

Uranyl (II) sorption onto Lewatit TP 214 resin

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Abstract— This study aims to investigate uranyl (II) removal by the liquid-solid extraction technique using Lewatit TP 214 resin containing thiourea group in polystyrene-divinylbenzene matrix, in batch process. The optimal conditions for UO₂(II) extraction were determined by studying the effects of parameters such as the contact time (0-180mn) with different mass of resin (0.015g, 0.1g, 0.3g), pH level (2-6), the initial concentration of the UO₂(II) ions (10⁻⁵-10⁻³M), ionic strength (CH₃COONa, NaCl) and temperature (293-323°K). The results showed remarkable affinity of resin towards uranyl (II) cations. The maximum uptake values of UO₂(II) was 19.45 mg/g. Percentage removal increases with increasing initial pH solution, uranyl (II) cations removal was better in initial pH values of 4.5, at room temperature. The addition of NaCl salt has a negative effect on the extraction process whereas CH₃COONa does not affect much. The uptake kinetic for uranyl (II) onto Lewatit TP 214 was best described by the pseudo second order model. The Sips isotherm fit well obtained equilibrium data compared to the Freundlich and Langmuir isotherm. The thermodynamic data for uranyl (II) cations sorption onto Lewatit 214 resin, indicate that the process endothermic ($\Delta H^\circ = + 4.84 \text{ KJ.mol}^{-1}$). Thermodynamic study showed also positive ΔG° values, indicating that the sorption process of uranyl (II) is not spontaneous. The quantitative elution study of uranyl can be realized with acetic acid.

Keywords— Liquid-Solid extraction, Uranyl (II), Lewatit TP 214 resin, Thermodynamics parameters.

I. INTRODUCTION

Uranium and its compounds are potential toxic and radioactive environmental pollutants [1], [2], [3], especially in mining and nuclear industry, so the migration of uranium in nature is important in this context [4]. In the aim to eliminate and separate this pollutant from wastewater, many papers were reported methods for separation and recovery of uranium from aqueous solutions [5], [6], such as ionic exchange, chemical precipitation [7], [8], membrane dialysis [9], flotation [10], [11], bio-concentration [12], liquid-liquid extractions [13], [14], solid-liquid separation [15], [16], [17]. At present, solid-liquid separation is recognized as the widest application prospect because it can work more efficiently and it is environment-friendly. It is also the most common technique used for metal pre-concentration in aqueous phase. It is simpler to operate and easier to separate. Various adsorbents including chelating resins and ion exchange resins are used in extraction of metal ions [18], [19]. Lewatit TP 214 is a monospherical, macroporous chelating resin with thiourea groups, having a high affinity for metal cations. The objective

of this research is to carry out a sorption of uranyl (II) ions from aqueous solutions, using Lewatit TP 214 resin. The effects of analytical parameters, such as adsorption kinetic, isotherm study and temperature were investigated.

II. EXPERIMENTAL

A. Reagents

All solutions were prepared from analytical grade chemicals and distilled water. Commercially Lewatit TP 214 resin, was purchased from Fluka Analytical, UO₂(CH₃COO)₂.2H₂O, Arsenazo III, acetic acid, hydrochloric acid (37%) and ammonium acetate were provided from Sigma-Aldrich. Sodium hydroxide ($\geq 97.0\%$, pellets), sodium chloride and sodium acetate (NaCl, CH₃COONa) were purchased from PROLABO Rectapur. A stock solution of 10⁻³ mol. L⁻¹ of UO₂(CH₃COO)₂.2H₂O was prepared by dissolving 0.4241 g in 1L of distilled water. The diluted solutions of uranyl ions were prepared by appropriate dilution of the stock solutions. The initial pH of the sample solutions was adjusted in the desired range by adding dilutes CH₃COOH or NaOH solutions.

