ISSN : 0974 - 7486 Volume 13 Issue 9

Materials Science

An Indian Journal

Full Paper

MSAIJ, 13(9), 2015 [308-316]

Kinetics of extraction process of uranium from El-Missikat mineralized shear zone, Eastern Desert, Egypt

E.A.Gawad

Nuclear Materials Authority, P.O. Box 530, El Maadi, Cairo, (EGYPT)

E-mail: egawwad@yahoo.com; egawwad1966@gmail.com

ABSTRACT

The extraction process of uranium from El-Missikat by anion exchange resin (Lewatit MonoPlus M500) was investigated. The extraction condition contact time, temperature, pregnant feed pH, resin/ leach liquor ratio and agitation rate were studied. The optimum process operating parameters were pH of 1.8; contact time 30 min.; Resin-leach liquor ratio (R/L) 1:50 and agitation rate 200 rpm at temperature 25°C. The extraction efficiency of uranium was about 95%. The experimental data were well interpreted with a shrinking core model with surface diffusion control. The extraction, process follows the kinetic model:

$1-(1-X_f)^{2/3} = k_{ap}\int_0^t C\,dt$ with an apparent activation energy of 20.1 kJ/mole.

KEYWORDS

Extraction;
Uranium;
Anion exchange resin;
Lewatit mono plus M500;
Non-linear;
Kinetics;
Shrinking core model;
Surface diffusion;
Pseudo first order;
Lagergren's rate equation;
Equilibrium isotherm;
Fritz-schlunder;
Adsorption four parameters models.

INTRODUCTION

The study area of Gabal El-Missikat is one of the most important localities in the central Eastern Desert of Egypt for occurrence of uranium deposits; El-Missikat covers an area of about 80 km^2 and includes Gabal El-Garra and Gabal El-Gidami in addition to Gabal El-Missikat[1]. El- Missikat uranium prospect area lies at about 3 km, midway between Safaga, on the red Sea coast and Qena in the Nile Valley. It is roughly bound by longitudes 33^o 15' - 33^o 28' E and latitudes 26^o 24' - 26^o 30' N where the mineralogical studies revealed the presence of uranium minerals such as uranophane, uraninite, soddyite and renadite[2].

Gabal El-Missikat consists of rocks are essentially compound of quartz, potash feldspars, sodic plagioclase and biotite. The main accessory minerals are sulfides, magnetite, zircon, apatite, fluorite, titanite, monazite, xenotime, uranothorite, rutile and uraninite. Hematite, epidote, muscovite and chlorite are present as secondary minerals[3].

The industrial application of ion exchange is widespread and ranges from water softening[4], wastewater treatment[5] and analytical chemistry[6] to the purification of high cost pharmaceutical derivatives[7] as well as precious metals[8]. Although the resins used in these operations are generally efficient, they tend to degrade as they age. This leads to increasing regeneration and rising cost owing to higher eluant usage and the subsequent disposal of increased amount of eluate.

The aim of this work is to investigate a simple extraction process of relatively low grade uranium-REE ore material from El-Missikat, Eastern Desert, Egypt by using Lewatit MonoPlus M500. This paper considers the kinetic aspects of uranium extraction. The effects of the main system variables on the extraction rate were examined, the kinetic model and the apparent activation energy were determined

EXPERIMENTAL

Characterization of the sulphate leach liquorm

The sulphate leach liquor loaded with the dissolved uranyl ions obtained from the previous leaching step after which the solution pH was adjusted at the required working value[9]. The loaded solution was contacted with the Lewatit mono plus M500 anion exchange resin. The stock of leach liquor was adjusted to the optimum pH for the pregnant feed solution to be introduced to the ion exchange extraction system. TABLE (1) shows the concentration of Uranium, REEs, and Fe_2O_3 in sulphate leach liquor. Series of experiments was carried out upon 10 ml sample portion of sulphate leach liquor. Uranium extraction efficiency was calculated according to the following equation:

$$\text{Extraction Efficiency of Uranium, \%} = \frac{\text{Extraction Metal ion conc.}}{\text{Original Metal ion conc.}} \times 100$$

Analytical procedures and instrumentation

The ore was analyzed for its major and minor elements using the reported methods.

