Adsorption isotherms and kinetics study for U(VI) removal by excellent sorbent materials graphene oxide and functionalised graphene oxide

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Abstract. In this paper, the graphene oxide (GO) and carboxylic functionalized graphene oxide (COOH-GO) were synthesized for the removal of U(VI) ion in samples of water. The structures of prepared GO and COOH-GO were confirmed by X-ray diffraction (XRD), Scanning electron microscope (SEM), Fourier transformed infrared (FTIR) spectroscopy, Raman spectra, and high-resolution transmission electron spectroscopy (HR-TEM). An adsorption study was carried out for these and it has been found that COOH-GO has more excellent adsorption property at 4.5 pH. The batch adsorption was studied successfully by the effect of initial uranium concentration, pH of the medium, sorbent dose, temperature, and contact time efficiency. The adsorption isotherms were studied successfully for Langmuir and Freundlich. The kinetics were studied successfully and fitted for the pseudo-first-order and pseudo-second-order model. The maximum adsorption capacities at pH 4.5 were calculated for COOH-GO, GO, and graphite. The thermodynamic studies revealed that adsorption is endothermic and spontaneous.

1. Introduction

The recovery and removal of heavy radionuclide uranium metal are one of the most challenging problems in the current scenario. Uranium is radio-toxic, chemo-toxic, and a long half-life substance. With the fast growth of different activities, the discharge of uranium into water is a serious problem. Therefore, the removal of heavy toxic metals of uranium from water samples is a hot topic of research [1, 2]. The superior and most significant techniques sorption [3-5] has been broadly used for the purification of waste water (e.g., precipitation [6], bio reduction and reverse osmosis [7], and ion exchange [8, 9]) due to cost-effective, easy technique and no secondary toxic waste. However, most of the sorbents’ materials have some disadvantages viz., less sorption ability, highly expensive, and less eco-friendly. Therefore, it is extremely important to develop cheaper & eco-friendly sorbent materials along with high sorption capacity.

In recent times, GO and COOH-GO has concerned with significant attention for their outstanding sorption capacity like cheapness, environmentally friendly, abundance, high stability, etc. All these properties have proved that GO and COOH-GO possess positive sorption ability for the removal of heavy metals like Pb [10], Hg [11], Co, and Sr [12]. Therefore, it is important to decorate GO and
COOH-GO with other large molecular compounds to find some better-quality properties in practical applications [13].

In GO and COOH-GO, the high number of oxygen-containing groups such as hydroxyl (-OH) and carboxyl (-COOH) are accountable to their high surface area, excellent sorption capacity, and specific electronic properties [14, 15]. However, it is commonly known that some cations like Mg2+, Ca2+, Na+, and K+, which are generally present in wastewater, most likely produce some interference for the adsorption capacity of sorbent [16].

The maximum sorption efficiency of GO for U (VI), as reported by Li et al. 2008, was 299 mg/g at pH 4 [17, 18]. Nowadays, heavy toxic metal pollution in water is a very serious problem for all kinds of living organisms. Thus, the sorption study of heavy metals in the water samples is currently a big area of research for researchers. Therefore, in the current perspective, low-cost materials such as GO and its derivatives are more useful in U(VI) sorption study.

Thus, in the present study, the surface of GO was modified to COOH-GO by using a monochloroacetic acid and formed a novel carboxylic functionalized graphene oxide (COOH-GO) composite. The structure and morphology of GO and COOH-GO were characterized successfully by UV-VIS, FT-IR, XRD, HR-TEM, and Raman shift [19]. In this modified COOH-GO, different functional groups such as carboxylic group (-COOH), alcoholic group (-OH), and epoxy (-O-) groups are effectively decorated on the layer of the graphene sheet. The effect of initial concentration, pH, amount of sorbent dose, temperature, and contact time on the sorption behaviour of U(VI) onto GO and COOH-GO was studied. Further, the adsorption isotherms were developed for Langmuir and Freundlich isotherm models. The kinetic studies were also fitted for the pseudo-first-order and pseudo-second-order model. The thermodynamic parameters were also studied for checking the sorption as endothermic or exothermic and spontaneous or nonspontaneous [20-22].

