Uranium Removal from Aqueous Solution Using Ion-exchange Resin DOWEX® 2x8 in the Presence of Sulfate Anions

M. R. Kosari, H. Sepehrian, R. Salamat Ahangari

Department of Energy Engineering, Sharif University of Technology, Azadi Avenue, Tehran, Iran.

Nuclear Science and Technology Research Institute, End of North Karegar Avenue, Tehran, Iran

Department of Chemistry, Faculty of Basic Science, Azarbaijan Shahid Madani University, Tabriz, Iran

The current study was aimed at uranium (VI) ions adsorption using an anion exchanger resin, Dowex®2x8, in the presence of sulfate anions. Evaluation of operational parameters including contact time, pH, initial concentration of uranium ions, and presence of various anions (including phosphate, sulfate, chloride, fluoride, and nitrate) in the solution was assessed on sorption performance of Dowex 2x8. Employing the Langmuir and Freundlich binding models, isotherm analysis was performed to clarify the relation between uranium ions adsorbed on the resin and the concentration of remaining uranium ions in the aqueous phase. To reveal the rate-limiting step of the sorption process, kinetic modeling using pseudo first-order and pseudo second-order equations was also carried out. Maximum sorption capacity for Dowex 2x8 anionic exchanger resin on uranium removal process was found to be 303.03 mmol g⁻¹. It was also disclosed that existence of diverse anion contents in the solution could affect the uranium sorption using Dowex 2x8 anion exchanger resin.

1. INTRODUCTION

Recently, uranium, the heaviest and radioactive element among rare-abundant elements in the earth's surface, has been found to have essential role for supplying the required energy of human life. Two important steps for extraction of uranium from its minerals including mining and milling processes have propagated great deals of processed and unprocessed uranium into the environment with both natural and anthropological events.

Having two kinds of toxicity including chemical and radioactive, uranium can severely affect human body. After uranium entrance to the body, it will mix with blood and absorb by different tissues like kidneys,
bones and skin, in which it can cause different cancers due to its radioactivity. Inhalation of insoluble uranium compounds is more dangerous because of its accumulation in respiratory tract and having no tendency to leave [1].

As for removal of toxic metals from contaminated media, so far various methods and materials have been investigated [2-7]. However, most of those methods for complete removal of heavy metals are inefficient due to their high costs, technical problems, and production of toxic chemical sludges. Among separation techniques, adsorption due to its merits such as low cost, easy operation and high efficiency has deserved special attention toward the removal of heavy metals [8]. On the other hand, grate deal of attempts was made by researchers for use of new adsorbents. Diverse group of synthetic and natural adsorbents were developed and used to reach the highest efficacy in adsorption of heavy metal ions, but still, most of researchers are seeking to find new adsorbents having considerable advantages such as maximum adsorption capacity, low cost and regeneration ability.

Metal ions adsorption mechanism on the surface or on the active sites of the adsorbents can be related to the nature of sorbents. Recently, many reports have been focused on the use of ion exchange resins including strong and weak acidic/basic anion or cation exchanger resins as sorbents [9-11]. The interchange of ions between two phases happens in an ion exchange process. When a resin- a cross-linked polymer network-consisting of ion to which is electrostatically bound, encounters with a solution including ions of the same charge, an ion exchange can occur that the extent of which depends on the concentration of the ion(s) in the solution [12]. The mechanism for an anions exchange between an insoluble phase and a solution phase can be depicted as below [12] (Equation (1)):

\[
\text{[Polymer]} - X^A + B^- \rightarrow \text{[Polymer]} - X^B + A^-. 
\]  

(1)

For the removal of macromolecules such as uranium, so far many techniques have been proposed and uranium removal in different conditions was investigated. There are various specific and general sorbents, which can adsorb uranium singly or in a matrix. Iminodiacetic acid, namely IDA, is a specific sorbent for uranium removal that its uranium adsorption just effectively occur around pH=2.5 [13]. In addition, graphene oxide (GO) is a general sorbent with the ability of adsorption of uranium along with other ions through the aqueous solutions [14]. However, there are operational problems through industrial application such as interference of uranium with other anions for sorbents surface or active sites of the sorbent. As a matter of fact, it was confirmed that existence of different anion contents whether single or binary could adversely influence on uranium removal using various sorbents or ion exchanger resins.

