Synthesis of a Novel Composite Hydrous Titanium Oxide-Hydroxyapatite for Adsorbing Uranium from Waste Effluents

Amr H Ali*, Shaimaa MA Esmaeel, Salah A Zaki and Mohammed S Hagag
Nuclear Materials Authority, P.O. Box 530 Maadi, Cairo, Egypt

ABSTRACT

In this paper, a novel composite (HAP@HTO) derived from hydrous titanium oxide (HTO) extracted from Rosetta ilmenite mineral and hydroxyapatite (HAP) was formed by co-precipitation method, specified and used for uranium preconcentration from its solutions. Batch tests were performed to investigate its selectivity towards uranium; maximum adsorption efficiency reached at pH 2.5, 120 minutes contact time, 900 mg L⁻¹ uranium concentration and adsorbent ratio (0.1g/75 mL). The equilibrium data fitted well with Langmuir adsorption isotherm. From kinetics and thermodynamics data; process was fast, fitted well with pseudo-second order, spontaneous and exothermic. The percentage desorption of uranium reached its maximal at 15 minutes equilibrium time using 1 mol L⁻¹ H₂SO₄. Thereby, (HAP@HTO) composite has promising potential applications in extracting U (VI) from its aqueous solutions in nuclear fuel field and environmental pollution cleanup.

Keywords: Ilmenite; Titanium hydroxide; Uranium; Langmuir; Elution

INTRODUCTION

One of the most popular methods of extraction and concentration of micro-quantities of elements is their sorption from its solutions with synthetic adsorbents. Therefore, obtaining adsorbents based on synthetic materials of organic and inorganic origin is one of the major problems of analytical chemistry. And the development on their basis of methods of concentration and the excretion of trace elements are always important. Methods of immobilization of reagents on the surface of various adsorbents and their use for concentrating metals in various objects are devoted to a number of works [1-4]. An important direction in the practice of using synthetic adsorbents is the targeted synthesis of new selective adsorbents and the improvement of the analytical characteristics of the already known by introducing functional analytical groups into the sorbent matrix that can interact with metal ions to form complexes, chelates, or ionic associates.

A set of technologies were developed for uranium removal and recovery from its ores, nuclear fuel effluents, mine tailings, seawater and other waste sources in consideration of the dual significance of uranium in nuclear power generation as well as its strategic importance [5-8]. Solid phase extraction (SPE) or solid–liquid extraction is more valuable technique compared with others due to the following advantages: insolubility of the applied solid in the aqueous phase, its low rate of physical degradation besides its high sorption capacity as well as its good flexibility, low costs, kinetic properties, absence of emulsion, safety with respect to hazardous samples and easier to operate in the automated analytical techniques [9-12].

Hydroxyapatite is an ideal material for long-term containment of contaminants because of its high sorption capacity for actinides and heavy metals, low water solubility, high stability under reducing and oxidizing conditions, availability, and low cost [13]. It was conducted in stabilization of a wide variety of metals (e.g., Cr, Co, Cu, Cd, Zn, Ni, Pu, Pb, As, Sh, U and V) by many investigators [14,15]. Among the adsorption materials, the hydrous titanium oxide has attracted attention as adsorbent due to its large surface area, high adsorption rate, heat and radiation resistance, free from the interference of other ions, insoluble in water and its photo catalytic action. It can be used for purification of ground water and industrial wastewater[16].

Additionally, preparation and design of composite particles consisting of cores covered by shells of different chemical compositions have attracted much interest due to their superior catalytic, optical, and electrical properties, which are different

*Corresponding to: Amr H Ali, Nuclear Materials Authority, P.O. Box 530 Maadi, Cairo, Egypt, Tel: 201224335661; E-mail: amr_nma@yahoo.com

Received: October 16, 2020; Accepted: November 25, 2020; Published: November 30, 2020


Copyright: 2020 © Ali AH, et al. This is an open access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
from those of single-component materials [17]. These interesting properties of core-shell materials are due to structure, size, morphology, composition of their shells and cores [18]. Among core-shell particles of various compositions, those made of core with inexpensive compounds and a reactive shell have received particular interest because of the functional and economic advantages that they can provide [15]. Arranging of reactive materials as thin shells on proper low cost cores greatly magnifies their use, and can also significantly enhances their properties via the so-called strain and ligand effects of the core substrate on the shell compound [19].

