

The Mathematical Models for Uranium Extraction from Nitric Acid Medium Using TBP Impregnated Amberlite XAD-4 Resin

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Summary: Uranium equilibrium distribution between the tributyl phosphate (TBP) impregnated Amberlite XAD-4 polymeric resin support and 5.5 N nitrate aqueous acid solution was converted from curve to straight line by the Langmuir equation. From the resultant straight line, the constants “Q” and “K” were determined to be used in the mathematical models validities. The values of these constants were found to be 223.312 and 0.3919 respectively. On the other hand, the adsorption and elution kinetics data resulting from the fractional approach to equilibrium “Y” were used in calculations for evaluating the diffusion control during uranium adsorption (from nitric acid medium and the nitric acid/aluminum nitrate medium) and during the elution. The corresponding mass transfer coefficients were then determined. The mathematical model validity for diffusion through liquid film reveals that another rate process controlling the mass transfer, while the diffusion through the combined liquid film and solid indicates validity the equation of controlling the mass transfer rate process. On the other hand, the mass transfer rate during the elution step was controlled by the diffusion through solid, however, the diffusivity inside the TBP impregnated resin beads “ D_p ” was $165.2 \times 10^{-12} \text{ m}^2/\text{s}$.

Key words: Uranium, tributyl phosphate, Amberlite XAD-4, impregnated resin, nitric acid, adsorption, elution, kinetics, diffusion, liquid film, mathematical models.

Introduction

The great advance in recent years drives towards reducing both capital and operating costs considered in uranium recovery, concentration and purification processes as well as the need for flowsheet simplification. This leads to the adoption of new extraction technique using the so called Solvent-Impregnated Resin "SIR" which behave as ordinary resins and bridges the gaps between the two commonly used extraction systems, ion exchange resin and solvent extraction, through combining the distinctive advantages of them⁽¹⁾. Solvent impregnated resins are obtained by simple immobilization of the common

extracting solvent onto an insoluble non-functional polymeric beads support⁽²⁾. Amberlite-XAD polymeric support series have actually resulted in very high efficiency than the other different supports such as silica gel, kieselguhr, and activated carbons⁽³⁾.

Tributyl phosphate (TBP) is one of the most common solvents used in uranium extraction from nitric acid medium, specially in the refining processes, with a free nitric acid concentration from 0.5 to 3 M⁽⁴⁾. Presence of free nitric acid actually increases the extraction efficiency due to the salting-out effect, which enhances the distribution coefficient of uranium⁽⁵⁾. However, inorganic nitrate salts have been used with great success as salting-out agent in the nitrate extraction systems. Aluminum nitrate has proved to be the most effective salting-out agent in uranium extraction from nitrate medium by TBP, where the extractability of the uranyl nitrate complex is greatly enhanced⁽⁴⁾.

When aqueous solutions of uranyl nitrate and nitric acid were contacted with TBP, the following reversible reactions take place at equilibrium:



The elution process is considered as the reverse process to the extraction one. In this regard, the extracted uranium is eluted (re-extracted) from the loaded TBP solvent using distilled water. It was recommended to use acidified distilled water (0.01 M HNO₃) during the elution step to prevent hydrolysis of the eluted uranyl nitrate and subsequent precipitation; a matter which would cause serious problems⁽⁶⁾.

Mathematical models can be useful in all phases of chemical engineering, from research and development to plant design and operation, and even economic studies. Mathematical models can be useful in plant design in the fields of exploring the sizing and arrangement of processing equipment for dynamic performance, studying the interactions of various parts of the process especially material recycle and heat integration, evaluating alternative process and control strategies and simulating start-up, shutdown, and emergency situations and procedures. In plant operation the mathematical models can be also useful in the

fields of troubleshooting control and processing problems, aiding in start – up and operator training, studying the effects of and the requirements for expansion (bottleneck – removal) projects and finally optimizing plant operation⁽⁷⁾.

