Optimization of The process Factors Affecting Extraction of Uranium from Acidic Solution Using Activated Carbon and Kinetics Studies of The adsorption Process

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Abstract

Activated carbon exhibits a great potential as an adsorbent because of its favorable physical/chemical surface characteristics. The objective of this research is to investigate the feasibility of activated carbon for the adsorption of uranium from aqueous solutions. All laboratory experiments were conducted at ambient temperature by following a batch adsorption technique. The impact parameters that affect the uranium adsorption such as stirring time, pH of the solution, initial uranium concentration have been optimized. The obtained results indicate that the adsorption is pH dependent. The maximum adsorption capacity of U (VI) took place at pH 5.0 for 60 minutes contact time and initial uranium concentration of 125 ppm. The experimental adsorption data was described using Langmuir and Freundlich adsorption isotherm models. Equilibrium adsorption data fitted the Langmuir adsorption isotherm well with $R^2 = 0.9773$. The values of parameters calculated from the kinetic models were best fitted to the pseudo-second order kinetic model, with the correlation coefficient of $R^2 = 0.9810$.

Keywords Adsorption, uranium, activated carbon, adsorption isotherms, adsorption kinetics.

1. Introduction

To support the use of nuclear power as a sustainable electric energy generating technology, long-term supply of uranium is very important [1]. Many processes have been proposed for uranium (VI) recovery from solutions. Chemical precipitation, ion exchange, solvent extraction, liquid membrane, and adsorption are the most commonly used methods; each has its merits and limitation in application [2-5]. Adsorption technique has attracted attention in recent decades in many physical, chemical, and biological processes in the nature because of its effective and economic method with high potential for the removal of uranium, recovery and recycling of metal ions from liquid solution. Adsorption is also widely used in water and wastewater treatment [6-8]. Among many types of adsorbent materials, Activated carbon is the most versatile adsorbent because of its high surface areas that range from 500 to 1500 $m^2g^{-1}$, polymodal porous structure (essentially microporous), presence of a wide spectrum of surface functional groups, high adsorption capacity, their higher thermal radiation resistance, compared with organic exchanger resins, and also their acid-base stability, compared with inorganic sorbents and variable surface chemical composition. As a consequence, there are numerous applications in many fields, for example in gas or liquid phases [9-11]. Two main processes are adopted to produce activated carbon, carbonization and activation respectively. First, the carbonization process is heating the raw material in the absence of air to remove any associated atoms to the carbon in order to get pure carbon. Dehydrating agent can be added during the carbonization process. Second, the activation process is done by passing oxidative hot gases such as carbon dioxide and steam through the carbon at very high temperatures varies between 315 and 925°C to remove any noncarbonaceous material and to form the pores of the activated carbon surface [11]. It was found that the activated carbon and modified activated carbon can be a useful tool in the uranium recovery from crude phosphoric acid with highly efficiency and cheap cost [12, 13]. High U
(VI) removal efficiencies could be achieved by using activated carbon derived from coconut husk [14]. It was indicated that biochar materials prepared from pyrolysis of Bamboo, Eucalyptus and Macauba nuts can be used for the removal of uranium ions from liquid wastes [15]. It was demonstrated that sawdust activated carbon (SDAC) and its amine form (SDACA) have a high sorption capacity for uranium and can be successively used for the fast removal of U (VI) ions from aqueous solutions [16]. The purpose of the present research was to investigate the removal efficiency of U (VI) ion using activated carbon from a synthetic solution and a pregnant solution obtained from Allouga pilot plants, southwestern Sinai, Egypt. Batch adsorption technique was conducted to study the effective parameters on the adsorption process such as contact time, pH and initial concentration of metal ions.

2. Material and Methods

2.1 Preparation of Sorbents

The used activated carbon (AC) was supplied by Ubichem Limited, UK, size of 2-4 mm. It was washed with distilled water several times to remove dirt and particulate materials and to remove trapped air from the pores.