1- Generally, the samples used in this work were weighed using an analytical balance produced by Shimadzu (AY 220).
2- The hydrogen ion concentration of the different solutions was measured accurately using the pH-meter model (HAANA pH-mV-temp).
3- Total REE was determined by arsenazo III where the absorbance of its complex was measured at the wavelength 650nm[10] by using UV-spectrophotometer "single beam multi-cells-positions model SP-8001", Metretech Inc., version 1.02.
4- ICP model (Prodigy Axial high dispersion ICP-OES-USA) used for determination individual REE.
5- An atomic absorption model G.B.C.A.A, was used for measuring trace elements.
6- The X-ray fluorecence technique (XRD) was used to identify the unknown minerals using a PHILIPS X'UNIQE II spectrometer analyzing crystal.
7- Uranium was determined by titration against ammonium Meta vanadate[11]

RESULTS AND DISCUSSION

Extraction results

Effect of contact time on uranium extraction efficiency

The effect of contact time on the extraction efficiency of uranium was investigated for El-Missikat leach liquor using the studied anion exchange resin for various contact times from 5 to 90 minutes. The other experimental parameters were kept constant, involving R/L ratio of 1/50 for resin, a uranium initial concentration of 480 ppm, pH of 1.8 with Lewatit at ambient temperature (≈ 25 °C). The results of uranium extraction efficiencies for the resin were graphically plotted in Figure (1). It is worthy to mention that, the extraction kinetics of resins determines the required time to reach equilibrium during adsorption from the pregnant leach liquids. This will consequently determine the maximum residence time required for the solution-resin contact during extrac-

TABLE 1 : Chemical composition of the prepared pregnant solution from El-Missikat

Components	*Concentration, g/l*
Uranium	0.665
REEs	0.350
Fe_2O_3	6.38

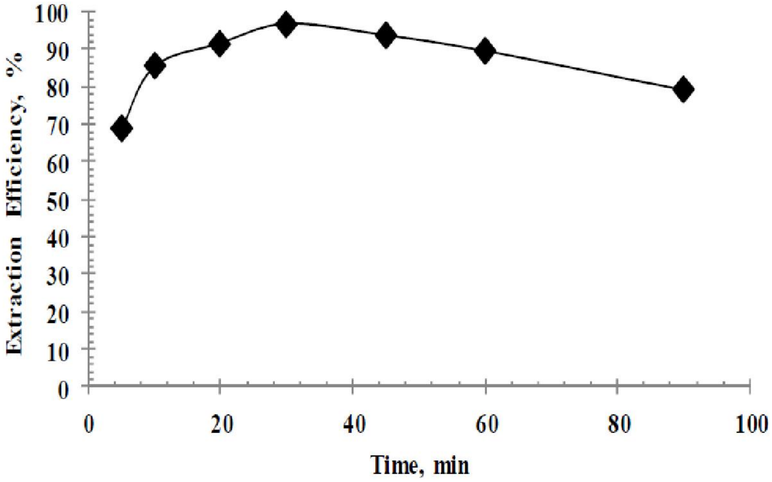

Figure 1 : Effect of contact time on uranium extraction efficiency

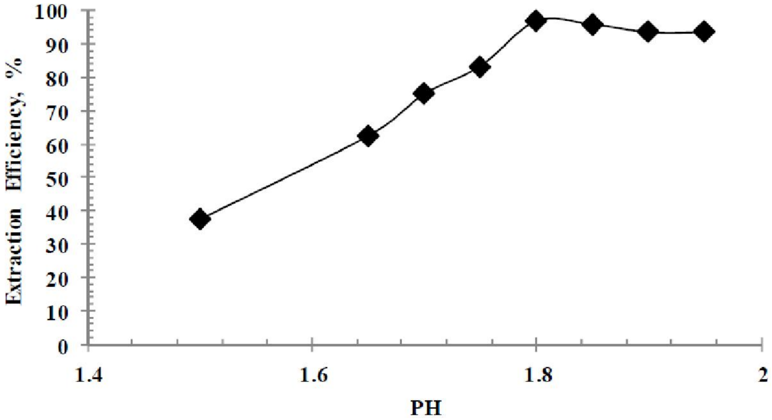

Figure 2 : Effect of pH on uranium extraction efficiency

tion in the fluid-bed column and would affect both flow rate and resin/solution ratio during operation. From the obtained data, a sharp increase in the uranium extraction efficiency for the resin was observed by increasing the contact time from 1 to 30 minutes to reach 95.4 after 30 min. with Lewatit and. Prolongation the contact time to 90 minutes shows slight influence on re-extracting uranium from the resin. Therefore, the contact time of the phases for 30 min. may be enough.