Mathematical models are usually much cheaper, safer and faster to conduct the kinds of studies on a mathematical model than experimentally on an operating unit (this is not to say that plant tests are not needed). They are also a vital part of confirming the validity of the model and of verifying important ideas and recommendations that evolve from the model studies. However, the empirical correlations for stirred tanks⁽⁸⁾ or fluidized beds^(9, 10) could be predict the mass transfer controlling rates from the kinetic data.

Experimental

Materials and Reagents

A dry uranium peroxide concentrate sample, assaying about 70% U_3O_8 , prepared from the Egyptian mineralization of Gattar V (35 km west of Hurgada City) was used for these experiments. Tributyl phosphate (sp. Gr. 0.98, assay 98% and mol. wt. 266.32 from Aldrich) was used to impregnate Amberlite XAD-4 hydrophobic polyaromatic nonionic resin (surface area 725 m^2/g , average pore diameter 40A°, pore volume 0.98 ml /g and wet mesh size 20 – 60, from Sigma). The impregnated resin sample was containing 1.15 g TBP/g resin.

Procedures

Set of uranium extraction equilibrium experiments was performed upon solutions of concentrations 17.5 and 35 to 140 g U/ l through 35 increasing. The other conditions that kept constant during the tests were total nitrate normality of 5.5 N and agitation of the solution with 10 g impregnated resin (S/R ratio of 5) in a glass beaker using a digital mechanical stirrer for 45 min. at 200 rpm and ambient temperature. Filtrate samples from each test were collected and analyzed against the remaining uranium (**c**) (g U/ l) after extraction where the corresponding uranium concentration in the TBP impregnated resin (**q**) (g U / l w.s.r) was calculated according to the following equation:

$$q = (\text{original U conc.} - \text{remaining U conc. "c"}) \times \text{Ratio}$$

Consequently, the distribution coefficient ($D = q / c$) was correlated by the Langmuir equation:

$$q = (Q K c) / (1 + K c)$$

or $q / c = Q K - K q$

The constants "Q" and "K" can be then determined from the equilibrium linear form of this equation by a least squares fit through the resultant values of "q" and "c" from the relationship between (q) and (q / c).

The relevant effective parameter which could be applied for modeling, to determine the adsorption kinetics in a stirred tank reactor, indeed involve the effect of contact time on the fractional approach to equilibrium during uranium adsorption and elution by the working impregnated resin. For adsorption kinetic studies, set of experiments was conducted using a total nitrate normality of 5.5 N in two extraction systems with 5.5 N nitric acid in the first and in the other 1.0 N $\text{HNO}_3 + 1.5 \text{ M Al} (\text{NO}_3)_3$. In these experiments, two grams of the solvent impregnated resin were used for each contact time of 1, 3 and 5 to 30 min. through 5 minutes increments. The other experimental conditions were fixed at an initial uranium concentration of 35 g U/l, solution to resin ratio of 5, agitation the phases at 200 rpm at ambient temperature. The fractional approach to equilibrium (Y) was then calculated according to the following equation:

$$Y = \frac{(\text{original conc.} - \text{remaining conc.})}{(\text{original conc.} - \text{remaining conc. at equilibrium})}$$

Uranium elution kinetic experiments were conducted using distilled water as an eluant. However, the resin beads were firstly washed before the elution using nitric acid solution having the same normality of the extraction solution. Two milliliters of the wet settled loaded solvent impregnated resin (2 ml w.s.r) were used during testing each contact time of 1, 3 and 5 to 30 min. through 5 minutes increment. The other experimental conditions were fixed at 70.5 g U/l w.s.r solvent impregnated resin, an eluate to w.s.r ratio of 5, agitation of phases at 100

rpm at ambient temperature. Fractional approach to equilibrium (Y) was calculated according to the following equation:

$$Y = \text{eluate conc.} / \text{eluate conc. at equilibrium}$$

The equilibrium and kinetic results obtained from the experimental work for uranium extraction, from nitric acid and aluminum nitrate media, were applied to determine the rate controlling process and to choose the appropriate equations that describe the kinetics of the overall process.