B. Apparatus

All pH measurements were performed with a WTW 3310 Set 2 digital pH meter. The extraction of UO₂²⁺ on resin was studied by batch technique. A shaker (Haier model) was used for removal experiments except for temperature effect where a magnetic stirrer (RCT Basic IKAMAG Stirrer with ETS-D5 Temperature Controller) was used. Specord® 210 Plus model analytic Jena UV-Vis spectrophotometer was used to determine UO₂²⁺ as Mⁿ⁺-Arsenazo III complex in aqueous phase [20], [21], [22] and PFP7 Flame Photometer JENWAY was used to determine Na⁺ concentration.

C. Extraction and analysis procedure

In aqueous phase, the UO₂²⁺ concentration was determined spectrophotometrically with Arsenazo III. In a test tube, which contained 2 mL of ammonium acetate/HCl buffer at pH=2.0 [23], were added to 100 μ L of UO₂²⁺ solution to be analysed and 100 μ L of Arsenazo III solution (10⁻³ mol. L⁻¹). Arsenazo III reacts with UO₂²⁺ to form a blue complex which can be estimated at $\lambda_{\text{max}} = 651 \text{ nm}$ [23], [24].

The general method of extraction, used for this study, was described as follows: 0.015 g (w), 0.030 g (w) and 0.100 g (w) of Lewatit TP 214 resin was equilibrated with 4 mL (v) of metal ions solution of known concentration in a stoppered

Pyrex glass flask at the temperature ($22 \pm 1^\circ\text{C}$) in a shaker for predetermined time. The resin was separated by filtration and the filtrate was analysed by UV-Vis spectrophotometer in presence of Arsenazo III for uranyl ions content [24].

The extraction of UO_2^{2+} ions on the resin at four different temperatures 20, 30, 40 and 50°C was investigated. For temperature effect, a magnetic stirrer was used and stirring speed was 250 round per minute to maintain resin particles in suspension. All data reported are based on the average of three replicate measurements.

The percentage of metal ions that was sorbed on the resin (i.e. extraction yield, Y) was determined by comparing its concentrations before and after extraction (Eq. (1)).

$$Y(\%) = \frac{C_i - C_e}{C_i} \cdot 100$$

The amount of metal uptakes at time t, q_t (mg g^{-1}), was calculated by Eq. (2):

$$q_t(\text{mg/g}) = \frac{C_i - C_t}{w} \cdot V$$

The distribution coefficient (K_D) of the uranyl ions between the aqueous solution and the solid resin was also calculated from Eq. (3):

$$K_D(\text{mL/g}) = [M]_{\text{resin}} / [M]_{\text{aq}} = \frac{C_i - C_e}{w} \cdot V / C_e$$

Where $[M]_{\text{resin}}$ and $[M]_{\text{aq}}$ is UO_2^{2+} ions concentration in resin phase (mg. g^{-1}) and in aqueous solution (mol. L^{-1}) respectively. C_i , C_t and C_e are respectively the initial, time t and equilibrium UO_2^{2+} concentration (g. L^{-1}). V is the volume of the solution (4 mL). w is the mass of the resin used.

D. Desorption procedure

After saturation of the Lewatit TP 214 resin by the uranyl ions, it can be regenerated for another extraction, using the following acids: HNO_3 , HClO and CH_3COOH . We can determine the best eluting with help of Eq. (4).

$$\text{ElutionYield}(\%) = 100 \cdot \frac{C_{\text{elution}}}{C_i - C_e}$$

Where,

C_{elution} is the concentration of UO_2^{2+} (mol L^{-1}) after acid treatment.

III. RESULTS AND DISCUSSIONS

A. Effect of pH

The pH value plays an important role in the sorption studies onto chelating resins, because the pH of the solution can influence the aqueous chemistry of uranyl and the properties of functional groups of resin. Effect of solution pH on the UO_2^{2+} removal ions from the aqueous solution using Lewatit TP 214 was investigated in the pH range of 2.0 to 6.0 using, 4 mL of $1.0 \cdot 10^{-3}$ mol. L^{-1} UO_2^{2+} ions solutions and 0.100 g of chelating resin. Fig. 1 shows that UO_2^{2+} percent removal increase with increasing pH solution and a maximum value were reached, (86,20 %) at an initial pH near 6.0. This

is due to the favourable conditions for the complex formation of uranyl with functional groups of resin in this pH region, at low pH values, the decrease of the percent may be attributed to the partial protonation of the active groups (thiourea) and the competition of H^+ with UO_2^{2+} onto sorption sites of Lewatit TP 214 resin. So, the following sorption studies will be carried out at $\text{pH} = 4.5$.