2.2 Preparation of Uranium Solutions

2.2.1 Synthetic Solution

A Stock standard solution of uranium (VI) assaying 1000 ppm was prepared by dissolving a predetermined amount of UO$_2$(NO$_3$)$_2$.6H$_2$O (1.782 g), Sigma–Aldrich, USA in 1000 mL of de-ionized water. For experiments the required concentration was prepared by diluting the stock solution in marked flasks.

2.2.2 A real Solution

Pregnant solution of uranium was obtained from Allouga pilot plants, southwestern Sinai, Egypt. The metal ions concentrations in the pregnant solution are shown in Table 1.

2.3 Adsorption Tests

Adsorption experiments were carried out by a batch technique at ambient temperature. The effect of various parameters on the absorption process including the initial concentration of U (VI), contact time, and the optimum pH were studied. Each of the controlling factors has been studied alone by varying its range and keeping all the other factors fixed. The ranges of each factor were as follow: pH from 1 to 7, contact time from 15 to 90 minutes and initial concentration from 25 to 1000 mg/L. Equilibrium adsorption experiments were conducted by agitating 0.3 g of activated carbon with 50 ml of uranium solution using magnetic stirrer at 120 rpm. In all stages of the experiment, 0.1 N solutions of NaOH and H$_2$SO$_4$ were used to adjust the pH for sulfate solutions and .1 N solutions of NaOH and .1 N HNO$_3$ for nitric solutions. The pH measurements were carried out using Digital pH meter model DM-21, together with a combined glass electrode obtained from HANA. The U (VI) concentration remaining in the supernatant solution and in the real solution was analyzed by an oxidimetric titration method against ammonium metavanadate [17]. The content of Na was determined by a flame photometric technique. $SO_4^{2-}$ was analyzed by UV-VIS spectrophotometer (Shimadzu UV-160). Other elements in the real solution were measured by atomic absorption spectrometer (model Unicam 969, Unicam Ltd., Cambridge, UK).

Table 1: Chemical analysis of the pregnant solution of uranium

<table>
<thead>
<tr>
<th>Element</th>
<th>Conc. (ppm)</th>
<th>Element</th>
<th>Conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^{3+}$</td>
<td>6350</td>
<td>Cu$^{2+}$</td>
<td>258</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>28</td>
<td>Ni$^{2+}$</td>
<td>26</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>6845</td>
<td>U$^{5+}$</td>
<td>134.4</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>174</td>
<td>Ca$^{2+}$</td>
<td>337</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>7520</td>
<td>$p^{5+}$</td>
<td>75</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>115</td>
<td>$SO_4^{2-}$</td>
<td>9765</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 The effect of pH

The solution pH is considered as the most dominant parameter that has a clear effect on the adsorption phenomena in most cases. This is mainly due to the fact that the pH of the aqueous solution affects the surface charge of the adsorbents, and it can influence the degree of ionization and speciation of the adsorbates [18]. The uptake capacity of adsorbates from the aqueous solution is affected by the value of the pH of the solution. This is mainly due to the fact that hydrogen and hydroxide ions are being adsorbed strongly by activated carbon, so the adsorption of other ions is influenced by the pH of the solution [19-20]. In order to obtain the optimum pH value for uranium adsorption, several batch experiments were carried out by differentiating the pH values from 1 to 7.0 and the other parameters
were kept constant at 0.3 g of activated carbon for 60 minute contact time at room temperature and 25 ppm initial uranium concentration using magnetic stirrer at 120 rpm. Figure 1 indicates that at low pH the uranium (VI) extraction efficiency and adsorption capacity are very low. This is attributed to the exaggerated protonation of the active sites at activated carbon surface where the H ions are small and fast and this often excludes formation of links between UO$_2^{2+}$ ions and the active site. At pH value of 5, linked H$^+$ is emitted from the active sites and adsorbed amount of uranium ions is generally found to increase where the extraction efficiency and adsorption capacity achieve the highest value (95.2% and 3.98 mg/g respectively). On the other hand, further increases in the pH beyond five caused precipitation of the uranium hydroxide, which was accompanied by a decrease of uranium adsorption [21].