2. Experimental Part

2.1 Reagents, Materials, and Characterization

The chemicals were used as received such as graphite fine powder (particle size 250 µm) and NaNO3 (99% Sodium nitrate) of Loba Chemie Pvt. Ltd., CICH₂COOH (>99.0% Monochloroacetic acid), potassium permanganate (>98.5% KMnO₄), sulphuric acid (98%H₂SO₄), sodium hydroxide (>97%, NaOH), hydrochloric acid (35%HCl), and hydrogen peroxide (30%H₂O₂) from Sigma Aldrich (Mumbai, India). Uranium standard solution, Accustandard, USA was used as received. The pH meter of Hanna Instruments, USA; LED fluorimeter, model name LF-2a from Quantalase Inc. Indore, India; Merck millipore deionized (DI) water; Fourier Transform Infrared (FT-IR) Spectroscopy from Agilent Technologies, UK; Scanning Electron Microscopy (SEM) model name SEM Zeiss EVO 18, USA; Raman Spectra from Research India (model name RIAR-0403, India); High-resolution transmission electron microscope (HR-TEM) instrument (JEM-2100, Make- JEOL, Japan) were used.

2.2 Synthesis of Graphene Oxide (GO) and Carboxylic Functionalized Graphene oxide (COOH-GO)

The GO was synthesized by using a modified Hummer’s method [23]. The brief procedure has been discussed in our previous paper [19]. Further, the functionalization of GO has been carried out by using monochloroacetic acid. In this method, the synthesized graphene oxide powder (0.10 g) was taken in a 500 ml beaker and then added 100 ml millipore water and sonicated for 30 minutes. Then, 2.4 g monochloroacetic acid and 2 g of sodium hydroxide were added to the graphene oxide solution and was sonicated for 3 hours. The above mixture was purified by repeated washing and was neutralized by adding 0.25M of hydrochloric acid dropwise until the pH of the resulting mixture becomes 7 [23]. Finally, the obtained residue of carboxylic functionalized graphene oxide (COOH-GO) was dried by using a hot air oven for 24 hours at 45°C [19, 24, 25].
2.3 Uranium (VI) Batch Sorption Study

Uranium batch sorption study was carried out by using LED fluorimeter for COOH-GO, GO, and graphite at the desired pH. All the sorption procedure occurred under room temperature and atmospheric air unless the condition was specified. The sorption % of U(VI) and sorption equilibrium capacity (mg/g) of U(VI) were observed by using equations 1 and 2, respectively.

\[
\text{U(IV) Sorption \%} = \frac{C_i - C_e}{C_i} \times 100 \% \\
\text{U(IV) Sorption capacity (mg/g)} = \frac{(C_i-C_e) \times V}{m}
\]

Where, \(C_i\) is the initial concentration of U(VI) before sorption, \(C_e\) is the equilibrium concentration or final concentration after U(VI) sorption, \(V\) = the volume of solution in mL, and \(m\) is the amount of adsorbent in mg.

2.4 The Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm equation was given as follows (Eq. 3) [26]:

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

The Langmuir’s adsorption isotherm can also be written as linear form (Eq. 4 and Eq. 5), where, \(q_e\) (mg/g) = Equilibrium sorption capacity of U(VI) adsorbed on adsorbent surfaces, \(q_{\text{max}}\) = Maximum sorption capacity of U(VI) adsorbed to form a complete monolayer coverage on adsorbent surfaces, \(K_L\) = Langmuir’s isotherm sorption constant related to the binding affinity between U(VI) and sorbent materials. The most important features of the Langmuir isotherm equation was the enthalpy of sorption constant or Langmuir’s isotherm sorption constant (\(K_L\)). The \(q_{\text{max}}\) would be calculated by a linear Langmuir sorption isotherm equation given as follows:

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}K_L} \times \frac{1}{C_e} + \frac{1}{q_{\text{max}}}
\]

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}K_L} + \frac{C_e}{q_{\text{max}}}
\]

The separation factor (RL) was calculated by using Eq. (6).

\[
R_L = \frac{1}{1+C_i \times K_L}
\]

Where, \(R_L\) = the dimensionless Langmuir constant which indicate the adsorption possibility either favourable \((0 < RL > 1)\), unfavourable \((RL > 1)\), linear \((RL = 1)\) or irreversible \((R_L = 0)\).

2.5 The Freundlich Adsorption Isotherm

This was based on adsorption on a heterogeneous surface Eq. 7a [27]:

\[
q_e = K_f C_e^{1/n}
\]

Where, \(K_f\) = Freundlich constant and \(1/n\) = Adsorption intensity which calculated the adsorption process is either unfavourable \((1/n > 2)\) or favourable \((0.1 <1/n < 0.5)\)

Taking the logarithm in both sides, the linear form of equation (Eq. 7b) is given below:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]
2.6 Kinetic Study
Adsorption rate of U(VI) on COOH-GO and GO were calculated for pseudo-first-order and pseudo-second-order kinetic models.
For pseudo 1st order model, the Eq. 8 is followed [28].
\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  
(8)

Where, \(q_e\) = sorption capacity (mg/g) at equilibrium, \(q_t\) = sorption capacity (mg/g) at time \(t\) and \(k_1\) (min\(^{-1}\)) = rate constant at equilibrium
For pseudo 2nd order model, the Eq. 9 is used [29].
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
\]  
(9)

Where, \(k_2\) (g mg\(^{-1}\)min\(^{-1}\)) = rate constant at equilibrium sorption.
For both the models the linear coefficient regression (R\(^2\)) values had been used for the prediction of the best-suited sorption isotherm.

3. Results and Discussion

3.1 FT-IR Spectra
The FT-IR spectra of GO show peak values at 3418.9 cm\(^{-1}\) for hydroxyl (O-H) stretching vibration, 1725.2 cm\(^{-1}\) for ketonic (\(>\text{C}=\text{O}\)) stretching vibration, and 1120.5 cm\(^{-1}\) for epoxide (\(-\text{C}-\text{O}-\text{C}-\)) stretching vibration. The two doublet peaks were observed due to tautomerism of keto and enol form at 1627.5 cm\(^{-1}\) & 1725.2 cm\(^{-1}\)[30]. However, upon comparing FTIR of GO to COOH-GO, a slight shift is observed because of the increase of the -COOH domain group. The COOH-GO peak values at 3408.6 cm\(^{-1}\) for hydroxyl (O-H) stretching vibration, 1731.2 cm\(^{-1}\) for ketonic (\(>\text{C}=\text{O}\)) stretching vibration and 1113.8 cm\(^{-1}\) for epoxide (\(-\text{C}-\text{O}-\text{C}-\)) stretching vibration were observed [19, 31, 32].

3.2 Raman Spectra
The Raman spectrum of GO and COOH-GO shows two peaks that are the G band and the D band. The D band value at 1332.4 cm\(^{-1}\) and G band value at 1579.5 cm\(^{-1}\) because of \(sp^2\) and \(sp^3\) hybridised carbon atoms for GO were observed (Figure 1). The D band value ~1345.5 cm\(^{-1}\)and G band value ~1595.6 cm\(^{-1}\) because of \(sp^2\) and \(sp^3\) hybridised carbon atoms for COOH-GO were observed (Figure 1). The intensity ratio \(I_D/I_G\) was calculated to be 1.1824 and 1.1952 for GO and COOH-GO, respectively [19, 33-35].
Figure 1. Raman Spectra of COOH-GO and GO.