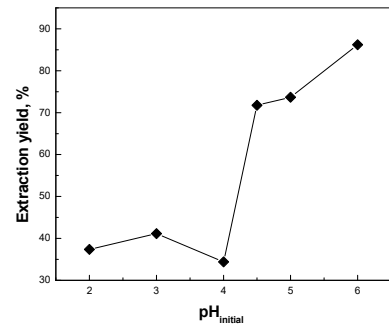


Fig. 1 Removal of uranyl ions by Lewatit TP 214 resin as a function of initial pH. $[\text{UO}_2^{2+}] = 10^{-3}$ mol. L^{-1} , $w = 0.100$ g, $V = 4$ mL, $\Phi = 250$ rpm, $T = 22 \pm 1$ C and Time=60 min.

B. Effect of contact time

To study the effect of contact time, we obtained the extraction yields at different times and different weights of resin (Fig. 2). It is seen that the extraction efficiency increases rapidly with increasing time. The time needed for Lewatit TP 214 to adsorb the maximum of uranyl was 60 min (for $w = 0.100$ g, 41.80 %, 7.09 mg. g^{-1}).

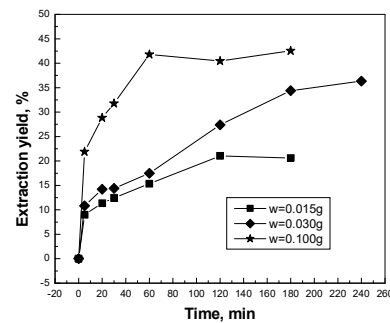


Fig. 2 Removal of uranyl ions by Lewatit TP 214 resin as a function of time with three different weights of resin. $[\text{UO}_2^{2+}] = 10^{-3}$ mol. L^{-1} , $\text{pH}_{\text{initial}} = 4.5$, $V = 4$ mL, $\Phi = 250$ rpm, $T = 22 \pm 1$ C.

C. Adsorption kinetics

Kinetics of sorption describing the solute uptake rate, which, in turn, governs the residence time of the sorption reaction, is one of the important characteristics defining the efficiency of sorption [25]. The linear form of the pseudo-first-order rate equation by Lagergren is expressed as Eq. (5):

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t$$

The linear form of the pseudo-second order rate equation is given as [26];

$$t/q_t = 1/q_e^2 + t/q_e$$

Where,

q_e and q_t are the amounts of sorbed UO_2^{2+} on the resin Lewatit TP 214 at equilibrium and at time t , respectively ($mg \cdot g^{-1}$),

k_1 is the first-order adsorption rate constant (min^{-1}),

k_2 is the pseudo-second-order adsorption rate constant ($g \cdot mg^{-1} \cdot min^{-1}$).

Using a weight of 0.100g of Lewatit TP 214 resin, the correlation coefficients (R^2) for the pseudo-first-order equation and the theoretical q_e values calculated from the pseudo-first-order equation are not in agreement with the experimental data (Table I), suggesting that this adsorption system is not a pseudo-first-order reaction. High correlation coefficients are obtained when employing the pseudo-second-order model and the calculated equilibrium sorption capacity is similar to the experimental data (Table I). This indicates that the pseudo-second order model can be applied to predict the adsorption kinetic.

