well fitted to pseudo second order kinetic model at 500 mg/L uranium concentration. The change in the thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) indicates that the adsorption process is a spontaneous exothermic random process. Loaded hexavalent uranium ions were stripped from the loaded composite using 0.25M nitric acid. Optimum conditions were applied to purify the dissolved uranium content from a leaching solution of a granite sample from El-Missikat area, Central Eastern Desert, Egypt.

**Keywords:** Magnetite-Dowex 50WX8, Ion-exchange, Uranium, Thermodynamics, Kinetics

### Introduction

Uranium is the conventional nuclear fuel used for nuclear power plants for peaceful applications. The growing demand of uranium supply is due to its prospective features [1]. Uranium milling processes have resulted in progressive exploration and development of advanced techniques to produce massive uranium concentrates worldwide [2-4]. Various techniques involved the recovery and separation of uranium out leaching solutions, including direct precipitation, solvent extraction, chromatographic separation, ion-exchange techniques, membrane dialysis, solid-liquid extraction, filtration, composite-in-pulp, bio-sorption and electro-deposition [5-27]. Most of such methods face technical and financial obstacles related to selectivity and duration of separation process and safety measures while dealing with hazardous materials applied in large

quantities. Ion-exchange separation is considered one of the most reliable methods to remove trace levels of ions, due to its cost-effectiveness, simplicity and versatile nature [28, 29]. Adsorption processes, especially ion-exchange techniques are applied commercially for isolation, pre-concentration and recovery of uranium ions from its solutions using specific composites. Among these composites; Amberlite IRA (100 mesh), Dowex-1X8 [30]. Amberlite IRA 402 is commonly used for uranium adsorption from sulfate solutions [31]. Adsorption of uranium onto Amberlite CG-400 composite is applicable from phosphate media [32]. Several studies covered the nature of uranium (VI) separation by Amberlite IRA-910 as well as Amberlite IR-118H [33, 34]. Uranium can also be recovered from acidic leach liquor using Ambersep 920U SO<sub>4</sub> composite [35].

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Different natural materials such as clays, seaweed and biomass, as well as synthetic materials including activated carbon, composites, and mesoporous silica have been used to adsorb heavy metals [36]. Uranium removal by chelating composites is a promising technique that has been reported in many studies [37, 38]. The only drawback of ion-exchange techniques is its high cost and the requirements for advanced pretreatment systems. Recently, the application of iron oxides, especially magnetite nano-particles for heavy metals removal have been investigated, due to their minute size, magnetic separation and the ease of synthesis, coating and modification [39-42]. However, magnetite nano-particles lose some of their magnetic properties due to aerial oxidation. Coating with inorganic shell such as silica and carbon was studied and was found to be capable of improving the chemical stability of magnetite nano-particles [43 - 45]. The use of magnetic composites in separation of heavy metals has been studied exclusively [46].

Early in 1995, magnetic ion-exchange composites were applied for the removal of organic matter [43]. Magnetic composites are easily isolated from solutions through application of an external magnetic field and are characterized by their high uptake capacity compared to free magnetic nano-particles [44].

It was found that in sulfate leach liquors of El Missikat ores that Mo in its hexavalent state is similar to the hexavalent U and thus may form anionic complexes of the type  $\text{MoO}_2(\text{SO}_4)_n^{2-2n}$ . These can be adsorbed more strongly than uranium complexes and are not removed by normal elution process, which leads to the reduction of uranium capacity of the composite [47]. El-Missikat granite ore materials have been subjected to direct agitation leaching technique using diluted sulfuric acid beside sulfatization roasting, as well as pressurized alkaline leaching processes. Alkaline leached proved to be more effective in recovering most of uranium content (95.6%), while the leaching extent of Mo was 93.1 %. However, the recovery of both U and Mo would be greatly facilitated when using this technique [48].

In this work, magnetite-Dowex 50WX8 composite was prepared using co-precipitation method. The prepared composite has been synthesized, characterized and tested to calculate adsorption kinetics and thermodynamic parameters of uranium adsorption from El-Missikat leach liquor.

## Experimental

### *Dowex 50WX8 characteristics*

A strong acid cation-exchange Dowex 50WX8 composite of Dow Co. was used in this work to synthesize magnetite-Dowex 50WX8 composite. The used composite contains exchangeable  $\text{H}^+$  ions. The porous nature of the polymeric structure provides the composite its superior adsorption capacity of large ions. It retains its activity from sulfonic groups. Dowex 50WX8 has excellent regeneration efficiency due to cross-linked polystyrene, excellent physical stability and high adsorption capacity. The structure of Dowex 50WX8 provides an excellent stability towards organic as well as inorganic decomposition. The adsorption capacity of the applied composite was found to be 1.7 meq/ml. It means that, the uptake capacity of Dowex 50W-X8 for uranium (VI) adsorption is 67.43 mg/g.

### *Synthesis of (Magnetite-Dowex 50WX8) composite*

One gram of Dowex 50W-X8 composite was put in beaker containing one gram of each of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and Ferric oxide. The mixture of Dowex and iron salts was diluted to 300 ml with distilled water, heated to 80 °C while stirred at 200 rpm for 3 hours. After cooling, ammonium hydroxide solution was added to precipitate iron at pH 10-12 [49]. The solution was filtered and washed with distilled water. The obtained precipitate was dried at 80°C. The prepared magnetite-Dowex 50WX8 composite was synthesized at optimum conditions, except for iron sulfate salts that have been used instead of iron chloride ones.

### *Characterization of adsorbent*

#### *Fourier transform infrared spectrometer characterization*

Fourier-transform infrared spectroscopy (FTIR) is a technique used to identify molecular and functional groups [50]. FTIR model "Thermo Scientific Nicolet IS10" instrument via KBR pressed disc method, in a range starting from 400 to 4000  $\text{cm}^{-1}$  wave number was used. The obtained Data of Dowex 50WX8 as well as the prepared magnetite-Dowex 50WX8 composite are shown on (Fig.1a and 1b). From which, the peak is observed at 3501  $\text{cm}^{-1}$  corresponding to O-H stretching. The C-H stretching in alkene appeared at 2932  $\text{cm}^{-1}$ , while the band at 1643  $\text{cm}^{-1}$  correspond to C=C of alkene. The bands at 1496, 1452, 1413  $\text{cm}^{-1}$  are related to C=C ring stretching. The peaks obtained

at 1185 and 1126  $\text{cm}^{-1}$  stand for S-OH and S(=O)<sub>2</sub> respectively. The two bands at 1039 and 1006  $\text{cm}^{-1}$  are attributed to S-O-C stretching. The C=C in alkene appeared at 836  $\text{cm}^{-1}$ . The band at 677  $\text{cm}^{-1}$  is due to C-S stretching band. Finally, the peaks at 580 and 621  $\text{cm}^{-1}$  are related to atactic polystyrene Fig. (1a).

