Uranium Sorption Using Lewatit MonoPlus M500 from Sulphate Media

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Abstract: The present work has focused on the uptake behavior of uranium (VI) from sulfuric acid media by using Lewatit MonoPlus M500 resin. The influence of parameters, namely pH, U (VI) initial concentration, contact time and temperature were investigated. The optimum conditions were explicated via the sorption kinetics, the isotherm models and the thermodynamic data to determine the behavior of the uranium adsorption. The studied resin is an efficient sorbent for U (VI) ions with maximum sorption capacity q_{max} 181.82 mg g^{-1} and agreed with both the pseudo-second order kinetic model and Langmuir isotherm. Thermodynamic characteristics showed that the process was spontaneous ($\Delta G° < 0$) and exothermic ($\Delta H° < 0$) in nature. Finally, by application of the results to increase the uranium assay and purity in the working impure uranium concentrate which produced at Gattar pilot plant, Egypt. The assay increase from about 36% up to 71%, while the purity up to 94%.

Keywords: Uranium, Sorption, Sulphuric Media, Lewatit Mono Plus M500

1. Introduction

Ion exchange resins are the most important and versatile mediums used in the treatment of aqueous solutions. Constantly growing demands on water quality requires increasing sophistication of both the ion exchange resins and the related application technologies. With Lewatit MonoPlus, a new range of ion exchange resins, these systems are taken to a new level. In the early 1980's Bayer was the first company to develop a process for producing monodispersive ion exchange resins. There are different types of monodispersive ion exchangers, such as: (1) Cation exchanger: a. strongly acidic, gel type, e.g. MonoPlus S108, b. strongly acidic, macroporous, e.g. Lewatit MonoPlus ASP 112 [1], and K-14chS (TOKEM-145-9.5) resin [2]. c. slightly acidic, macroporous, e.g. Lewatit CNP 80. (2) Anion exchanger: a. strongly alkaline, gel type, e.g. MonoPlus M 500. b. strongly basic, macroporous, e.g. MonoPlus 800 [1], and A-14chS (TOKEM-845-8) [2]. c. weakly basic, macroporous, e.g. Lewatit® MonoPlus MP 64 [3], and Lewatit MP 62 WS. (3) Acrylic exchanger, e.g. Lewatit VPOC 1071. (4) Inert resin, e.g. Lewatit IN 42 [1].

Lewatit MonoPlus ion exchange resins have a considerable number of advantages over heterodisperse types. The bead size diameter for Lewatit MonoPlus lies between 0.55 and 0.75 mm, depending on the type. This type of resins is characterized by monodispersity higher than 90% (more than 90% of all beads are within 0.05 mm of the given bead diameter); therefore the above-mentioned monodispersive form of resins gives high efficiency, higher stability and extremely robust results in their long lifetimes. In practice, this advantage leads to higher permitted differential pressures, allowing greater resin bed depth and higher velocities. Moreover, their good kinetic properties cause reduction of required bed depth and ion leakage and permit shorter cycle times. The better kinetic properties, the better exchange behavior resulting in lower regenerate and rinse water demand. Increase of regeneration efficiency and unit capacity (total capacity is improved by about 10% compared to the heterodisperse one) as well as decreases in the amount of resin required (smaller column) and operating costs are the results of their high operating capacity [4].

From the literature, Lewatit MonoPlus resins are widely applied in a range of industries such as purification of organic liquids as the removal of glycerin from biodiesel, recovery of reusable materials (chromium, molybdenum,

copper, gold), uranium extraction, separation of the rare earths, wastewater treatment, waste air purification and soil purification.

Lewatit MonoPlus M 500 and Lewatit FO36 are used in separation of As(III) and As(V) species from natural and drinking water [5]. Lewatit MonoPlus M 500, Lewatit MonoPlus M 600 and Lewatit MonoPlus MP 500 used in sorption of heavy metal ions—Cu(II), Co(II), Ni(II) and Fe(III)— from aqueous solutions containing iminodisuccinic acid (IDS) or EDTA [6]. Lewatit MonoPlus MP 600 has been studied for the simultaneous sorption recovery of Pt(IV), Pd(II) and Rh(III) present in chloride solution collected from the leaching platinum group metal-containing spent automotive catalyst [7]. Lewatit FO36 can be successfully used for the adsorption of Cr (VI) from aqueous solutions using the batch method [8]. A chelating resin of a new generation with the bi's-picolylamine functional groups, namely Lewatit MonoPlus TP-220 was applied in selected noble metal recovery such as palladium(II), platinum(IV), gold(III) and base metals such as Cu(II), Co(II), Ni(II) and Zn(II) [9]. Sorption recovery of palladium(II) present in chloride and chloride−nitrate(V) solutions can be achieved by applying the commercial strongly basic anion exchanger Lewatit MonoPlus SR-7 [10].

Uranium was extracted from carbonate leach liquor using Lewatit Mono plus M500 as anion exchange resin with 77% extraction efficiency. Bell curve was achieved from the elution process with 89.5% elution efficiency [11]. Also, the adsorption behavior of Lewatit mono plus M500 resin was studied by batch experiments to determine the optimum conditions for uranium removal rare earths sulfate liquor contaminated with traces of uranium as radioactive contaminates [12].

This paper describes the applicability of Lewatit MonoPlus M 500 in uranium(VI) removal from the sulphate solution attained from Gattar pilot plant, Nuclear Materials Authority, Egypt. Kinetic and equilibrium studies of the sorption process and regeneration and reuse of this resin were considered.

2. Experimental

2.1. Reagents and Solutions

All reagents used were of analytical reagent grade. The standard uranium sulphate solution was prepared by dissolving uranyl sulphate trihydrate $UO_2SO_4.3H_2O$ obtained from Ibilabs, Florida, USA. The working Lewatit MonoPlus M500 resin was purchased from Lanxess (Germany). The physicochemical properties and brief specifications of this resin are presented in Table 1. Prior to use, resin pretreatment was carried out by washing with distilled water, followed by contacting with 0.5 M sulfuric acid for several times to remove organic and inorganic impurities from its synthesis and was finally aired-dried.

Table 1. Characteristics of the Lewatit MonoPlus M500 ion exchange resin。

Resin type	Strongly basic anion exchange resin, type 1	
Matrix	Crosslinked styrene-divinylbenzene (gel)	
Structure	gel type beads	
Ionic form as shipped	Cl⁻	
Functional group	Quaternary ammonium	
	— CH₂ - N(CH₂-CH₂-CH₃)₃Cl	
Appearance	yellow, translucent	
Operating temperature	max. 70°C	
Operating pH-range	0 – 12	
Mean bead size	0.62 (+/- 0.05)	
Stability	pH range	0 – 14
	Temperature range	-20°C - 40°C
Regenerant	NaOH	

2.2. Apparatus and Analytical Procedure

The quantitative analysis of uranium was achieved spectrophotometrically by UV single beam spectrophotometer model SP-8001'', Metretech Inc., version 1.02 using Arsenazo III method [13] and curtained by an oximetric titration against ammonium metavanadate method using N-phenyl anthranilic acid indicator (Sigma-Aldrich) [14]. All experiments were carried out three times and only the average values were reported.