TABLE I
KINETIC MODELLING OF UO_2^{2+} IONS SORPTION ONTO LEWATIT TP 214 RESIN

W,g	Pseudo First order rate model	Pseudo second order rate model
0.015	q (thé.)=16.96 q (exp.)= 23.76 $k_1(min^{-1})=0.0196$ R = 0.9916	q (thé.)= 25.88 q (exp.)= 23.76 $k_2(g \cdot mg^{-1} \cdot min^{-1})=2.0470 \times 10^{-3}$ R = 0.9852
0.030	q (thé.)=19.92 q (exp.)=19.45 $k_1(min^{-1})=0.0144$ R = 0.9242	q (thé.)= 24.21 q (exp.)= 19.45 $k_2(g \cdot mg^{-1} \cdot min^{-1})=7.8484 \times 10^{-4}$ R = 0.9318
0.100	q (thé.)=2.53 q (exp.)= 7.21 $k_1(min^{-1})=0.0221$ R = 0.5281	q (thé.)= 7.47 q (exp.)= 7.21 $k_2(g \cdot mg^{-1} \cdot min^{-1})=1.7173 \times 10^{-2}$ R = 0.9971

D. Effect of initial metal concentration

The extraction equilibrium of uranyl ions between aqueous solution and resin can be described by a sorption isotherm.

The extraction experiments were performed using different initial concentration of UO_2^{2+} at $T=22 \pm 1$ °C. Extraction yield of uranyl sorption on Lewatit TP 214 were presented in Fig. 3 as a function of the initial concentration of uranyl ions in the aqueous medium.

The results obtained are shown in Fig.3. It has been seen that sorption capacity increases with increasing initial UO_2^{2+} ions concentration onto chelating resin. The maximum sorption capacity was $12.47 mg \cdot g^{-1}$. This result indicates that Lewatit TP 214 resin is an effective sorbent in treatment of diluted uranyl solutions in batch process.

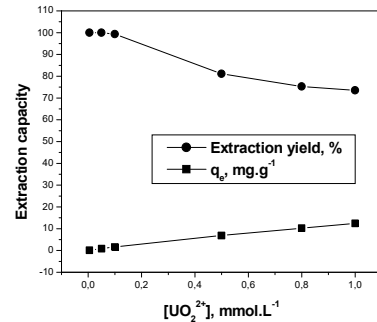


Fig. 3 Removal of uranyl ions by Lewatit TP 214 resin as a function of initial UO_2^{2+} concentration, $w = 0.100$ g, $pH_{initial}=4.5$, $V = 4$ mL, $\phi = 250$ rpm, $T=22 \pm 1$ C and Time=60 min.

E. Isotherm adsorption

The sorption data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. Classical adsorption models, Langmuir (Eq. 7) and Freundlich (Eq. 8), were used to describe the equilibrium between adsorbed UO_2^{2+} ions on the Lewatit TP 214 resin site [26]. For the interpretation of both models, we have used the following equations [27].

$$C_e / q_e = C_e / q_m + 1 / (q_m \cdot K_L)$$

$$Lnq_e = LnK_F + nLnC_e$$

Where,

C_e is the equilibrium concentration of uranyl ($mg \cdot L^{-1}$),
 q_e is the amount of uranyl sorbed on the Lewatit TP 214 resin ($mg \cdot g^{-1}$),

K_L is the Langmuir adsorption constant ($L \cdot mg$),

q_m is the maximum amount of uranyl that can be sorbed,

K_F is the Freundlich adsorption constant and,

n is a constant that indicates the capacity and intensity of the adsorption, respectively.

The Sips isotherm is a combined form of Langmuir and Freundlich models [28]. When approaches a low value, the Sips isotherm effectively reduces to Freundlich, while at high, it predicts the Langmuir monolayer sorption characteristic. The model can be written as:

$$q_e = q_{ms} K_S C_e^{1/n} / (1 + K_S C_e^{1/n})$$

The Sips linear equation model is expressed as:

$$1/q_e = 1/q_{ms} K_S x1 / C_e^{1/n} + 1/q_{ms}$$

Where q_{ms} ($mg \cdot g^{-1}$) is the sips maximum adsorption capacity, K_S (g^{-1}) is the Sips model isotherm constant, and $1/n$ is the sips model exponent.

