Application of response surface methodology for uranium(VI) adsorption using hydroxyapatite prepared from eggshells waste material: study of influencing factors and mechanism

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ABSTRACT

Hydroxyapatite (HAp) was synthesized from biowaste hen eggshells by wet precipitation method in which calcium hydroxide and phosphoric acid were used as precursors. The effectiveness of uranium(VI) adsorption onto HAp was investigated by batch adsorption experiments from aqueous solutions. The obtained HAp powder was characterized by X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectrometry, point of zero charge and Scanning electron microscope. The factors and levels used during the experiments were pH (2–5), adsorbent mass (0.01–0.05 g), and initial U(VI) concentration (100–310 mg L⁻¹). A Box–Behnken design combined with analysis of variance was used to interpret the main effect influencing the adsorption. The results showed that pH was the most significant parameter affecting U(VI). The kinetic data correlates well with the pseudo-second-order model. The adsorption isotherms fitted the Langmuir-1 type model with the $q_{\text{max}} = 175.22$ mg g⁻¹ at 25 °C. The calculated value of the mean free energy indicates the chemisorption process. Under optimal conditions, the uranium effluent derived from the precipitation of ammonium uranyl carbonate removal performance of 98% was achieved. This study proved that HAp prepared from eggshell was an ecofriendly and low-cost adsorbent and was very effective for the adsorption of U(VI) from aqueous solutions.

Key words | adsorption, hydroxyapatite, kinetics, mechanism, thermodynamics, U(VI)

HIGHLIGHTS

- The adsorbent (hydroxyapatite (HAp)) was synthesized by wet precipitation method from biowaste hen eggshells in order to removal the U(VI).
- The U(VI) is significantly adsorbed as 98.34% by HAp.
- The optimum sorption conditions were determined.
- The maximum adsorption capacity obtained from Langmuir-1 isotherm was $175.22$ mg g⁻¹ at 25 °C.
- The kinetic data correlates well with the pseudo-second-order model.

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Uranium (U) is one of the most important representatives of the actinide family used in the fuel nuclear cycle. It is a naturally occurring element with abundance in the Earth’s crust of 2 mg kg$^{-1}$. Due to its chemical toxicity, the occurrence of elevated levels of uranium in drinking water poses a health risk. The United States Environmental Protection Agency introduced a standard for drinking water of a maximum value of 30 μgL$^{-1}$ (Chung et al. 2019). The World Health Organisation recommended the same value of uranium concentration in drinking water. This element is a possible harmful pollutant in the environment, hence, investigating the concentration of uranium in the environment is significant because of its radioactivity and chemical toxicity. It has been reported that radioactivity affects humans negatively and can cause skin erythema, cataract, cancer, and genital system injury (Bjørklund et al. 2020). In the past few years, many methods have been used for U(VI) removal from industrial wastewaters and radioactive wastes. Several specific techniques have been implemented for the removal of uranium from aqueous solutions, such as precipitation (Kornilov et al. 2020), ion exchange (Foster et al. 2020), and membrane processes (Hoyer et al. 2014) but these are expensive and have economical and technical disadvantages such as operational costs and important energy consumption, and they are ineffective when metals are present in high concentrations in aqueous solution. Currently, adsorption or biosorption is an economically feasible alternative method for removing trace metals from radioactive effluents (Nibou et al. 2011; Chegrouche et al. 2016). Many different adsorbents have been used to remove and recover U(VI) from radioactive effluents, including resins (Donia et al. 2009), olive stones (Kütahyalı & Eral 2010), sepiolite (Linghu et al. 2017), and graphene (Zhao et al. 2020). Each of them has its advantages and limitations in application. The use of low-cost adsorbents for the U(VI) sorption is widely proposed nowadays. Hydroxyapatite (HAp) is one of many adsorbents which are being used. The efficiency of HAp depends on various parameters such as low water solubility, and high capacity of sorption for heavy metals, and high stability under reducing oxidizing conditions (Ghahremani et al. 2017). HAp is widely used for chromatographic purposes (Chen et al. 2019) and is suitable for several biomedical applications, e.g. artificial bone and surface of teeth (Toledano et al. 2019). Many studies have reported the use of HAp in the removal of rare earth (Attia et al. 2019), heavy metals (Zou et al. 2019), and actinide (Imam et al. 2019). Many processes have synthesized HAp through various routes, including hydrothermal technique (Jung et al. 2019), solid-state reaction (Ramesh et al. 2016), wet precipitation method (Ul Hassan et al. 2019), low-temperature synthesis (Cestari et al. 2020), and sol-gel technique (Chen et al. 2020). Only a few researchers are interested in the chemical synthesis of HAp prepared from eggshells (Patel et al. 2020; Yu et al. 2020). Eggshells are generally intended
as a waste material and naturally valueless on a laboratory and industrial scale. This present work focuses on the biosorption of U(VI) by HAp obtained from biowaste hen eggshells. The study concerns the evaluation of the effects of selective parameters, such as the pH solution, the initial U(VI) concentration, and the adsorbent mass on the adsorption process. The experiments were carried out using Box–Behnken design combined with response surface methodology (RSM) to examine the main effects and their interactions of the parameters considered. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectrometry, point of zero charge (PZC), and Scanning electron microscopy (SEM) were used to characterize the adsorbent. Several statistical analyses were used to interpret the main factors and their interactions influencing the uranium uptake on this HAp. The adsorption kinetics models and the equilibrium isotherm related to the process were also investigated in this study.