Environmental scanning electron microscope (ESEM), Philips XL30, Nuclear Material Authority (NMA), Egypt, was used in order to obtain information about Lewatit MonoPlus M500 surface morphology also, the purity of final precipitate of uranium qualitatively. The FTIR spectroscopy was employed to confirm the interactions between Lewatit MonoPlus M500 resin and uranium ions using 4100 Jasco-Japan infrared spectrophotometer, Cairo University.

2.3. Sorption Experiments

In order to organize, establish and understand an adequate design model for the removal of uranium from aqueous media, isotherms, kinetics, thermodynamic and desorption studies are essential basic prerequisites. These studies were carried out using the batch experiments method.

Sorption experiments were conducted using a batch technique to determine the optimum adsorption conditions, including pH, contact time, initial metal ion concentration and temperature, so batch experiments were carried out by contact of 0.1 g of Lewatit MonoPlus M500 with 10 ml of

uranium sulfate synthetic solution (of 200 mg/L initial uranium concentration) in a stopped conical flasks and placed on mechanical shaker at room temperature. The adsorption efficiency of uranium by the resin under discussion was estimated by means of the recovery degree (R, %), which is the difference between its equilibrium and initial concentrations as the following equation:

$$R = (C_o - C_e/C_o) \times 100\% \qquad (1)$$

and the equilibrium sorption capacity is expressed as

$$q_e = (C_o - C_e) \times V/M \qquad (2)$$

Where C_o and C_e are the original and the equilibrium concentrations of uranium (mg/L), respectively, V is the volume of the aqueous phase (L), and M is the weight of the resin used (g).

For elution process, the loaded uranium was eluted from the Lewatit MonoPlus M500, through applying a number of eluting agents with different concentrations.

3. Results and Discussion

3.1. Effect of pH

The pH of the aqueous solution plays an important role in the whole adsorption process and particularly on the adsorption capacity, influencing the surface charge of the adsorbent, the degree of ionization of the materials, and the dissociation of functional groups such as, carboxyl, hydroxyl and amino on the active sites of the adsorbent [15]. It can also influence the aqueous chemistry of uranium [16]. The mobility of the other ions in the medium is affected by concentration of H^+ ions. Moreover, it also affects interest and capacity of adsorbents for target species. There is always a competition between H^+ ions and target species depending on pH in the medium [17]. Especially, if there are polyphonic or polycationic species in their solution, interactions are fairly affected by the pH of the medium.

The effect of initial solution pH was investigated by preparing a series solution having a different pH within the range 0.5 to 2.8, adjusted by using either 0.5M H_2SO_4 or 0.5M NaOH. As a result of this experiment, it was observed that the uranium adsorption efficiency, increased from 37.2% at pH 0.5 to a maximum value of 90.6% at pH 1.8 and then declines slowly from 90.6% to 82.5% as shown in Figure 1. The bivalent $[UO_2(SO_4)_2]^{2-}$ and in particular the tetravalent uranium sulfate complexes $[UO_2(SO_4)_3]^{4-}$ at lower pH were found to have a high affinity for the anionic exchange resins [18, 19].

So, pH 1.8 of the sample was selected for further experiments. In the adsorption cycle or step, the uranium anionic complexes are adsorbed on the resin and their interaction may be represented as follows, where R represents the fixed ion-exchange sites of the resin, and X^- equals sulfate anions.
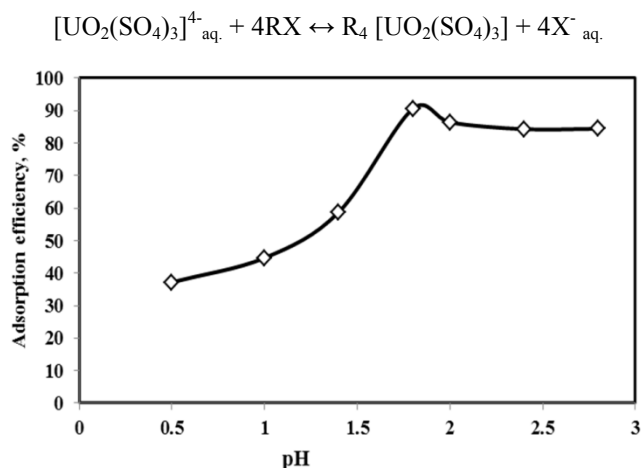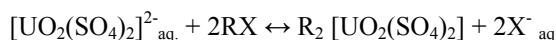
$$[UO_2(SO_4)_2]^{2-}_{aq.} + 2RX \leftrightarrow R_2[UO_2(SO_4)_2] + 2X^-_{aq}$$

$$[UO_2(SO_4)_3]^{4-}_{aq.} + 4RX \leftrightarrow R_4[UO_2(SO_4)_3] + 4X^-_{aq.}$$

Figure 1. *pH dependence of the uranium adsorption efficiency.*

3.2. Effect of Resin/ Liquid (Sulphate Solution) Ratio (R/L)

A series of (R/L) ratios was performed from 1/15 to 1/70 under constant uranium concentration, at room temperature for 30 min time and pH 1.8. The obtained data are plotted in Figure 2. It was observed that the adsorption efficiency, increased with increasing the pregnant feed solution from 1/15 to 1/50 for the resin, more increase in the pregnant feed solution gave a slight increase in uranium adsorption efficiency, so the ratio 1/50 was recommended the optimum ratio.
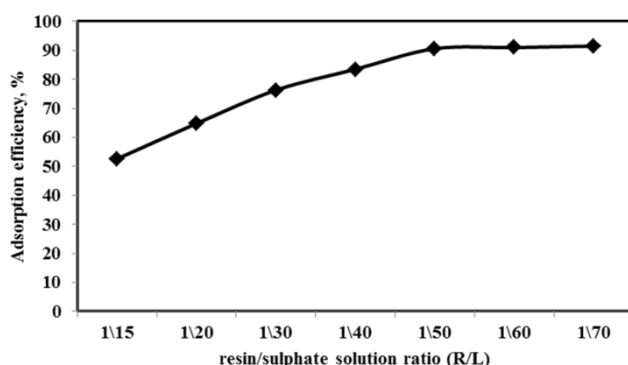

Figure 2. *Effect of resin/ liquid (sulphate solution) ratio on uranium adsorption.*

3.3. Effect of Uranium Initial Concentration

The initial concentration of uranium was studied by contacting 0.1 g of Lewatit MonoPlus M500 with 10 ml of uranium sulfate synthetic solution of different initial concentration of uranium ranging from 10 mg/L to 1000 mg/L for 30 min., pH 1.8, and 200 rpm at room temperature.

