Removal of uranium(VI) from acetate medium using Lewatit TP 260 resin

Abdelhakim Kadous · Mohamed Amine Didi · Didier Villemin

Received: 5 December 2010/Published online: 4 January 2011
© Akadémiai Kiadó, Budapest, Hungary 2011

Abstract Removal of uranium(VI) ions from acetate medium in aqueous solution was investigated using Lewatit TP260 (weakly acidic, macroporous-type ion exchange resin with chelating aminomethylphosphonic functional groups) in batch system. The parameters that affect the uranium(VI) sorption, such as contact time, solution pH, initial uranium(VI) concentration, adsorbent dose and temperature have been investigated. Results have been analyzed by Langmuir and Freundlich isotherm; the former was more suitable to describe the sorption process. The moving boundary particle diffusion model only fits the initial metal adsorption on the resin. The rate constant for the uranium sorption by Lewatit TP260 was 0.441 min⁻¹ from the first order rate equation. The total sorption capacity was found to be 58.33 mg g⁻¹ under optimum experimental conditions. Thermodynamic parameters (ΔΗ = 61.74 kJ/mol; ΔS = 215.3 J/mol K; ΔG = −2.856 kJ/mol) showed the adsorption of an endothermic process and spontaneous nature, respectively.

Keywords Solid phase extraction · Ion exchange resin · Uranium(VI) · Lewatit TP 260

Introduction

Uranium, a toxic and weak radioactive heavy metal, is relatively widespread in the environment, and as a naturally occurring element it is found at low levels in all rocks, soils and waters, the removal of uranium from wastewater is of great importance [1, 2]. Traditional solvent extraction such as liquid–liquid extraction, which uses extensive amounts of organic solvents [3, 4]. Solid phase extraction (SPE) has been a basic and powerful method of concentrating desired analytes, like metal ions. This technique has often been pointed out to be tedious and/or time consuming.

A special attention is focused on the techniques which are characterized by a considerable reduction or complete elimination of organic solvents [5–8]. The use SPE have been proved to be more advantageous in view of their total insolubility in aqueous phase, low rate of physical degradation, high sorption capacity for metal ions, low organic solvent inventory and good flexibility in working conditions. The organic extractant can be grafted to an inert polymeric support like polystyrene, and recently many works using this technique have been reported for uranium extraction [1, 2, 9–14]. In recent years, a number of Lewatit commercial resin such as Lewatit TP-208 [15], Lewatit TP 260 [16, 17], Lewatit Mono plus SP 112 [18], Lewatit MP 62 [19], Lewatit MP-64 [20], Lewatit TP-207 [21], Lewatit S-100 [22] and Lewatit CNP-80 [23], have been used to remove heavy metals from wastewater. Ion-exchange is highly effective, low-cost material, efficient and easy to operate among the physicochemical treatment processes. In the present work, the Lewatit TP 260 resin was applied as a new sorption material for uranium(VI) extraction in batch process. The effects of analytical parameters, adsorption kinetic, isotherm studies, desorption process and temperature effect were investigated.
Experimental

Instrumentation

Visible spectra were measured using Perkin-Elmer-Lambda 300 UV–Vis spectrophotometer. pH measurements were taken on a potentiometer Consort C831.

Reagents

Lewatit TP 260 resin was purchased from Fluka (Table 1). Uranyl acetate dehydrate, sodium nitrate, sodium acetate, sodium chloride, sodium sulfate and Arsenazo III were obtained from Merck. Hydrochloric acid (36%) and nitric acid (65%) were purchased from Reidel-de-Haen.

Procedure

The Lewatit TP 260 resin has been investigated in liquid–solid extraction of uranyl cation. 0.06 g of resin was added to 5 mL of uranyl solution (with known concentration and fixed pH) in a 50 mL glass flask. The mixture was stirred for 120 min. The aqueous phase was separated from the resin by filtration. The uranyl concentrations in the aqueous phase were determined, before and after extraction spectrophotometrically with Arsenazo III at pH 2 [24]. The absorbance of Arsenazo III–uranium(VI) complex was measured at 651 nm.