MATERIALS AND METHODS

Preparation of HAp

Synthesis of calcium oxide from eggshells

The eggshells were first washed by water and then rinsed three times by distilled water. Washed eggshells were dried in an oven at 30 °C overnight. The dried product was extracted from the membranes in order to obtain a homogeneous solid. The product was washed with deionized water and then dried at 80 °C for 12 h. Finally, the obtained solid was sifted, crushed, and stored in a desiccator. The hen’s eggshells were used to synthesis calcium oxide (CaO) after they were boiled for 45 min in water and calcined at 900 °C for 2 h. Above 850 °C, the calcium carbonate (CaCO₃) was transformed into CaO on the eggshell according to the chemical reaction Equation (1) (Sopyan et al. 2008)

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \uparrow
\]  

Preparation of calcium hydroxide

The amount of calcined eggshell was dispersed in a beaker containing distilled water. In this reaction the CaO is transform into calcium hydroxide (Ca(OH)₂) as shown in the following Equation (2):

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \Delta\text{H}^\circ
\]  

Synthesis of HAp powders

The HAp compounds were prepared via the solution-precipitation method (Mobasherpour et al. 2007). Briefly, 300 g of Ca(OH)₂ was dispersed in a beaker containing distilled water under magnetic stirring (type IKAMAG REO), then 824 mL of a solution of phosphoric acid (1.128M) was added drop by drop. The precipitation formation was observed at pH 8.5, the solution was kept for 24 h at 20 °C, which causes the precipitation hardening, followed by 1 h of agitation and before being left for 24 h until maturation. The chemical reaction Equation (3) for this process is given as follows:

\[
10\text{Ca(OH)}_2 + 6\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 18\text{H}_2\text{O}
\]  

The solid was filtered under vacuum, washed with the mixture (distilled water–ethanol), and dried in the oven at 80 °C for 24 h. Then, the dried product was calcined at 400 °C for 2 h under air atmosphere and ground. The HAp presented Ca/P ratio of 1.73.

Reagents

A stock of U(VI) was made by dissolving 2.131 g of UO₂(NO₃)₂·6H₂O(99%) in distilled water. The working solutions were made by dilution of the stock solution to obtain the desired concentration (100–310 mg L⁻¹). The pH buffer solutions (4, 7, and 9) were used to calibrate the pH meter. The pH of each solution was adjusted with pH meter (OHAUS) by adding nitric acid (HNO₃) or sodium hydroxide (NaOH). All reagents were supplied by BDH Company (Germany).

Point of zero charge

The experiments were carried out under batch technique. First, 0.01 g of HAp was added to a 50-mL Erlenmeyer flasks containing a solution of potassium nitrate (KNO₃) (0.1 M) adjusted to different pH (4.5, 5.5, 6.5, 7.5, 8.5, and 9.5). The initial pH solution (pHi) was adjusted by potassium hydroxide (KOH) (0.1 M) and HNO₃ (0.1 M). The prepared solution was agitated by a magnetic stirrer at 2.5 Hz for 24 h at 24 °C. Thereafter, the final pH solution (pHf) of the supernatant liquid was measured after filtration through 0.42-μm Whatman filter paper. The PZC is equal to the value of initial pH when the ΔpH equal to zero.
Analysis of U(VI)

The U(VI) concentration in all batch adsorption experiments was determined by the arsenazo III method as follows: 500 µL to 1 mL of U(VI) were introduced into 25-mL flasks, paratitrogen was used as an indicator to adjusted the pH solution to 2.07 by NaOH (0.1 M) and HCl (0.1M), 1 mL of chloroacetic acid buffer (10%), 1 mL of ethylendiaminetetraacetic acid (0.1 M), and 2 mL of arsenazo III (0.03%). The final solution was added and deionized water was added up to the graduation mark. The mixture of reagents was left for 10 min to achieve equilibrium. The absorbance of the matured solution was been determined to be HAp with a very intense peak located at 2θ = 31.79° with hkl (211), the estimated value was 34.29 nm and confirmed the formation of nanocrystalline of the prepared HAp.

The FTIR spectrum of HAp was taken before and after the sorption of U(VI) Figure 1(b). As seen from the spectrum of absorption peaks, the observed bands at 1,600 cm⁻¹ and 3,457 cm⁻¹ were attributed to the –OH stretching vibration in the HAp structure (Zhou et al. 2020). The band observed at 1,414 cm⁻¹ corresponds to the presence of CO₃²⁻, the characteristic bands of different vibrations of the tetrahedron PO₄³⁻ were observed between 500 cm⁻¹ and 1,000 cm⁻¹, the bands observed at 1,022 cm⁻¹ and 560–603 cm⁻¹ were assigned to the ν₅ PO₄³⁻, ν₄ PO₄³⁻, respectively (Guo et al. 2020). Moreover, the identified band located at 872 cm⁻¹ was assigned to the HPO₄²⁻ vibration band. Additionally, the Raman spectroscopy of the HAp shown in Figure 1(c) confirmed the presence of phosphate band, located at 958.83 cm⁻¹, which is due to the stretching and librational modes of ν₁, PO₄³⁻ group, the bands located at 1,044.82 and 1,069.39 is characteristic for ν₃ PO₄³⁻ (Borkowski et al. 2016).