Currently, uranium (VI) ions sorption using an anion exchanger resin, namely Dowex 2x8, was investigated as a function of contact time, initial concentration, pH and diverse anions in the solution. For better understanding of the sorption process, a mathematical description by applying isotherm and kinetic models on experimental data was eventually performed.

2. EXPERIMENTAL

2. 1. Materials

Uranium nitrate (UO$_2$(NO$_3$)$_2.6$H$_2$O) used for the sorption experiments was of analytical grade with 99.99% assay. Sodium sulfate (Na$_2$(SO$_4$)$_2$) was also used in the current study as phosphate anion source. Dowex 2x8, a strongly basic anionic exchanger resin, 200-400 mesh was obtained from Sigma-Aldrich (Milwaukee, WI, USA). Other chemicals and reagents used were of analytical grade from Merck (Darmstadt, Germany).

2. 2. Sorption Experiments

Batch sorption experiments were implemented to evaluate sorption properties of Dowex 2x8 anion exchanger resin for uptake of uranium ions from aqueous solution. In a typical test, 20 mg of adsorbent were added into 10 ml of U(VI) solution whose initial concentration was situated on a certain value. Additionally, sulfate anions with specific concentration (2655 mg L$^{-1}$) existed in the solution. After a desired time of stirring and attaining equilibrium, adsorbent was segregated from solution by filtration. Consequently, the remained 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 (2) and (3)):

\[
q (\text{mg g}^{-1}) = \left( C_i - C_f \right) \times \frac{V}{m} 
\]  

(2)

\[
\% \text{uptake} = \frac{\left( C_i - C_f \right)}{C_i} \times 100 
\]  

(3)

Working solution pH effect on the removal behavior of Dowex 2x8 was determined at a constant temperature of 25°C for 2 h. In batch tests, 20 mg of the adsorbent was equilibrated with 10 ml of the solution containing 200 mg L$^{-1}$ of U(VI) ions at various pH quantities. The adsorption of uranium was investigated in the pH range of 2-9.

Isotherm analysis was performed for assessment of the relationship between the amount of uranium ions adsorbed on Dowex 2x8 surface and concentration of remaining metal ions in solution. Out of several binding models, the Freundlich and Langmuir isotherms have been extendedly used to describe the experimental results of sorption isotherm. The aforementioned isotherm models are mathematically represented in linear forms as (Equations (4)-(6)):
Langmuir isotherm [15]:

$$\frac{c_e}{q_e} = \frac{1}{q_{\text{max}}b} + \frac{c_p}{q_{\text{max}}}$$  \hspace{1cm} \text{Linear form} \hspace{1cm} (4)

Freundlich isotherm [16]:

$$q_e = k_f C_e^{1/n}$$  \hspace{1cm} (5)

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$  \hspace{1cm} \text{Linear form} \hspace{1cm} (6)

Kinetics analysis was carried out to reveal the rate-limiting step of sorption process such as chemical reaction or mass transfer. On that account, two kinetics models, namely pseudo first-order and second-order, are applied on experimental data of uranium sorption onto Dowex 2x8. The pseudo first-order and second-order formulas are expressed by (Equations (7) and (8)) [17]:

Pseudo first-order model:

$$\log \left( \frac{q_e}{q_e-q_f} \right) = \log \left( \frac{q_{\text{max}}}{K_1} \right) + \frac{1}{K_1} t$$  \hspace{1cm} (7)

Pseudo second-order model:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{\text{max}}} + \frac{t}{q_{\text{max}}}$$  \hspace{1cm} (8)

The solution resemblance to real effluent was employed to assess the anion effect on sorption performance of Dowex 2x8 anion exchanger resin. For this purpose, adsorption properties of the resin were tested during the presence of various anion contents in the solution with a concentration range of those anions.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

Performing pH tests on uranium removal, sorption efficiency of uranium ions versus pH values was sketched in Figure 1. The result shows that Dowex 2x8 anion exchanger resin is capable of uptaking U(VI) ions in pH ranges 2 to 9 effectively. This behavior can be ascribed to capacity of active sites existing on resin’s surface for holding U(VI) ions and their affinity towards various uranium anionic species.