This study deals with the preparation of a core-shell structure composed of calcium hydroxyapatite hydrous titanium oxide. The fabricated composite will be subjected, in batch reactor, with uranyl ions waste aqueous solution to investigate its sorption characteristics in aqueous solution under different experimental conditions.

**MATERIALS AND METHODS**

**Chemicals and reagents**

All chemicals used were of analytical grade purity and were used without further purification. Ammonia solution (NH₄OH) was supplied from Readel, Germany. Calcium nitrate (Ca(NO₃).4H₂O) was supplied from Win Lab, UK while dis-ammonium hydrogen phosphate ((NH₄)₂HPO₄) was a product of VEB, Germany. Both was supplied from Win Lab, UK while dis-ammonium hydrogen phosphate ((NH₄)₂HPO₄) was a product of VEB, Germany. Both hydrochloric acid and sodium hydroxide were obtained from Adwic, Egypt.

**Preparation of titanium leach liquor from ilmenite processing**

A sample of East Rosetta beach ilmenite concentrate (Table 1) was used in the present work to prepare the working Ti leach liquor by applying the optimum conditions previously determined and which have resulted in 95% leaching efficiency of titanium [20]. These conditions involved ilmenite leaching after grinding to -200 mesh size in concentrated HCl solution (12 mol L⁻¹) in 1/8 S/L ratio at 80°C for 90 minutes and adding 10% Fe powder. The ilmenite dissolution reactions can be represented as follows:

\[
\text{FeO}.\text{TiO}_2 + 4\text{HCl} \rightarrow \text{TiOCl}_4 + \text{FeCl}_2 + 2\text{H}_2\text{O}
\]

\[
\text{FeO}.\text{TiO}_2 + 6\text{HCl} \rightarrow \text{TiCl}_4 + \text{FeCl}_3 + 3\text{H}_2\text{O}
\]

After filtration and washing, the assay of the obtained leach liquor was found to be attaining 41.6 g TiO₂/L equivalent to 25 g Ti/L together with 60 g Fe₂O₃/L in hydrochloric acid concentration 5 mol L⁻¹.

**Composite preparation**

The hydroxyapatite coated with hydrous titanium oxide (HAP@HTO) was decided to be constructed by applying calcium hydroxyapatite as a core and hydrous titanium oxide as an active shell. They were prepared by firstly dropping a solution of 0.387 M (NH₄)₂HPO₄ into an equal volume of 0.5 M Ca(NO₃)₂ solution bearing titanium to precipitate calcium hydroxyapatite (HAP) and the reaction was terminated at pH 11 which could produce the stoichiometric Ca/P ratio of 1.67. After further stirring for 30 minutes, HAP precipitate was filtered and washed repeatedly to remove the unwanted ions. Secondly, chloride solution bearing titanium was added to HAP precipitate at 5 mL minutes⁻¹ rate with continuous stirring. A shell of hydrous titanium oxide was then precipitated on HAP surface by adding NH₄OH till pH attained a value of 10. The mixture was left for settling wherein the supernatant was separated. The precipitate was then washed thoroughly with distilled water until constant pH value was sequentially attained. Finally, the composite was dried, pulverized, sieved and stored in a desiccator for further usage.