The value of the PZC is the value when the electric density charges on the surface of the adsorbent equal zero. Above this value, the surface is negatively charged, below this value, the surface is positively charged. In our case, the value of PZC was found to be 7.17, and the HAp acted as a buffer for the pH range of 4.5–9 (Figure 1(d)).

The SEM micrograph of the HAp powder using back-scattered electronics is shown in Figure 2(a). Their regular form was observed on HAp and the particle size distribution of HAp presented in Figure 2(b) indicates the predominance of average particle size of 350 µm in the powder. The parameters of D(0.1) was found to be equal to 69.66 µm, and this critical value means that only 10% of particles had less than 69.66 µm.

Batch adsorption experiments

The adsorption experiments were carried out in batch. Different U(VI) concentrations were prepared (100, 205, and 310 mg L⁻¹) from the solution of 1 g L⁻¹ in a 50-mL beaker. In this study, 17 batch adsorption experiments designed by the Box–Behnken approach were carried out, taking into account the effect of initial U(VI) concentration (100–510 mg L⁻¹), adsorbent mass (0.01–0.05 g), and initial
pH (2–5). Samples were collected at different time intervals, filtered through 0.42-μm Whatman filter paper, and the U(VI) concentration was analyzed using a ultraviolet–visible method. The distribution constant $K_d$ (mL g$^{-1}$) and the percentage of adsorption (%) were calculated using Equations (5) and (6):

$$K_d = \frac{\text{amount of metal in adsorbent}}{\text{amount of metal in solution}} \times \frac{V}{M}$$  \hspace{1cm} (5)

$$\text{Adsorption uptake} (\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100$$  \hspace{1cm} (6)

where $C_0$ and $C_e$ are the initial and the final equilibrium concentration of U(VI), $V$ is the volume of the solution (L), and $M$ is the mass of HAp (g). The adsorption capacity ($q_t$) at time $t$ is calculated using Equation (7):

$$q_t = \left(\frac{C_0 - C_t}{M}\right) \times V$$  \hspace{1cm} (7)

Modelling by full factorial design

The Box–Behnken design for the three independent variables was used to optimize parameters selected in this study. These designs allow the experimenter to run the experiences on three levels ($-1$, $0$, $+1$). The experiences are projected in a sphere dimension. The Box–Behnken design allows the possibility to start the study of $n$ factors by allowing the addition of other factors in the same design without losing the results of the experiments already done. The number of experiments can be calculated using Equation (8):

$$N = p^3 + p + \alpha$$  \hspace{1cm} (8)

where $p$ is the number of independent variable and $\alpha$ is the number of replicates.
central point experiment. The relationship between the coded and real values was determined from Equation (9).

\[
X = X_i - \frac{(X_{\text{max}} + X_{\text{min}})}{2} \cdot \frac{(X_{\text{max}} - X_{\text{min}})}{2}
\]

where \( X \) is the coded value; \( X_i \) is the real value; \( X_{\text{max}} \) and \( X_{\text{min}} \) are the maximum and minimum actual values, respectively.

The ranges and levels of independent variables employed in this study are given in Table 1. The second-order polynomial equation was used to correlate the U(VI) adsorption and the dependent variable (Equation (10)):

\[
Y_{\text{PREDICTED}} = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_i x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon
\]

where \( Y_{\text{PREDICTED}} \) is the predicted response of U(VI) adsorption; \( \beta_0 \) is the global mean; \( \beta_i \) the linear coefficients; \( \beta_{ij} \) the interaction coefficients; \( \beta_{ii} \) the quadratic coefficients; and \( \varepsilon \) is the residuals which is the difference between the experimental and predicted values. The Box–Behnken design matrix for the real and coded values along with experimental and predicted values for U(VI) adsorption efficiency (%) by HAp are shown in Table 2.
RESULTS AND DISCUSSION

Effect of contact time

The contact time was estimated as one of the important parameters affecting the sorption. Our study range was taken at the initial U(VI) concentration of 104.51 mg L\(^{-1}\) for 150 min in different beakers numbered from 1 to 10 which include various times (15–150 min) with 0.05 g of HAp at pH 3 as shown in Figure 3(a). The kinetic had a two-step process. It started quickly and then continued slowly until a pseudo-equilibrium condition was reached. The U(VI) uptake increased with an increase in contact time up to 90 min and, after that, the U(VI) uptake became constant. The high number of active surface sites available may explain the initial faster metal ion uptake on the HAp surface (Li et al. 2019). The active binding groups with higher affinities are occupied first. The percentage adsorption of U(VI) was achieved at 95%. To assure the equilibrium, the contact time was set up at 105 min and stirred for all further studies.

Effect of initial pH

The initial pH solution was investigated in this study and is depicted in Figure 3(b). As shown, at pH 2, the low rate of adsorption uptake was observed at 36.14%. The increase of the positive charge H\(^{+}\) and uranyl ion (UO\(_2\)\(^{2+}\)) restricts the adsorption. The maximum value of adsorption was found at pH 3.5 at 96.67%, with the maximum U(VI) removal capacity reaching 99.69 mg g\(^{-1}\). At this pH value, the uranyl ion species is predominant, which makes the adsorption favorable as observed by (Liu et al. 2016). Above pH 3.5, the uranium removal decreased and the uranyl ions complexes were transformed to UO\(_2\)(OH)\(^{+}\), (UO\(_2\)\(^{+}\))(OH)\(^{2+}\), (UO\(_2\)\(^{2+}\))(OH)\(^{3+}\), (UO\(_2\)\(^{3+}\))(OH)\(^{4+}\), (UO\(_2\)\(^{4+}\))(OH)\(^{5+}\), which fact prevents the adsorption.