On the other hand, the prepared (magnetite-Dowex 50WX8) composite showed two bands at 532 and 455  $\text{cm}^{-1}$  that are attributed to Fe-O bending. The O-H band is shifted to 3336  $\text{cm}^{-1}$ . The band at 2932  $\text{cm}^{-1}$  disappeared, indicating the formation of magnetite composite. Absorbance bands for most groups have been shifted for the prepared magnetite composite due to the precipitation of iron on Dowex50WX8. This attitude confirms the coordination bonding of Fe to the Sulfur atom of the strong cation exchange Dowex 50WX8 Fig.

(1b).

#### *Environmental scanning electron microscope "ESEM"*

ESEM has become a powerful device for material examination [51]. Environmental scanning electron microscope Philips XL30 ESEM FEG has been used at the working temperature of the emitter 1800°K, 25-30 KV accelerating voltage, 1-2mm beam diameter and 60-120s counting time, minimum detectable weight concentrations ranging from 0.1 to 1 wt%, while the realized precision is below 1%.

The image of the surface of magnetite-Dowex 50WX8 composite is shown in Fig. (2). After iron precipitation, homogeneous brilliant spots are observed on the composite beads that are free of agglomeration. The size of the composite is 50 nm

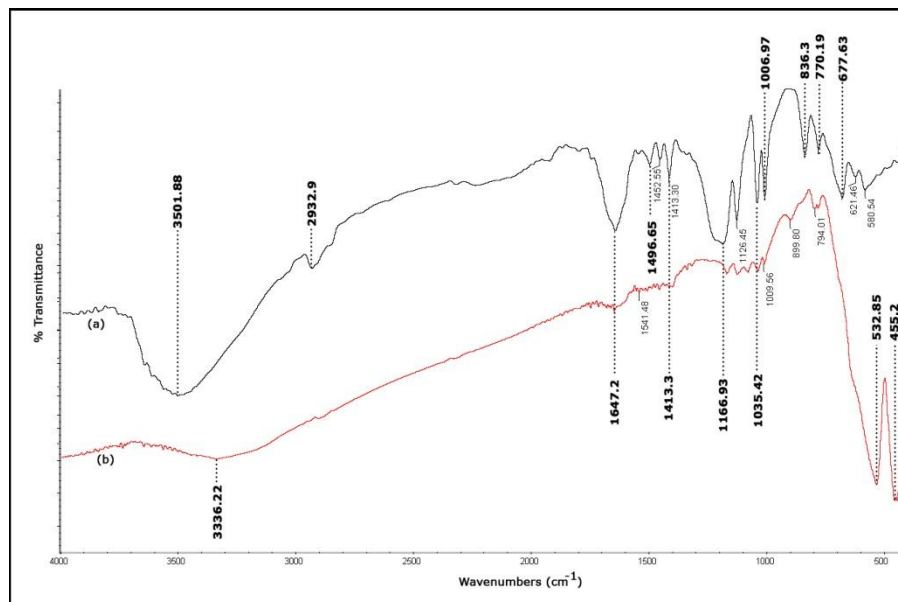


Fig. (1): FTIR chart of the Dowex 50WX8 (a) and prepared (magnetite-Dowex 50WX8) composite (b)

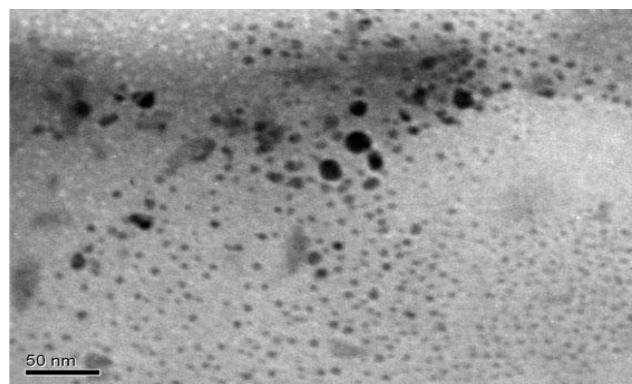


Fig. (2): SEM of prepared (magnetite-Dowex 50WX8) composite

*Analytical procedures*

Uranium was measured volumetrically by oxidation-reduction titration Vs  $[\text{NH}_4]\text{VO}_3$  [52]. Data was collected and compared to spectrophotometric analysis of U by Metertech Inc (SP-8001) using Arsenazo III method at  $\lambda$  655 nm [53]. Major oxides such as silica, alumina and titanium oxides were quantified spectrophotometrically via standard analytical techniques while sodium and potassium oxides were measured using flame photometer.  $\text{Fe}_2\text{O}_3^T$ , CaO and MgO have been determined by volumetric titration [54]. Each sample was analyzed in triplicate. Trace elements were analyzed using ICP-MS at Henri Poincare University laboratories, Nancy, France [55]. Quality control of the analyses was confirmed using international geostandards

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*El-Missikat sample*

El Missikat uranium prospect lies at midway along Qena-Safaga road in the Central Eastern Desert of Egypt Fig. (3). El Missikat prospect, as a wide shear zone striking ENE-WSW direction, comprises generations of silica veins crosscut in a wide younger granite pluton Fig. (4). Some of these silica injections are associated with uranium and other valuable minerals.

*Preparation of El-Missikat sample*

The studied El-Missikat sample was attacked using mixture of acids HF,  $\text{HNO}_3$ ,  $\text{HClO}_4$  and HCl, to quantify major oxides inside the samples collected

from El-Missikat shear zone, Central Eastern Desert, Egypt Table (1). The analyses of trace elements (ppm) were determined and shown in Table (2).

*Preparation of El-Missikat leach liquor*

To prepare the leach liquor, El-Missikat samples were leached at optimum conditions to ensure the maximum uranium leaching efficiency (83.3%) with minimum contamination of unwanted species. Optimum conditions are -200 mesh grinding size, 0.2M  $\text{HNO}_3$ , 3:1 Liquid: solid ratio, 200 rpm agitation speed for 3 hours at 60 °C. After cooling, the solution was filtered then, uranium was measured in leach liquor.

The obtained leach liquor uranium concentration was found to be 2000 mg/L, while the concentration of uranium in El-Missikat ore sample was 2400 mg/L Table (1).

*Adsorption studies*

Batch adsorption experiments were performed by agitation of the pregnant solution together with a certain amount of composite for a certain time at a definite temperature till equilibrium was achieved. In order to estimate the best conditions for uranium adsorption from solution using (magnetite-Dowex50WX8) composite, the mixture was mechanically stirred at 200 rpm at variable pH values from pH 1 to pH 7, while changing the composite amount and uranium concentrations along from 50 to 1000 ppm at different agitation time intervals from 5 to 120 minutes and variable degrees of temperature. The composite was filtered off and uranium was measured in the filtrate each time. Adsorption capacity for uranium ( $q_e$ , mg/g) as well as uranium adsorption efficiency (%E) and distribution coefficient ( $K_d$ ) were calculated from the mathematical relations:

$$q_e = (C_o - C_e) \times v / m \quad (1)$$

$$E (\%) = 100 (C_o - C_e) / C_o \quad (2)$$

$$K_d = [(C_o - C_e) / C_e] \times V / m \quad (3)$$

Where;  $C_o$  and  $C_e$  are uranium concentrations initially and at equilibrium state respectively measured in ppm, V is the aqueous solution volume, while m is the mass of the dry composite in grams.