From Figure 3, the uranium ions sorption increased with the initial concentrations of metal ions, increasing at the beginning and then reached to surface saturation at high concentrations. This indicated that, at lower initial concentrations of uranium ions, the sorption sites on the adsorbent were sufficient for the metal ions, the sorption relied on the amount of metal ions transported from the

bulk solution to the surfaces of the sorbents. However, at higher initial concentrations of UO_2^{2+} ions, the adsorption sites on the surfaces of the sorbents reached to saturation, and the sorption of UO_2^{2+} ions achieved equilibrium [20, 21]. This could be due to a higher probability of collision between uranium ions and the adsorbent surface and a better driving force, which lessens the mass transfer resistance, the sorption sites on the surfaces of the sorbent reached to saturation, and the sorption of uranium ions achieved equilibrium [22, 23].
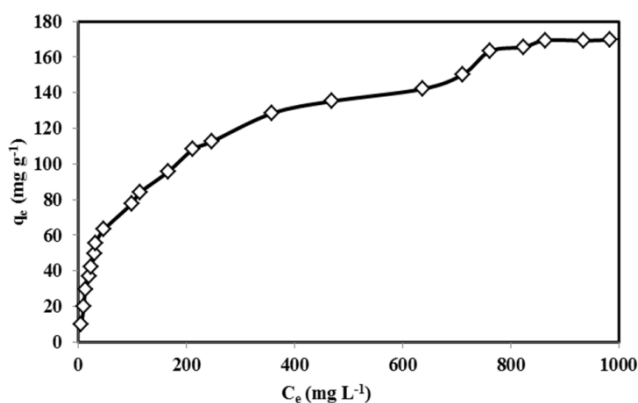

Figure 3. Effect of uranium initial concentration on the sorption capacity.

Sorption isotherms studies

The metal ions can be adsorbed from their solutions onto the surface of solid sorbent by several mechanisms. To investigate the best fitting isotherm model, the sorption experiments were conducted at the previously found optimum conditions.

Sorption isotherm studies are extensively used to provide information about the amount of adsorbed ion by a certain adsorbent and about the interaction between the adsorbents and adsorbate [24].

The Sorption equilibrium data have been analyzed using various isotherm models, such as the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models [23]. Non-linear regression method was applied to the results in order to see the harmony between experimental results and theoretical models. Though the fit of experimental data by a given equation does not necessarily means that the mechanisms associated with the model are verified, this may help in interpreting the adsorption mechanism.

i. Langmuir Isotherm Model

The Langmuir [22] isotherm is based on the following assumptions: (a) adsorbents are chemically adsorbed at a fixed number of well-defined sites; (b) a monolayer of the adsorbent is formed over the surface of the adsorbent when it gets saturated; (c) each site can hold only one adsorbate species; (d) all sites are energetically equivalent; (e) interactions between the adsorbate species do not exist.

The Langmuir isotherm equation is depicted by Eq.(3):

$$C_e / q_e = (1/q_{max.}) C_e + (1/b\ q_{max.}) \qquad (3)$$

where q_e is the amount of adsorbent adsorbed at the

equilibrium (mg g^{-1}), C_e is the supernatant adsorbate concentration at the equilibrium (mg L^{-1}), b is the Langmuir equilibrium constant (L mg^{-1}), and q_{max} is the maximum adsorption capacity of the adsorbent (mg g^{-1}) assuming a monolayer of adsorbate uptake by the adsorbent. So, the adsorption increases with concentration until active center on the surface is fulled by analyte ions. The adsorbed amount reaches a plateau and equilibrium with increasing concentration.

Experimental results are plotted as shown in Figure 4 using the linearized Langmuir equation, and the parameters of the model are summarized in Table 2.

For further analysis of the adsorption process, a dimensionless constant (or the separation factor) (R_L), which reflects the essential characteristic of Langmuir model, can be obtained from the constant b from Eq.(4):

$$R_L = 1/ (1 + b\ C_o) \qquad (4)$$

where b (L mg^{-1}) refers to the Langmuir constant and C_o is denoted to the adsorbate initial concentration (mg l^{-1}). In this context, lower R_L value (from 0.92 to 0.09) reflects that adsorption is more favorable. In a deeper explanation, R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [23, 25].

From this research work, the maximum monolayer coverage capacity (q_{max}) from the Langmuir isotherm model was determined to be 181.82 mg g^{-1}, b (Langmuir isotherm constant) is 0.0091 L mg^{-1}, R_L (the separation factor) is from 0.92 to 0.09 indicating that the equilibrium sorption was favorable and the R^2 value is 0.989 proving that the sorption data fitted well to Langmuir Isotherm model.

ii. Freundlich Isotherm Model

Freundlich [26] isotherm model is an exponential equation, and assumes that the concentration of adsorbate on the adsorbent surface increases as the adsorbate concentration increases. Theoretically, using this expression, an infinite amount of adsorption will occur. Similarly, the model assumes that the adsorption could occur via multiple layers instead of a single layer. The equation has a wide application in heterogeneous systems. Eq.(5) shows the Freundlich isotherm model;

$$\log q_e = \log k_f - 1/n \log C_e \qquad (5)$$

where k_f (the Freundlich isotherm constant) is an approximate indicator of adsorption capacity, and n is the Freundlich exponent (dimensionless) is the heterogeneity factor [23] and it is a function of the strength of adsorption in the adsorption process [27]. If n = 1 then the partition between the two phases are independent of the concentration. If a value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption [28]. It is accepted that heterogeneity of surface is increased if n value approaches to 1. From the data in Table 2, that a value of 1/n = 0.46 while n = 2.19 indicating that the sorption process is favorable and the R^2

value is 0.932.

iii. Dubinin–Radushkevich (D-R) Isotherm Model

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [29, 30]. The linearized form of the D-R equation is given by Eq.(6):

$$\ln q_e = \ln q_D - K_{DR}\,\varepsilon^2 \qquad (6)$$

where q_D is the theoretical isotherm saturation capacity, K_{DR} is related to the mean free adsorption energy per molecule of adsorbate and ε ($kJ^2\,mol^{-2}$) is the Polanyi potential and it is expressed as follows Eq.(7):

$$\varepsilon = RT \ln(1 + 1/C_e) \qquad (7)$$

where R is the universal gas constant (8.314×10^{-3} $kJ\,mol^{-1}$ K^{-1}) and T is the absolute temperature, K.

The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E_{DR} per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the relationship [31, 32]:

$$E_{DR} = (2K)^{-1/2} \qquad (8)$$

It is commonly accepted that physical adsorption corresponds to mean adsorption energy below 8 $kJ\,mol^{-1}$ while chemical adsorption requires mean adsorption energy greater than 8-16 $kJ\,mol^{-1}$ [23, 33]. One of the unique features of the Dubinin-Radushkevich (DRK) isotherm model lies on the fact that it is temperature-dependent, which, when adsorption data at different temperatures are plotted as a function of the logarithm of the amount adsorbed (Ln q_e) vs ε^2 the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve [23].

In the present work, the experimental adsorption data were fitted based on the aforementioned isotherm models. All parameters were obtained from the slopes and intercepts of the fitted straight lines of the three isotherm plots are shown in Figure 4 and are summarized in Table 2. Based on Table 2, the correlation coefficients (R^2) of the linear form of the Langmuir model were nearly closer to ≈ 1.0 than the values obtained with the Freundlich model and a maximum adsorption capacity (181.82 mg g^{-1}) close to that experimentally determined ($\approx$ 169 mg g^{-1}). This was expectable based on the shape of sorption isotherms: the saturation plateau is consistent with the asymptotic trend associated with the Langmuir equation, while the Freundlich equation means an exponential trend. Calculated R_L value (from 0.92 to 0.09) was less than 1 while the value of n was greater than 1 reflects that adsorption process is more favorable. This suggests that uranium occurs through monolayer sorption onto a surface, with a finite number of identified sites, which are homogeneously distributed over the adsorbent surface.