**Batch mode adsorption and desorption studies**

Batch adsorption experiments were carried out by stirring the aqueous solution with the prepared composite in glass beaker at 400 rpm for a period of 180 minutes using a magnetic stirrer. 0.1 g of composite was added to different volumes from aqueous sample (10-100 mL) containing various concentrations of U (VI) at temperatures of [25-55(±2)°C]. The pH of the working solutions was adjusted to 2.5. When the adsorption equilibrium was reached, it was filtered to separate the two phases. The quantity of uranium loaded on the composite was calculated using equation 1, i.e. by taking the difference between the initial and residual concentrations of uranium in solution and dividing it by the weight of the adsorbent. The removal or adsorption efficiency (R) was defined as the U sorption percentage relative to the initial concentration equation 2:

\[
q_e = \frac{C_0 - C_e}{M} \times V
\]

\[
R = \frac{C_0 - C_e}{C_0} \times 100
\]

Where \( q_e \) (mgg⁻¹) is the amount of uranium loaded per unit weight of the adsorbent; \( C_0 \) and \( C_e \) are the initial and equilibrium (or any time) uranium or interfering ions concentration (mg L⁻¹), respectively; \( V \) is the volume per liter of solution and \( M \) is the weight (g) of the adsorbent (HAP@HTO) composite. To desorb uranium from the (HAP@HTO) composite adsorbent, a variety of stripping agents were examined, including HCl, H₂SO₄, Na₂CO₃, double distilled H₂O and HNO₃. Uranium analyzed spectrophotometrically in the corresponding aqueous phases by Arsenazo (III) reagent using Lambda UV/VIS spectrophotometer (Perkin-Elmer, USA) [21]. Also, U (VI) was analyzed by redox titration method against ammonium metavanadate in the presence of diphenylamine sulfonate indicator prior to titration; proper reduction of U (VI) was performed using ferrous sulfate [22].

**Instruments**

The surface characteristic of the synthesized resin was characterized using Fourier Transform Infrared spectrophotometer (FTIR) model Thermo Scientific Nicolet IS10, Germany. The powder X-ray diffraction patterns was recorded with AP-Analytical X-Ray Diffraction equipment model XPert PRO with Monochromator, Cu-radiation (λ=1.542Å) at 45 K.V., 35 M.A. and scanning speed 0.030/sec. were used. The reflection peaks between 2θ ~20 and 60°, corresponding spacing (d, Å) and relative intensities (I/I₀) were obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files. SEM model Philips XL 30 ESEM (25-30 k e V accelerating voltage, 1-2 mm beam...
diameter and 60-120 s counting time). Minimum detectable weight concentration is ranging from 0.1 to 1 wt % with realized precision lower than 1%. Inductive Coupled Plasma Optical Emission Spectrometry was employed for trace concentrations of metal ions (Prodigy Axial high dispersion ICP-OES-USA model).

Liquid waste sample

The used liquid waste sample in this study was obtained from disposal waste derived from ores products project at Anshas site, Nuclear Materials Authority, Egypt. The waste solution was collected from (washing, scrubbing, raffinate, solvent regeneration solutions, leaching and several precipitation tests). The waste solution precipitated by sodium hydroxide. The formed hydroxide precipitate washed several times with distilled water to remove the excess NaOH, then dried and about 60 g from the dried cake dissolved with HNO₃. A sample from the wetted raffinate precipitated cake was analyzed against their constituents using (ICP–OES), it was indicated that the wetted cake contained about 1.45% U. The chemical composition of the hydrous cake is tabulated in (Table 2).

RESULTS AND DISCUSSION

Composite characterization

Characterization of HAP@HTO composite with FT-IR: IR band changes from Figures 1 & 2 may reveal the adsorption of uranium ions onto (HAP@HTO) composite. The characteristic band of TiO₂ appears at 745 cm⁻¹ is slightly affected in intensity after uranium adsorption. The bands at 1000 cm⁻¹ represented phosphate group. 1469.54 cm⁻¹ indicates the presence of carbonate groups (CO₃²⁻) it can be identified as Ca₁₀(PO₄)₆CO₃. Broadband > 3300 cm⁻¹ represented water stretching.

X-ray analysis: The phase structure of the synthesized sample was investigated by XRD and some of data are given in Figure 2, the shell structure of HAP@HTO is HTO. So, the diffractogram clarified that the sample is amorphous.