Optimization of the U(VI) adsorption by HAp

Experimental design

By applying the least squares method on the design matrix solved using JMP 10.0, the coefficients of the second-order
polynomial regression model of U(VI) adsorption was established as follows (Equation (11)):

\[
\text{U(VI) \% adsorption efficiency} = \frac{94.96 - 20.70 \text{pH}}{C_0^{20.70}} + \frac{8.94 \text{pH} \times \text{initial U(VI) concentration}}{C_0^{16.11}} + \frac{12.29 \text{initial U(VI) concentration} \times \text{adsorbent mass}}{C_0^{12.29}} + \frac{38.70 \text{pH}^2 + 4.74 \text{initial U(VI) concentration}^2}{C_0^{38.70}} + \frac{18.56 \text{adsorbent mass}^2}{C_0^{18.56}}
\]

(11)

Analysis of variance

Analysis of variance (ANOVA) was carried out to describe the coefficients of the quadratic model and their effects. The significance of the model was evaluated from the Fisher variation ratio (F) and probability value (p > F). Table 3 summarizes the regression results of the quadratic model by ANOVA. The value of F-model was greater than F-tabulated, (F-model = 94.44 > F-tabulated = 3.68) with a very low probability of p-value (p-model > F = 0.001) at a 95% of confidence level which indicated the significance of the model. The R² and R² adjusted values were calculated in Figure 4(a) and found to be 0.99 and 0.981, respectively.

Table 3 | ANOVA analysis for adsorption of U(VI) by HAp through Box-Behnken design

| Source                                | Df | Coef. | Effect | S² | t ratio | SS² | F-value | (SS²/Df)² | Prob.> F |
|---------------------------------------|----|-------|--------|----|---------|-----|---------|-----------|----------|
| Model                                 | 9  | 94.96 | -      | -  | -       | 17,738.62 | 94.44 | 1,970.95 | <0.001   |
| X1 – pH                               | 1  | -20.71| -41.41 | 3.23 | -12.82 | 3,429.93 | 164.35 | 3,429.93 | <0.0001  |
| X2 – Initial U(VI) concentration (mg L⁻¹) | 1  | -16.21| -32.42 | 3.23 | -10.04 | 2,102.13 | 100.73 | 2,102.13 | <0.0001  |
| X3 – Adsorbent mass(g)                | 1  | 16.33 | 32.65  | 3.23 | 10.11  | 2,132.19 | 102.17 | 2,132.19 | <0.0001  |
| X1 × X2                              | 1  | -8.95 | -17.90 | 4.57 | -3.92  | 320.32  | 15.34  | 320.32   | 0.0058   |
| X1 × X3                              | 1  | -16.11| -32.22 | 4.57 | -7.05  | 1,038.17 | 49.74  | 1,038.17 | 0.0002   |
| X2 × X3                              | 1  | 12.29 | 24.59  | 4.57 | 5.38   | 604.65  | 28.97  | 604.65   | 0.001    |
| X1²                                  | 1  | -38.71| -77.41 | 4.45 | -17.39 | 6,308.43 | 302.28 | 6,308.43 | <0.0001  |
| X2²                                  | 1  | 4.75  | 9.49   | 4.46 | 2.13   | 94.84   | 4.54   | 94.84    | 0.0705   |
| X3²                                  | 1  | -18.57| -37.13 | 4.45 | -8.34  | 1,451.44 | 69.55  | 1,451.44 | <0.0001  |
| Error (SSₑ)                           | 7  |       |        |     |         | 146.08 | 20.86  |           |          |
| Total                                 | 16 |       |        |     |         | 17,884.71 |       |           |          |
| Lack of fit                           | 3  |       |        |     |         | 142.03 | 46.81  | 47.34    | 0.0014   |
| Pure error                            | 4  |       |        |     |         | 4.04   | 1.01   |          |          |
| R²                                    |    | 99.18 |        |     |         |        |        |          |          |
| R² adjusted                           |    | 98.13 |        |     |         |        |        |          |          |

aNon-significant, bsum of squares, cmean square.
demonstrating that the model could not explain 0.019% of variation. The significance of each parameter was estimated by Student t-test and p-value. The critical value of the t-test was written according to the number of the model parameters at 95% confidence level, which equals $t_{0.05,9} = 2.26$. All values of the Student t-test model lower than 2.26 are not statistically considered significant. In our case, the coefficients of $X_1$, $X_2$, $X_3$, $X_1X_3$, $X_1X_2$, $X_1^2$, and $X_3^2$ have t-test greater than 2.26 and p-value >0.05, which were considered to be significant, while the t-test and p-value of the coefficient $X_2^2$ (t-test = 2.13 and p-value = 0.07) was found to be less than t-test critical and p-value, which is considered to be statistically not significant. The coefficients of $X_1$ and $X_2$ have a negative effect on the response, and these factors should be minimized to increase the removal of U(VI). While the coefficients of $X_3$ have a positive effect on the response, this factor should be maximized to increase the removal of U(VI). The plot $Y_{\text{PREDICTED}}$ versus Studentized residuals was evaluated to check the adequacy of the quadratic model Figure 4(b). It is obvious that they have no visible pattern or irregular structure between the experimental and predicted response, showing that the variance of original observation was constant and it was not essential for the transformation of variables response (Behera et al. 2018). Moreover, the small value of standard deviation (1.10) revealed the closest value between the experimental and predicted data for the U(VI) adsorption by HAp. The final step of ANOVA is to use the sum of squares of each parameter as a tool to highlight the results of the statistical tests. As seen in Figure 4(c), the bars of pH and pH² contribute more to the adsorption process compared to the other factors with a contribution percentage of 20 and 36, respectively.