3.3 HR-TEM for Carboxylic Graphene Oxide and Graphene Oxide
The direct images of GO and COOH-GO were observed by using high-resolution transmission electron microscopy (HR-TEM). This technique is a very powerful and helpful tool for the atomic scale level of sp$^3$ hybridized carbon [36, 37]. The exfoliated sheet and larger surface area were observed for different nanometer level for GO and COOH-GO [38]. The more amorphous nature was observed for COOH-GO as compared to GO due to more number of carboxylic groups (figure 2a and 2b).

Figure 2. (a) HR-TEM image of GO.
3.4 Effect of pH on Uranium Sorption

The solution pH affects strongly the sorption rate of the radionuclide. Therefore, the sorption of U(VI) was studied in pH range of 2-12 which is similar to the previously reported paper [33, 39], and pH maintained by using 0.01M HCl and 0.01M NaOH (figure 3). The maximum sorption order was found to be COOH-GO > GO > graphite at 4.5 pH. The study suggested that the uranium removal is more due to the presence of more carboxyl functional groups in COOH-GO at low pH level. The COOH-GO and GO have been most likely decorated with negative surface charge and this group has an electrostatic attraction with U(VI) of \( \text{UO}_2^{2+} \) positive charge species at lower pH region [19]. However, at higher pH, the sorption was decreased and was believed to be due to the formation of the negatively charged stable uranium carbonate complexes like \( [\text{UO}_2(\text{CO}_3)]^{4-} \) in solution [40, 41]. Thus, the electrostatic repulsion was observed between the negative complex of uranium and the negative sorbent surface of materials at a higher pH range.

The conditions for the experiments are, pH = 2-12, U(VI) concentration = 10µg/mL, mass of sorbent = 10 mg, volume of sample = 10 mL [Figure 3].

![Figure 2. (b) HR-TEM image of COOH-GO.](image)

![Figure 3. Effect of pH for sorbent materials.](image)
3.5 Effect of Contact Time
The effect of the contact time period was taken from 10 to 140 minutes with interval values 10, 20, 30, 40, 50, 60, 80, 100, 120, and 140 minutes for sorbent materials. This study shows 87.6%, 92.9%, 95.9% of sorption was occurred for graphite powder, GO, and COOH-GO, respectively [23]. These sorption results were well with those reported in the literature and the time required to attain equilibrium is 100 minutes [12, 19].

3.6 Effect of Sorbent Dose
The sorption amount increases regularly from 5 to 70 mg with a very fast increase from 5 to 10 mg. The order of maximum sorption is in the order COOH-GO > GO > graphite [12, 23]. When the dose of sorbents varied from 5 to 70 mg, the sorption percentage increased from 37% to 94% [19].

3.7 Sorption Isotherm
The equilibrium study was developed for U(VI) removal in water samples. The initial concentrations were varied from 10 to 200 µg/mL, and all other parameters were kept constant [23]. The sorption capacity of sorbent materials versus the equilibrium concentration of the U(VI) (Figure 4) shows that more adsorption capacity for COOH-GO was observed due to its more negative charge potential and porous nature than GO and graphite. The initial concentration of U(VI) affects the sorption of sorbent materials. The effect of initial concentration data were used for two theoretical models Langmuir and Freundlich adsorption isotherm. Langmuir’s isotherm shows monolayer adsorption of U(VI) onto the sorbent which has a finite number of sorption sites but Freundlich’s isotherm supports the sorption occurs on the heterogeneous surface of the sorbent (Figure 5, 6) [42]. The plotted graph showed the Langmuir isotherm model best fits for the sorption of U(VI) due to the formation of a monolayer on COOH-GO, GO, and graphite. The sorption isotherm gives very important information about the surface nature, adsorption capacity, and binding affinity of the sorbent substances which help to know the binding mechanism of sorbate to the sorbent [43].