Results and discussion

Effect of pH

The retention of Uranium(VI) on resin from acetate medium was studied in the pH range from 2.7 to 10.1 and the results obtained are shown in Fig. 1. From the figure it was observed that the retention of Uranium(VI) on the resin increases with the pH from 2.7 to 4.1, then the adsorption capacity decreases with pH increase. From Fig. 2 it can be seen that maximum uranium retention obtained at pH 4.1 could be due to the presence of $\text{UO}_2(\text{CH}_3\text{COO})^{2+}$ and $(\text{UO}_2)_2(\text{OH})_4^{2+}$ which is in equilibrium with the $\text{UO}_2^{2+}$, $\text{UO}_2(\text{OH})_2\text{H}_2\text{O}$ and $\text{UO}_2(\text{CH}_3\text{COO})_2$, the complexes formed between $\text{UO}_2(\text{CH}_3\text{COO})^{2+}$ & $(\text{UO}_2)_2(\text{OH})_4^{2+}$ and functional group are more stable.

Depending on the pH of solution the aminophosphonate functionality can be represented in the structures in scheme 1 [26].

According to our experimental condition of initial pH (4.1), the form (c) in scheme 1 is more appropriate to be considered and the possible coordination mechanism for the interaction between $\text{UO}_2(\text{CH}_3\text{COO})^{2+}$, $(\text{UO}_2)_2(\text{OH})_4^{2+}$ and the aminophosphonate function my be illustrated by Scheme 2.

![Fig. 1 Effect of initial pH of the aqueous solution on the retention of uranium(VI) on Lewatit TP 260 resin. [Uranium(VI)]$_{0}$ = 2 mmol L$^{-1}$. Resin quantity = 0.06 g, aqueous volume = 5 mL, contact time = 120 min](image1)

![Fig. 2 Distribution diagrams of uranyl ion (2 mmol L$^{-1}$) in acetate media using Medusa and Hydra programs [25]. R styrene–divinylbenzene (macroporous) matrix](image2)
Effect of resin amounts

Figure 3 shows the yield recovery of uranyl ions from the solution containing 1.19 mg of Uranium(VI) (1 mmol L⁻¹; aqueous volume = 5 mL) as a function of resin amounts. The recovery increases with increasing amount of functionalized resin available for uranium complexation. The highest yield recovery (98%) was obtained at a 0.1 g of resin, for values higher than 0.1 g, the extraction the yield does not change.
Metal loading capacity

The retention capacity of the resin was determined by equilibrating 0.06 g of the Lewatit TP 260 with 5 mL of uranyl ion solutions at different concentrations [0.5–6 mmol L\(^{-1}\)]. The amount of uranyl ion needed for saturation was obtained as follows:

\[
q (\text{mg/g}) = \frac{(C_0 - C_e) \times V \times 238.029}{W}
\]

where \(C_0\) and \(C_e\) denote the initial and equilibrium concentrations of Uranium(VI) in the aqueous phase (mol L\(^{-1}\)), \(V\) is the volume of the aqueous phase (5 mL), \(W\) is the weight of the grafted resin (0.06 g) and 238.29 is the molar weight of Uranium (g/mol).

The experimental capacity obtained is 58.33 mg/g (Fig. 4). This sorption capacity is higher than chelate modified solid phase extraction procedures reported in literature as polyethyleneimine-phenylphosphonamidic acid (30.66 mg/g) [11], \(N'\)-dimethyl-\(N'\)-dibutyl malonamide functionalized polymer (18.78 mg/g) [13], succinic acid impregnated amberlite XAD-4 (12.33 mg/g) [27], gelamid (28.98 mg/g), gel-benzamide (18.64 mg/g) [28] and natural clinoptilolite zeolite (0.7 mg/g) [2].