Effect of pregnant feed pH on uranium extraction efficiency

From the previous mentioned studies on uranium extraction systems using strong base anion exchange resins, it was thought that the pH of the pregnant leach solution might be influenced. Thus an attempt to choose the suitable operating pH that verifies maximum resin equilibrium exchange capacity for uranium, pH of the leaching solution was varied from 1.5 to 1.95. The other experimental conditions were fixed at an R/S ratio of 1/40, a uranium initial concentration of 480 ppm, mixing the leach liquor with the resin for 30 minutes at ambient temperature (≈ 25^{o}C). The result of uranium extraction efficiency for the resin was graphically given in Figure (2). From the obtained results, the uranium extraction efficiency using Lewatit was increased from pH 1.5 to 1.8 and then slightly decreased in extraction efficiency with the pH up to 1.9.

Effect of resin/ leach liquor ratio (R/S) on uranium extraction efficiency

The effect of resin/ leach liquor ratio (R/S) from 1/15 to 1/50 was studied under the conditions of uranium initial concentration such a 480 ppm, pH of 1.8 for Lewatit 30 minutes at ambient temperature(≈ 25 ^{o}C). The result of uranium equilibrium exchange capacity for the resin was graphically plotted in Figure (3).

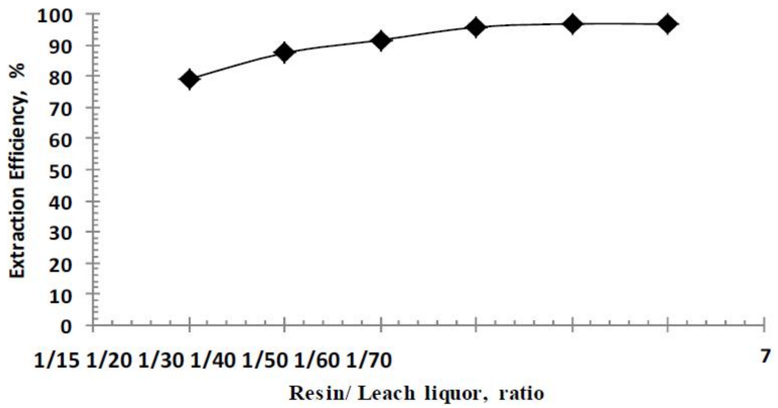

Figure 3 : Effect of LewatitMP-500/solution ratio on uranium extraction

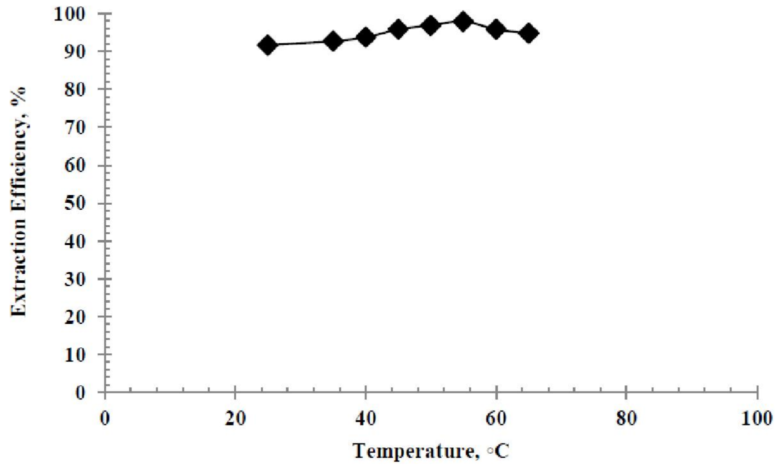

Figure 4 : Effect of extraction temperature on uranium extraction efficiency

The results of resin/solution ratio effect revealed that the uranium concentration on the used resin increases gradually with the pregnant feed solution from 1/15 to 1/50 for the resin. Uranium extraction with 1/50 ratio was then fixed constant for Lewatit with the feed solution ratio to 1/50. As a result, the resin/ leach liquor ratio of 1\50 was the more efficient ratio for the Lewatit resin.