As can be seen, as pH quantity increases, the amount of H+ ions decreases and uranium ions uptake is gently reached to maximum sorption efficiency and is remained at a plateau after pH 3. Achieving the high efficiency may be by virtue of the formation of different complexes of uranium in the presence of hydroxyl ions and sulfate anions in the medium. Thus, sorption of U(VI) species at pH>2 than pH=2 enhances because all of uranium dioxide cations in the form of $UO_2^{2+}$ at pH<2 change to anionic species such as $UO_2$SO$_4^{2-}$ and (UO$_2$)OH$_4^{2-}$ at higher pHs whose affinity towards Dowex 2x8 anion exchanger resin are huge.

3.2. Isotherm Study

Adsorption rate of uranium ions onto the resin showed a striking variation with the initial concentration of uranium ions (Figure 2a). It is obvious that adsorption efficiency increased with increasing the initial concentration of uranium (VI) ions. The Langmuir and Freundlich isotherms were applied to experimental data. 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 [18]. While, the Freundlich isotherm model assumes that enthalpy of adsorption is independent of the amount adsorbed and heterogeneous surface is involved in the sorption process [19].

Concerning with Figure 2b, parameters of Langmuir model can be calculated from the trend line equation. Based on Freundlich isotherm data (see Figure 2c), by plotting log $q_e$ vs. log $C_e$, amounts of $K_1$ and n parameters can be evaluated from the intercept and slope, respectively. An analogous between Langmuir and Freundlich isotherms indicates that the former model can satisfactorily fit experimental data. It can be concluded that the sorption process is affected by the formation of monolayer coverage of the sorbate (uranium) on the homogenous sorbent surface. The isotherm constants given in Table 1 show good agreement between experimental data and the Freundlich isotherm result based on regression value. The maximum adsorption capacity ($q_{\text{max}}$) of the Dowex 2x8 anion exchanger resin was found to be 303.03 mmol g$^{-1}$.

3.3. Kinetics Study

To perceive the relation between the contact time and sorption performance of Dowex 2x8 anion exchanger resin, equilibrium experimental data of uranium (VI) ions were measured at different time intervals up to 24 h.

Regarding the profile illustrated in Figure 3a, the amount of uranium (VI) ions sorption efficiency of the adsorbent increased with time and equilibrium condition was achieved after 2 h.
Figure 2. (a) Effect of initial concentration of uranium ions on Dowex 2x8 sorption behavior, (b) Langmuir adsorption isotherm curve of U(VI) ions uptake and (c) Freundlich adsorption isotherm curve of U(VI) ions uptake. Conditions: initial pH value: 3 sulfate concentration= 2655 mg.l⁻¹, agitation time: 2 h, and temperature= 25°C.

TABLE 1. Isotherm constants for uranium (VI) adsorption onto Dowex 2x8 anion exchanger resin

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>q_max (mmol g⁻¹)</td>
<td>303.03</td>
<td>82.5</td>
</tr>
<tr>
<td>equation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>n</td>
<td>1.72</td>
<td>1587.44</td>
</tr>
<tr>
<td>equation</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

On account of investigating the governing mechanism on U(VI) ions sorption, the rate of uranium ion sorption, one of the important traits that portrays sorption efficacy, was determined by applying the pseudo first-order and pseudo second-order kinetic models (Table 2).

The pseudo 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 [20]. An examination of kinetics outcome shows that pseudo second-order model fitted the kinetic data of the Dowex 2x8 anion exchanger resin better than that of pseudo first-order. The affirmation of pseudo second-order model indicates that the concentration of both sorbate (uranium) and sorbent (Dowex 2x8) are involved in the rate-limiting step of the sorption process [21].

3. 4. Effect of Various Anions on Uranium Removal One factor that leads to debilitation of most sorbent’s effectiveness in uranium sorption process is the presence of interfering ions.