Adsorption kinetics

The rate of loading of uranium(VI) onto Lewatit TP260 was studied at initial concentration of uranium(VI) 3 mM (Fig. 4) for 0, 5, 15, 30, 60, 90, 120 and 180 min.

The kinetics of uranium(VI) adsorption on Lewatit TP260 resin follows the first order rate expression given by Lagergren [29].

\[
\log (q_e - q) = \log q_e - K_{ads} \frac{t}{2.303}
\]

where \(q\) and \(q_e\) are the amounts of uranium(VI) adsorbed (mg g\(^{-1}\)) at time, \(t\) (min) and equilibrium time (120 min), respectively and \(K_{ads}\) the rate constant of adsorption. Linear plots of \(\log (q_e - q)\) versus \(t\) (Fig. 5) show the applicability of the above equation for the resin. The correlation coefficients of linear plot obtained for Lagergren plot is 0.9960, for 0.3 mM of uranium(VI) solution. The \(K_{ads}\) calculated from the slopes of Fig. 5 is 0.0254 min\(^{-1}\).

Adsorption isotherm

The adsorbed amounts of uranyl ions on resin have been determined as a function of the metal concentration in the supernatant (\(C\)) at the equilibrium state and ambient temperature. The Langmuir treatment [30] is based on the
assumption that (i) maximum adsorption corresponds to saturated monolayer of adsorbate molecules on the adsorbent surface, (ii) the energy of adsorption is constant and (iii) there is no transmigration of adsorbate in the plane of the surface

\[
\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0}
\]  

(3)

where \(C_e\) is the equilibrium concentration (mg L\(^{-1}\)), \(q_e\) the amount adsorbed at equilibrium and \(q_0\) and \(b\) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of \(C_e/q_e\) versus \(C_e\) shows that adsorption obeys Langmuir adsorption model (Fig. 6). The correlation coefficient for the linear regression fits of the Langmuir plot was found to be 0.9996. \(q_0\) and \(b\) determined from the Langmuir plot were found to be 63.371 mg g\(^{-1}\) and 0.0165 g mg\(^{-1}\) respectively. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, \(R_L\) which is defined by Eq. 4:

\[
R_L = \frac{1}{1 + bC_0}
\]  

(4)

where \(b\) is a Langmuir constant and \(C_0\) is the initial concentration of uranium(VI). \(R_L\) values observed between 0 and 1 indicate favourable adsorption of uranium(VI) onto SA resin (Table 2).

The Freundlich equation was also applied to the adsorption, this equation is basically empirical but is often useful as a means of data description. It generally agrees quite well compared to Langmuir equation and experimental data over a moderate range of adsorbate concentrations.

The Freundlich isotherm is represented by Eq. 5:

\[
\log \left( \frac{x}{m} \right) = \log K_f + \left( \frac{1}{n} \right) \log C_e
\]  

(5)

where \(C_e\) is the equilibrium concentration (mg L\(^{-1}\)) and \(x/m\) the amount adsorbed per unit mass of resin. A plot of \(\log(x/m)\) versus \(\log C_e\) (Fig. 7) is linear and the constants \(K_f\) and \(1/n\) were found to be 0.2598 and 0.9435, respectively. The value of \(1 < n < 10\) shows a favourable adsorption of uranium(VI) onto SA resin. The correlation coefficient for the Freundlich plot was found to be 0.94352 indicating that the fit of the experimental data of Langmuir is better.

Sample volume

The effect of the volume of sample solution on the recovery of uranium(VI) was studied by passing 5–20 mL volume. The results are shown in Fig. 8. The extraction of uranium(VI) with Lewatit TP 260 was not affected by sample volume below 200 mL.