*Elution studies*

Different agents have been tested for such purpose; HNO<sub>3</sub>, HCl and H<sub>2</sub>SO<sub>4</sub> acids were used to strip uranium ions from the loaded composite. In each

experiment, 25 mg of the loaded composite were shaken with 10 ml of each eluting agent at variable concentrations for 30 minutes at room temperature.



Fig. (3): Location map of El-Missikat granite, Central Eastern Desert, Egypt

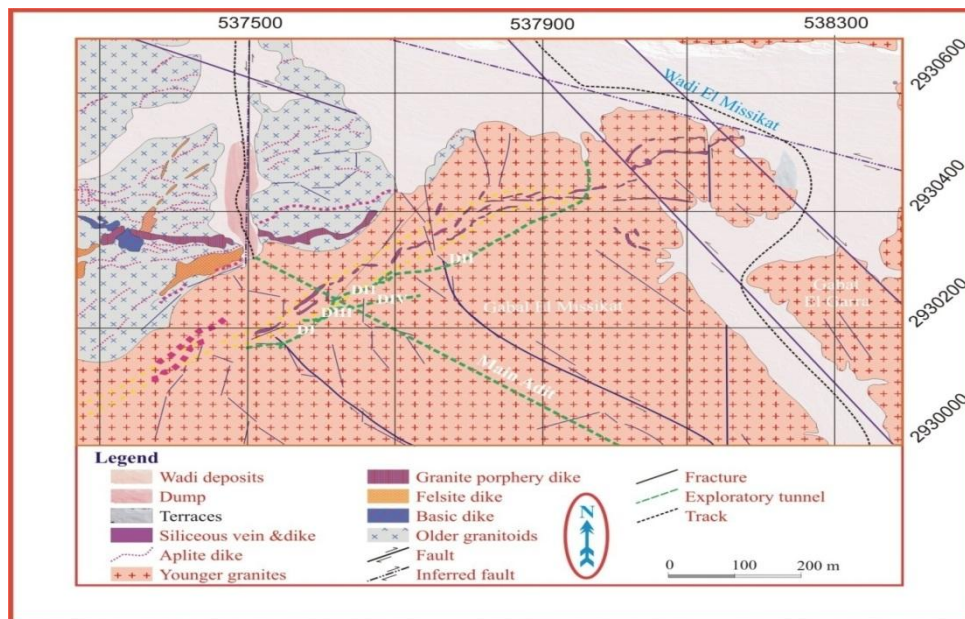


Fig. (4): El Missikat granite, shear zone and the Silica veins, after [56]

**Table (1): Chemical composition of major oxide (wt %) and uranium concentration (mg/L)**

<b>Major oxides</b>	<b>Wt %</b>
<b>SiO<sub>2</sub></b>	92.7
<b>Al<sub>2</sub>O<sub>3</sub></b>	2.9
<b>TiO<sub>2</sub></b>	N.D*
<b>Fe<sub>2</sub>O<sub>3</sub><sup>T</sup></b>	0.67
<b>CaO</b>	1.67
<b>MgO</b>	N.D*
<b>Na<sub>2</sub>O</b>	N.D*
<b>K<sub>2</sub>O</b>	N.D*
<b>P<sub>2</sub>O<sub>5</sub></b>	N.D*
<b>L.O.I</b>	1.74
<b>Total</b>	99.7
<b>U</b>	2400 (mg/L)

\*N.D= not detected (under limit of detection)

**Table (2): Trace elements content (ppm) using ICP-MS technique**

<b>Trace elements</b>	<b>(ppm)</b>
<b>Ba</b>	200
<b>Rb</b>	4.75
<b>Sr</b>	22.7
<b>Ta</b>	21.4
<b>Nb</b>	130
<b>Zr</b>	177
<b>Y</b>	157
<b>Th</b>	20.8
<b>Pb</b>	1868
<b>Zn</b>	177
<b>Hf</b>	12
<b>Ni</b>	6
<b>Ga</b>	10.3
<b>Mo</b>	1570

## Results and Discussion

### *pH of uranium solution*

The pH value of the uranium solution is so important for successful uranium adsorption by any composite. The pH value directly affects both the soluble aqueous uranium species present in solution as well as the composition of active sites on the adsorbent surface [57]. The retention of uranium (VI) on prepared (magnetite-Dowex 50WX8) composite was studied in pH range 1-7 using 10 ml uranium solution conc. 500 ppm, 0.025 grams of composite and 200 rpm agitation speed for 30 minutes. The obtained results indicated that uranium (VI) adsorption efficiency rises with pH range from 1 to 4 (adsorption efficiency= 95%, and  $q_e$ = 190 mg/g) and then, adsorption decreases with increasing pH till 7 (Fig. 5). The maximum sorption capacity for uranium ions was found to be at the pH value of 4 for the prepared (magnetite-Dowex 50WX8) composite. This may be attributed to the limitation of uranium adsorption below the pH value of 3, due to the electrostatic repulsive forces between the prepared (magnetite-Dowex 50WX8) composite and metal ions, and the hindering of metal ions sorption on the surface [58, 59]. At the pH value of 4, the adsorption increases due to the enhanced ionization of sorption sites owing to the competition between uranium and  $H_3O^+$ . At pH 5, most of the metal ions precipitate as hydroxides.

### *Contact time*

The influence of varying contact time was monitored while fixing other conditions that affect uranium adsorption. The agitation time was varied from 5 to 120 minutes. It was found that the uranium adsorption efficiency on the prepared (magnetite-Dowex 50WX8) composite increased as time of agitation was increased Fig. (6). Adsorption nearly reached equilibrium after 30 minutes. Furthermore, there was no significant change in uranium adsorption by the studied composite in the next 60 minutes. Uranium uptake slowly increased from 79 % at the first 5 minutes till 95 % through 30 minutes (adsorption efficiency =95%,  $q_e$ = 190 mg/g). Beyond this time, no change in adsorption occurred; this revealed that equilibrium was reached.

### *Uranium solution concentration*

A series of solutions, 10 ml each, with different uranium concentration from 50 to 1000 ppm were

contacted with 25 mg of composite at a pH value of 4 and 200 rpm agitation speed for 30 minutes. Results obtained are presented in terms of adsorption efficiency and maximum uranium uptake ( $q_e$ ) in Fig. (7), which reveals that the adsorption of uranium on the prepared composite decreases from (98-95%) with (50-500 ppm) and drops to 50% with 1000 ppm solution. A solution of initial uranium concentration of 500 ppm was found to be suitable enough as it corresponds to an adsorption efficiency of 95% and  $q_e$ = 190 mg/g).

### *Temperature variance*

For testing this factor, adsorption efficiency was monitored at a temperature range from 25°C to 100°C, while fixing all other variables; 500 ppm uranium concentration, pH 4 and 200 rpm stirring speed for 30 minutes. The results are presented in Fig. (8) that shows that the efficiency of uranium adsorption by the studied composite decreases from 95% at 25°C to 50% at 100 °C. It was concluded that the best temperature to perform uranium adsorption by the studied medium was room temperature, (adsorption efficiency =95%,  $q_e$ = 190 mg/g).