Uranium Determination Method

Uranium was determined in the samples by Redox Titrimetry⁽¹¹⁾ through reduction to the tetravalent state with excess iron(II) in strong phosphoric acid medium containing sulfamic acid where the excess of iron(II) was oxidized to iron(III) by nitric acid and molybdate(VI) catalyst while uranium(IV) remains unchanged. Uranium in the solution is then back oxidized to the hexavalent state using standardized potassium di-chromate " $K_2Cr_2O_7$ " titrant. Uranium concentration was calculated as follows:

$$\text{g/l } U_3O_8 \text{ in sample} = \frac{\text{titrant (ml)} \times N (K_2Cr_2O_7) \times \text{meq. } (U_3O_8) \times 1000}{\text{sample aliquot (ml)}}$$

Results and Discussion

Equilibrium Isotherm for Uranium Extraction by the Impregnated Resin

Equilibrium isotherm for uranium extraction from aqueous nitric acid medium using TBP impregnated resin was constructed (Fig. 1) then linearized by the correlated Langmuir equation (Fig. 2) where the straight line equation was:

$$y = - 0.3919 x + 87.516$$

Accordingly, the constant " K " is "0.3919" and the constant " $Q K$ " is "87.516", consequently the constant " Q " would be "223.312". These constants will be used in the proposed mathematical models.

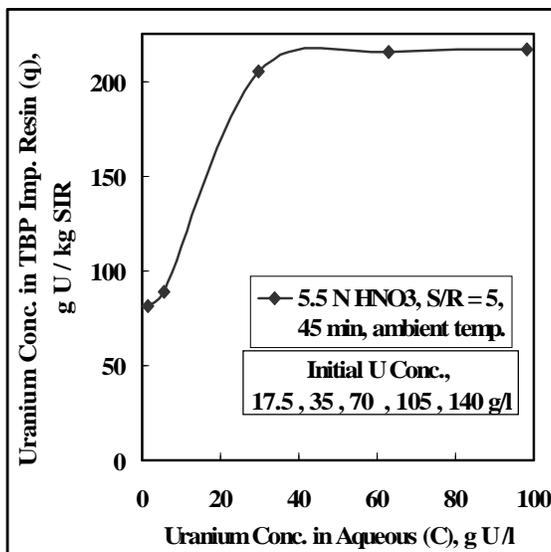


Fig. (1): Equilibrium Curve for Uranium Extraction by the TBP Impregnated Resin

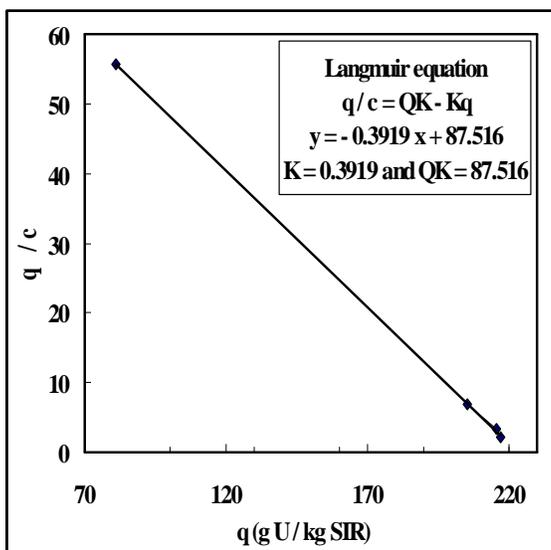


Fig. (2): Straight Line of the Equilibrium Data using Langmuir Equation

Fractional Approach to Equilibrium during Uranium Adsorption

The fractional approach to equilibrium during uranium adsorption from 5.5 N nitric acid and 1.0 N HNO₃ + 1.5 M Al (NO₃)₃ using TBP impregnated resin was illustrated in Fig. (3). From this figure, it is clear that the fractional approach to equilibrium was rapidly increased in the first 5 minutes to be 0.74 in case of uranium extraction from 5.5 N nitric acid and increased more rapidly to 0.83 in case of extraction from 1.0 N HNO₃ + 1.5 M Al (NO₃)₃. This fractional