Effect of electrolytes on Uranium(VI) extraction

Sodium salts are the major component in soil and sediment samples, a study their influence for quantitative uranyl extraction becomes essential [31]. The influence on the extraction of Uranium(VI) was studied at varying concentrations (0.1–100 mmol L\(^{-1}\)) of NaNO\(_3\), NaCl, Na\(_2\)SO\(_4\) and CH\(_3\)COONa (Fig. 9).
data are plotted as fractional attainment of equilibrium adsorption \( F \) versus time in Fig. 10. It is seen that the initial concentration of uranium has a slight effect on the rate of adsorption. The adsorption onto ion exchange resins must be considered as a liquid–solid phase reaction which includes several steps [32]:

i) the diffusion of ions from the solution to the resin surface,

ii) the diffusion of ions within the solid resin,

iii) the chemical reaction between ions and functional groups of the resin.

The adsorption of the metal is governed by the slowest of these processes. The kinetic models and the rate equations for the above three cases have been established. The exchange of ions can be described by the Nernst–Planck equations which apply to counter diffusion of two species in an almost homogeneous media [33]:

If the liquid film diffusion controls the rate of exchange, the following relation can be used (Fig. 11):

\[ -\ln(1 - F) = kt \]  

(6)

If the case of diffusion of ions in the resin phase controlling process, the equation used is:

\[ -\ln(1 - F^2) = kt \]  

(7)

In both Eqs. 6 and 7, \( k \) is the kinetic coefficient or rate constant.

After testing both mathematical models proposed for diffusion in the adsorption of uranium(VI) onto the resin, this is best fitted when the metal uptake is film diffusion controlled (Table 3).

In Eq. 8 \( k \) is:

\[ k = \frac{D_l \pi^2}{r_0^2} \]  

(8)

Diffusion study

The adsorption of uranium(VI) on the Lewatit TP260 from uranyl acetate solution at initial concentrations of 3 mM was studied as a function of time at 25 °C. Experimental

---

Fig. 8 Effect sample volume on the recovery of uranium ions. Resin quantity = 0.06 g. [Uranium(VI)] = 2 mmol L\(^{-1}\). Initial pH = 4.1, contact time = 120 min

Fig. 9 Effect of salt concentration on the extraction of Uranium(VI) with grafted resin. Resin quantity = 0.06 g. aqueous volume = 5 mL, initial pH = 4.1. Contact time 120 min, [Uranium(VI)] = 2 mmol L\(^{-1}\)

The results show an increase in extraction efficiency in the presence of CH\(_3\)COONa; this is due to the stability of the complex formed between UO\(_2\)(CH\(_3\)COO)\(^-\) and aminophosphonate, this increase is almost constant in interval concentration [1–100 mM]. However, for NaNO\(_3\), NaCl and Na\(_2\)SO\(_4\) we observe the decrease of extraction; this could be due to the screen effect of Na\(^+\) which affects the diffusion of ions within the resin. From a concentration of 8 mM the extraction yield increases again for NaNO\(_3\) and Na\(_2\)SO\(_4\), this can be explained by the effect of ionic strength which becomes important from this concentration for these two salts.

Fig. 10 Rate of uranium(VI) adsorption on Lewatit TP260. Resin quantity = 0.06 g. aqueous volume = 5 mL, initial pH = 4.1, [Uranium(VI)] = 3 mM
Table 3 Kinetic parameters of uranium(VI) adsorption on grafted resin

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ (min$^{-1}$)</td>
<td>0.029</td>
</tr>
<tr>
<td>$D_r \times 10^4$ (cm$^2$/min)</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Fig. 11 Plot of Eq. 6 for uranium(VI) adsorption on Lewatit TP260. Resin quantity = 0.06 g, aqueous volume = 5 mL, initial pH = 4.1, [Uranium(VI)] = 3 mM

where $D_r$ is the diffusion coefficient in the resin phase and $r_0$ is the average radius of resin particle. Thus, the values of the adsorption rate constant and of the diffusion coefficient in the resin phase calculated from the slope of the straight lines (Fig. 11) are summarized in Table 3.