### *Composite dose*

The influence of composite dose has been investigated ranging from 10 to 250 mg mixed with 10 ml volume of uranium solution at optimum conditions of other factors. The results in Fig. (9) shows that the adsorption efficiency changed from 85 % using only 10 mg of composite till reaching 95% using 25 mg and then, remained constant with increasing composite dose. Therefore, the required composite dose to adsorb uranium (VI) was chosen to be 25 mg, (adsorption efficiency =95 %,  $q_e$ = 190 mg/g). Increasing the adsorbent dose provides more available sorption sites and high surface area. It can be concluded that the composite gives a higher uranium adsorption using the prepared (magnetite-Dowex50WX8) composite.

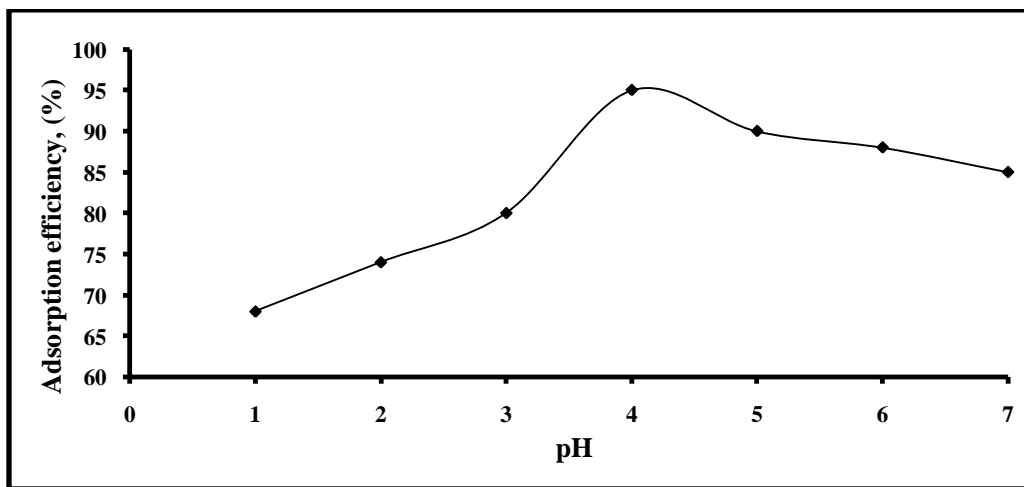
### *Desorption and regeneration of the prepared composite*

Three eluting agents were tested to determine which offers the best elution efficiency. Different concentrations of the tested acids were prepared from 0.12M to 1.0M. A volume of 10 ml of the prepared eluent solution was allowed to contact with 25mg of the composite for 30 minutes. The results obtained in Table (3) clarify that desorption

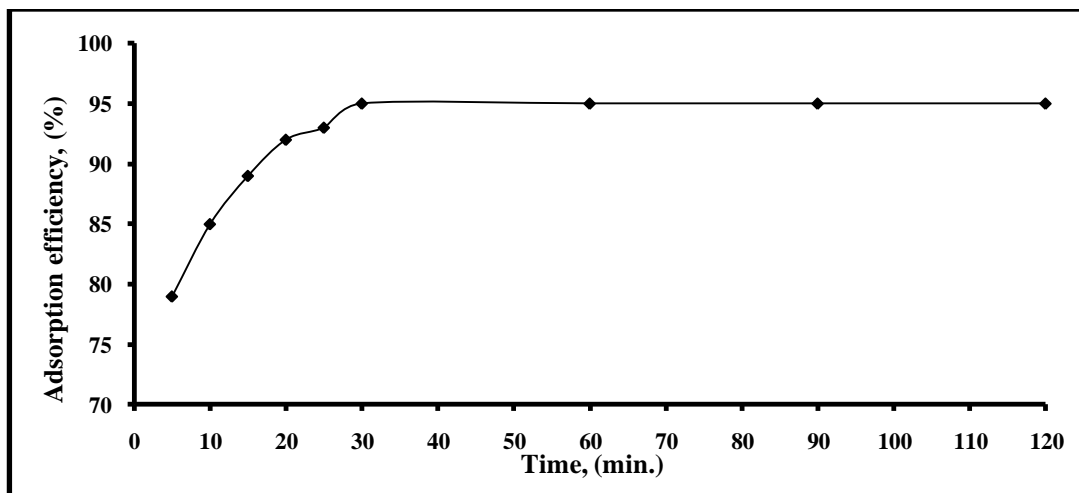
efficiency increased as acid concentration of the eluting solution increased. The best elution efficiency was found to be 99% with 50 ml of 0.25M HNO<sub>3</sub> or 0.75M H<sub>2</sub>SO<sub>4</sub> and 85% with 1M HCl acid solution from 25 mg loaded composite. The uranium loaded onto the prepared composite was dissolved using 0.25M HNO<sub>3</sub>. The adsorption-elution process was repeated several times till adsorption efficiency was reduced to 85% and elution was reduced to 90% after ten cycles. This indicated the superior affinity of the prepared magnetite-Dowex 50WX8 composite for uranium recovery.

#### *Stability of the prepared (magnetite-Dowex 50WX8) composite*

A series of prepared 10 ml of different HNO<sub>3</sub> concentrations ranging from 0.1 to 3M were mixed with 25 mg of the prepared composite at 200 rpm for 30 minutes at room temperature. The prepared composite was separated and Fe content was measured in the filtrate. Iron dissolution was not detected by 0.1-0.6M HNO<sub>3</sub>. Beyond this concentration, iron dissolution increased from 0.035 % by 0.7M HNO<sub>3</sub> to 5% by 3M HNO<sub>3</sub> Table (4). Accordingly, a recommended concentration of HNO<sub>3</sub> in the range 0.1- 0.6M was added to keep the stability of the prepared composite and to prevent unwanted dissolution of iron.



**Fig. (5):** Effect of pH on uranium adsorption efficiency using the prepared (magnetite- Dowex 50WX8) composite  
*Adsorption conditions: 500 ppm uranium concentration, 30 min. contact time, room temperature and 25 mg composite dose*



**Fig. (6):** Effect of contact time (min.) on uranium adsorption efficiency using the prepared (magnetite-Dowex 50WX8) composite  
*Adsorption conditions: 500 ppm uranium concentration, pH 4, room temperature and 25 mg composite dose.*