approach was steadily increased in the further 5 minutes of contact to reach 0.88 and 0.94 in case of the two extraction media of nitric acid without and with aluminum nitrate respectively. However, the fractional approach to equilibrium of 0.99 was reached after 25 minutes in case of uranium extraction from nitric acid medium alone, and was 0.98 after only 15 minutes in presence of aluminum nitrate.

The results reveal that about half of the time is required to approach equilibrium in case presence of aluminum nitrate during uranium extraction by the TBP impregnated Amberlite XAD-4 resin. This is obvious from the value of fractional approach to equilibrium of 0.96 at 20 minutes in case of nitric acid medium alone and about the same level of 0.94 at only 10 minutes in presence of aluminum nitrate.

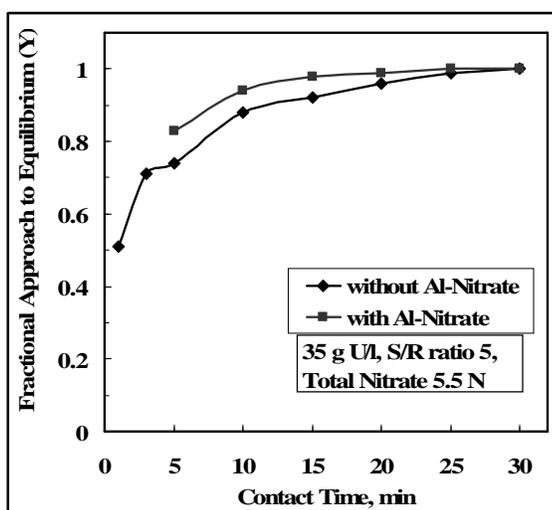


Fig. (3): Effect of Contact Time on the Fractional Approach to Equilibrium during Uranium Adsorption using SIR

Adsorption Controlling Rates

Uranium extraction equilibrium data besides adsorption kinetics from nitric acid medium by the studied TBP impregnated resin would be applied upon the proposed mathematical models to determine the mass transfer controlling rate. After determining the mass transfer controlling rate, the corresponding mass transfer coefficient would be then calculated from the slope of the straight line

resulted from drawing the relationship of the corresponding mathematical model equation of mass transfer control.

Evaluation of Diffusion through the Liquid Film

The rate of mass transfer through the liquid film is given by:

$$dq / dt = k_f a_p (c_o - c_i)$$

where: k_f (m/s) is the liquid film coefficient, and
 a_p (m^2/m^3) is the specific surface area of resin beads.

When the overall rate of mass transfer is determined only by diffusion through the liquid film, there are effectively no concentration differences inside the resin beads and therefore “ c_i ” equals the concentration “ c^* ” that is in equilibrium with “ q ”. The rate of mass transfer is then given by:

$$dq / dt = k_f a_p (c_o - c^*)$$

When the adsorption is controlled by film diffusion, stirred tank reactor in a constant volume is the appropriate model⁽⁸⁾. The liquid to resin volume ratio “ F ” is constant and the mass balance would be:

$$f_1(Y) = (QF / z + bF / 2 z) \log \{ (1 - \beta Y) / (1 - Y) \} - (F/2) \log \{ (1 - Y) - \beta Y(1 - Y) \}$$

$$= k_f a_p t$$

Where: $b = - [Q + F/K + Fc_o]$, $z = (b^2 - 4QFc_o)^{0.5}$, $\beta = (b + z) / (b - z)$