The values of K_F, 1/n and R^2 in the Freundlich model (Figure 4) are reported in Table 2. The value of 1/n is less

than 1; whatever the concentration and the temperature: this means that the sorption is a favorable process over the entire concentration range [23, 34]; however, the correlation coefficient is lower than in the case of the Langmuir equation.

Meanwhile, from the Dubinnin-Radushkevich (D-R) isotherm, the plot of ln q_e versus ε^2 gives a straight line with the slope K and the intercept ln q_D shown in Figure 4. The parameters of the model are reported in Table 2. The calculated value of the mean adsorption energy (E_{DR}) is 1.6 $kJ\,mol^{-1}$ which is below 8 $kJ\,mol^{-1}$, suggesting that the uptake of uranyl ions was driven by physisorption process based on van der waals forces.
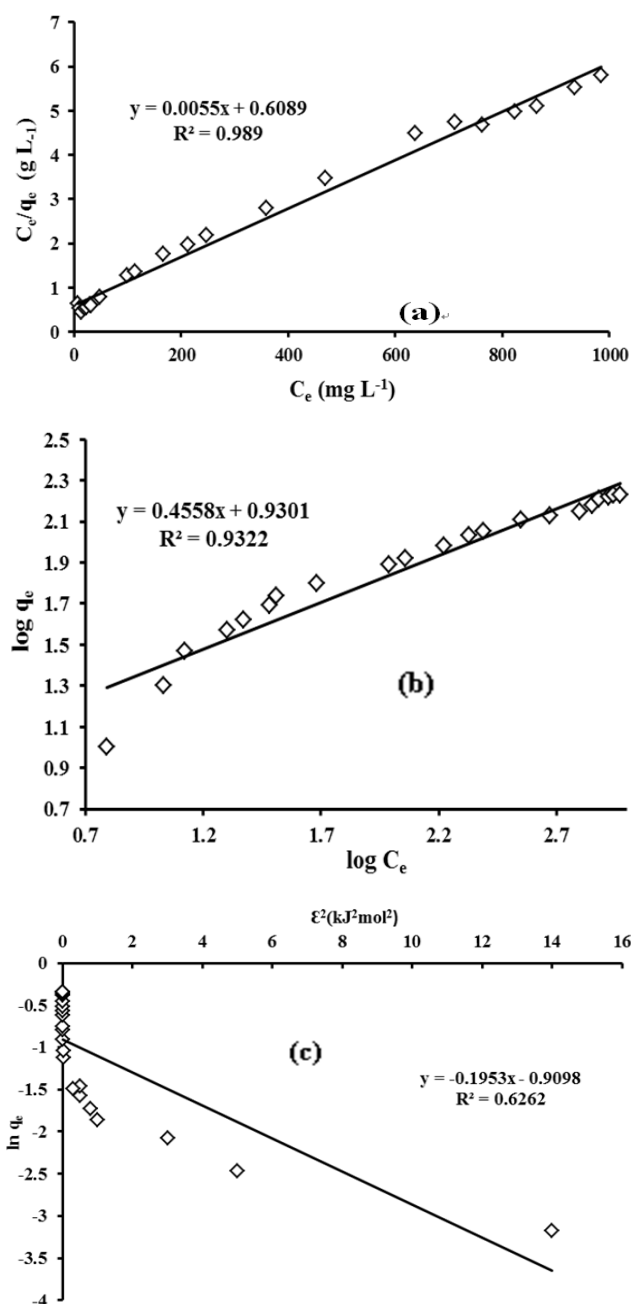

Figure 4. Isotherms models: (a) Langmuir, (b) Freundlich and (c) D-R for U(VI) sorption onto Lewatit MonoPlus M500.

Table 2. *Isotherm constants for U(VI) ions sorption.*

Model	Parameters		
Langmuir	q_{max} 181.82 mg g^{-1}	b 0.0091 L mg^{-1}	R^2 0.989
Freundlich	n 2.19	k_f 8.51 mg g^{-1}	R^2 0.932
Dubinin-Raduskevich	$q_{max, D-R}$ 95.83 mg g^{-1}	E_{DR} 1.6 kJ mol^{-1}	R^2 0.626

A comparison between the adsorption capacity of Lewatit MonoPlus M500 resin and some other adsorbents is provided in Table 3. Since these experiments were not systematically obtained under similar experimental conditions, the strict comparison of absolute values is not easy; this simply gives an overview of the potential of the present sorbent against other materials.

Table 3. *Comparison between the adsorption capacity of U(VI) on various adsorbents.*

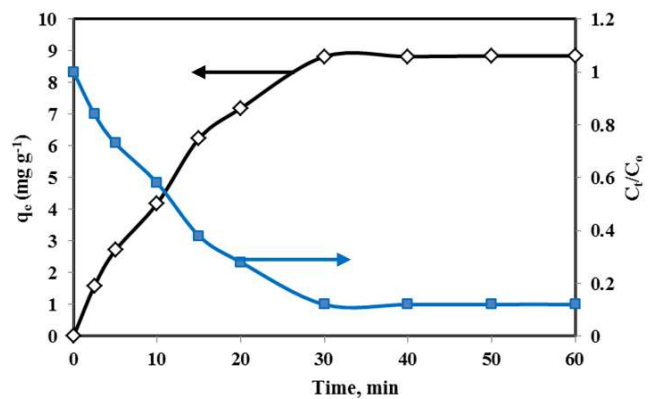| Adsorbent	U (VI) sorption capacity q_{max} (mg g^{-1})	References
Amberlite IR-910	64.27	[35]
Ambersep 920U SO$_4$	58	[36]
Amberjet 1200 H	133	[37]
Lewatit TP260	6	[38]
Lewatit MonoPlus M500 resin	181.82	Present work

3.4. Effect of Equilibration Time and Sorption Kinetic Studies

The effect of the equilibrium time on the adsorption of UO_2^{2+} ions was investigated from 0 to 90 min, while other factors were fixed at 0.1 g of Lewatit MonoPlus M500 in 50 ml; 200 mg U l^{-1} were agitated at 200 rpm at 25 ±1°C.

Figure 5 shows a plot of the sorption capacity (q_t, mg U g^{-1}) versus time (t), the plot reveals that the kinetics of UO_2^{2+} ions adsorption mainly consists of two stages: an initial rapid stage related to the instantaneous external surface adsorption of metal ions, that takes place for the first 30 min of contact and represents more than 90% of the total amount adsorbed, indicate that the UO_2^{2+} ions adsorption process proceeded fast and reached saturation levels gradually due to the strong affinity of the uranium ions for Lewatit MonoPlus M500 resin (correlated to both the affinity of these reactive groups for uranyl ions and to the increased number of reactive groups). The second stage in the process corresponds to a slow phenomenon limited by the strong decrease in the availability of sorption sites (most of them being occupied; this corresponds to the approach to saturation). Based on these results a contact time of about 30 min is sufficient to achieve the equilibrium.