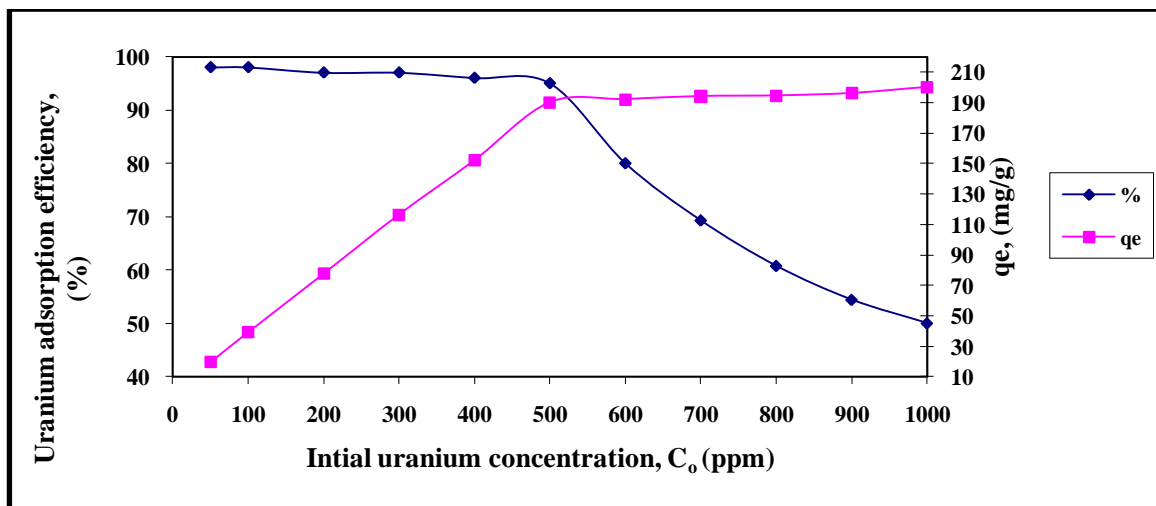


Fig. (7): Effect of initial uranium concentration (ppm) on uranium adsorption efficiency using the prepared (magnetite-Dowex 50WX8) composite

Adsorption conditions: pH 4, 30 min. contact time, room temperature and 25 mg composite dose.

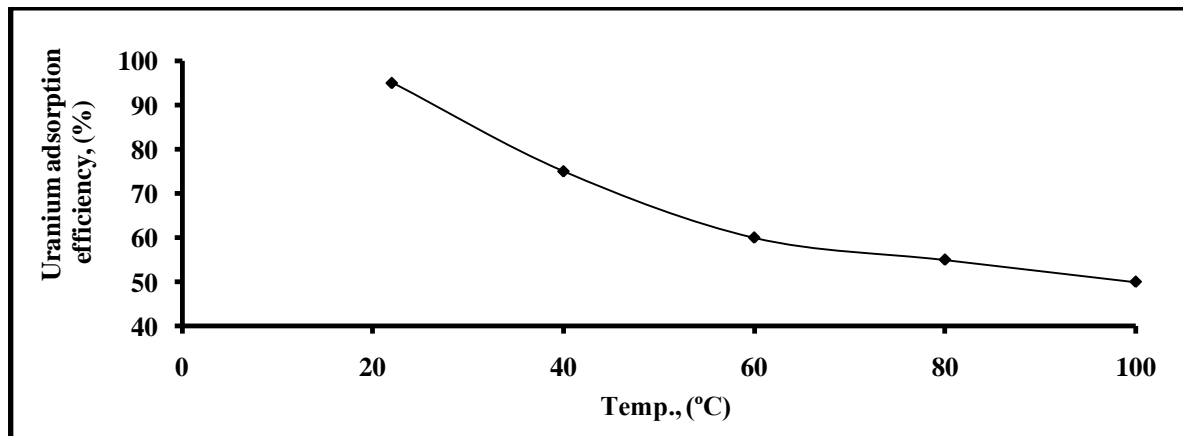


Fig. (8): Effect of temperatures on uranium adsorption efficiency using the prepared (magnetite-Dowex 50WX8) composite

Adsorption Conditions: 500 ppm uranium concentration, 30 min. agitation time, pH 4 and 25 mg composite dose.

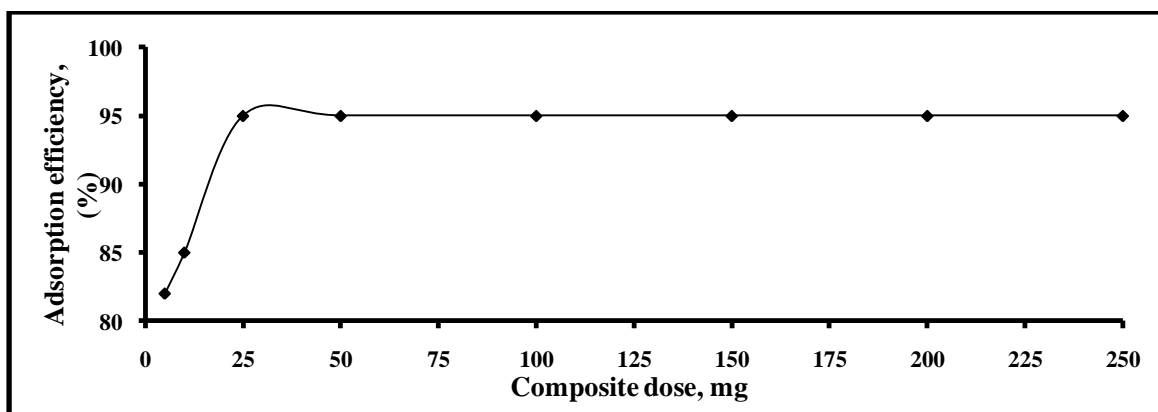


Fig. (9): Effect of composite dose on uranium adsorption efficiency using the prepared (magnetite-Dowex 50WX8) composite

Adsorption conditions: 500 ppm uranium concentration, 30 min. contact time, room temperature and pH 4.

Table (3): Effect of eluting agents on uranium loaded onto prepared (magnetite-Dowex 50WX8) composite

Concentration, (M)	Elution efficiency, %		
	HNO <sub>3</sub>	HCL	H <sub>2</sub> SO <sub>4</sub>
0.12	91	75	76
0.25	99	80	84
0.5	99	83	95
0.75	99	83	99
1	99	85	99

*Adsorption conditions:* 500 ppm uranium concentration, 30 min. contact time, room temperature, 25 mg composite dose and pH 4.

Table (4): Effect of nitric acid concentrations (M) on the Fe<sub>2</sub>O<sub>3</sub><sup>T</sup> dissolution (%)

Nitric acid concentration, (M)	Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup> , (%)
0.1	-----
0.2	-----
0.3	-----
0.4	-----
0.5	-----
0.6	-----
0.7	0.035
1	0.5
1.25	0.7
1.5	0.85
1.75	1
2	3
3	5

### Adsorption equilibrium studies

Adsorption isotherms were used to characterize the uptake mechanism of uranyl ions by the prepared composite. Uranium ions can be adsorbed by several mechanisms that depend on the density and distribution of adsorption sites, surface area, and affinity of the adsorbent. The mechanism of adsorption also depends on the composition of the aqueous solution [60, 61]. Sorption experiments were conducted at optimum conditions. 10 ml of solution with initial U conc. of 500 mg/L are contacted with 25 mg of the prepared composite at a pH value of 4 and stirred at 200 rpm for 30 minutes at room temperature. Langmuir and Freundlich models were utilized to correlate experimental data. Langmuir model is built on a principle that adsorption mainly occurs as a monolayer surface of the adsorbing material and that adsorption energy is unchanged, while no migration of the adsorbed molecules occurs across the surface [62]. Langmuir model isotherm can be represented mathematically by the following relation:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{bq_{max}} \quad (4)$$

Where;  $C_e$  is the equilibrium concentration of uranium in the solution (mg/L),  $q_e$  is the amount of uranium adsorbed per weight unit of composite at equilibrium time (mg/g),  $q_{max}$  is the saturated monolayer adsorption capacity (mg/g) and  $b$  is the Langmuir constant (L/mg). The linear plots of  $C_e/q_e$  Vs  $C_e$  are shown in Fig. (10). As shown from Table (5), the values of maximum capacities ( $q_{max}$ ) are so close to those of experimental values with correlation coefficient  $R^2 = 0.9997$ . The results indicate that the U adsorption process obeys Langmuir isotherm model which implies that the prepared composite is homogeneous in the liquid phase and it is similar to the monolayer adsorption process.