This mathematical equation for liquid film control model was tested using the kinetic data of the two extraction cases, nitric acid medium alone and in presence of aluminum nitrate. Results of testing the validity of the equation are illustrated in Fig. (4) in case of uranium extraction from nitric acid medium and Fig. (5) in case of extraction from nitric acid medium in presence of aluminum nitrate. From these figures, it is obvious that the resultant straight lines in the two cases were achieved revealing the equation validity for liquid film diffusion control. The correlation coefficient “ R^2 ” in the first case was “0.889” while in the

second case was “ 0.9359 ”. The relative lower value of correlation coefficient in the first case indicates that another rate controlling the mass transfer with the film diffusion.

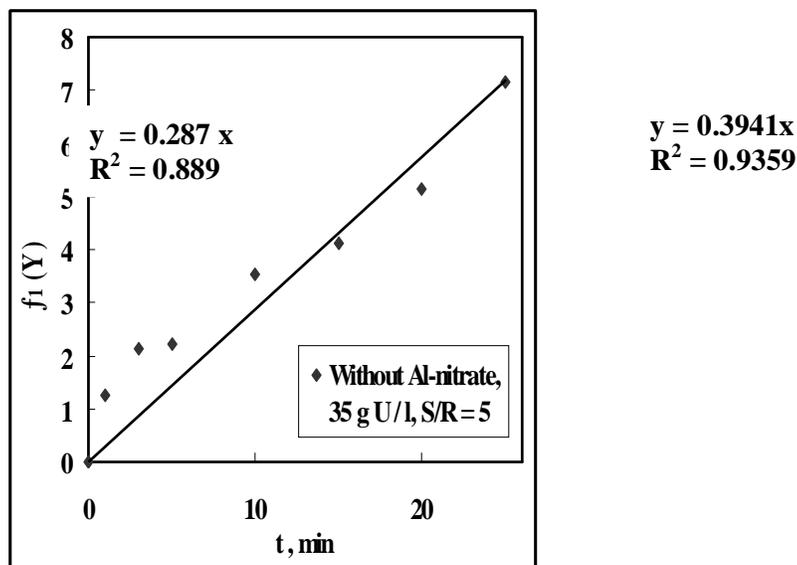


Fig. (4): Evaluation of Film Diffusion Control Equation for Uranium Extraction without Presence of Al-nitrate

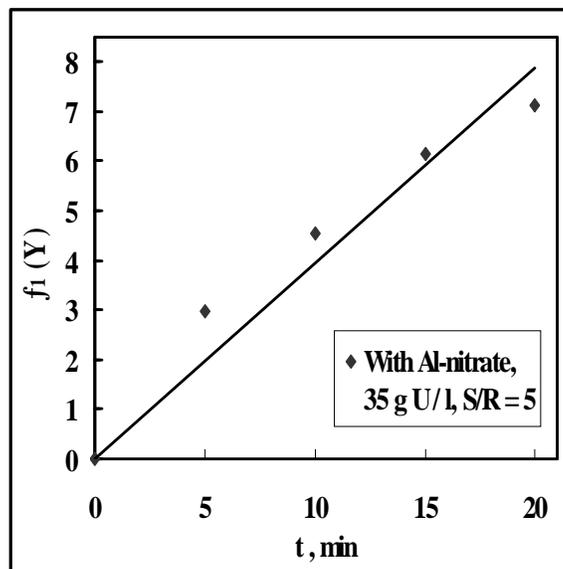


Fig. (5): Evaluation of Film Diffusion Control Equation for Uranium Extraction with Presence of Al-nitrate

The values of “ $k_f a_p$ ” were determined from the slope of straight lines which are “0.287” in case nitric acid medium and “0.3941” in presence of aluminum nitrate. Accordingly, the mass transfer coefficient for liquid films “ k_f ” would be 4×10^{-4} and 5.5×10^{-4} $\mu\text{m/s}$ in the two cases respectively. Comparing this “ k_f ” value with the data obtained from Levestrel OC 1023 (TBP Impregnated Resin)^(12, 13) which was 14.4 $\mu\text{m/s}$ at U concn. 0.1g/l, it was found that the mass transfer coefficient based on liquid film of the worked Amberlite XAD-4 impregnated resin decreased sharply. This result reveals that the resistance decreases for diffusion through liquid film. This is of course due to the high driving force resultant from the high initial uranium concentration in the studied aqueous solution.