Kinetic studies

The study of adsorption kinetics is important in the treatment of aqueous effluents because it provides valuable pieces of information on the reaction pathways and the mechanism of adsorption reactions. Many kinetic models were developed to evaluate the intrinsic kinetic adsorption constants such as the pseudo-first order rate equation (PFORE), the pseudo-second order rate equation (PSORE) and the resistance to intraparticle diffusion (RIDE).

Figure 5. *Effect of time on the adsorption of U(VI) ions.*

i. Pseudo-first-order rate equation (PFORE)

The pseudo-first order of Lagergren assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake to time. The kinetic was expressed as in the following Eq.(9) [25]:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303) \, t \qquad (9)$$

where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and time t (min), respectively. k_1 (min^{-1}) is the rate constant of PFORE. The constants can be determined experimentally by plotting of log (q_e- q_t) against t.

ii. Pseudo-second-order rate equation (PSORE)

The model [20, 39, 40] is based on the assumption that the adsorption follows second order chemisorptions and predicts the behavior over the whole range of concentration and is in agreement with an adsorption mechanism being the controlling step rate. This model is represented as equation (10) [39-41]:

$$t / qt = 1/k_2 \, q_e^2 + (1/q_e) \, t \qquad (10)$$

k_2 (g mg^{-1} min^{-1}) is the rate constant of PSORE and the constants can be determined experimentally by plotting of t/qt against t.

iii. Resistance to Intraparticle diffusion model (RIDE)

For systems controlled by the resistance to intraparticle diffusion complex models exist; however, a first diagnostic on the impact of this mechanism in the control of uptake kinetics can be obtained using a simplified Eq.(11):

$$q_t = k_{int} \cdot t^{0.5} + c \qquad (11)$$

where q_t (mg g^{-1}) is the amount of metal ions adsorbed at time t (min), and k_{int} (mg g^{-1} min$^{-0.5}$) is the intraparticle diffusion constant. According to Eq. (11), a plot of $q_t \sim t^{0.5}$ should be a straight line with a slope k_{int} and intercept c.

In the present study, experimental data have been fitted by the aforementioned kinetic models. The rate constants, calculated U(VI) equilibrium uptakes, and corresponding correlation coefficients were calculated and have been reported in Table 4 and shown in Figure 6. In the case of pseudo first order kinetic equation, the calculated sorption

capacity value (q_e cal. = 11.85 mg g^{-1}) significantly deviated from the experimental ones (q_e exp. = 8.82 mg g^{-1}) and also the correlation coefficient was very low. While in pseudo second order the predicted U(VI) uptake (q_e cal. = 9.74 mg g^{-1}) was consistent with the experimental one. Additionally, the correlation coefficient for the pseudo second order kinetic equation (R^2 = 0.9911) was much higher than in the case of the pseudo first order (R^2 = 0.9864). The (RIDE) model show poor correlation coefficient (R^2 = 0.8462) if compared with the correlation coefficient of pseudo second-order model, this means that the (RIDE) model is not playing a significant role in the control of uptake kinetics and the pseudo-second order sorption mechanism is the predominant and the rate limiting step is the chemical sorption mechanism.

Table 4. *Kinetics parameters for U(VI) ions sorption.*

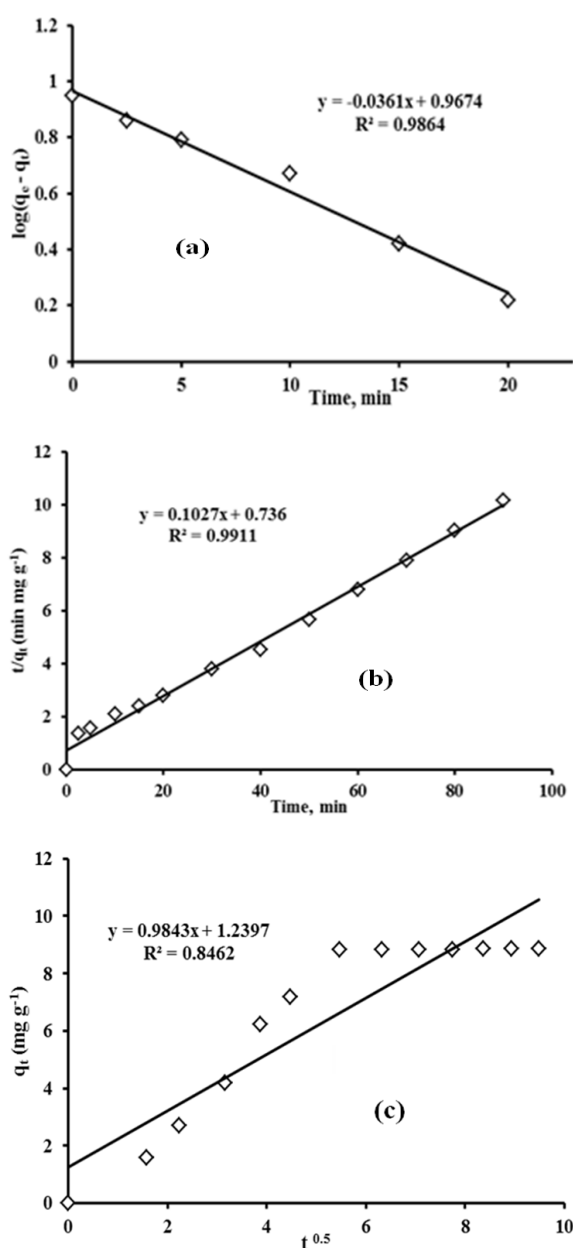| Model	Parameters		
Pseudo-first order rate equation (PFORE)	K_1 9.8×10^{-2} min^{-1}	q_e 11.85 mg g^{-1}	R^2 0.986
Pseudo-second order rate equation (PSORE)	K_2 0.014 g mg^{-1} min^{-1}	q_e 9.74 mg g^{-1}	R^2 0.991
Resistance to intraparticle diffusion equation (RIDE)	C 1.2397 mg g^{-1}	K_{int} 0.9843 mg g^{-1} min-	R^2 0.626

Figure 6. *Kinetic models: (a) PFORE, (b) PSORE and (c) RIDE for U(VI) sorption onto Lewatit MonoPlus M500.*