$R_L$  is a dimensionless constant that stands for a separation factor and is used in the prediction of the degree of spontaneity of the sorption process. The value of that constant is calculated from the assumptions of Langmuir model by the following relation [63]:

$$R_L = 1 / (1 + bC_o) \quad (5)$$

Where;  $b$  is Langmuir constant and  $C_o$  is the initial concentration of uranium in solution (ppm). If  $R_L=0$ , this indicates that the isotherm is

irreversible, if ( $0 < R_L < 1$ ) then, the sorption process is favorable, if ( $R_L = 1$ ) then, the isotherm is linear and if ( $R_L > 1$ ) then, the sorption process is said to be unfavorable. The results show that ( $0 < R_L < 1$ ) in all cases, indicating that the sorption process is always favorable, according to Langmuir model isotherm.

Freundlich isotherm model assumes that adsorption occurs on a solid surface with heterogenous distribution of energies of the active sites, in a manner that the adsorption is accompanied by interactions between the adsorbed ions [64]. The Freundlich model isotherm can be illustrated mathematically by the following relation:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \quad (6)$$

Where;  $C_e$  is the equilibrium concentration of uranium in the solution (mg/L),  $q_e$  is the amount of uranium adsorbed per weight unit of composite at equilibrium time (mg/g).  $K_f$  is the adsorption capacity (mg/g) and  $1/n$  (L/mg) is the Freundlich constant related to the intensity of adsorption. The Freundlich constants  $K_f$  and  $1/n$  are calculated from the slope and intercept of the  $\log q_e$  vs.  $\log C_e$  plots Fig. (11). Adsorption isotherm parameters of Langmuir and Freundlich for adsorption of uranium onto the prepared composite are shown in Table (5). The value of  $K_f$  is lower than that of the untreated composite at room temperature. From the obtained data, the adsorbent does not obey Freundlich model isotherm.

### Sorption kinetics studies

The study of the kinetic parameters helps to predict the adsorption rate and gives overall information helpful to design and model any extraction process. Both pseudo-first order and pseudo-second order diffusion models were applied to analyze the kinetics of the sorption process of U (VI) onto the prepared composite. Sorption kinetics was studied at uranium concentration of 500 mg/L at pH 4, 200 rpm stirring speed and room temperature. The results were applied to both models. The pseudo first-order model can be mathematically represented by following relation [65]:

$$\text{Log}(q_e - q_t) = \log q_e - (K_1 / 2.303)t \quad (7)$$

Where;  $q_t$  and  $q_e$  stand for the quantity of uranyl ions adsorbed by the composite at time  $t$  and at

equilibrium in (mg/g), respectively. " $k_1$ " is the adsorption rate constant that can be estimated by plotting  $\text{Log}(q_e - q_t)$  Vs  $t$  Fig. (12).

From Table (6), the sorption capacity was determined from the intercept of the plots and was found to be 13.42 mg/g. The correlation coefficient  $R^2$  for this model was 0.6943 at 500 mg/L initial U(VI) concentration by the prepared (magnetite-Dowex 50WX8) composite. It was found that the adsorption processes did not follow pseudo first-order model.

the results were also applied to pseudo-second order kinetic model in the following form [66]:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e) t \quad (8)$$

Where;  $k_2$  is the rate constant (g/mg min). The straight lines of plots of  $t/q_t$  against  $t$  have a slope  $1/q_e$  and intercept at  $1/k_2 q_e^2$  (Fig. 13). The calculated value of  $q_e$  was 192.30 mg/g and correlation coefficient ( $R^2$ ) = 1, (Table 6). The results obtained obeyed the pseudo second-order model in a perfect manner at 190 mg/g. Accordingly, the pseudo second order model is suitable to describe the kinetic process of U (VI) adsorption by the prepared composite. The kinetic process is mainly controlled by the chemi-sorption that involves chemical bonding between uranyl ions and the composite active sites [67, 68].

#### *Thermodynamics of uranium adsorption*

The change in energy of molecules accompanying the adsorption process is concerned to the laws of thermodynamics. It helps to understand the appropriate mechanism of the studied adsorption process. Thermodynamic parameters studied involve the change in enthalpy or energy content ( $\Delta H$ ), change in entropy or randomness ( $\Delta S$ ) and the change in Gibbs' free energy ( $\Delta G$ ). These can be mathematically estimated by the following relations [69]:

$$\Delta G = -2.303RT \log k_d \quad (9)$$

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

$$k_d = (C_o - C_e)/C_e \times V/m \quad (11)$$

Where;  $K_d$  stands for the adsorption equilibrium constant,  $R$  is the universal gas, and  $T$  is temperature in °K. On plotting a graph of  $\text{Log } K_d$  Vs  $1000/T$ , the value  $\Delta H$  is estimated from the slope, while the value of  $\Delta S$  is estimated from the intercept Fig. (14).

The thermodynamic parameters estimated are listed in Table (7). The negative values of  $\Delta H$  suggest an exothermic nature of the adsorption of uranium onto the prepared composite. The value of  $\Delta G$  ensures that the reaction is spontaneous.

#### *Uranium (VI) adsorption from the studied leach liquor using the prepared (magnetite-Dowex 50WX8) composite*

From the obtained results, it was evident that the prepared (magnetite-Dowex 50WX8) composite is efficient for U(VI) adsorption from solution. A leach liquor of El-Missikat area containing 2000 mg/L uranium (VI) was used under the previously determined optimum conditions; pH 4, 200 rpm agitation speed for 30 minutes by 4L of the leach liquor with 10 grams of the prepared (magnetite-Dowex 50WX8) composite. The obtained results showed that uranium (VI) adsorption efficiency reached 95%. The loaded composite was easily stripped from U (VI) ions by 100 ml of 0.25M  $\text{HNO}_3$  solution. The eluted uranium content was precipitated using  $\text{H}_2\text{O}_2$  at pH 2. A quantity of 2.5g ( $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ ) was precipitated. Uranium content in the precipitate was 61% and the purity of uranium in the obtained uranium concentrate was 86.5 %. A comparison of the uptake capacity (mg/g) of different adsorbents toward uranium is shown in Table (8).