![Figure 4. Sorption capacity graph for C_e versus q_e.](image)

The sorption result was shown in Table 1 shows that the values of the linear regression coefficient (R^2 > 0.999) was best fitted with Langmuir isotherm whereas Freundlich adsorption isotherm for COOH-GO, GO, and graphite (Table 2) has R^2 < 0.99. So it was confirmed that the monolayer sorption of U(VI) on COOH-GO, GO, and graphite surface occurs. The calculated value of q_max (maximum sorption capacity)
was observed to be 148.36, 128.53, and 116.14 mg/g for COOH-GO, GO, and graphite, respectively (Table 1). The RL (separation factor) value is less than one and was observed that the adsorption process is favourable [23].

![Figure 5. Langmuir adsorption isotherm between $1/C_e$ versus $1/q_e$](image)

From above Eq. 4, Intercept = $1/q_{max}$, $q_{max}$ were calculated. The value of $K_L$ was calculated as $1/slope \times q_{max}$, The value of $R_L$ were calculated as $1/(1+C_i \times K_L)$.

**Table 1.** Langmuir model for U(VI) sorption onto COOH-GO, GO, and graphite.

| Parameters       | Sorbent materials |
|------------------|--------------------|
| $y = mx + c$     | COOH-GO            |
|                  | $y = 0.2203x + 0.00674$ |
|                  | GO                 |
|                  | $y = 0.2483x + 0.00778$ |
|                  | Graphite           |
|                  | $y = 0.4939x + 0.00861$ |
| $R^2$            | 0.9997             |
| $q_{max}$ (mg/g) | 148.36             |
| $K_L$ (L/mg)     | 0.0305             |
| $R_L$            | 0.2464             |

| Parameters       | Sorbent materials |
|------------------|--------------------|
|                  | GO                 |
|                  | $y = 0.2483x + 0.00778$ |
|                  | Graphite           |
|                  | $y = 0.4939x + 0.00861$ |
| $R^2$            | 0.9996             |
| $q_{max}$ (mg/g) | 128.53             |
| $K_L$ (L/mg)     | 0.0313             |
| $R_L$            | 0.242              |

| Parameters       | Sorbent materials |
|------------------|--------------------|
|                  | Graphite           |
|                  | $y = 0.4939x + 0.00861$ |
| $R^2$            | 0.9997             |
| $q_{max}$ (mg/g) | 116.14             |
| $K_L$ (L/mg)     | 0.0174             |
| $R_L$            | 0.3645             |
From Eq. 8, slope, $K_f$ and Log $K_f$ were calculated.

**Table 2.** Freundlich model for U(VI) sorption onto COOH-GO, GO, and graphite.

| Parameters       | COOH-GO         | GO           | Graphite       |
|------------------|-----------------|--------------|----------------|
| $y = mx + c$     | $y = 0.6587x + 0.8153$ | $y = 0.6619x + 0.6619$ | $y = 0.6715x + 0.5437$ |
| $R^2$            | 0.9884          | 0.9839       | 0.9817         |
| $1/n$            | 0.6587          | 0.6619       | 0.6715         |
| $K_f$            | 6.5369          | 4.5911       | 3.4974         |

3.8 Kinetic Studies for Sorption

The kinetic study of both pseudo 1$^{st}$ order [28] and pseudo 2$^{nd}$ order rate equation [29] were applied for the sorption rate and its study of kinetic mechanism was done by using Eq. 8, and 9, respectively.

3.8.1 Pseudo 1$^{st}$ order model

The equation (Eq. 8) is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$  \hspace{1cm} Eq...(8)

Where, $q_e$ = sorption capacity (mg/g) at equilibrium, $q_t$ = sorption capacity (mg/g) at time t and $k_1$ (min$^{-1}$) = rate constant at equilibrium.