3.2 Effect of Initial Uranium Concentration

Effect of initial uranium concentration on the adsorption efficiency was studied using a fixed mass of activated carbon (0.3 g), contact time 1 h, a solution volume of 50 ml and pH 5 using magnetic stirrer at 120 rpm at room temperature (25 °C±1). The range of initial uranium concentrations was up to 1000 ppm. From Figure 2 it can be revealed that the maximum extraction efficiency is 97.2 % at 125 ppm initial uranium concentration. This increase could be attributed to an increase in the interaction of uranium (VI) ions with the sufficient surface active sites of activated carbon and to the higher mobility of uranyl ions (UO$_2^{2+}$) at lower initial concentrations [22]. Further increase of the initial uranium concentration has adverse effect on uranium adsorption efficiency as a result of increasing competition with uranium ions for the free active sites. It can be noticed also from Figure 2 that the uranium adsorption capacity of the activated carbon increased with increasing initial uranium concentration and reached a maximum value at uranium concentration of 600 ppm. Beyond this initial uranium concentration, uranium adsorption capacity of the activated carbon remained constant at 46.4 mg/g.

3.3 Adsorption Isotherm Models

If the adsorbent and adsorbate are contacted long enough, equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by adsorption isotherms. An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. The adsorption isotherm is also an equation relating the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution at a given temperature. Various isotherms such as Langmuir and Freundlich isotherms had been used to evaluate the equilibrium characteristics of the adsorption processes. Langmuir and Freundlich isotherms are the most widespread isotherms used to characterize the solid-liquid adsorption system. The parameters of the isotherm equations were calculated by linear regression analysis.

3.3.1 Freundlich Isotherm

The Freundlich model supposes an exponential trend. The Freundlich equation predicts that the ion concentrations on the adsorbent will increase as long as there is an increase in the ion concentration in the liquid. The empirical model was shown to be consistent with an exponential distribution of active centers and characteristic of heterogeneous surfaces.

![Figure 1: Effect of pH on uranium ions adsorption onto activated carbon surface (0.3 g activated carbon, 25 ppm uranium initial concentration, 120 rpm stirring speed for 60 min)](image1)

![Figure 2: Initial uranium concentration, ppm concentration on its adsorption onto activated carbon surface (0.3 g activated carbon, pH 5, 120 rpm stirring speed for 60 min)](image2)
The linear form of this isotherm is expressed as:
\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\] (3)

Where \(C_e\) is the equilibrium concentration (mg/L), \(K_f\) and \(n\) are Freundlich constants with \(n\) giving an indication of how favorable the adsorption process is (mg/g) (L/mg) and \(1/n\) is related to the adsorption capacity of the adsorbent. From Figure 3 it can be suggested that the sorption of the uranium complex ions obeys Freundlich isotherm over the entire range of the studied sorption concentration. The numerical values of the constants \(1/n\) and \(K_f\) are computed from the slope and intercept by means of a linear least square fitting method and are given in Table 2. It can be seen from these data that the Freundlich intensity constant \((n)\) is greater than unity for the studied uranium ion. This has physicochemical significance with reference to the qualitative characteristics of the isotherms, as well as to the interactions between metal ion species and modified activated carbon. Where \(n = 5.6\) indicating that the sorption of uranyl ions onto activated carbon is favourable and the \(R^2\) value is 0.9359.