Evaluation of the Diffusion through Combined Liquid Film and Solid

There is no simplified analytical equations exist to determine the mass transfer diffusion rate through both the liquid film and the solid. However, simplified expressions have been used in which the rate coefficient is an empirical function of the aqueous concentration⁽¹⁴⁾ or of the resin concentration⁽¹⁵⁾. In the case where diffusion through the liquid film strongly affects the overall rate, the following equation is proposed here:

$$dq/dt = k_m a_p [c - (q/q^*) c]$$

where: “ q^* ” is the concentration in resin in equilibrium with liquid.

In this equation the unknown concentration at the surface, “ c_i ” is approximated by $\{(q/q^*) c\}$ then,

$$f_2(Y) = (QF/z) \log \{(1 - \beta Y)/(1 - Y)\} = k_m a_p t$$

The mathematical equation for the combined liquid film and solid control model was tested using also the kinetic data of the two extraction cases, under the conditions that previously mentioned.

Results of testing validity of the equation are illustrated in Fig. (6) in case of uranium extraction from nitric acid medium, and in Fig. (7) in case of extraction from nitric acid medium in presence of aluminum nitrate. From these figures, it is obvious that the resultant straight lines in the two cases were achieved revealing the validity of the equation for the combined liquid film and solid diffusion control. The correlation coefficient “ R^2 ” in the first case was “0.957” (equal “0.889” for diffusion through liquid film) while in the second case of extraction it was “0.9921” (equal “0.9359” for diffusion through liquid film). This result indicates that the combined diffusion through liquid film and solid is controlling the mass transfer rate process.

The values of “ $k_m a_p$ ” were determined from the slope of the straight lines which are “0.5938” in case of extraction from nitric acid medium and “0.8529” in case of presence aluminum nitrate. Accordingly, the mass transfer coefficient for combined films “ k_m ” would be 0.83×10^{-3} and $1.2 \times 10^{-3} \mu\text{m/s}$ in the two cases respectively. Comparing this “ k_m ” value with the data obtained from Levestrel OC 1023^(12, 13) ($5 \mu\text{m/s}$ at U concn. 1.0 g/l), it was found that, the mass transfer coefficient for combined films decreased sharply. This result reveals that the resistance decreases for diffusion in both liquid film and through solid of the worked Amberlite XAD-4 impregnated resin. This is of course due to the high

driving force resultant from the high initial concentration of uranium in the aqueous solution.

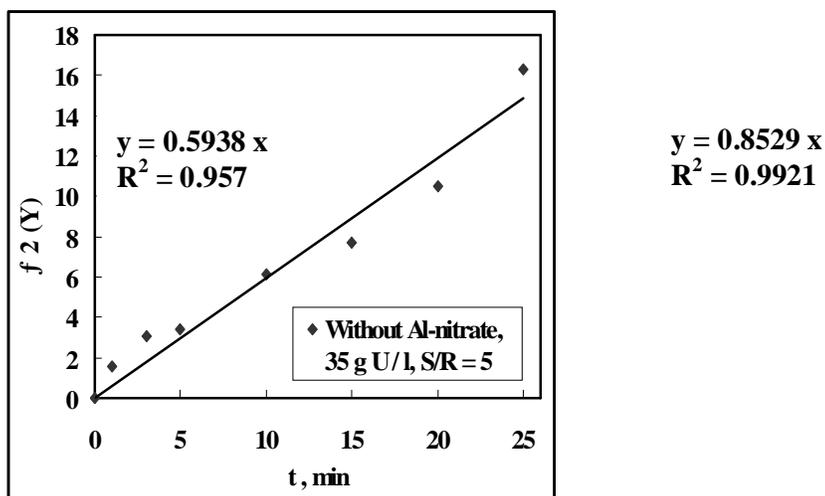


Fig. (6): Evaluation of Film and Solid Diffusion Control Equation for Uranium Extraction without Presence of Al-nitrate