TABLE II
ADSORPTION ISOTHERM MODELS FOR UO_2^{2+} IONS SORPTION ONTO LEWATIT TP 214 RESIN

q_m (exp),	Freundlich isotherm	Langmuir isotherm	Sips isotherm
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mg. g ⁻¹			
12.47	K _F = 203.02 g ⁻¹ n = 0.3195 R ² = 0.9851	K _L = 1.69×10 ⁵ L.mg ⁻¹ q _m = 11.71 mg. g ⁻¹ R ² = 0.9383	K _S = 7.65×10 ⁵ L.mg ⁻¹ q _{ms} = 9.46 mg. g ⁻¹ R ² = 0.9882 1/n = 1.4688

From the Table II, it appears that the experimental data agree with those theoretically expected by the Sips isotherm. The correlation coefficient is 0.9882. The theoretical value of the maximum retention capacity (q_{ms}) is 9.46 mg. g⁻¹, quite close to the experimental value 12.47 mg. g⁻¹.

F. Effect of ionic strength

The influence on the extraction of uranyl and sodium were studied at varying concentrations (0-1 mol. L⁻¹) of NaCl and CH₃COONa. From Fig. 4, it can be seen that the addition of the CH₃COONa salt increases the extraction yield of uranyl ions in the salt concentration range between 0 to 0.3 mol. L⁻¹, this can be explained by the fact that the increase in the ionic strength increase the adsorption of the UO₂²⁺ ions on the resin. Then, the extraction yield decreases slightly (from 69.86% to 64.85%) in the salt concentration range (from 0.3 to 1.0 mol. L⁻¹) where the extraction competition begins.

However, from Fig. 5, it can be seen that the addition of the salt NaCl has a great negative influence on the extraction yield, it drops it from 36.77% to 4.47% in the salt concentration range. (From 0 to 1 mol. L⁻¹). This result can be explained by a competition between the UO₂²⁺ and Na⁺ cations on the active sites of the Lewatit TP-214 resin.

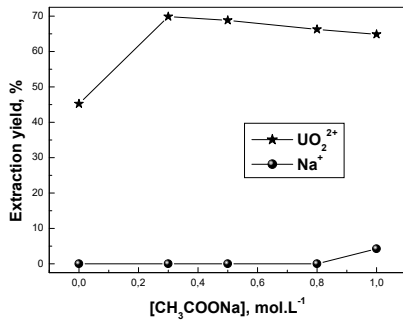


Fig. 4 Removal of uranyl and sodium ions by Lewatit TP 214 resin as a function of initial concentration of NaCl.

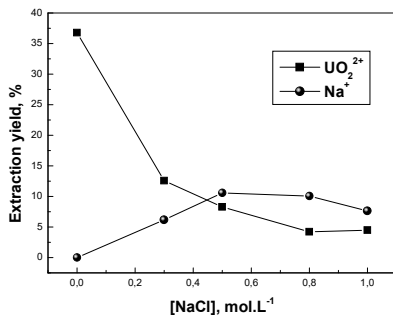


Fig. 5 Removal of uranyl and sodium ions by Lewatit TP 214 resin as a function of initial concentration of CH₃COONa.

G. Thermodynamic parameters

The effect of temperature on the removal of uranyl from acetate solution by Lewatit TP 214 resin was studied for the determination of thermodynamic data such as, the Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°). ΔG° was calculated using the following equations [25]:

$$\Delta G = \Delta H - T.\Delta S$$

$$\Delta G = -RT.LnK_D$$

Where, R is the gas constant (8.314 J mol⁻¹ K⁻¹), and T the temperature (K).

The relation between K_D, ΔH° and ΔS° can be described by Van't Hoff correlation in Eq. (13).

$$LnK_D = \Delta S / R - \Delta H / RT$$

Fig. 6 shows that an increase in temperature, in the range of 20 - 50 ° C, increases the extraction efficiency from 58.2 to 62.15%. These results indicate that uranyl sorption on the Lewatit TP 214 resin is an endothermic and not spontaneous process, as supported by the positive values of ΔH° and ΔS° (Table III), decrease in ΔG° values with increase in temperature showed that the sorption was most favourable at higher temperature.