Surface morphology studies

SEM images of the composite macrostructure before and after uranium adsorption Figures 3a & 3b showed the rudimentary on the surface (Figure 3a). After adsorption, these pores were occupied with uranium ions (Figure 3b).

Factors affecting the adsorption process

Effect of pH: The pH value of the aqueous solution is an important variable which control the adsorption process of the metal ion at the solid-liquid interface. Therefore, pH effect on uranium adsorption onto (HAP@HTO) composite was examined in pH range of 1 to 3.5, while the other experimental parameters were fixed. As can be seen in Figure 4, uranium adsorption efficiency and uptaking increased by pH increasing up to 2.5 then starts decreasing again. The pH solution could affect the mechanism of uranium adsorption through the hydrolysis of the uranyl ions. At (high acidity) lower pH below 2.5, adsorption efficiency was decreased due to competition occurs between the H⁺ ions, which are small and fast, and the uranium species, which are also positive, and adsorption is not favored. Thus, the presence of a higher concentration of H⁺ ions in the reaction mixture caused a reduction in the uranium uptake. In contrast, increasing solution pH resulted in the adsorbent surface becoming more negatively

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Chemical composition of Heavy Metals and trace elements for the Precipitated Cake by (ICP–OES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Conc., %</td>
</tr>
<tr>
<td>U</td>
<td>1.45</td>
</tr>
<tr>
<td>As</td>
<td>0.49</td>
</tr>
<tr>
<td>Cd</td>
<td>0.05</td>
</tr>
<tr>
<td>Ca</td>
<td>0.15</td>
</tr>
<tr>
<td>Pb</td>
<td>0.86</td>
</tr>
<tr>
<td>Se</td>
<td>UDL</td>
</tr>
<tr>
<td>Ag</td>
<td>UDL</td>
</tr>
<tr>
<td>Sr</td>
<td>0.24</td>
</tr>
<tr>
<td>Zn</td>
<td>1.11</td>
</tr>
<tr>
<td>Cu</td>
<td>10.07</td>
</tr>
<tr>
<td>Cr</td>
<td>4.67</td>
</tr>
<tr>
<td>Al</td>
<td>7.35</td>
</tr>
<tr>
<td>V</td>
<td>1.77</td>
</tr>
<tr>
<td>Na</td>
<td>4.24</td>
</tr>
<tr>
<td>K</td>
<td>4.18</td>
</tr>
<tr>
<td>Ca</td>
<td>2.88</td>
</tr>
<tr>
<td>Mg</td>
<td>3.11</td>
</tr>
<tr>
<td>Fe</td>
<td>20.50</td>
</tr>
<tr>
<td>Ni</td>
<td>0.53</td>
</tr>
<tr>
<td>Mn</td>
<td>0.41</td>
</tr>
<tr>
<td>Ba</td>
<td>1.53</td>
</tr>
<tr>
<td>Co</td>
<td>0.08</td>
</tr>
<tr>
<td>B</td>
<td>UDL</td>
</tr>
</tbody>
</table>

UDL=under detection limit
charged, which resulted in the more favorable adsorption of positively charged species [23]. At pH >2.5; showing gradual decrease of uranium adsorption, due to the domination of the negatively charged uranium species within the bulk solution.

**Effect of contact time:** Contact time was studied in a range of 15-180 minutes while other controlling factors were kept constant. The adsorption efficiency increased from 30.33% at 15 minutes till reached its maximum value 42.5% at 120 minutes, as shown by Figure 5. Furthermore, no significant increase in uranium adsorption took place, revealing that equilibrium state has been reached. The adsorption behavior shows that at the starting stage, adsorption takes place in fast way on the external surface of the adsorbent followed by a slower process. The trend in uranium adsorption gives an indication that the binding may be occurred due to conjugation with functional groups located on the surface of the composite. These results agree with [24] who found that, 120 minutes as contact time is efficient for lead adsorption on the surface of tobacco and also stated that at a fixed adsorbent dosage at lower concentrations, the ratio of number of metal ions to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration. While at higher concentrations, the available sites of adsorption become fewer and subsequently the removal of metals depends on the initial concentrations.

