



Adsorptive Behavior of an Amberlite Anion Exchanger Resin for Uranium (VI) Sorption in the Presence of Sulfate Anions

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ABSTRACT

Uranium (VI) sorption using an anionic exchanger resin, namely Amberlite IRA910, in the presence of sulfate anions was the subject of current study. Batch sorption experiments were carried out to evaluate the influence of operational parameters such as pH, contact time, initial concentration and existence of various anions (including phosphate, sulfate, chloride, fluoride, and nitrate) in the solution on Amberlite IRA910 sorption behavior. Experiments revealed that uranium adsorption was fulfilled at pH>3 and 50 min to amount of 80%. Kinetics study revealed that the pseudo-second-order model showed better curve-fitting regression of the experimental data than the pseudo-first-order one. Freundlich isotherm was also provided well mathematical description of sorption process than the Langmuir one. Uranium adsorption capacity of the sorbent was 1666.6 mmol g⁻¹. It was also revealed that the existence of various anion species in the solution could strongly affect the sorption of uranium using the Amberlite IRA910 anion exchanger resin.

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1. INTRODUCTION

Nowadays, nuclear energy, which is generated by bombarding uranium nucleus with neutrons in nuclear reactors, draws much attention from different countries as sustain and low-pollutant source of energy than fossil fuels. Uranium, the origin of nuclear energy, was distributed on earth's surface and in its rock minerals by an average concentration about 0.1%. The lowest of such concentration needs the largest amount of rocks for preparation of adequate amount of uranium through uranium processing needed for handling nuclear reactors. Treatment of such large quantity of rocks generates immense amount of liquid effluents and sewages. Therefore, particular processes for safe treatment and disposal of the uranium wastes must be developed.

Removal of heavy metals from contaminated media (e.g. uranium wastes) so far was investigated using various techniques including ion exchange, chemical precipitation, solvent extraction, and adsorption [1-6]. Among these, the later deserves a particular position for heavy metal removal [7-9]. High removal efficiency merit as well as low-cost, easy operation, and simplicity of adsorption technique convert it to a reliable method for practical purposes between researchers.

In recent years, several types of adsorbents have been exploited for uptake of uranium from the solution through adsorption process. Functionalized molecular sieves mesoporous and nanoporous, strongly basic ionic exchangers, and impregnated nanocomposites are only few examples [10-13]. Nevertheless, most of the utilized sorbents adsorb the uranium ions from an acidic solution (i.e. leach liquor) generated through uranium processing. Hence, require to such technique that could improve uranium-bearing effluent's treatment for the final disposal into the environment is strongly felt. Such an adsorbent should probably be traced in the realm of anion exchanger resins.

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Uranium ion adsorption in the presence of anions, in particular sulfate anion has not been studied yet. Additionally, uranium adsorption using anion exchanger in the presence of other obtruding anions (binary effect) has not been investigated. The current study was examined the uranium adsorption using the Amberlite IRA910 anion exchanger resin as sorbent from aqueous solution by the batch equilibrium method and the effects of different operational parameters including pH, contact time, initial concentration and interference anions (single and binary) were investigated.

2. EXPERIMENTAL

2. 1. Materials Amberlite IRA910 anion exchange resin, 200-400 mesh used in the current study was purchased from Rohm and Haas chemical Co. (France). A stock of uranium (VI) solution with given concentration was prepared by dissolving an appropriate amount of uranium nitrate, $(\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, into distilled water. Other chemicals and reagents used in the present work were of analytical grade from E. Merck (Darmstadt, Germany).

2. 2. Sorption Experiments All adsorption experiments were done by a batch method using 20 mg of Amberlite IRA910. In this procedure, the resin was added to a 10 mL uranium (VI) solution of desired concentration in the presence of sulfate anions with concentration of 2655 mg L^{-1} regarding to the actual effluent. After shaking the resulted solution for a given time using a water shaker bath, it was filtered and the remainder solution was analyzed by an inductively coupled plasma-atomic emission spectrometry (ICP-AES), for its uranium content. The sorption capacity (q , mg g^{-1}) and sorption percentage (uptake, %) were calculated using following equations (Equations (1) and (2)):

Adsorption capacity

$$q \text{ (mg g}^{-1}\text{)} = (C_i - C_f) \times \frac{V}{m} \quad (1)$$

$$\text{Uptake (\%)} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (2)$$

where, C_i and C_f stand for initial and final concentration of uranium ions before and after sorption (mg L^{-1}), V is the volume of uranium ions solution (L), m is the mass of resin (g), and q is the adsorption capacity of the Amberlite IRA910 (mg g^{-1}).