**Pareto chart**

To visualize the effect of the quadratic model parameters, the Pareto diagram was used is presented in Figure 4(d).
The bars of the standardized effects of each parameter were evaluated in this diagram. The length of the bar $X^2$ was below $p$-value, which shows that this coefficient contributed weakly to the response.

**Interaction plot**

To better analyze the effect of each parameter influencing the response, the interaction plot was investigated and is shown in Figure 5. The concept of the graphs was based on the study of the effect of one parameter on the response as a function of the high and low level of another parameter. As can be seen, the percentage of U(VI) adsorption reaches its maximum when the pH and U(VI) concentration are at their low levels (2 and 100 mg L$^{-1}$, respectively), and the adsorbent mass is at a high level (0.05 g). Also, there is a strong interaction with the three factors between the pH and adsorbent mass, and the percentage of U(VI) adsorption increases when the pH and adsorbent mass varied from low to high level. Furthermore, a low percentage (20%) of U(VI) adsorption was observed at low pH and adsorbent mass.

**Modelling by RSM**

The RSM is one of the most relevant steps on the analysis of the optimal parameters influencing the adsorption of U(VI) on HAp and is illustrated in Figure 6(a)–6(c), designed by Origin 9.5. The surface plots of the interaction of the three parameters are not linear and the graphs show a very strong interaction between pH and adsorbent mass. It can be seen in Figure 6(a) that at a constant value of concentration (237.55 mg L$^{-1}$), the adsorption increases with an increase of adsorbent mass at a pH range of 2.00–3.50. The maximum adsorption efficiency is observed as red, which reached 83–99% at pH 2–3.5 and absorbent mass 0.02–0.05 g. The UO$_2^{2+}$ ions species predominates in the solution, which makes the adsorption favorable. Figure 6(b) shows that at a fixed value of pH 3, the response surface...
area has three regions which give three ranges of response. The blue area shows a percentage of U(VI) removal between 40 and 60%, the green color shows a percentage of U(VI) removal between 70 and 90%, and the red color shows the optimum region with a high percentage of U(VI) adsorption >90%. In this region, the combination parameters varied from (0.02–0.05 g) for the adsorbent mass and from 100 to 205 mg L$^{-1}$/$C_0$ for the initial U(VI) concentration.

In Figure 6(c), the RSM shows the influence of pH and initial U(VI) concentration on the adsorption at a constant value of adsorbent mass (0.04 g), the adsorption of U(VI) increase with an increase of pH and initial U(VI) concentration, and the optimum region of the two parameters located in the red color situated at pH 2–3 and 270.10–310 mg L$^{-1}$ for initial U(VI) concentration. The optimum values obtained by RSM were pH 3.50, initial U(VI) concentration 270.1 mg L$^{-1}$, and adsorbent mass 0.04 g.

**Kinetic studies**

To investigate the kinetics of U(VI) onto HAp, the pseudo-first-order, pseudo-second-order (with linear and nonlinear form), and intraparticle diffusion are used and presented in Table 4 and Figure 7(a)–7(c) where $k_1$ and $k_2$ are the equilibrium rate constant of pseudo-first-order and pseudo-second-order (mg g$^{-1}$ and g mg$^{-1}$ min$^{-1}$, respectively), and $k_3$ is the constant of the intraparticle diffusion (mg g$^{-1}$/min$^{0.5}$).

As shown in Table 4, the pseudo-second-order kinetic model shows excellent linearity with a high correlation coefficient ($R^2 = 0.99$) at the initial U(VI) concentration of 100 mg L$^{-1}$ and adsorbent mass 0.05 g compared to the

| Kinetic models | Equation | Parameters | Linear form | Non-linear form |
|----------------|----------|------------|-------------|-----------------|
| Pseudo-first-order rate | $ln(Q_t - Q_e) = ln Q_e - \left(\frac{k_1}{2.303}\right)t$ | $q_e$ (mg g$^{-1}$) and $k_1$ (mg g$^{-1}$) | 47.14 and 0.09 | 99.01 and 0.06 |
| Pseudo-second-order rate | $\frac{t}{Q_t} = \frac{1}{k_2 Q_e} + \frac{1}{Q_e}t$ | $q_e$ (mg g$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) | 104.82 and 0.001 | 108.55 and 9.78 $\times 10^{-04}$ |
| Intraparticle diffusion model | $Q_t = k_3t^{0.5} + C$ | $k_3$ (mg g$^{-1}$/min$^{0.5}$) and C | 62.29 and 3.48 | – |
other kinetic models, and the electrons sharing or exchanging between the HAp might be accruing by chemisorptions.