Effect of extraction temperature on uranium extraction efficiency

The temperature of the extraction process in the range from 25 to 65°C was studied its effect on uranium extraction efficiency for El-Missikat leach liquor using the studied anion exchange resin. The other experimental conditions were fixed at an R/S ratio of 1/50 for the Lewatit resin, a uranium initial concentration of 480 ppm, pH of 1.8 with 30 minutes contact time. The result of uranium extraction efficiency for the resin was graphically plotted in Figure (4).

From the obtained data, it was observed that a sharp decrease in the uranium extraction efficiency from 97.9% to 94.7 for Lewatit with increasing the extraction temperature from 55 to 60°C. So it was better to hold extraction at room temperature.

Effect of initial uranium concentration on extraction efficiency

Initial uranium concentration of the studied feed solution has an effect on the equilibrium extraction by anion exchange resins[12]. This in turn, has a clear effect upon both the resin to liquid ratio and the number of contacts needed for resin saturation. Both effects would consequently provide some basic data to choose the suitable concentrations and number of stages. To study this factor, the effect of initial uranium concentration was investigated in the range of 500 to 1700 ppm under the fixed conditions of an R/L ratio of 1/50 for the resin, mixing the solution of 200 rpm, pH of 1.8 with 30 minutes contact time at ambient temperature. The results of uranium equi-