**Effect of adsorbent dose:** Effect of adsorbent dose on U(VI) adsorption efficiency and uptaking onto (HAP@HTO) composite was studied under the following conditions: S/A varied from (0.1 g/10 mL) to (0.1 g/100 mL), initial uranium concentration 900 mg L⁻¹, at room temperature (25±2)°C, 15 minutes., and pH 2.5. The results illustrated below in Figure 6; it is clear that; by increasing solution volume leads to increasing uranium uptake and decreasing adsorption efficiency till complete saturation of the adsorbent reached at (0.1 g/75 mL). Therefore, it was chosen for the subsequent experiments. Apparently, at this ratio uranium ions occupy most of the vacant adsorption sites.

**Effect of uranium initial concentration:** Uranium initial concentration was varied from 250 to 1500 mg L⁻¹ under the following conditions: 0.1 g of adsorbent, 75 mL of solution, (25 ± 2)°C, contact time 45 minutes and pH 2.5. The results are shown below in Figure 7 which illustrated that maximal uranium uptake was reached at uranium concentration of 900 mg L⁻¹ with 42.5% adsorption efficiency. This is attributed to higher mobility of uranyl ions (UO₂²⁺) in the dilute solutions and strong interaction of the ions with the adsorbent, in agreement with the data of Mezenner and Bensmaili [25]. At uranium concentrations higher than 250 mg L⁻¹, the competition of uranium ions for free active sites becomes stronger, which negatively affects the adsorption efficiency. In this case, the adsorbed uranium amount increased further relative to the value obtained at 900 mg L⁻¹. Therefore, it was chosen as optimum uranium concentration.

**Effect of temperature:** Temperature affect on adsorption efficiency and uranium uptaking by (HAP@HTO) composite was studied in temperature range of 25 to 55(± 2)°C. Figure 8; showed that there is a sharp decrease in both uptaking and adsorption efficiency of U (VI) by temperature increasing. So, the temperature has a negative effect on U (VI) adsorption efficiency.
Adsorption kinetics and mechanism

Several experiments carried out at different temperatures (25–55°C) were evaluated by using the simple Lagergren equation 3 to determine the rate of adsorbing interactions assuming pseudo first order kinetics:

$$\log(q_e - q_t) = \log(q_e) - k_1 t$$

(3)
Where $q_t$ and $q_e$ are the amounts of uranium adsorbed (mg/g) at time $t$ (minutes) and equilibrium time (60 minutes), respectively, and $(k_1)$ is the pseudo first order Lagergren desorption rate constant (minutes$^{-1}$). The $(k_1)$ values could be obtained by plotting $\log (q_e - q_t)$ versus ($t$) for adsorption of uranium at different temperatures as shown in Figure 9; the values of the first order rate constant $(k_1)$ and correlation coefficient $(R^2)$ obtained from these plots are listed in (Table 3). The values of $(k_1)$ indicate that rate of desorption process increased with temperature. The first order mechanism suffered from inadequacies when applied to uranium sorption on the prepared composite. The experimental $(q_e)$ values differed from the corresponding theoretical values. Thus, the interaction of uranium with the prepared composite does not follow the first order kinetics. In order to insure the description of the kinetics, second order kinetic equation was applied. The pseudo second order kinetics can be represented by the following linear equation 4:

$$\frac{t}{q_t} = \frac{1}{K_q q^2} \left( \frac{1}{q_e} \right) t$$

Where $(k_2)$ is the second order rate constant (g mg$^{-1}$ minutes$^{-1}$). The kinetic plots of $(t/q_t)$ versus ($t$) for uranium are shown in Figure 10. The plots showed straight lines with good linearity temperatures. The calculated correlation coefficients are closer to unity for the pseudo second order kinetic model. The calculated equilibrium adsorption capacity $(q_e)$ is consistent with the experimental data. The $k_2$ values show the applicability of the above equation for the composite. Therefore the sorption reaction can be approximated more favorably by the pseudo second order sorption as the predominant mechanism.