When the adsorption of metal ion involves mass transfer accompanied by chemical reaction the process can be explained by the moving boundary model. This model assumes a sharp boundary that separates a completely reacted shell from an unreacted core and that advances from the surface toward the center of the solid with the progression of adsorption. In this case, the rate equation is given by:

$$3 - 3(1 - F)^{2/3} - 2F = kt$$  \( (9) \)

The graphical correlation in Fig. 3 of $3 - 3(1 - F)^{2/3} - 2F$ versus $t$ shows that the moving boundary particle diffusion model fits only the initial adsorption on the Lewatit TP260 resin. The linear regression analysis of functions $3 - 3(1 - F)^{2/3} - 2F$ versus time are also given in Table 4.

The uranium(VI) uptake is best explained by the liquid film diffusion controls (Eq. 6, $r^2 = 0.998$).

Effect of temperature on extraction equilibrium

The effect of temperature on the sorption of 2 mM solution of uranium(VI) ions under optimum conditions of pH, weight of resin and shaking time was studied. Different thermodynamic parameters were computed using Van’t Hoff equation in the form (10).

$$\log K_e = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R}$$  \( (10) \)

$$\Delta G = RT \ln K_e$$  \( (11) \)

where $\Delta H$, $\Delta S$, $\Delta G$, and $T$ are the enthalpy, entropy, Gibbs free energy, and temperature in Kelvin, respectively. The values of equilibrium ratio ($K_e$), was calculated at each temperature using the relationship $K_e = F_a/(1 - F_a)$, where $F_a$ is the fraction of U(IV) ions adsorbed at equilibrium (Figs. 12, 13).

The plot of $\log K_e$ vs $1/T$ is a straight line as shown in Fig. 14, with correlation coefficient $r = 0.9947$. The numerical values of $\Delta H$, $\Delta S$ are computed from the slope and intercept of the graph are given in Table 4. The negative value of Gibbs free energy as shown in Table 4 indicates the spontaneous nature of sorption from bulk or aqueous phase, while positive values of $\Delta H$ reflects the endothermic sorption behavior (Table 5).

The increase in entropy favors the stability of the sorbed complex via covalent interaction type chemisorption. The main source of this entropy gain may be due to the rupturing of the hydration zone formed around a central metal atom in mother liquid to a great extent and direct interaction of Uranium(VI)–Functional group complex with resin that results in net positive entropy effect [34].

![Fig. 12 Plot of Eq. 7 for uranium(VI) adsorption on Lewatit TP 260. Resin quantity = 0.06 g, aqueous volume = 5 mL, initial pH = 4.1, [Uranium(VI)] = 3 mM](image-url)
indicates the strong affinity of Uranium(VI)–Resin sorption is related to pore filling of the resin that is energetically homogenous and close to the size of Uranium(VI)–Resin complex.

**Conclusion**

A commercial sorbent the Lewatit TP260 was tested on uranium(VI) extraction. The extraction efficiency was determined as a function of various parameters such as time, pH, uranium concentration, extractant to uranium ratio, sample volume and electrolytes effect. The experimental capacity obtained is 58.35 mg/g. The kinetics of uranium(VI) adsorption on grafted resin follows the first order rate expression given by Lagergren. The equilibrium isotherm for sorption of the investigated metal ions has been modeled successfully using the Freundlich isotherm. The uranium(VI) uptake is best explained by the liquid film diffusion controls. The thermodynamic parameters confirm the entropy driven endothermic nature of chemisorption. The high value of entropy is due to the chelate effect of Uranium(VI)–Functional group complex which counteracts the enthalpy effect. The negative value of Gibbs free energy ($\Delta G$) indicates the spontaneous nature of sorption.

**Acknowledgments** We gratefully acknowledge the Rhom and Haas Company for their generous gift of chloromethyl polystyrene and the Tassili program No. 10 MDU799 for their financial support.

**References**