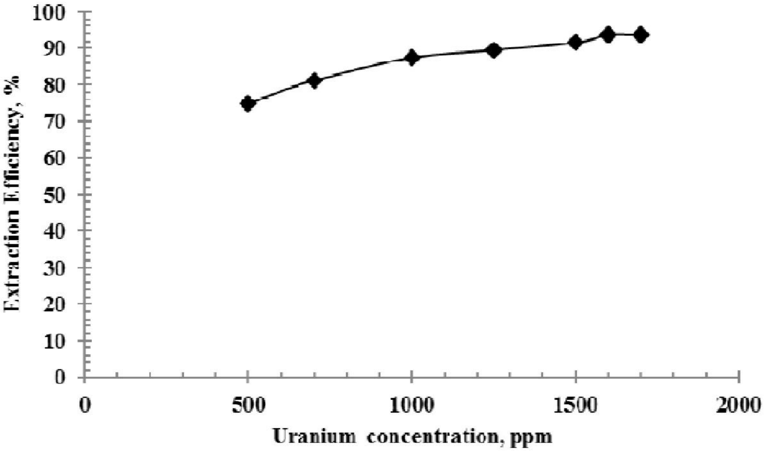

Figure 5 : Effect of initial uranium concentration on uranium extraction

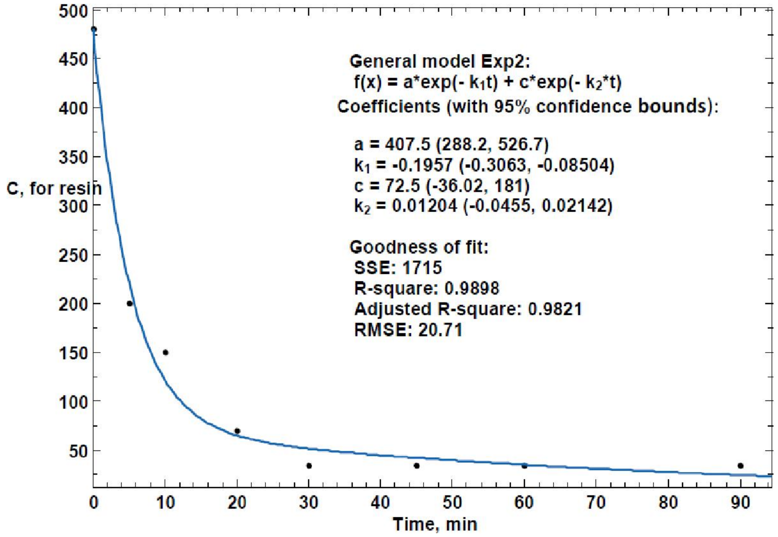

Figure 6 : Effect of Time on uranium extraction

librium exchange capacity for the resin were graphically represented in Figure (5). From the results, it is clear that the uranium extraction efficiency increases from 75% to 94% with the initial uranium concentrations from 500 to 1700 ppm for Lewatit. Accordingly, increasing the uranium concentration of the pregnant leach solution would increase uranium extraction efficiency for the Lewatit resin MonoPlus M500.

Extraction kinetics of uranium

Effect of time

Linear regression was frequently used to determine the most fitted model throughout the years and the method of least squares has been frequently used for finding the parameters of the models. However, transformations of non-linear isotherm equations to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least squares[14, 15, 16]. By using nonlinear steps for determining the type of reaction and the isotherm, Figure (6) presents the effect of the reaction time on the uranium extraction rate at 25°C under conditions of pH of 1.8; contact time 30 min.; Resin-leach liquor ratio (R/L) 1:50 and agitation rate 200 rpm. The results show that the extraction rate of uranium increases as the time increases. In order to obtain the kinetic equation and the apparent activation energy for the Extraction of uranium in the experimental data in Figure (6) were correlated to various kinetic models for solid-liquid reactions. Several equations were studied including[17, 18, 19, 20]:

$$1\text{-}3\,(1\text{-}X_f)^{2/3} + 2\,(1\text{-}X_f) = k_{Dap'}\int_0^t C\,dt \qquad (1)$$

$$1 - (1 - X_f)^{1/3} = k_{Cap}, \int_0^t C\, dt \qquad (2)$$

$$X_f = k_{Fap}, \int_0^t C\, dt \qquad (3)$$

$$1 - (1-X_f)^{2/3} = k_{Sap}, \int_0^t C\, dt \qquad (4)$$

Steps for determining the type of reaction and the isotherm

The nonlinear fitting uranium concentration vs. time

From this Figure (6): there is a pseudo shifted first order reaction;

a and c are initial concentrations of the main and shifted reaction respectively

t : time of reaction in min and

k_1 and k_2 are rates of the main and shifted reaction respectively

Definite integration of the gained equation

$$\int_0^t (ae^{-k1t} {}_{+} ce^{-k2t}) \text{ dt}$$

Plot $f(x_f)$ vs integration

Model equations are in the form $f(X_f) = S\int_0^t C\, dt$

Where the slope S and the function $f(X_f)$ are different for each controlling mechanism. The integral on the right hand side of this equation can be easily estimated by arithmetic means by nonlinear fitting. The values of this integral are shown in TABLE (2). In Figure 7, the function $f(X_f)$ is plotted against the integral for all models. The next step is to find out which function is linear with zero intercept. The results are shown in TABLE 2.

Where X_f is film diffusion control, D_s is the effective diffusion coefficient of fluid phase reactant in the solid (ash), k_c is reaction kinetics control and k_s is surface diffusion controlled step.

It is obvious that the best fit is given by the surface diffusion controlled equation. The slope of the line is 0.003 L/mg min = k_s and from which the apparent activation energy =ΔG*=-R*T*ln (k_{ap}) = ΔG*= (-8.134*298*ln (0.0003))/1000

TABLE 2 : $f(X_f)$ versus t data

time	$k_{ap}\int_0^t C\, dt$	X_f	D_s	k_c	k_s
0	0	0	0	0	0
5	1.65E+03	6.29E-01	1.93E-01	2.82E-01	4.84E-01
10	2.47E+03	7.42E-01	3.00E-01	3.63E-01	5.94E-01
20	3.33E+03	9.21E-01	6.07E-01	5.72E-01	8.16E-01
30	3.90E+03	1.00E+00	1.00E+00	1.00E+00	1.00E+00
45	4.60E+03	1.00E+00	1.00E+00	1.00E+00	1.00E+00
60	5.18E+03	1.00E+00	1.00E+00	1.00E+00	1.00E+00
90	6.07E+03	1.00E+00	1.00E+00	1.00E+00	1.00E+00