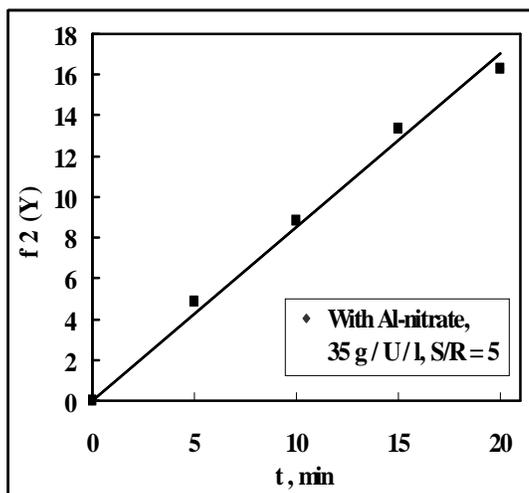


Fig. (7): Evaluation of Film and Solid Diffusion Control Equation for Uranium Extraction with Presence of Al-nitrate

Evaluation of the Diffusion through Solid

Results of studying the elution kinetics through varying the contact time in term of fractional approach to equilibrium during uranium elution process are graphically represented in Fig. (8). From these results, it is clear that the

fractional approach to equilibrium was rapidly increased in the first 5 minutes (0.69), while this fractional approach was steadily increased in the further 5 minutes of contact to reach 0.86. However, the fractional approach to equilibrium of 0.94 and 0.99 was reached after 15 and 20 minutes respectively. The results of fractional approach to equilibrium are also used in the calculations to evaluate the diffusion control during uranium elution process and determining the corresponding mass transfer coefficients.

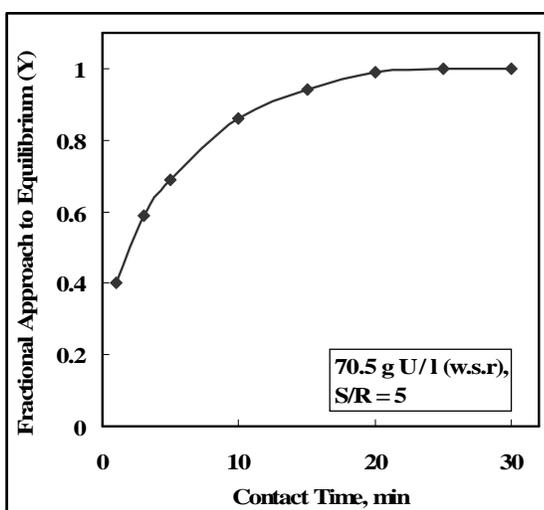


Fig. (8): Fractional Approach to Equilibrium during Uranium Elution from the Loaded SIR

A simplified approximation of the analytical equations for diffusion into and from spheres for constant diffusivity, “ D_p ”, has been given by Vermeulen⁽¹²⁾. Thus, when the rate of mass transfer is controlled by the solid diffusion, as in the case of elution process, the diffusion model through the solid would be:

$$dY / dt = \emptyset (60 D_p / d_p^2) (Y^{*2} - Y^2) / 2 Y$$

Accordingly, $f_3(Y) = -\log(1 - Y^2) = (60 D_p / d_p^2) t$

The correction factor “ \emptyset ” is given by⁽¹⁶⁾:

$$\emptyset = 0.59 / (1 - 0.41 B^{0.5}) \quad \text{for } B < 1, \text{ and}$$

$$\phi = 1$$

$$\text{for } B \geq 1$$

where: $1/B = K c_0 + 1$

Result of testing the validity of solid diffusion model is illustrated in Fig. (9) from which it is clear that a straight line was achieved and the correlation coefficient “ R^2 ” was “0.9958”. This reveals validity of the model and the diffusion through solid controlling the mass transfer rate during the elution process. However, from the straight line slope, the value of “ $60 D_p/d_p^2$ ” was “0.0562”, accordingly, the diffusivity inside resin beads “ D_p ” is found to be $165.2 \times 10^{-12} \text{ m}^2/\text{s}$. Comparing this “ D_p ” value with the data obtained from Levextrel OC 1023^(12,13), it was found that, an increase in this value revealing the decrease in resistance inside the particles of the worked Amberlite XAD-4 impregnated resin.

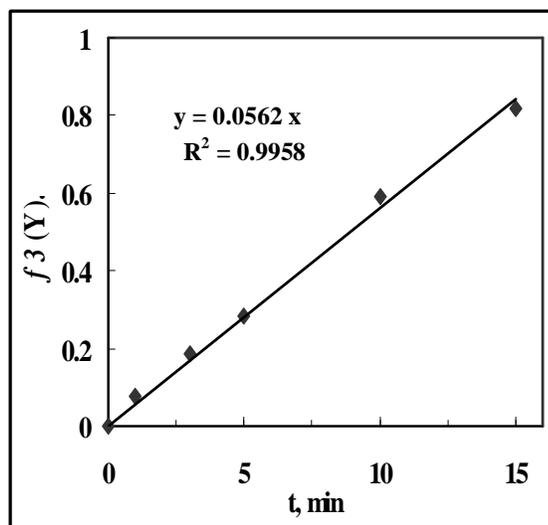


Fig. (9): Evaluation of Solid Diffusion Control Equation for Uranium Elution from Loaded SIR

Conclusion

The fractional approach to equilibrium was more rapid in case of extraction from 1.0 N HNO₃ + 1.5 M Al (NO₃)₃ medium than the case of 5.5 N nitric acid alone during uranium extraction by the working TBP impregnated Amberlite XAD-4 resin. The mathematical equation for the combined liquid film and solid control model was valid for uranium extraction from both nitrate media where the mass transfer coefficient “ k_m ” found to be $0.83 \times 10^{-3} \mu\text{m/s}$ for extraction from nitric acid medium and $1.2 \times 10^{-3} \mu\text{m/s}$ for extraction from nitric acid/Al (NO₃)₃ medium. On the other hand, the mathematical equation for the solid diffusion control model was valid during uranium elution where the diffusivity inside resin beads “ D_p ” found to be $165.2 \times 10^{-12} \text{m}^2/\text{s}$.

Symbols

- a_p** is the specific surface area of resin beads (m^2/m^3).
- b** constant = $- [Q + F/K + Fc_0]$
- B** constant
- c** concentration in the aqueous phase (g U/l)
- c_i** concentration in liquid at resin surface (g U/l)
- c₀** concentration in liquid at start of run (g U/l)
- c*** concentration in liquid in equilibrium with resin (g U/l)
- D** distribution coefficient (q / c).
- d_p** diameter of resin beads (m).
- D_p** diffusivity inside resin beads (m^2 / s).
- F** ratio of liquid volume to freely settled resin volume.
- K** constant.
- k_f** mass transfer coefficient based on liquid film ($\mu\text{m} / \text{s}$)
- k_m** mass transfer coefficient for combined films ($\mu\text{m} / \text{s}$)
- Q** constant.
- q** concentration in resin (g U / l).
- q*** concentration in resin in equilibrium with liquid (g U / l resin).
- Y** fraction approach to equilibrium during adsorption or elution.
- Y*** value of Y at resin surface.
- z** constant = $(b^2 - 4QFc_0)^{0.5}$
- β** constant = $(b + z) / (b - z)$
- Ø** correction factor

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