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TABLE 2. Kinetic parameters for uranium removal using Dowex 2x8 anion exchanger resin

<table>
<thead>
<tr>
<th>Model</th>
<th>( k ) (min(^{-1} ))</th>
<th>( q_e ) (mmol g(^{-1} ))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first-order</td>
<td>0.419</td>
<td>0.861</td>
<td>0.9694</td>
</tr>
<tr>
<td>Pseudo second-order</td>
<td>1.548</td>
<td>8.203</td>
<td>1</td>
</tr>
</tbody>
</table>

The problem that often seems to be challenging is that most of ions existing in the solution have trivial or strong tend to the adsorbent. Hence, the effect of interfering ions on uranium sorption, a challenge which must be met, was evaluated in the presence of sulfate (0-2655 mg l\(^{-1} \)), nitrate (0-1000 mg l\(^{-1} \)), chloride (0-2527 mg l\(^{-1} \)), fluoride (0-4842 mg l\(^{-1} \)), and phosphate (0-300 mg l\(^{-1} \)) ions. It can be seen from Figure 4 that, chloride and nitrate ions severely affect uranium uptake using Dowex 2x8 resin rather than the others. The result additionally showed that the presence of high amounts of sulfate, fluoride, and phosphate ions had no interference for uranium sorption in contrary with Cl and NO\(_3\) ions. Having considered the negative impact of Cl and NO\(_3\) ions on the resin performance, it is recommended that before using Dowex 2x8 for uranium sorption, a relevant process for elimination of those ions from the solution should be performed.

3.5. Anion Exchange Mechanism As a result of inauguration of Dowex 2x8 resin into uranium solution, the following exchange reaction can happen between uranyl ions and the active sites on the surface of the resin (Equation (9)):

\[
[\text{Dowex}] - \text{Cl}^{-} + [\text{U}] \rightarrow [\text{Dowex}] - \text{U}^{4+} + \text{Cl}^{-} \quad (9)
\]

The result showed that (based on Figure 4 data) the presence of some anions in the solution can decrease the adsorption efficiency. This effect can be attributed to the formation of various ionic complex between uranium and those anions contents which inhibit the sequestering uranium complexes on the active sites of the resin. As another possible explanation for uranium uptake by Dowex 2x8, we mention the space inhibition of uranium molecule that can play a negative role in sorption process. Under such condition, uranium embedded among the resin’s active sites’ dentates and they hold uranium complexes in the matrix of resin (Figure 5). Adversely, this phenomenon can attribute to the decrease of uranium removal from solution. As there are other anions such as sulfate, fluoride, chloride, nitrate, and phosphate in the solution, by formation of uranium complexes, they have more opportunity to be adsorbed on resin active sites.

4. CONCLUSION

Briefly, current work investigates affinity of Dowex 2x8 anion exchanger resin towards sorption of uranium ions in the presence of sulfate ions. During the sorption experiments, the operational parameters influencing on U(VI) adsorption onto the resin, including pH, initial concentration, contact time and anion effect were studied. It was disclosed that the sorption strongly occurs at pH 3 and it will remain constant in the afterward pH quantities. To be able to understand the observed phenomena, we employed isotherm and kinetic models to depict the adsorption mathematically. Isotherm study showed that the Freundlich binding model was consistent with experimental data compared to the Langmuir model, indicating the sorption process was influenced by the formation of monolayer coverage of the sorbate (uranium) on the homogenous sorbent surface. Pseudo second-order kinetic model better estimated the result than the pseudo first-order kinetic model. This revealed that the concentration of both sorbate (uranium) and sorbent (Dowex 2x8) are involved in the rate-limiting step of the sorption process. Anions effect including sulfate, nitrate, chloride, fluoride, and phosphate ions on uranium sorption using the Dowex 2x8 resin was investigated. The result showed that the presence of anionic elements such as fluoride, phosphate and sulfate did not affect the
sorption process, while the presence of Cl and NO₃ ions had negative impact on uranium removal. Thus, before using Dowex 2×8 for uranium sorption, a relevant process for elimination of those interfering ions from the solution should be done. The maximum adsorption capacity (q_{max}) of the Dowex 2×8 anion exchanger resin was found to be 303.03 mmol g⁻¹.

5. REFERENCES

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