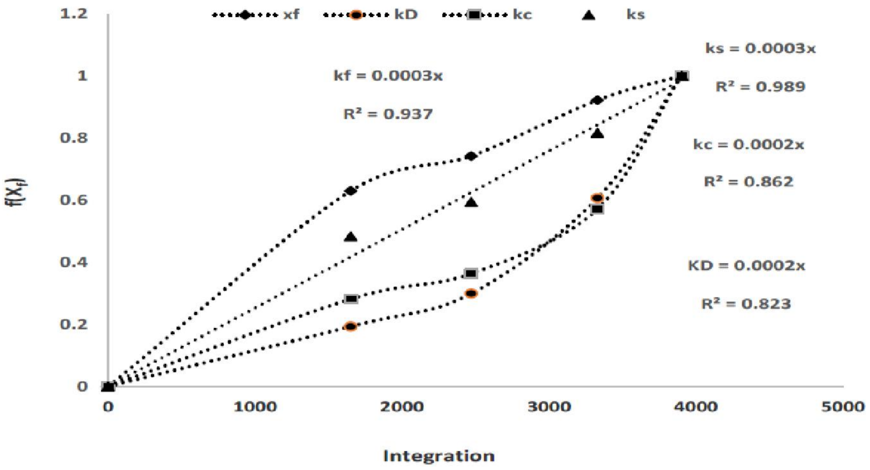

Figure 7 : the application of the shrinking-core models

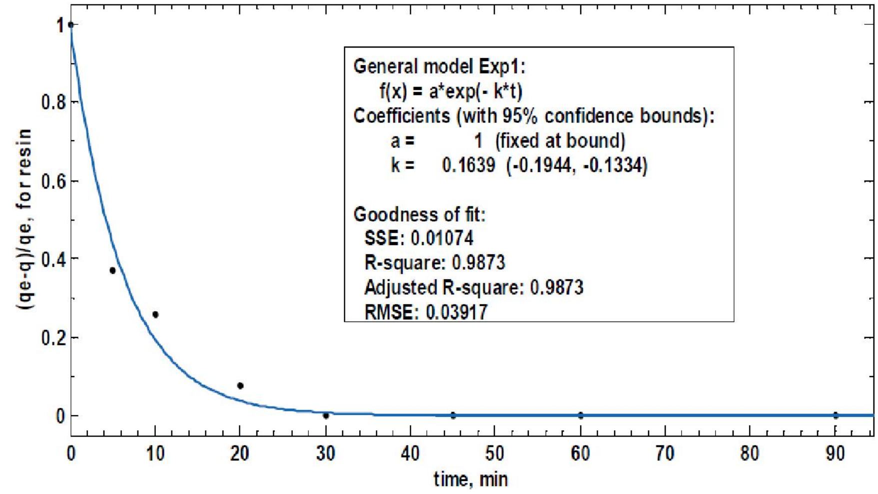

Figure 8 : Pseudo first order reaction

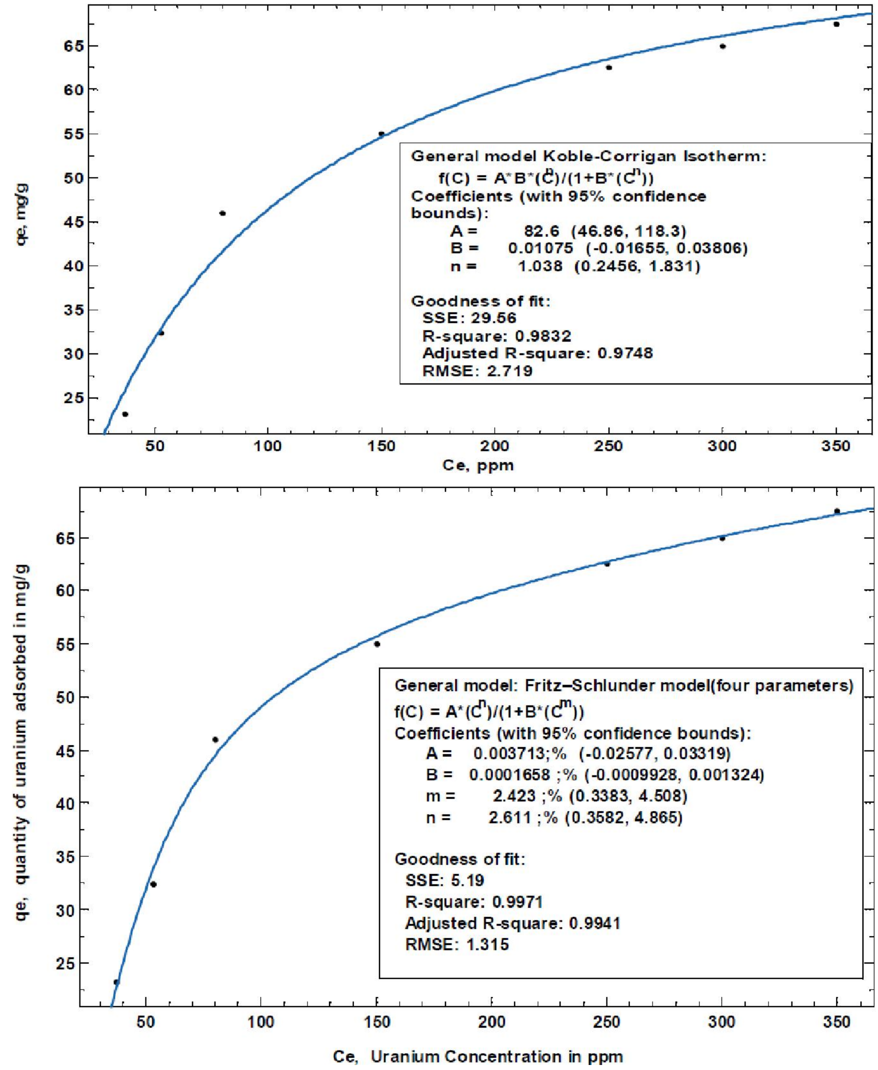

Figure 9 : Fritz-Schlunder isotherm for uranium extraction using anion exchange resin (Lewatit mono plus M500)

ΔG^*=20.097 kJmol^{-1} ^{f}K^{-1}

Determination the order of reaction

To determine the order of this reaction the known models were tested for first and second orders using non-linear technique and the best one is the Pseudo-first-order kinetic model (Lagergren's rate equation). In this model, the kinetic rate in differential form and its analytical solution by integration and rearrangement can be expressed as

$dq/dt=k(qe-qt)$

$(q_e-q)= q_e*e^{-kt}$

$(q_e-q)/q_e=e^{-kt}$

; k is the reaction rate

Figure (8) represents this relation

Determination the equilibrium isotherm

For the determination of adsorption isotherm, many known models were tested from two to five parameters and the best models are four-parameter models and further detailed studies are going to be accomplished in the nearest future work. Figure (9) represents the Fritz-Schlunder model that fits the relation between equilibrium concentration Ce and quantity of uranium adsorbed qe

CONCLUSIONS

Uranium can be easily extracted from Uranium/REE ore by using anion exchange resin (Lewatit MonoPlus M500). Using conditions of pH 1.8; contact time 30 min.; Resin-leach liquor ratio (R/L) 1:50 and agitation rate 200 rpm at temperature 25°C, gave extraction efficiency of about 97% for uranium. The reaction order of the uranium adsorbed by this resin is pseudo first order reaction. Hence, the extraction rate of uranium strongly matches with the Fritz-Schlunder model. The extraction kinetics of uranium showed that the rate of uranium extraction using Lewatit MonoPlus M500 is surface diffusion controlled and follows the shrinking core model $1- (1-X)^{2/3} = k_{sap} \int_0^t C\,dt$ with an apparent activation energy of 20.1 kJ/mol.

REFERENCES

[1] N.A.Mohamed; Distribution and extraction of uranium and some trace elements from the mineralized zones of El-Missikat- El-Eredya area, Eastern Desert, Egypt, ph.D. Cairo Univ., 184 **(1995)**.