3.5. Effect of Temperature on Sorption Process and Thermodynamic Parameters

The temperature of the solution is an important parameter for the adsorption of UO_2^{2+} ions; an increase or decrease in temperature will change the equilibrium capacity of the adsorbents during the process of adsorption. Also thermodynamic parameters are used to explain the mechanism of adsorption. The effect of temperature on uranium adsorption on the resin was studied at different temperature in the range 298K to 343K. The sorption of uranyl ions decreases with increasing the temperature as shown in Figure 7.
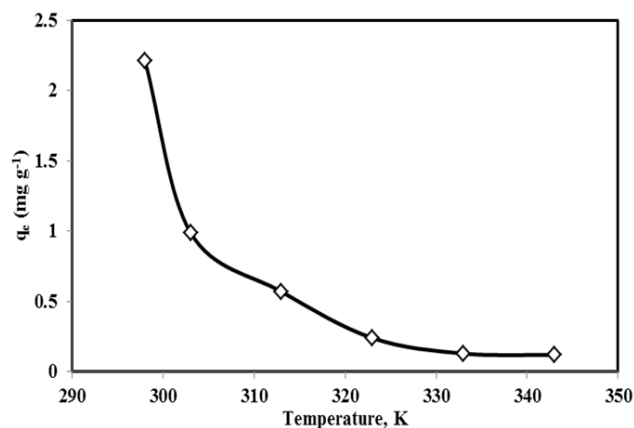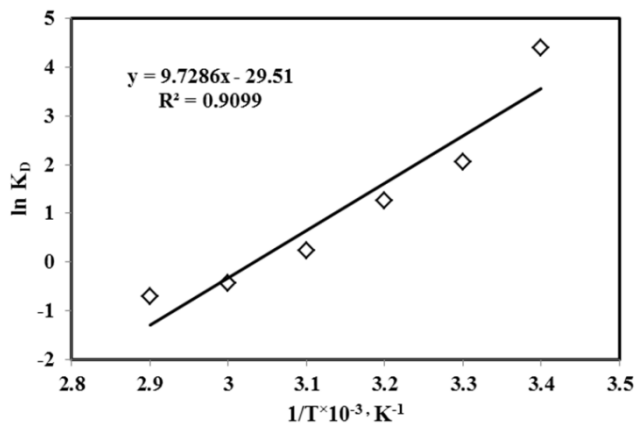

Figure 7. *Effect of temperature on adsorption efficiency of Lewatit MonoPlus M500.*

This decrease in the uranium uptake capacity with increasing temperature might be due to a decreasing effect on the surface activity where at high temperature, the thickness of the boundary layer would decrease due to the increasing tendency of U(VI) to escape to the solution phase [12].

The uranium adsorption at room temperature (298K) reached 88.2% and decreased down to 4.64% at 343K: the reaction is by exothermic nature. This is confirmed by the determination of the enthalpy change ($\Delta H°$), the entropy change ($\Delta S°$) and the Gibbs free energy ($\Delta G°$) of the reaction which are reported in Table 5 and shown in Figure 8.

Table 5. *Thermodynamic parameters of U(VI) ions sorption.*

$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1}mol^{-1})	$\Delta G°$ (kJ mol^{-1})						R^2
		298K	303K	313K	323K	333K	343K	
-80.884	-245.35	-7.769	-6.542	-4.089	-1.635	0.817	3.271	0.9099

Figure 8. *Van't Hoff plots of lnK$_D$ against 1/T for U(VI) ions sorption.*

Figure 9. *FTIR spectrum of Lewatit MonoPlus M500 before (a) and after (b) uranium loading.*

From Table 5, it is clear that $\Delta H°$ has negative value which confirms the exothermic nature of the sorption process. In addition, the negative $\Delta S°$ value suggests decreasing the system randomness at the solid-liquid interface during the adsorption process. The negative value of $\Delta G°$ which decrease with increasing temperature indicates the spontaneous nature of the sorption process and it's more efficient at low temperature.

4. FTIR Study for Both Free and Loaded Lewatit MonoPlus M500 with U(VI)

FTIR spectroscopy was employed to confirm the interaction between Lewatit MonoPlus M500 resin and uranium ions. The spectra of resin before and after uranium adsorption were presented in Figure 9 (a, b). From the figure, it has been realized that some characteristic peaks representing the major groups of the studied resin have a sharp intensity that turned to medium intensity after the adsorption experiments. This indicates that the studied sorbant is able to form complex with U(VI) metal ions in the sulfate solution. Accordingly, the bands of various intensity occurring at 3423.99 cm^{-1}, 3020.94 cm^{-1} and 2923.56 cm^{1-} associated with valence vibrations of a C-H bond in an aromatic ring and the methylene group (-CH$_2$) in the polystyrene chain. The bands at about 1482.99 cm^{-1} as well as 1422.24 cm^{-1} assigned to scissoring vibration of the methylene group in the polystyrene chain, the bands at 1381.75 cm^{-1} corresponding to benzene ring vibration. The frequencies 1625.7 cm^{-1} and 830.2 cm^{-1} correspond to the skeleton aromatic stretching and bending vibrations respectively, of the alkene C=C bonds in the ring plane [42].
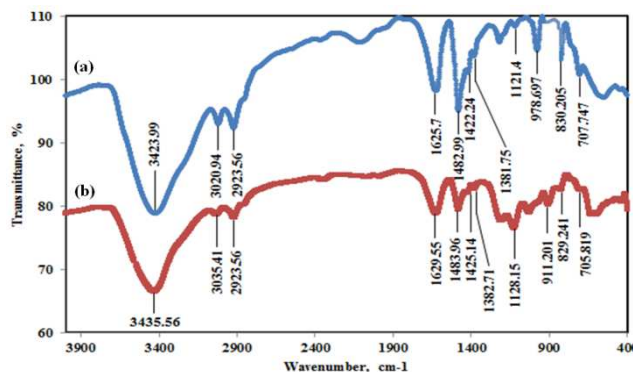
On the other hand, there are characteristic bands at 1121 cm^{-1} and 707.74 cm^{-1} assigned to C-N antisymmetric and symmetric stretch vibration absorption, respectively. In addition, the peaks related to the quaternary nitrogen appear at 978.68 cm^{-1} [9]. It is thus possible to mention that Lewatit MonoPlus M 500 resin exhibits, indeed, good affinity towards the U(VI) metal ions in sulphate solution. The FTIR showed new absorption bands which weren't assigned in the spectrum of Lewatit MonoPlus M 500 resin; a characteristic peak of UO$_2^{2+}$ has been clearly observed at 911.2 cm^{-1} [43- 48]. U(VI) metal ions have replaced the sulfate ions in the adsorption step and to be released by elution. It has also to be mentioned that, it is clearly evident that the formed complex between U (VI) metal ions and the resin would take place by the reaction of uranium metal ions and sulfate ions [49].