### 3.3.2 Langmuir Isotherm Model

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [24, 25]. Based upon these assumptions, Langmuir represented the following equation:

\[
\frac{1}{q_e} = \frac{1}{K_L \cdot Q_o} \cdot \frac{1}{C_e} + \frac{1}{Q_o}
\] (4)

Where: \(C_e\) is the equilibrium concentration of adsorbate (mg/L\(^{-1}\)), \(q_e\) is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), \(Q_o\) is the maximum monolayer coverage capacity (mg/g) and \(K_L\) is Langmuir isotherm constant (L/mg). Figure 4 indicated that a plot of \(1/q_e\) versus \(1/C_e\) would result in a straight line with a slope of \(1/K_L \cdot Q_o\) and intercept of \(1/Q_o\). The Langmuir parameters given in Table 2 can be used to predict the affinity between the sorbate and the sorbent using the dimensionless separation factor, \(R_L\) expressed as in the following Equation [26]:

\[
R_L = \frac{1}{K_L \cdot Q_o}
\] (5)

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q_o) (mg/g)</td>
<td>(K_L) (L/mg)</td>
</tr>
<tr>
<td>45.25</td>
<td>0.373</td>
</tr>
</tbody>
</table>

From Langmuir Isotherm model \(Q_o\) was determined to be 45.25 mg/g, \(K_L\) (Langmuir isotherm constant) is 0.059 L/mg, \(R_L\) (the separation factor) is 0.373 indicating that the equilibrium sorption was favourable and the \(R^2\) value is 0.9773 proving that the sorption data fitted well to Langmuir Isotherm model.

Comparing the parameters of isotherms, it can be stated that the adsorption of uranium (VI) on activated carbon fits the Langmuir isotherm model because it gives a higher correlation coefficient \((R^2=0.9773)\) value than Freundlich isotherm model \((R^2=0.9359)\).
3.4 Effect of Stirring Time

The impact of stirring time on the adsorption efficiency on activated carbon has been investigated by performing a series of adsorption experiments under the following conditions: 0.3 g of adsorbent, 50 ml of U (VI) solution, 125 ppm initial uranium concentration and pH 5.0 at ambient temperature using magnetic stirrer at 120 rpm. The adsorption experiments were carried out at stirring times ranging from 15 to 90 min. From Figure 5 it can be revealed that the adsorption efficiency and adsorption capacity were increased with increasing contact time until 60 minutes. A further increase in contact time has no effect on the uranyl ions adsorption. This relatively rapid attainment of equilibrium may be related to the large surface area and adequate active sites of the activated carbon. The maximum adsorption efficiency and adsorption capacity were 97.2 % and 20.25 mg/g respectively.

3.5 Adsorption Kinetics

Kinetic models were applied to the experimental data in order to understand the potential rate controlling steps and mechanism of reaction. The adsorption of uranium (VI) onto activated carbon was analyzed using pseudo first order and pseudo second-order models. The linear form of pseudo first order model was given by Equation 6 [27]:

\[
\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t
\]  

(6)

Where \( q_e \) and \( q_t \) are the amount of U (VI) ions adsorbed onto activated carbon at equilibrium (mg/g) at time t, respectively and \( K_1 \) is the adsorption rate constants of pseudo-first-order model (1/min). Values of \( K_1 \) and \( q_e \) were calculated from the slope and intercept of the straight line of plotting \( \log(q_e - q_t) \) versus t, respectively as seen from Figure 6 and Table 3.

The linear pseudo-second order model can be represented as equation 7 [28, 29]:

\[
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e}
\]  

(7)

Where \( K_2 \) is the equilibrium rate constant of pseudo second order adsorption (g/mg/min). Values of \( K_2 \) and \( q_e \) were calculated from the slope and intercept of the straight line of plotting \( \frac{t}{q_t} \) versus t as shown in Figure 7 and Table 3.
The results obtained for each of the kinetic models show a good compliance with the pseudo second order equation, where the values of correlation coefficient $R^2$ and the calculated $q_e$ are 0.981 and 47.1 mg/g, respectively.