The effect of pH on the U(VI) ions adsorption was investigated at room temperature for 2 h. In order to assess the pH effect, 20 mg Amberlite IRA910 anion exchanger resin was added into 10 mL solution with uranium initial concentration of 5 mg L^{-1} in the pH ranges over 2 to 8.

For revealing the relationship between the amount of U(VI) ions adsorbed on the resin and the concentration of residual uranium ions in the aqueous phase, study of adsorption isotherm was carried out. For achieving this goal, the initial uranium concentration changed from 5 to 250 mg L^{-1} . Afterward, Langmuir and Freundlich isotherms were applied on experimental results. The Langmuir sorption isotherm model is based on the assumption that all the sorption sites are energetically identical and sorption occurs on a structurally homogeneous sorbent [14]. The Freundlich isotherm model depicts both multilayer sorption and sorption on heterogeneous surface. The Langmuir and Freundlich isotherms are represented by following equations (Equations (3) and (4)):

Langmuir isotherm [15]

$$\frac{C_e}{q_e} = \frac{1}{q_{max} k_l} + \frac{C_e}{q_{max}} \quad (3)$$

Freundlich isotherm [15]

$$\log q_e = \log k_f + \frac{1}{n} C_e \quad (4)$$

where, q_e (mg g^{-1}) and q_{max} (mg g^{-1}) are the amount of uranium ions adsorbed per unit weight of the resin and the maximum sorption capacity, respectively. C_e ($\mu\text{mol L}^{-1}$) is the equilibrium concentration of the uranium ions in solution, and k_l ($\text{L } \mu\text{mol}^{-1}$) is Langmuir isotherm constant, which relates to the energy of sorption. k_f ($\text{mg g}^{-1} \mu\text{mol}^{-1}$) is the measure of sorption capacity and also referred to as adsorption capacity, while n is the heterogeneity factor and related to adsorption intensity.

In order to kinetics study, pseudo first-order and pseudo second-order kinetic models were applied on experimental result to specify the mechanism of sorption process. The kinetics models are formulated as follows (Equations (5) and (6)):

Pseudo first-order model [16]

$$\log \left(\frac{q_e}{q_e - q_t} \right) = \left(\frac{K_1}{2.303} \right) t \quad (5)$$

Pseudo second-order model [16]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where, K_1 (L min^{-1}) and K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) stand for the rate constant of adsorption. Values of K_1 and K_2 were calculated from the straight line graph of $\log(q_e - q_t)$ versus t , and (t/q_t) versus t for different initial concentrations of the uranium (VI) ion, respectively.

3. RESULTS AND DISCUSSION

3. 1. pH Effect Uranium uptake using the Amberlite IRA910 anion exchanger resin in the presence of sulfate anions was performed for investigating the pH effect and the result was sketched

in Figure 1. As seen, as long as H^+ ion concentration decreases from pH 2 to 4, the amount of uranium uptake increases and it reaches to a plateau at pH 4 and remains constant till pH about 8. Under such condition, it also observes that maximum efficiency on uptake of uranium ions was also occurred. This phenomenon may be due to the formation of different complexes of uranium in presence of hydroxyl ions and sulfate anions in the medium. Hence, adsorption of uranium species at $pH > 2$ than $pH = 2$ increases because all of uranium ions in form of UO_2^{2+} at $pH < 2$ convert to anionic species such as $UO_2SO_4^{2-}$ and $(UO_2)OH_4^{-}$ at higher pHs whose their affinity towards Amberlite IRA910 anion exchanger resin are great.

3. 2. Isotherm Study Figure 2a shows the effect of initial concentration of U(VI) ions on sorption behavior of Amberlite IRA910 anion exchanger resin. Obviously, increasing of uranium concentration causes an intense increase in sorption capacity. For determination the isotherm of sorption process, as illustrated in Figures 2b and 2c, the Freundlich isotherm showed better estimation of experimental data than the Langmuir one regarding to their regression values (R^2). Thus, the sorption process is affected by the formation of monolayer coverage of the sorbate (uranium) on the homogenous sorbent surface. The amounts of isotherm constants are also tabulated in Table 1.