5. Scanning Electron Microscope (SEM) for Both Free and Loaded Lewatit MonoPlus M500 with U(VI)

The morphologies of Lewatit MonoPlus M500 resin before (a) and after (b) U(VI) uptake are presented in Figure 10 (a, b). As seen in Figure 10 (a, b), the surface of resin before and after absorption was smooth, well-ordered and has a good uniformity, but after the adsorption the resin surface become more brilliant and brighter than before adsorption, this demonstrates that the sorption of U(VI) ions have taken place onto the resin, also the resin has the ability to resist the mechanical damage during experimental operation.
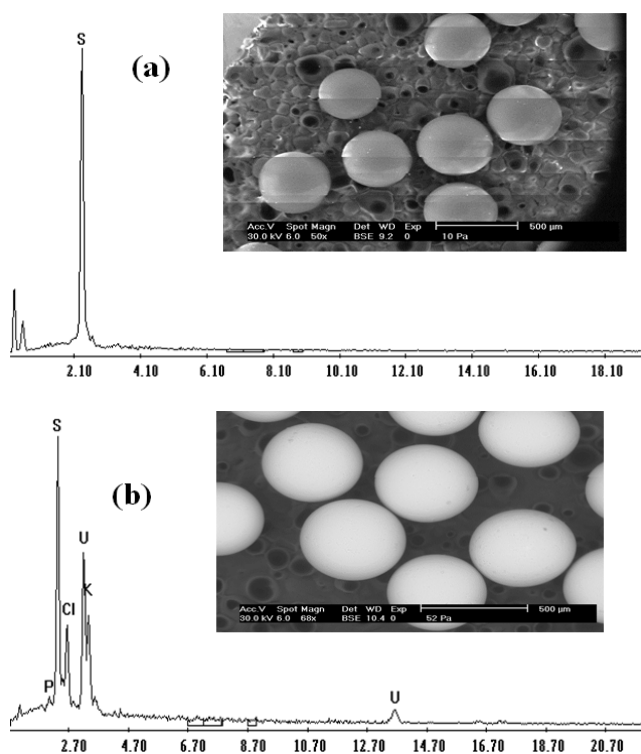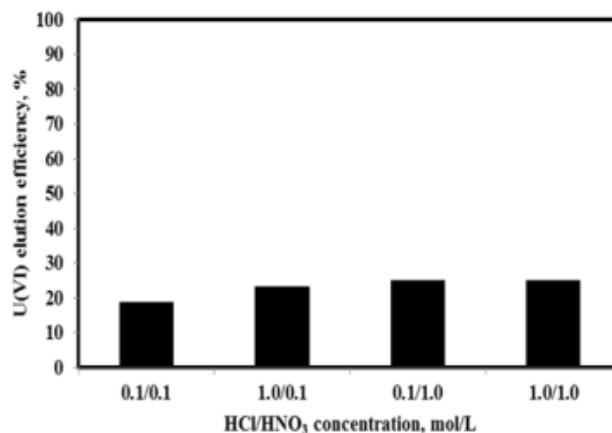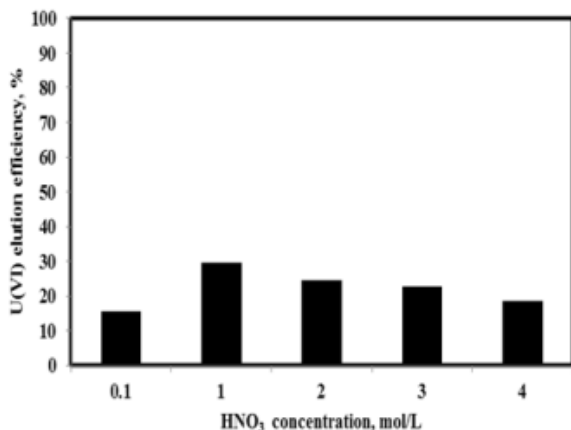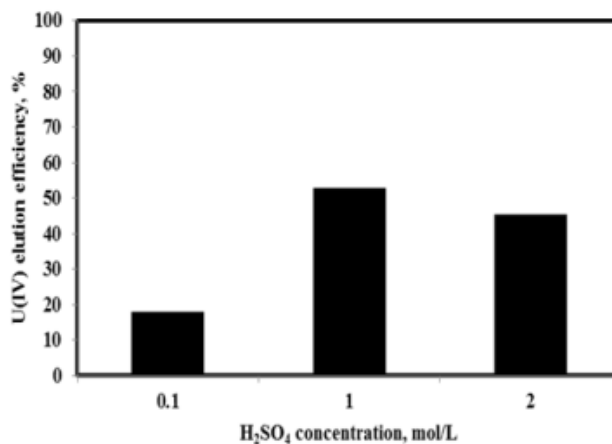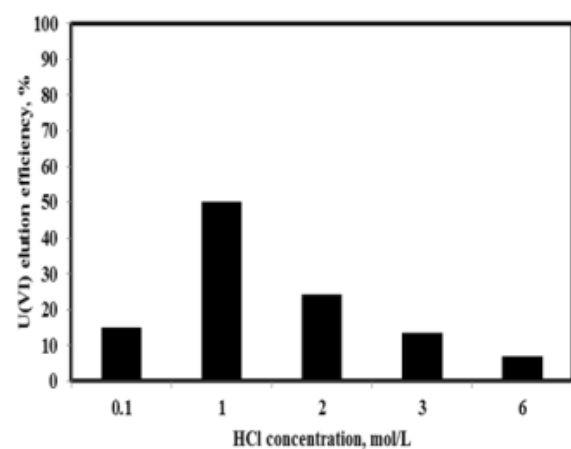
Figure 10. SEM images of Lewatit MonoPlus M500 before (a) and after (b) uranium loading.

6. Desorption Experiments and Reusability of Lewatit MonoPlus M500

To enhance the economic value of the sorption process, desorption process was studied. The desorption process will help to regenerate the spent adsorbent so that it can again be reused to adsorb uranium. Also the mechanism of uranium uptake as well as reusability of adsorbent can be better understood via desorption experiments.

6.1. Effect of the Eluting Agent type

The desorption characteristics of uranyl ions were analyzed by making use of various eluents were equilibrated with different portions of the resin containing a maximum of adsorbed uranium. Several eluents were tested: acidic (0.1-6.0 M HCl, 0.1-4.0 M HNO_3, 0.1-1.0 M HCl + 0.1-1.0 M HNO_3, 0.1-2 M H_2SO_4), basic (0.5-2.0 M NH_4OH) and (1.0 M HCl + 2.0 M NaCl, 0.5 M HCl + 2.0 M NaCl, 0.25 M HCl + 2.0 M NaCl) solutions. As can be seen from the presented data in the following Figure 11, the desorption efficiency of U(VI) from the Lewatit MonoPlus M500 is different depending on the eluting agents used. Also, NH_4OH solution is not a suitable agent in U(VI) removal from loading resins. In this case desorption efficiency is nearly null. It was obvious that (HCl 1.0 M / 2.0 M NaCl) has resulted in 99% U(VI) elution efficiency.
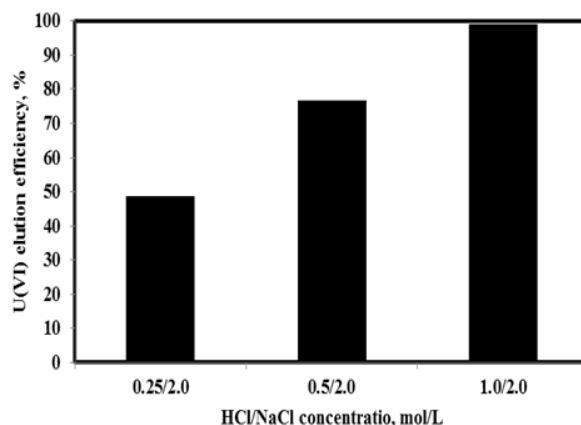
Figure 11. Elution possibility of U(VI) from Lewatit MonoPlus M500.

6.2. Reusability of Lewatit MonoPlus M500

To determine the reusability of the Lewatit MonoPlus resin M500, a repetitive adsorption-desorption cycles were achieved upon the same adsorbent dose using a fresh solution for each cycle under the optimum condition of adsorption and desorption. During the first 17th cycle the adsorption and desorption of uranium have been realized, after that the adsorption efficiency of the resin has decreased from 90.6% to reach 85% in the 23th cycle. Also, the desorption efficiency decreased from 96% to 90% in the 23th cycle. Therefore, the Lewatit MonoPlus M500 is a promising adsorbent that can be used to remove uranium in aqueous solution due to their high reusability and mechanical stability.