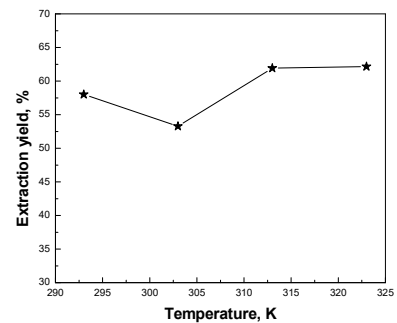


Fig.6 Removal of uranyl ions by Lewatit TP 214 resin as a function of temperature. [UO₂²⁺] = 10⁻⁴ mol. L⁻¹, pH_{initial}=4.5, w = 0.100 g, V = 4 mL, Ω = 250 rpm, and Time=60 min.

TABLE III
 THERMODYNAMIC PARAMETERS FOR THE REMOVAL OF UO₂²⁺ ON LEWATIT TP 214 RESIN

ΔH° (KJ. mol ⁻¹)	ΔS° (J. mol ⁻¹ K ⁻¹)	ΔG° (KJ. mol ⁻¹)	
		Temperature (°K)	Values
+4.84	+1.93	293	+4,2760
		303	+4,2567
		313	+4,2375
		323	+4,2182

H. Desorption study

In order to investigate the elution behavior of uranyl from the Lewatit TP 214 resin, elution experiments were conducted with using various eluting agents viz, CH₃COOH, HNO₃, and HClO of a concentration of 3 mol. L⁻¹. Firstly, Lewatit TP 214 resin is saturated with the solution of uranyl and elution

yield is calculated by Eq. 4. To a saturated sample of the resin (0.1 g), 4 mL of the selected acid was added and kept for 2 h. Though all the acids gave significant elution yields and the better yield was obtained with CH_3COOH (22%).

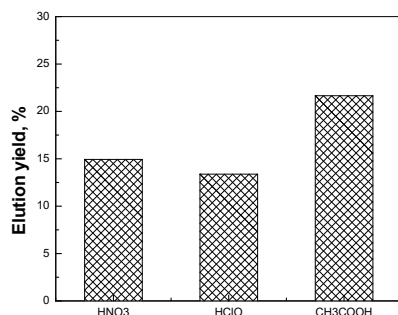


Fig. 7. Optimum eluants for quantitative recovery of uranyl.

IV. CONCLUSIONS

In this study, the sorption capacities of UO_2^{2+} onto Lewatit TP 214 were studied by batch tests conducted under various experimental conditions such as pH, contact time, initial UO_2^{2+} content and temperature. Based on the results, the following conclusions are summarized as below:

1. The sorption of UO_2^{2+} onto Lewatit TP 214 achieves equilibration at 60 min. The kinetic sorption of UO_2^{2+} onto this chelating resin follows the pseudo-second order model.

2. The equilibrium batch experiment data demonstrate that Lewatit TP 214 resin is an effective sorbent for the removal of UO_2^{2+} from aqueous solution with the maximum sorption capacity of 19.45 mg. g^{-1} , under the given experimental conditions.

3. The sorption of UO_2^{2+} on the resins is strongly dependent on pH and uranyl content. The adsorption process follows Sips isotherm.

4. The percentage removal decreases in the presence of CH_3COONa and NaCl as electrolytes salts.

5. The calculated thermodynamic parameters showed the feasibility, endothermic and not spontaneous nature of the sorption of UO_2^{2+} onto Lewatit TP 214 resin.

6. The results obtained in this study make Lewatit TP 214 resin as promising candidates for sorption, immobilization and pre-concentration of uranyl ions from acetate medium.

7. Desorption study of uranyl can be effected with acetic acid (3 mol L^{-1}) after 3 h of shaking.

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