**Thermodynamic studies**

Thermodynamic parameters such as free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) (Equations (12)–(14)) are presented in Table 5 by the slope $\ln(\rho_{wkd})$ versus $1/T$ (Rodrigues et al. 2018).

$$\Delta G^\circ = -RT \ln(\rho_{wkd})$$  \hspace{1cm} (12)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$  \hspace{1cm} (13)

$$\ln(\rho_{wkd}) = \Delta H^\circ / RT + \Delta S^\circ / R$$  \hspace{1cm} (14)

where: $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $k_d$ the equilibrium constant (mL g$^{-1}$), $T$ temperature (K), $\rho_w$ is the water density (mg L$^{-1}$), $\Delta H^\circ$ is the enthalpy change (kJ mol$^{-1}$), $\Delta S^\circ$ is the entropy change, and $\Delta G$ is the free energy change (kJ mol$^{-1}$).

$\Delta G^\circ$ values were calculated using Equation (13) and are presented in Table 5. The negative value of $\Delta G^\circ$ indicated the spontaneous reaction of the adsorption process, which became more spontaneous with an elevation in temperature.
which made it favored and possible. $\Delta G^\circ$ value decreased with increasing temperature, and suggesting that higher temperatures favored the adsorption of U(VI). The value of $\Delta S^\circ$ could describe the randomness during the adsorption process. Yet, the positive value of $\Delta S^\circ$ (80.27 J mol$^{-1}$K$^{-1}$) describes the affinity of the adsorbent for the U(VI) ions particles and confirmed the increased randomness at the solid-solution interface during adsorption. A positive value of $\Delta H^\circ$ (5.81 kJ mol$^{-1}$) confirmed the endothermic nature of the adsorption process. This result also supported that the adsorption capacity of HAp increases with increasing temperature. The equilibrium constant ($k_d$) increased with increasing temperature, which might be attributed to the increase in the pore size and the enhanced rate of intraparticle diffusion.

**Modelling the adsorption process**

The adsorption capacity of this system was inspected by Langmuir, Freundlich, Langmuir–Freundlich, Kahn, Redlich–Peterson, Temkin, and Dubinin–Radushkevitch (D–R). The results are summarised in Table 6 and presented in Figure 8(a)–8(d) and 8(g) according to the following equations:

The Langmuir equation was given by:

$$q_e = q_{\text{max}}KLC_e \left(1 + KLC_e\right)^{-1}$$

The Equation (15) can be rearranged to the following four linear forms:

**Langmuir-1**

$$\frac{C_e}{q_e} = \frac{1}{K_Lq_{\text{max}}} + \frac{1}{q_{\text{max}}}$$

**Langmuir-2**

$$\frac{1}{q_e} = \frac{1}{K_L}q_{\text{max}} \frac{1}{C_e} + \frac{1}{q_{\text{max}}}$$

**Langmuir-3**

$$q_e = q_{\text{max}} - \frac{1}{K_Lc_e}$$

**Langmuir-4**

$$\frac{q_e}{C_e} = K_Lq_{\text{max}} - K_Lq_e$$

The Freundlich equation was given by:

$$q_e = K_FC_e^1$$

The linearized form of the Equation (19) is given by:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Table 6 | Parameters values of several isotherms forms of U(VI) adsorption by HAp

| Model                      | Graphic linearization | Parameter | Values  |
|----------------------------|-----------------------|-----------|---------|
| Langmuir-1                 | $y = 0.00571x + 0.03743$ | $q_{\text{max}}$ (mg g$^{-1}$) | 175.22  |
|                            |                       | $K_L$     | 0.15    |
|                            |                       | $R^2$     | 0.99    |
| Langmuir-2                 | $y = 0.002551x + 0.001274$ | $q_{\text{max}}$ (mg g$^{-1}$) | 156.93  |
|                            |                       | $K_L$     | 0.5     |
|                            |                       | $R^2$     | 0.87    |
| Langmuir-3                 | $y = -2.080x + 795.2$ | $q_{\text{max}}$ (mg g$^{-1}$) | 159     |
|                            |                       | $K_L$     | 0.48    |
|                            |                       | $R^2$     | 0.77    |
| Langmuir-4                 | $y = -0.373x + 306.6$ | $q_{\text{max}}$ (mg g$^{-1}$) | 165.75  |
|                            |                       | $K_L$     | 0.37    |
|                            |                       | $R^2$     | 0.77    |
| Freundlich                 | $y = 0.159x + 4.360$ | $K_F$     | 78.25   |
|                            |                       | $n$       | 6.28    |
|                            |                       | $R^2$     | 0.96    |
| Non-linear Langmuir        |                       | $q_{\text{max}}$ (mg g$^{-1}$) | 160.49  |
|                            |                       | $K_L$     | 0.42    |
|                            |                       | $R^2$     | 0.80    |
| Non-linear Freundlich      |                       | $K_F$     | 77.63   |
|                            |                       | $n$       | 6.17    |
|                            |                       | $R^2$     | 0.95    |
| Kahn                       |                       | $q_{\text{max}}$ (mg g$^{-1}$) | 12.66   |
|                            |                       | $a_k$     | 12.66   |
|                            |                       | $b_k$     | 0.42    |
|                            |                       | $R^2$     | 0.80    |
| Langmuir–Freundlich        |                       | $q_{\text{max}}$ (mg g$^{-1}$) | 28.17   |
|                            |                       | $n$       | 0.16    |
|                            |                       | $K_{LF}$  | 423.07  |
|                            |                       | $R^2$     | 0.95    |
| Redlich–Peterson           |                       | $k$       | 100     |
|                            |                       | $a_{RP}$  | 0.94    |
|                            |                       | $b_{RP}$  | 0.90    |
|                            |                       | $R^2$     | 0.90    |
| Temkin                     | $y = 20.25x + 69.15$ | $A_T$ (L g$^{-1}$) | 69.15 |
|                            |                       | $B_T$ (kJ mol$^{-1}$) | 20.25 |
|                            |                       | $R^2$     | 0.94    |
| D–R                        | $y = -0.00036x + 5.06017$ | $q_{\text{max}}$ (mg g$^{-1}$) | 157.61  |
|                            |                       | $E$ (kJ mol$^{-1}$) | 36.76  |
|                            |                       | $R^2$     | 0.83    |
Figure 8 | Isotherm models of U(VI) adsorption on HAp: (a) Langmuir-1 type, (b) Langmuir-2 type, (c) Langmuir-3 type, (d) Langmuir-4 type, (e) Freundlich isotherm, (f) RL versus initial U(VI) concentration, (g) DR isotherm, (h) several isotherms models: (non-linear Langmuir, non-linear Freundlich, Langmuir–Freundlich, Kahn, Redlich–Peterson, Temkin).
Langmuir–Freundlich equation is given by:

\[ q_e = \frac{q_{\text{max}}(K_L C_e)^n}{q_{\text{max}}(K_L C_e)^n + C_e} \]  

(22)

The Kahn equation expression is given as:

\[ q_e = \frac{q_k b_k C_e}{(1 + b_k C_e) a_k} \]  

(23)

The Redlich–Peterson is given as follows:

\[ q_e = \frac{k_{\text{tr}} C_e}{(1 + a_{\text{tr}} C_e)^n} \]  

(24)

The Temkin equation is given as:

\[ q_e = B \ln A_T + B \ln C_e \]  

(25)

where \( C_e \) is the equilibrium concentration (mg L\(^{-1}\)), \( q_e \) the amount of metal ion adsorbent, \( q_{\text{max}} \) the maximum capacity of adsorption (mg g\(^{-1}\)), \( K_L \) is the sorption equilibrium constant of Langmuir (L mg\(^{-1}\)), \( K_F \) (mg\(^{1-1/n}\) L\(^{1/n}\) g\(^{-1}\)) is the Freundlich constant, \( K_{\text{LF}} \) (mg g\(^{-1}\)) is the Langmuir–Freundlich constant, \( a_{\text{tr}} \), \( k_{\text{tr}} \), \( a_k \), and \( b_k \) is the Kahn constant, \( k_{\text{tr}} \), \( a_{\text{tr}} \), and \( b_{\text{tr}} \) is the Redlich–Peterson constant, \( A_T \) and \( B \) is the Temkin constants (L g\(^{-1}\) and J mol\(^{-1}\), respectively).

The D–R isotherm model agrees with the Langmuir model in describing sorption in uniform pores, but it assumes a heterogeneous surface. The D–R equation was applied in the following linearized form (Kalal et al. 2011):

\[ \ln q_e = \ln q_d - 2K_{\text{DR}}RT \ln \left(1 + \frac{1}{C_e}\right) \]  

(26)

where \( K_{\text{DR}} \) is the activity coefficient related to the mean sorption energy (mol\(^2\)/kJ\(^2\)) calculated from the slope of \( \ln q_d \) versus \( RT \ln(1 + C_e) \), and \( q_d \) is the intercept plot of adsorption capacity (mg g\(^{-1}\)).

The mean free energy (\( E \)) was calculated from D–R using the Equation (27):

\[ E = \frac{1}{\sqrt{2K_{\text{DR}}}} \]  

(27)

The mean free energy \( E \) provides information about whether the sorption mechanism is physical or chemical. If the value of \( E \) is \(<16 \text{kJ mol}^{-1} \) means that the sorption is manifested by chemisorption. If the value of \( E \) is \(<8 \text{kJ mol}^{-1} \) the sorption process is affected by physical behavior (Table 6).

The \( R_L \) value indicates the sorption process (Equation (28)), which becomes favorable when \( 0 < R_L < 1 \). The calculated parameters are obtained from the fitting plots of the Langmuir Figure 8(f).

\[ R_L = \frac{1}{1 + K_L C_0} \]  

(28)

According to the results presented in Table 6, the Langmuir-1 isotherm equation represents the sorption process very well (Figure 8(a)), the \( R^2 \) values are all higher than 0.99, indicating a good correlation comparing to the other model, the monolayer coverage of U(VI) is formed on the HAp. Also, the indicated value of Freundlich (\( n = 6.28 \)) is found in the range of 1–10, which indicates the favorable adsorption process. The value of the mean free energy is found to be greater than 16 kJ mol\(^{-1}\), which confirms the chemisorptions process. Also, the value of \( R_L \) is found to be inside the range \( 0 < R_L < 1 \), which confirms the favorability of the adsorption of U(VI) by HAp.