7. Case Study

In the present work, we are studying the possibility of upgrading uranium in the impure crude uranium concentrate of Gattar pilot plant, from Nuclear Material Authority, Egypt.

For the upgrading procedure suggested in the present work a proper 1L sulphate solution has been prepared by dissolution of 10g of the crude concentrate in 30g/l sulpuric acid solution. During dissolution the gross amount of silica and other insoluble have been removed as insoluble residue which was then filtrated and washing until having 1 liter clear solution of the working crude uranium concentrate [50].

Table 6. Chemical analysis of the studied sample.

Element	Wt. %	Element	Wt. %	Element	Wt.%
U	35.8000	Fe	1.2234	Sr	0.0490
Ag	0.0668	K	0.2612	V	1.5270
Al	0.0886	Mg	0.4377	Zn	0.0095
Ca	2.1222	Mn	0.0174	Ce	0.0202
Cd	0.0046	Na	4.2794	Sm	0.6708
Co	0.0086	Ni	0.0266	Tb	0.1888
Cr	0.0094	P	0.0742	Ho	0.1080
Cs	0.0320	Si	0.0120	Tm	0.1024
Cu	0.0164				

The obtained clarified solution's pH was adjusted to be ready for sorption experiments. From the above giving, it was found greatly interesting to apply a suggested procedure for upgrading G. Gattar crude yellow cake via its proper treatment with Lewatit MonoPlus M500 resin.

Lewatit MonoPlus M500 resin has been tested for recovering uranium from impure crude uranium concentrate, the solution was adjusted to pH=1.8; contact time 30 min; resin-liquid ratio (R/L) 1:50 and agitation rate 200 rpm at room temperature. By calculating the accumulated loaded uranium and comparing the loading capacity (176.4 mg U/g resin) with the obtained theoretical capacity (181.82 mg U/g resin), the loading capacity of a uranium study solution decreased from 90.6% to 88.2% may be due to the competition between uranium and different ions in the studied sample.

The working sample of Lewatit MonoPlus M500 resin loaded with uranium has been eluted effectively by using (HCl, 1.0 M / 2.0 M NaCl) solution at room temperature for 30 min contact time. The desorption efficiency of uranium was 99%.

Precipitation of Uranium(VI)

Uranium was precipitated from the eluting solution by two ways using a) 25% ammonium hydroxide and b) hydrogen peroxide, respectively.

i) Precipitation by ammonium hydroxide

Uranium was precipitated as ammonium diuranate at pH 7.5 by drop-wise addition of 25% ammonium hydroxide on two cycles, the first cycle the purity of ammonium diuranate was 69.68%, but in the second one the purity was increased to reach about 94.81% and assaying up to 71.19% U has been obtained. The uranium precipitate was dried at 110°C and analysed for U(VI) using the Scanning Electron Microscope (SEM) for its elemental analysis as shown in Figure 12(a, b).
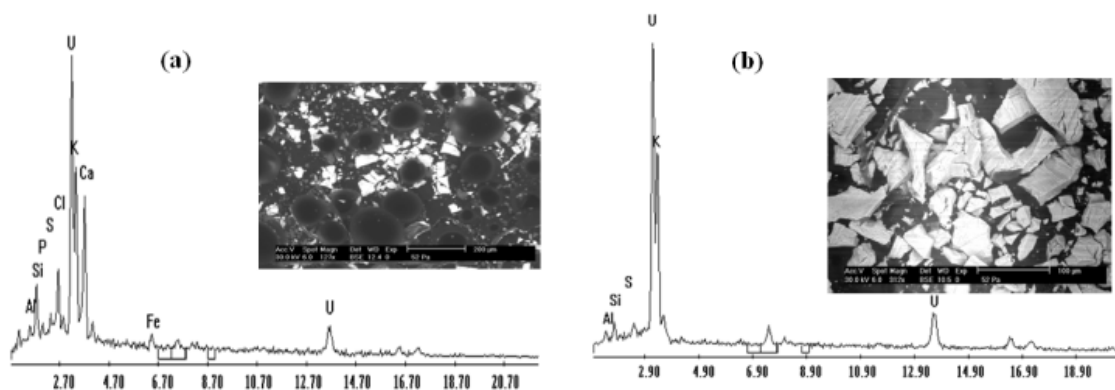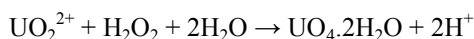
Figure 12. *U(VI) precipitation by NH₄OH (a) first cycle,(b) second cycle.*

ii) Precipitation by hydrogen peroxide

Uranium precipitated from acidic solutions with hydrogen peroxide as shown in the following equation:

$$UO_2^{2+} + H_2O_2 + 2H_2O \rightarrow UO_4.2H_2O + 2H^+$$

The precipitate was dried at 110-120°C for 48h and the SEM analysis for uranium product was has a purity of 94.67% from the first cycle as shown in Figure 13 and assaying up to 71% U has been obtained.
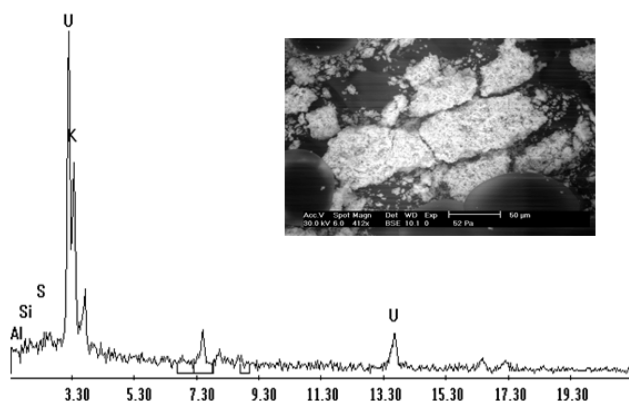

Figure 13. *U(VI) precipitation by H₂O₂.*

8. Conclusion

The attained results of the present work revealed that Lewatit MonoPlus M500 adsorbent could be used effectively for uranium adsorption and removal from the studied crude yellow cake acidic solution. In this study, the batch experiments method were performed to optimize the U(VI) sorption under various conditions, including pH, U (VI) initial concentration, contact time and temperature. The study on equilibrium sorption revealed that Langmuir isotherm model fits well to the experimental data confirming the monolayer adsorption of U(V) onto Lewatit MonoPlus M500 resin with maximum sorption capacity q_{max} 181.82 mg g⁻¹. Thermodynamic studies of the adsorption reaction of U(VI) with Lewatit MonoPlus M500 showed that the $\Delta H°$ of reaction equal to (-80.884 kJ mol⁻¹). The negative value of $\Delta H°$ indicates that the adsorption is an exothermic process, with a decrease in the randomness of the system shown by

negative value of entropy change $\Delta S°$ (-245.35 J K⁻¹ mol⁻¹). The negative value of $\Delta G°$ indicates that the adsorption process was spontaneous. A kinetic study showed that the adsorption process was reached to equilibrium within 30 min. The kinetic date fit well to pseudo-second order kinetic model which was more favorable as the predominant mechanism. Finally, the purity of uranium(VI) product from sulphate solution was 94.81% and 94.67% when using NH₄OH and H₂O₂ solutions, respectively. It has been shown that uranium can be removed from solution and recovered by using a system which can be applied multiple times. Therefore, it has potential application in large scale.

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