A comparative study for uptaking capacity (mgg$^{-1}$) of different adsorbents towards uranium is shown in (Table 4) [26-34].

### Adsorption isotherms

To describe the results obtained, we used the Langmuir and Freundlich isotherms respectively [35,36]. Langmuir model illustrated on Figure 11 assumes that the removal of metal...
ions occur on an energetically homogenous surface by monolayer sorption and there are no interactions between the adsorbate species on adjacent sites. The linear form of the Langmuir equation is shown below by equation 5:

\[
\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}
\]  

(5)

Freundlich isotherm Figure 12 is an empirical relationship describing the sorption of solutes from a liquid onto a solid surface. It assumes that different sites with several sorption energies are involved. The linear form of the equation is shown below by equation 6:

\[
\ln q_e = \ln k_f + \left(\frac{1}{n}\right) \ln C_e
\]  

(6)

where, \(q_e\) (mg g\(^{-1}\)) and \(C_e\) (mg L\(^{-1}\)) are the equilibrium concentrations of U(VI) in the solid and liquid phases, respectively, \(q_m\) (mg g\(^{-1}\)) is the monolayer capacity, \(b\) (Lmg\(^{-1}\)) is the equilibrium constant, \(k_f\) and \(n\) are characteristic constants related to the relative sorption capacity of the sorbent and sorption intensity, respectively. The
correlation coefficients ($R^2$) and corresponding parameters are presented below in (Table 5). Thus, comparing the isotherms applied with the experimental results, Langmuir isotherm describes the system more adequately than the Freundlich isotherm does i.e. Langmuir model suppose that, the adsorption occurs uniformly on the active sites of the sorbent, and once adsorbate occupies a site, no further sorption can take place at this site.

**Elution studies**

The reusability of (HAP@HTO) composite for preconcentration-separation of uranium was evaluated by elution studies. For such studies, a weighted amount of the adsorbent was shaken at the optimum conditions previously obtained to obtain a loaded amount. Desorption of uranium ions from loaded (HAP@HTO) performed in a batch mode. These factors include type of eluent agent, concentration of eluent agent and shaking time.

**Eluent agent type and its concentration effect**

Different elution agents with 1 mol L$^{-1}$ concentration such as HCl, HNO$_3$, H$_2$SO$_4$, Na$_2$CO$_3$ and DDW (double distilled water) were studied to recover adsorbed U (VI) from loaded (HAP@HTO). The obtained results in Figure 13; indicated that H$_2$SO$_4$ desorbs U (VI) more effectively than others used eluent agents. The required H$_2$SO$_4$ concentration to elute all adsorbed U(VI) from loaded composite was examined by varying its concentration from 0.25 – 1 mol L$^{-1}$. Figure 14 indicated that about 100% of adsorbed U(VI) can be recovered using 1 mol L$^{-1}$ of H$_2$SO$_4$.

**Contact time effect**

Elution experiments were carried out on loaded (HAP@HTO) with a fixed adsorbent dosage of 0.05 g/ 20 mL and with 1 mol L$^{-1}$ H$_2$SO$_4$ concentration. The results in Figure 15 showed that; elution of uranium increased with increasing contact time from 2-15 mins.
CONCLUSION

A new sorbent HAP@HTO was successfully synthesized, characterized and its applicability for uptaking uranium from its solutions was investigated. Uranium adsorption process followed a traditional Langmuir adsorption isotherm. The synthesized HAP@HTO adsorbent material had strong structural stability and good adsorption capacity for U(VI). The prepared adsorbent has been successfully applied for uranyl ions removal from waste sample solution. Thus, HAP@HTO exhibits the characteristics of a promising adsorbent in the area of separation science.

REFERENCES