3.6 Application of The studied Activated Carbon for A real Solution

The obtained optimum parameters for the adsorption of synthetic solution of uranium were applied for the removal of uranium from a real solution. The case study was carried out using batch experiment by contacting 0.3 g of activated carbon contact with 50 ml of a real solution for 60 minutes at pH 5 using magnetic stirrer at 120 rpm. After equilibration, the solution (case study) was filtered and analyzed to determine the uranium concentration. It was indicated that under the working conditions, the extraction efficiency of uranium decreased to 81.7 % compared to 97.2 % obtained in case of synthetic solution. This could be attributed to the competitive effect between uranium (VI) and cations for the active sites available for the adsorption process [30]. In a different trend, the presence of $Fe^{+3}$ enhances the adsorption of uranium onto the activated carbon due to formation of complexes between $Fe^{+3}$ and $SO_4^{2-}$, thus releasing uranium which in turn is adsorbed on activated carbon; or the binding of uranium complexes to $Fe^{+3}$ as well as onto activated carbon, a situation resembling a salt bridge set up (surface-uranium complex–Fe uranium complex) [30, 31].

4. Conclusion

On the basis of the obtained results in the investigation of adsorption of uranium on activated carbon using batch technique it may be concluded that: The activated carbon can be regarded as an effective sorbent for the removal of uranium from aqueous solutions. The adsorption of uranium on activated carbon obviously depends on pH values. The maximum loading of uranium ions on activated carbon (46.4 mg/g) was obtained by contacting 0.3 g of activated carbon with 50 ml U (VI) at pH 5 for 60 minutes at room temperature using magnetic stirrer at 120 rpm. Kinetics study illustrated that adsorption of U (VI) followed pseudo second-order kinetic model ($R^2$ value is 0.981). Sorption of uranium onto activated carbon was best described by the Langmuir isotherm model ($R^2$ value is 0.9773). In case of real solution, the extraction efficiency of uranium decreased to 81.7 % compared to 97.2 % due to the competition between uranium and other cations. This work illustrated that activated carbon can be regarded

![Figure 6: Pseudo first-order for the adsorption of uranium (VI) onto activated carbon](image1)

![Figure 7: Pseudo second-order for the adsorption of uranium (VI) onto activated carbon](image2)

| Table 3: Kinetic parameters of the U (VI) adsorption onto activated carbon. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Pseudo-first-order | Pseudo-second order |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $Q_o$(mg/g) | $K_1$(L/mg) | $R^2$ | $Q_o$(mg/g) | $K_2$(mg/g) | $R^2$ |
| 42.07 | 0.007 | 0.9152 | 47.1 | 0.0003 | 0.9810 |
as an effective adsorbent for the removal of U (VI) from aqueous solutions.

5. Conflicts of interest
There are no conflicts to declare.

6. Acknowledgments
The author appreciate the help of the Pilot Plant Department, Nuclear Materials Authority, Cairo, Egypt

7. References


[269] تحقيق العوامل المثلى التى تؤثر فى استخلاص اليورانيوم من محلول حمضي باستخدام الكربون النشط والدراسات الحركية لعملية الامتزاز

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ينظر الكربون النشط كمادة مثلى لاستخلاص اليورانيوم من محلول حمضي، وذلك بسبب خصائصه السطحية الكيميائية والفيزيائية. الهدف من هذا البحث هو دراسة جدوى استخدام الكربون النشط لاستخلاص اليورانيوم من المحاليل المائية. أجريت جميع التجارب العملية باستخدام تقنية الامتزاز الدفعي. تم تحقيق العوامل التي تؤثر على عملية الامتزاز مثل زمن التقليب وتركيز اليورانيوم ودرجة حامضية محلول التاليم. النتائج التي تم الحصول عليها تشير إلى أن عملية الامتزاز تعتمد على درجة حامضية محلول (\( \text{pH} \)). أقصى امتصاص لليوئانيوم يحدث عند الرقم الهيدروجيني 5 وعند التقليب لمدة 60 دقيقة عندما يكون التركيز الأولي لليوئانيوم 125 ppm. تم وصف بيانات الامتزاز الحركية باستخدام نماذج Langmuir and Freundlich. نتائج عملية الامتزاز متوافقة مع نموذج Langmuir. قيم العوامل المحسوبة من (kinetic models) تتوافق مع نموذج درجة (\( R^2 = 0.9810 \)).