The sorption kinetic curves were plotted for U(VI) sorption onto COOH-GO, GO, and graphite for both pseudo 1$^{st}$ order and pseudo 2$^{nd}$ order reaction and are shown in figure 7 and figure 8 (Table 3). In the initial 20 minute maximum and fast U(VI) sorption was observed than at 80 minutes [19, 23]. After 20 min, the sorbent become saturated with sorbate and eventually they attained the dynamic equilibrium [19, 43].
3.8.2 Pseudo 2nd order model

The equation (Eq. 9) is:

\[
\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
\]

Where, \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) = rate constants at equilibrium sorption.

For both the models the linear coefficient regression \( (R^2) \) values had been used for prediction of best suited sorption isotherm. The best-suited model was observed by using a linear regression coefficient \( (R^2) \) if the value is near 0.99 or one then this is best fitted kinetic model (Figure 7, 8). From table 3, it has been observed that for pseudo 2nd order model, the linear regression coefficient \( R^2 > 0.99 \). The observed data shows that the pseudo 2nd order kinetic model was followed. The rate-determining step depends on both concentration of U(VI) and sorbents [19, 43].

![Figure 7](image1.png)

**Figure 7.** Pseudo 1st order kinetic plot between time and ln(q\(_e\)-q\(_t\)).

![Figure 8](image2.png)

**Figure 8.** Pseudo 2nd order kinetic plot between time and t/q\(_e\).
Table 3. Parameters calculated for pseudo 1\(^{st}\) order and pseudo 2\(^{nd}\) order model.

| Observed Parameters | COOH-GO  | Sorbent materials | Graphite |
|---------------------|----------|-------------------|---------|
| Order of Kinetics   | Pseudo 1\(^{st}\) order | Pseudo 2\(^{nd}\) order | Pseudo 1\(^{st}\) order | Pseudo 2\(^{nd}\) order | Pseudo 1\(^{st}\) order | Pseudo 2\(^{nd}\) order |
| Intercept           | 1.8778   | 0.0188            | 2.2446  | 0.0366  | 2.6066  | 0.0622  |
| Slope               | -0.022   | 0.0103            | -0.0221 | 0.0105  | -0.0228 | 0.011   |
| q\(_e\) (mg/g)      | 6.5391   | 97.0873           | 9.4366  | 95.2381 | 13.5528 | 90.909  |
| q\(^2\) Square      | -        | 9425.959          | -       | 9070.295| -       | 8264.46 |
| k\(_1\)             | -0.00016 | -                 | -0.00016| -       | -0.0002| -       |
| k\(_2\)             | -        | 0.005643          | 0.003012| -       | -       | 0.00195 |
| R\(^2\)             | 0.5372   | 0.999             | 0.4497  | 0.997   | 0.4424  | 0.9929  |

3.9 Thermodynamic Studies for Sorption

The effect of temperature on U(VI) sorption was studied by using a water bath. The condition for sorption were C\(_0\) = 10 µg/ml, mass of sorbent = 10 mg, pH = 4.5, and volume of sample =10 mL. The sorption capacity of sorbent materials was taken as a function of temperature in Kelvin. In this study, the three different temperatures were taken that is 298K, 308K, and 318K for all three sorbents (Figure 9). The sorption capacity of U(VI) was found to increase with the increasing temperature which indicates the sorption of U(VI) is endothermic (Table 4). This result is similar to previously obtained results of U(VI) sorption by activated carbon [44, 45]. The Thermodynamic parameters ∆G\(^o\) (kJmol\(^{-1}\)), ∆H\(^o\) (kJmol\(^{-1}\)), and ∆S\(^o\) (Jmol\(^{-1}\)K\(^{-1}\)) were also calculated for sorption. The value of ∆H\(^o\) (kJmol\(^{-1}\)) and ∆S\(^o\) (Jmol\(^{-1}\)K\(^{-1}\)) were calculated by slope and intercept of linear line equation lnK\(_L\) versus 1/T by van’t Hoff equation [46].

\[
K_L = \frac{C_{eq}}{C_{e}}
\]

\[
\ln K_L = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}
\]

\[
\Delta G^o = \Delta H^o - T\Delta S^o
\]

Where, the value of K\(_L\) (mL/g) = the distribution coefficient of U(VI), T = temperature in Kelvin, and R = gas constant (8.314 J/(mol K)).