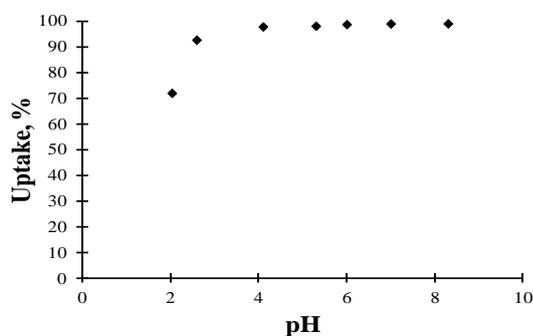


Figure 1. Effect of pH on uranium(VI) sorption using Amberlite IRA910 anion exchanger resin. Conditions: $C_0(U)$: 5 mg L^{-1} , sulfate concentration: 2655 mg L^{-1} , agitation time: 2 h, and temperature: 25°C

TABLE 1. Isotherm constants for uranium (VI) onto Amberlite IRA910 anion exchanger resin

Isotherm	Parameters		
	$q_{max}(\text{mmol.g}^{-1})$	$K_L(\text{L mM}^{-1})$	R^2
Langmuir Equation	1666.6	15	0.9807
Freundlich Equation	n	$K_f(\text{mmol g}^{-1} \text{mM}^{-1})$	R^2
	1.7658	6.604	0.9902

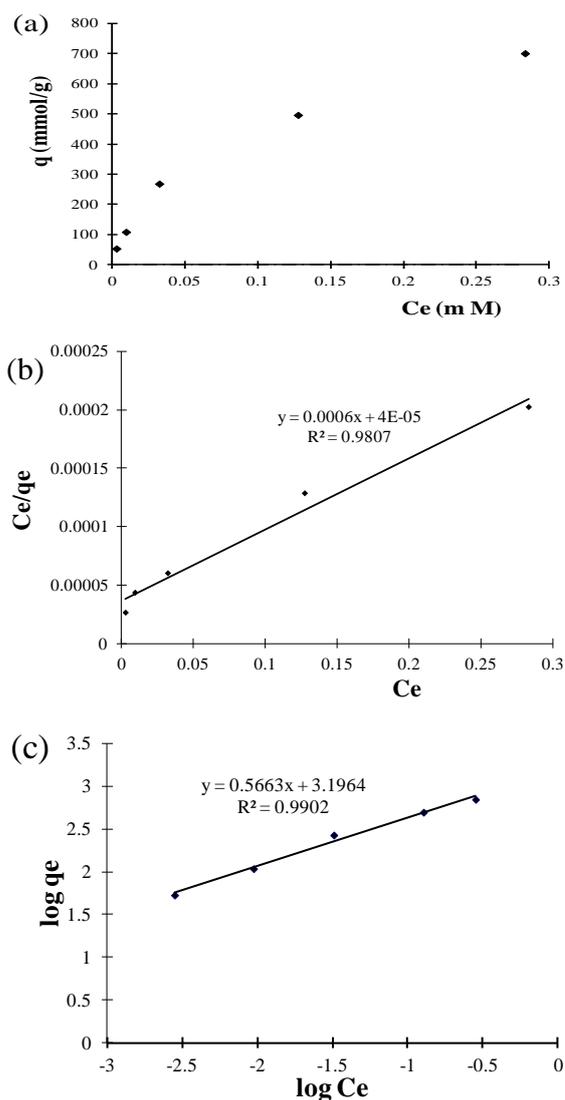


Figure 2. Sorption isotherm of Amberlite IRA910 for uranium (VI) sorption (a), Linearized Langmuir (b) and Freundlich (c) plots. Conditions: initial pH value: sulfate concentration= 2655 mg L^{-1} , agitation time: 2 h, and temperature= 25°C .

3. 3. Kinetics Study The sorption capacity of Amberlite IRA910 for uranium (VI) adsorption as a function of contact time is figured in Figure 3a over 200 min at the uranium initial concentration of 5 mg L^{-1} . It can be seen that the uptake of U(VI) ions were rapidly increased and a contact time of 60 min is approximately sufficient to achieve about 80% in removal of uranium ions. It is believed that the strong affinity of Amberlite IRA910 anion exchanger resin toward anionic species of uranium ions play a role in this process.

In order to assessment of uranium sorption using Amberlite IRA910 resin, kinetics studies were performed. To do so, the pseudo first- and second-order equations were applied on equilibrium sorption data.

The first order kinetic model has been used for the description of reversible equilibrium between liquid and solid phase, whereas, the second-order kinetic model assumes that the rate-limiting step may be chemical adsorption [17]. As shown in Figures 3b and 3c, based on their regression values (R^2), the pseudo second-order model is in appropriate agreement with experimental data the pseudo first-order one. Thus, the rate-controlling step of uranium (VI) ions sorption onto Amberlite IRA910 resin relates to chemical sorption. The amounts of kinetics constants were calculated (see Table 2).