**Mechanism**

According to the results published by Arey et al. (1999) and Skwarek et al. (2019) when the ratio of U (g)/apatite (g) >0.0011, the precipitation is dominated by other phenomena (ion exchange and adsorption) and the uranium interacts with the calcium and phosphate to precipitate in the form of cohenrovich or autinite. In our case, the calculated ratio U (g)/HAp (g) is found greater than 0.0011 (0.17), which confirms the predominance of uranium in high concentrations. The FTIR peaks after adsorption were calculated and illustrated in Figure 1(b). This shows the new peak observed at 921 cm\(^{-1}\) which is assigned to the antisymmetric stretching vibration mode of UO\(_2^2\), and the peaks of tetrahedron PO\(_4^3\) at 560,604 and 1,022 cm\(^{-1}\) have changed, which confirms the precipitation of phosphate onto UO\(_2\), as mentioned by Guo et al. (2020). Moreover, the considerable change of intensity peaks of OH observed at 1,600 cm\(^{-1}\) and 3,437 confirms the complexation of the surface group onto HAp. These results confirm that the U(VI) is captured onto the HAp surface.

Also in the area of the ratio U (g)/apatite (g) <0.0011 the uranyl ion can be manifested by ion exchange and sorption according to the following equations:
Sorption (Simon et al. 2008):

\[ \equiv \text{OH} + \text{UO}_2^{2+} \equiv \text{O} - \text{UO}_2^{2+} + \text{H}^+ \]  

(29)

\[ \text{O}_3\text{P} - \text{OH}^+ + \text{UO}_2^{2+} \equiv \text{O}_3\text{P} - \text{O} - \text{UO}_2^{2+} + \text{H}^+ \]  

(30)

Ion exchange (Rigali et al. 2016):

\[ \text{Ca}^{2+} + \text{UO}_2^{2+} \equiv \text{UO}_2^{2+} + \text{Ca}^{2+} \]  

(31)

Dissolution precipitation:

\[ \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \equiv 10\text{Ca}^{2+} + 6(\text{PO}_4)^{3-} + 2\text{OH}^- \]  

(32)

\[ 2\text{H}^+ + 2\text{UO}_2^{2+} + 2\text{PO}_4^{3-} + n\text{H}_2\text{O} \equiv \text{H}_2(\text{UO}_2)(\text{PO}_4)_2 \times n\text{H}_2\text{O} \]  

(33)

\[ \text{Ca}^{2+} + 2\text{UO}_2^{2+} + 2\text{PO}_4^{3-} + n\text{H}_2\text{O} \equiv \text{Ca}(\text{UO}_2)(\text{PO}_4)_2 \times n\text{H}_2\text{O} \]  

(34)

**Real test on uranium effluent**

In order to confirm the results of this study, a real test was carried out using the batch technique on uranium effluent derived from the precipitation of ammonium uranyl carbonate (AUC) according to the following reaction:

\[ \text{UO}_2(\text{NO}_3)_6\text{H}_2\text{O}_{(aq)} + 6\text{NH}_3(g) + 3\text{CO}_2(g) \rightarrow (\text{NH}_4)_4\text{UO}_2(\text{CO}_3)(s) + 2\text{NH}_4\text{NO}_3_{(aq)} + 3\text{H}_2\text{O}_{(l)} \]

The characteristics of the effluent and the parameters of this test are presented in Table 7 and the optimum value of RSM (pH = 3.5 and adsorbent mass = 0.04 g) were chosen. The experiments were repeated three times. The result was efficient with a rate of uranium elimination at 98.34%. This result fits well with the predicted value obtained at 100% with less residual error (−0.022).

**Comparison of the U(VI) adsorption capacities with other adsorbents**

To justify the validity of the HAp as an effective adsorbent for U(VI) adsorption, a comparison was made with other works carried out elsewhere using other adsorbents for a similar purpose (Table 8).

**CONCLUSION**

The results of this work revealed that HAp prepared from the eggshells was a very effective adsorbent for U(VI) in the batch technique. The XRD characterization results show that the nanocrystalline apatite phases were successfully formed in synthesis materials. The SEM imagery reveals that the powder has an irregular form with spherical grain size. The FTIR peaks after sorption show that U(VI) is precipitated onto the HAp surface. The statistical analysis shows that the pH has an important influence on the
removal of U(VI) in aqueous solution. The calculated values of $R^2$ and $R^2_{\text{adj}}$ show that the applied quadratic regression model has a very good fit for estimating the correlation between the experimental and predicted data. The results of RSM show the optimal conditions, which were pH 3.5, initial U(VI) concentration 270.10 mg L$^{-1}$, and adsorbent mass 0.04 g. It can be observed that under optimal conditions, the uranium effluent derived from the precipitation of AUC had a high adsorbency of 98%. The process kinetics follows the pseudo-second-order. The isotherms study of AUC had a high adsorbency of 98%. The energy was 36.76 kJ mol$^{-1}$.

Results of RSM show the optimal conditions, which were pH 3.5, initial U(VI) concentration 270.10 mg L$^{-1}$, and adsorbent mass 0.04 g. It can be observed that under optimal conditions, the uranium effluent derived from the precipitation of AUC had a high adsorbency of 98%. The process kinetics follows the pseudo-second-order. The isotherms study fitted better with the Langmuir-1 model than the other isotherm models, with a maximum capacity of 175.22 mg g$^{-1}$. The value of the calculated mean sorption energy was 36.76 kJ mol$^{-1}$ and confirms that the U(VI) can be manifested by chemisorption. This result proves that HAp prepared from eggshell is ecofriendly, low-cost, and highly adsorbent for the adsorption of U(VI) from aqueous solutions.

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AVAILABILITY OF DATA AND MATERIALS

All data are available without restriction.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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