#### **Conclusion**

The prepared (magnetite-Dowex 50WX8) composite used for uranium (VI) adsorption under optimum conditions by the applied batch technique showed a composite capacity of 190 mg/g at 298K using 10 ml of synthetic solution containing 500 ppm of uranium agitated with 25mg of composite at pH 4, 200 rpm agitation speed for 30 minutes. The obtained kinetic data obeyed pseudo second-order kinetic model that was adopted to represent the studied adsorption mechanism. Langmuir model isotherm was found to be more suitable to explain the present adsorption process. Maximum U (VI) desorption efficiency was achieved using 0.25M nitric acid solution. The prepared (magnetite-Dowex 50WX8) composite is higher for uptake capacity than other adsorbents. As a final step, the optimum conditions were applied for U adsorption from El-Missikat sample, Central Eastern Desert, Egypt after being leached with 95 % adsorption efficiency.

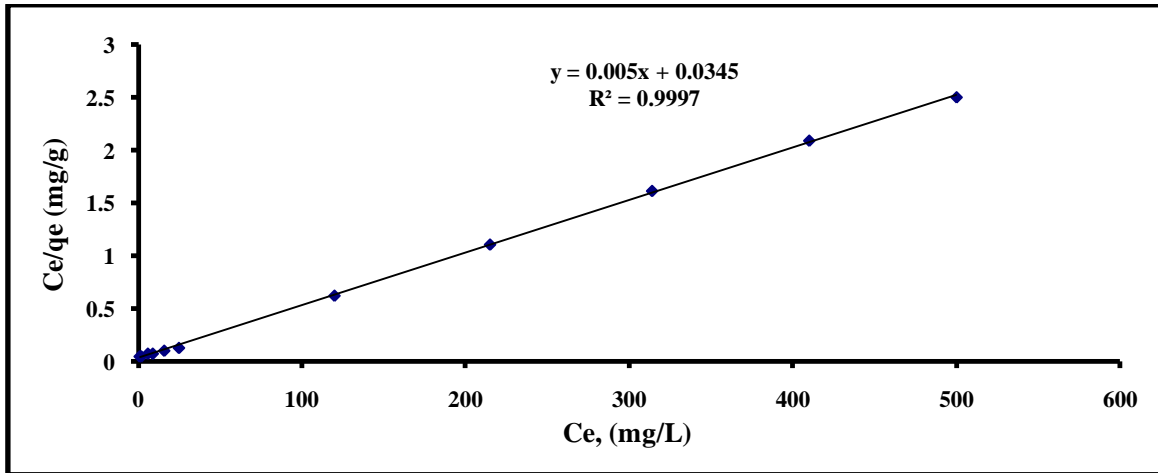


Fig. (10): Langmuir isotherm model of U (VI) adsorption onto the prepared (magnetite-Dowex 50WX8) composite

Table (5): Adsorption isotherm parameters of (Langmuir and Freundlich) for adsorption of uranium onto the prepared (magnetite-Dowex 50WX8) composite

Kinetic models	Parameters	298K
<b>Langmuir isotherm</b>	Equation	$Y=0.005x+0.0345$
	q max (mg/g)	200
	b (L/mg)	0.1449
	$R^2$	0.9997
<b>Freundlich isotherm</b>	Equation	$Y=0.3085x+1.592$
	$k_f$ (mg/g)	39.08
	1/n (mg min/g)	0.3085
	$R^2$	0.7594

**Adsorption conditions:** 500 ppm uranium concentration, 30 min. contact time, room temperature, 25 mg composite dose and pH 4.

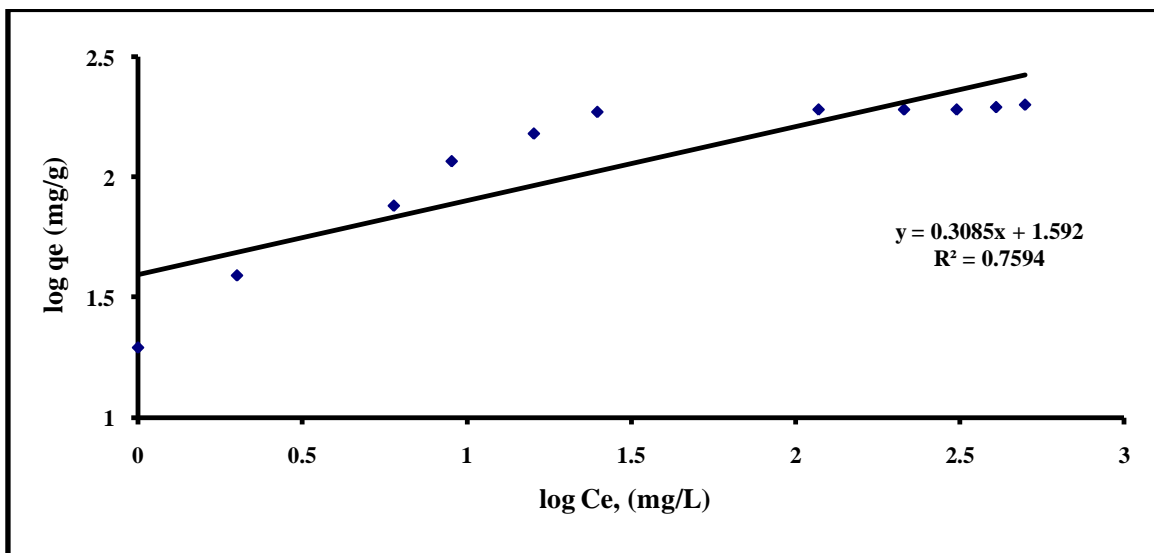


Fig. (11): Freundlich isotherm model of U (VI) adsorption onto the prepared (magnetite- Dowex 50WX8) composite

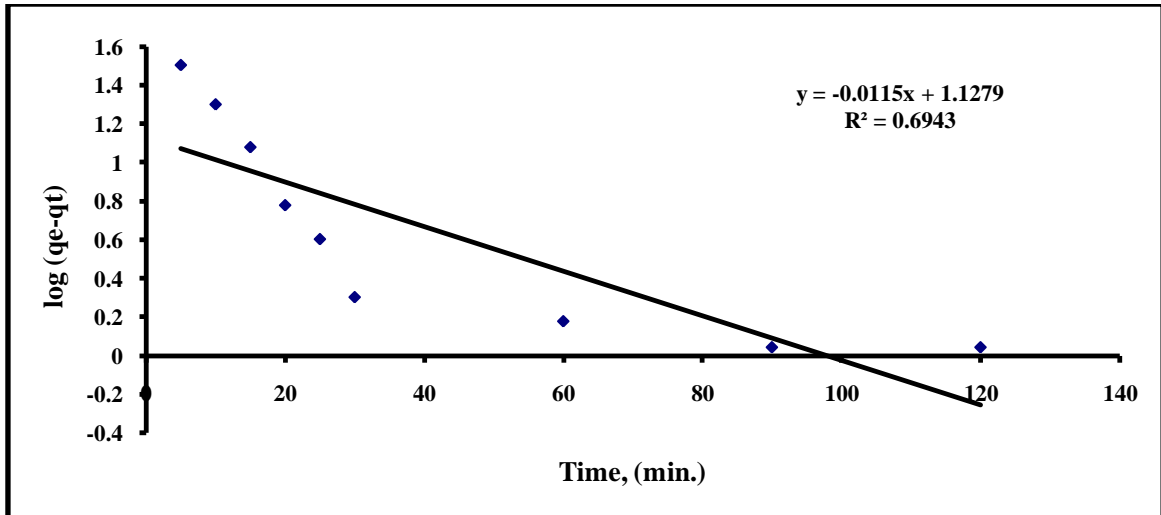


Fig. (12): Pseudo first order model of U (VI) onto the prepared (magnetite-Dowex 50WX8) composite