TABLE 2. Kinetics parameters for uranium removal using Amberlite IRA910 anion exchanger resin

	$k_1(\text{min}^{-1})$	0.0096
Pseudo first-order	$q_e(\text{mmol g}^{-1})$	2.1E-5
	R^2	0.65
	$k_2(\text{g mmol}^{-1} \text{min}^{-1})$	0.027
Pseudo second-order	$q_e(\text{mmol g}^{-1})$	10.504
	R^2	0.9996

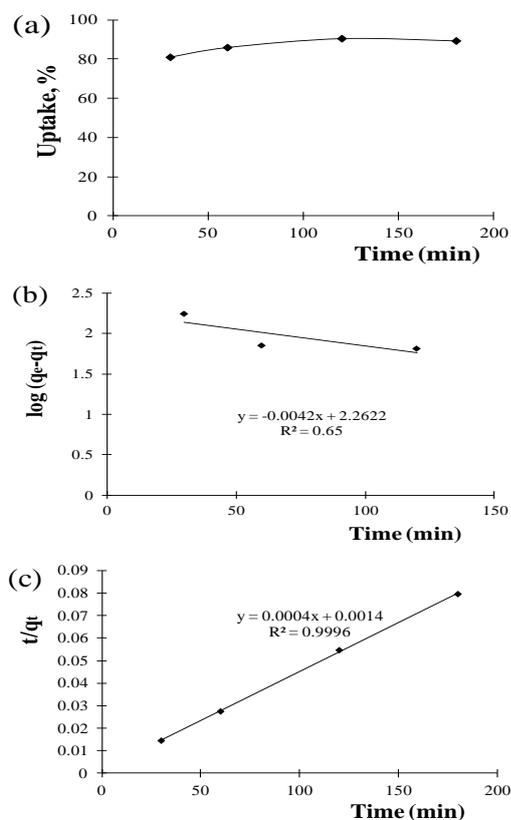


Figure 3. (a) Effect of contact time on U(VI) adsorption performance of Amberlite IRA910 anion exchanger resin, (b) Adsorption kinetics curve of pseudo first-order model and (c) linearized experimental data of pseudo second-order kinetics model plot

3. 4. Effect of Various Anions on Uranium Sorption

As an important factor on uranium sorption, simulation of the actual situation of effluent in this work was also performed. To do so, effect of presence of different anionic species, which existed in the effluent including phosphate, sulfate, chloride, fluoride, and nitrate are investigated during the sorption process.

The results representing in Figure 4 show that the presence of high concentration of the fluoride, sulfate and phosphate anions have no obstruction on uranium sorption, while, uranium uptake severely affected by the presence of chloride and nitrate anions.

The effects of chloride and nitrate ions variation on uranium sorption percentage in presence of constant concentration of fluoride (4000 ppm), sulfate (2655 ppm) and without any intrusive ion were represented in Figures 5a and 5b, respectively.

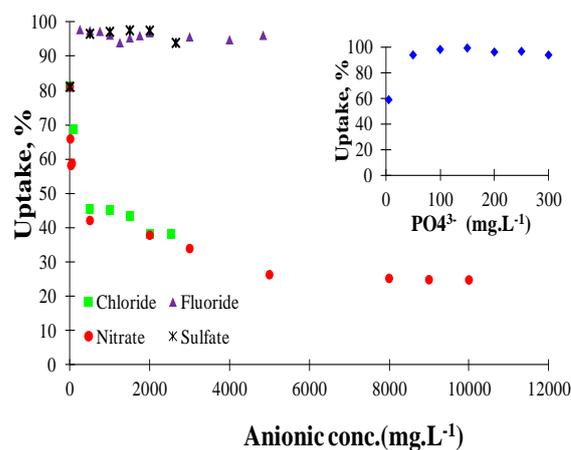
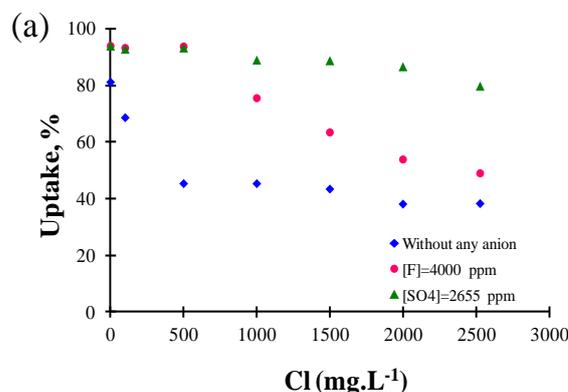


Figure 4. Effect of anions concentration on uranium (VI) sorption [sulfate (0-2655 mg.L⁻¹), nitrate (0-1000 mg.L⁻¹), chloride (0-2527 mg.L⁻¹), fluoride (0-4842 mg.L⁻¹), phosphate (0-300 mg.L⁻¹)]