[2] T.E.Amer, T.M.Ibrahim, S.A.Omar; Micro-probe studies and some rare metals recovery from El Missikat mineralized shear zone, Eastern Desert, Egypt, Assiut-Egypt, **(2)** 225-238 **(2005)**.

[3] T.M.Ibrahim; Geologic and radioactive studies of the basement-sedimentary contact in the area west Gabal El Missikat, Eastern Desert, Egypt, PhD.thesis, Mansoura University, El Mansoura, Egypt, 214 **(2002)**.

[4] H.M.Abdalla, A.H.El Afandy; Geochemistry and genesis of uranium mineralization at Missikat-Erediya area, Central Eastern Desert, Egypt, Egyptian Mineral., **16**, 1-33 **(2004)**.

[5] D.A.Clifford; Ion exchange and inorganic adsorption, Chap. 9 in: F.W. Pontius -Ed.., Water quality and treatment, A handbook of community water supplies, 4th Edition, McGraw-Hill, USA, American Water Works Association, 561–640 **(1990)**.

[6] B.A.Bolto, L.Pawlowski; Wastewater treatment by ion exchange, E & FN Spon, New York, USA, 262 **(1987)**.

[7] O.Samuelson; Ion exchange separations in analytical chemistry, Wiley, New York, USA, **(1963)**.

[8] J.Inczedy; Analytical applications of ion exchangers, Pergamon, Elmsford, NY, USA, 1966, 212 D.Feng, C.Aldrich Hydrometallurgy, **55**, 201–212 **(2000)**.

[9] K.Dorfner; Ion exchangers in pharmacy and medicine, Chap. 6 in: A.Fe´ Coers_Ed.., Ion Exchangers: Properties and Applications, Ann Arbor Sci.Publ., Ann Arbor, MI, USA, **(1972)**.

[10] Z.Marczenko; Spectrophotometric determination of elements, John Wiley& Sons, Inc., New York, **(1986)**.

[11] A.R.Eberle, M.W.Lerner, C.G.Cold Beck, C.J.Rodden; Titrimetric determination of uranium in product, Fuel and scrap materials after ferrous iron reduction in phosphoric acid, New Brunswick Laboratory, USAEC, **(1964)**.

[12] H.J.Small; Inorg.Nucl.Chem., **18**, 232 **(1961)**.

[13] P.P.A.D.Abrowski, S, M.B.Z.Hubicki; Adsorption of phenolic componds by activated carbon a critical review, Chemosphere, **58**, 1049–1070 **(2005)**.

[14] Liu Wei, Tang Mo-Tang, Tang Chao-Bo, He Jing, Yang Sheng-Hai, Yang Jian-Guang; Dissolution kinetics of low grade complex copper ore in ammonia"ammonium chloride solution [J], Transactions of Nonferrous Metals Society of China, **20(5)**, 910"197 **(2010)**.

[15] US EPA; Guidelines for water reuse, EPA/625/R-

04/108, U.S.Agency for Inter, Development, Washington, DC, USA, **(2004)**.

[16] N.Ghasemi, M.Ghasemi, S.Mashhadi, M.H.Tarraf; International congress on informatics, Environment, Energy and Applications-IEEA 2012 IPCSIT, IACSIT Press, Singapore, 38 **(2012)**.

[17] C.Moreno-Castilla; Adsorption of organic molecules from aqueous solutions on carbon materials, Carbon, **42**, 83–94 **(2004)**.

[18] I.H.Lee, Y.C.Kuan, J.M.Chern; Equilibrium and Kinetics of heavy metals ion exchange, J.Chinese Institute of Chem.Eng., **38**, 71-84 **(2016)**.

[19] B.Ozkaya; Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models, J.Hazard.Mater, **129**, 158–163 **(2006)**.

[20] K.Vijayaraghavan, T.V.N.Padmesh, K.Palanivelu, M.Velan; Bio.sorption of nickel (II) ions onto Sargassum wightii: application of two-parameter and three-parameter isotherm models, J.Hazard.Mater, **133**, 304–308 **(2006)**.