Table (6): Kinetic model parameters applied to uranium onto the prepared (magnetite- Dowex 50WX8) composite

Kinetic models	Parameters	298 K
First order parameter	$q_e$ (mg/g)	13.42
	$K_1$ ( $\text{min}^{-1}$ )	0.026
	$R^2$	0.6943
Second order parameter	$q_e$ (mg/g)	192.30
	$K_2$ (g/mg. min)	0.00614
	$R^2$	1

*Adsorption conditions:* 500 ppm uranium concentration, 30 min. contact time, room temperature, 25 mg composite dose and pH 4.

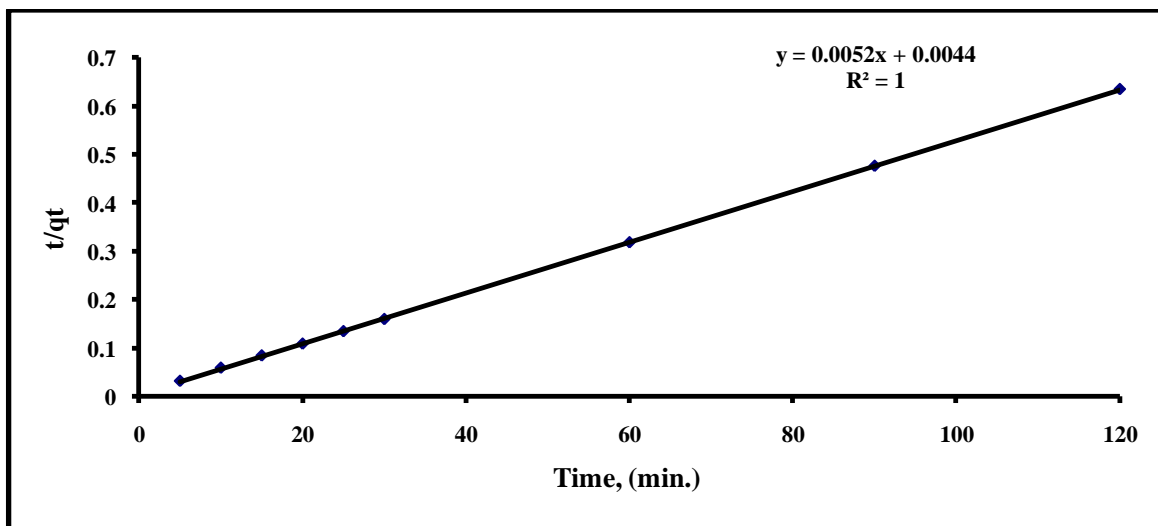


Fig. (13): Pseudo second order model of U (VI) onto the prepared (magnetite-Dowex 50WX8) composite

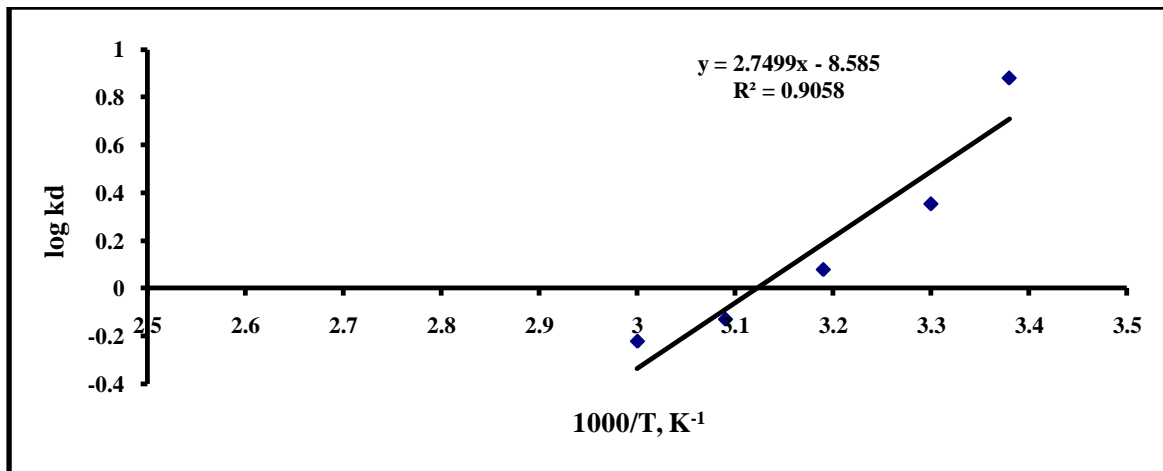


Fig. (14): A plot of  $\log K_d$  against  $1000/T$  for uranium adsorption onto the prepared (magnetite-Dowex 50WX8) composite

Table (7): Thermodynamic parameters for the uranium adsorption onto the prepared (magnetite-Dowex 50WX8) composite

Temperatures, (°C)	Temperatures,(°K)	$\Delta H$ , (KJ/mol)	$\Delta G$ , (KJ/mol)	$\Delta S$ , (KJ/mol. K <sup>-1</sup> )
22	295		-4.97	-0.1616
30	303	-52.65	-2.05	-0.1669
40	313		-0.474	-0.1666
50	323		0.797	-0.1654
60	333		1.409	-0.1623

Table (8): A comparison of the uptake capacity (mg/g) of different adsorbents toward uranium

Adsorbent	Capacity, (mg/g)	References
Dowex 1X8	89	[30]
Ambersep 920U SO <sub>4</sub>	58	[35]
Dowex 1X-8	69	[70]
Dowex 1X-8	73.6	[71]
Dowex 1X-8	134.86	[72]
Dowex 1X- 8	100	[73]
Dowex 2IK sulphate	95	[74]
Dowex 1X- 8	84	[75]
Amberlite XAD-4 functionalized with succinic acid	90	[76]
Purolite S985,	120	[77]
DOWEX 50 WX8	110	[78]
Lewatit MonoPlus TP 214	152.2	[79]
Dowex M4195	78	[80]
Dowex 1X	90	[81]
Amine-impregnated cellulose (AIC)	56.5	[82]
Dowex MSA-2	108.93	[83]
(ZMPP-TBP)	196.08	[84]
polyvinyl alcohol functionalized with amidoxime	42.84	[85]
Purolite A500	90	[86]
<b>Present work</b>	<b>200</b>	<b>L.A.Yousef</b>

### Recommendations

To keep the stability of the prepared (magnetite-Dowex 50WX8) composite and prevent iron dissolution, nitric acid concentration must not exceed 0.6M HNO<sub>3</sub>.

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