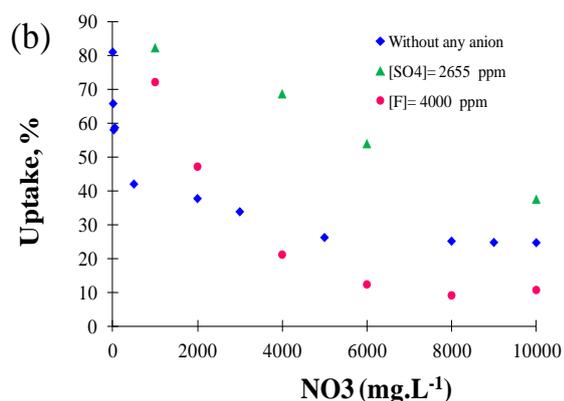


Figure 5. Anion effects on uranium (VI) ions sorption; (a) effect of chloride anion in presence of fluoride (F) and sulfate (SO_4) anions, and (b) effect of nitrate anion in presence of fluoride (F) and sulfate (SO_4) anions

Increasing Cl ions, when the solution includes only uranium ions, cause too much decreasing in uranium uptake percentage than that of fluoride or sulfate. Thus, while sulfate anions exist in the solution, uranium uptake can strongly occur using Amberlite IRA910 anion exchanger resin. Formation of uranium complexes with sulfate anions in the medium, which might have high affinity towards the resin, may be a reason. As well as chloride effect, in the same situation, the effect of nitrate ions profile on uranium sorption efficiency was investigated. As illustrated in Figure 5b, in this case, the presence of sulfate anions in the solution improved uranium uptake than two others status. By virtue of the mentioned reason, we also think that presence of sulfate anions play an important role on uranium sorption due to their complex formation traits with uranium species.

4. CONCLUSION

The present work evaluates sorption performance of Amberlite IRA910 in the removal of uranium ions from aqueous solution. Through the adsorption experiments, it was observed that adsorption of uranium ions onto Amberlite IRA910 strongly occur at pH 4 to about 8. Kinetics study revealed that the sorption kinetics is fast and obey from pseudo-second-order model as represented by its R-squared value. Therefore, the governing mechanism on adsorption rate-limiting step can be a chemical reaction. The Freundlich isotherm model was found to be fitted the isotherm equilibrium data better than the other model, indicating the sorption process is affected by the formation of monolayer coverage of the sorbate (uranium) on the homogenous sorbent surface. Investigation of presence of divers anionic elements such as fluoride, phosphate and sulfate on uranium sorption using Amberlite IRA910 anion exchanger resin was showed that the sorption efficacy

remained constant and did not change. While, existence of nitrate and chloride anions can severely influence uranium uptake because of obstruction effects. Meanwhile, it was revealed that presence of sulfate anions coinciding with nitrate or chloride anions could remarkably improve the sorption efficiency than the lack of sulfate anions. The maximum adsorption capacity (q_{max}) of the Amberlite IRA910 anion exchanger resin was found to be $1666.6 \text{ mmol g}^{-1}$.

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جذب یون‌های اورانیوم (VI) با استفاده از یک رزین تبادلگر آنیونی، Amberlite IRA910، در حضور آنیون‌های سولفات موضوع مقاله حاضر می‌باشد. آزمایش‌های جذب به صورت ناپیوسته به منظور بررسی اثر پارامترهای عملیاتی شامل pH، زمان تماس، غلظت اولیه و حضور آنیون‌های مختلف (شامل فسفات، سولفات، کلرید، فلوئور و نیترات) در محلول بر روی رفتار جذبی Amberlite IRA910 انجام شده است. آزمایشات نشان داد که جذب اورانیوم در $\text{pH} > 3$ و مدت زمان 50 min به میزان 80٪ انجام می‌گردد. مطالعه سینتیکی نشان داد که مدل شبه درجه دوم برازش منحنی رگرسیون بهتری از داده‌های آزمایشی نسبت به مدل شبه درجه اول دارد. ایزوترم فروندلیچ نیز توصیف ریاضیاتی بهتری از فرآیند جذب نسبت به ایزوترم لانگمویر نشان داد. ظرفیت جذب اورانیوم توسط جاذب برابر $166.6 \text{ mmol g}^{-1}$ بود. همچنین مشخص گردید که حضور گونه‌های مختلف آنیونی در محلول می‌تواند به طور زیادی فرآیند جذب یون‌های اورانیوم را با استفاده از رزین تبادلگر آنیونی Amberlite IRA910 تحت تاثیر قرار دهد.

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