From Table 4, all these parameters were calculated from the linear fitting line Eq. 11. The value of ∆G\(^o\) = -Ve (negative) indicates that the sorption is spontaneous in nature, ∆H\(^o\) = +Ve (positive) means sorption is endothermic in nature, and ∆S\(^o\) = +Ve means entropy of the system increases under these conditions [47].
Figure 9. Thermodynamic graph between \( \ln K_L \) versus \( 1/T \)

Table 4. Thermodynamic parameters for U(VI) adsorption on sorbent materials.

| Parameters        | Sorbent Materials |
|-------------------|-------------------|
|                   | COOH-GO | GO   | Graphite |
| Temp. in Kelvin   | 298     | 308  | 318     | 298     | 308  | 318   | 298     | 308  | 318   |
| \( \Delta G^\circ \) (kJmol\(^{-1}\)) | -2.02   | -2.70 | -3.73   | -1.46   | -2.28 | -2.83 | -0.96   | -1.76 | -2.20 |
| \( R \) (Jmol\(^{-1}\)K\(^{-1}\))    | 8.314   | 8.314 | 8.314   |
| \( \Delta H^\circ \) (kJmol\(^{-1}\)) | 23.28   | 18.92 | 17.49   |
| \( \Delta S^\circ \) (Jmol\(^{-1}\)K\(^{-1}\)) | 84.76   | 68.58 | 62.14   |
Table 5. Comparison of the U(VI) sorption capacities of GO and COOH-GO with other sorbent materials.

| Sorbent Materials                      | pH | Temp. (K) | Equilibrium time (min.) | $q_{\text{max}}$ (mg/g) | References |
|----------------------------------------|----|-----------|-------------------------|--------------------------|------------|
| GO                                     | 5  | 293       | 60                      | 122.4                    | [48]       |
| Reduced GO                             | 4  | 293       | n/a                     | 74.1                     | [33]       |
| Cyclodextrin-modified GO               | 5  | 288       | n/a                     | 97.3                     | [49]       |
| Multi-walled carbon nanotubes (MWCNTs) | 5  | 318       | 60                      | 39.5                     | [50]       |
| Activated carbon                       | 3  | 293       | 180                     | 28.3                     | [51]       |
| Graphite                               | 4.5| 298       | 80                      | 116.14                   | This study |
| GO                                     | 4.5| 298       | 80                      | 128.53                   | This study |
| COOH-GO                                | 4.5| 298       | 80                      | 148.36                   | This study |

4. Conclusion
The GO and COOH-GO were synthesized and characterized successfully by UV-VIS Spectroscopy, Fourier transformed infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Scanning electron microscope (SEM), Raman Spectra, and high-resolution transmission electron spectroscopy (HR-TEM). The GO and COOH-GO synthesis was cost-effective, environment friendly, and have high efficiency for U(VI) removal. The batch sorption experiment was studied successfully by the effect of pH, contact time, amount of sorbent dose, initial U(VI) concentration, and temperature. The removal of uranium was found to be more for COOH-GO than GO and graphite due to the presence of more oxygen-containing domains in COOH-GO. The adsorption isotherms were studied successfully and the sorption was best fitted for the Langmuir adsorption model ($R^2 > 0.99$) as compared to the Freundlich adsorption model confirming monolayer adsorption. The kinetics was studied successfully and was best fitted ($R^2 > 0.99$) for the pseudo-second-order model. The thermodynamic studies suggested that the adsorption was endothermic and spontaneous in nature.

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