A Novel Method for the Removal of Uranium by Using Carboxyl Functionalized Graphene Oxide

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Abstract. Graphene oxide (GO) and functionalized carboxylic graphene oxide (COOH-GO) were successfully synthesized by modified Hummer’s technique. The prepared GO and COOH-GO was characterized successfully by UV-Visible Spectroscopy, Fourier transforms infrared spectroscopy (FTIR), X-ray diffraction, Raman spectroscopy, Scanning electron microscopy (SEM)& Zeta potential. The removal of U(VI) heavy metal comparative study was done by using Graphite, GO & COOH-GO and the removal were confirmed by using LED fluorimeter. The effect of pH of medium, contact time, adsorbent dose, initial concentration of U(VI) were examined for the removal of U(VI). The extent of U(VI) removal has been found to be in the order of COOH-GO >GO> graphite. The U(VI) removal maximum efficiency was observed ~96% observed at pH 4.5. The higher removal efficiency is attributed to the higher negative surface charge of COOH-GO (zeta potential:-39.9 mV) in comparison to zeta potential of GO (-28.9 mV) &graphite (-21.6 mV).

Keywords: Removal of Uranium, Sorption study, Graphene Oxide, LED Fluorimeter.

1. Introduction

There are many different methods to remove heavy toxic metals from polluted water like ion-exchange, precipitation, electroplating, membrane separation, coagulation, disinfection (oxidation/ozonation), biological degradation, electro-kinetics, sorption, solution extraction and adsorption [1-3]. Among all these techniques, the most efficient and widely used technique is sorption technique due to its low cost, versatility & simplicity [4-6]. All type of sorbent has been highly used for removal of toxic elements, such as metal oxides, modified silica, metal-organic frameworks, biomass, carbon-based materials, clay minerals and so on [7, 8]. Among these, carbon-based materials are better for the removal of U(VI) heavy metal in pollutant water due to its catenation property and high surface area [9]. Especially, the carbon-containing substances such as GO and its derivates have their excellent physio-chemical properties with high surface area 2630 m²/g, ultra light weight, high mechanical strength, playing important role to remove heavy metal toxicity in polluted water [10-13].

GO was synthesized from graphite powder which has SP2 containing carbon. GO is one of the promising materials for the cleaning of environmental pollutants like heavy metals (Fe, Co, Ni, Cu, Pb, As, Cd, Hg & U, etc) as well as organic pollutants. It is arranged in a
hexagonal lattice with good electronic properties due to the $\pi$ and $\pi^*$ orbital's. It is the strongest material in the way of mechanical strength [14]. The application of GO and its derivative compounds are highly useful for the removal of various heavy metals. Further, GO make very stable dispersion in water and can be synthesized by wet or dry medium. The dry synthesis method consists of an oxidation reaction of graphene to atomic oxygen in an ultra-high vacuum [15-20]. However, in the wet synthetic method, the main source for the synthesis of GO is graphite due to its high natural abundances and low cost. In the wet synthesis approach, three main routes are possible. In the first route, graphite is converted to GO by mechanical method followed by oxidation while in second route exfoliation of graphite occurs in an aqueous medium followed by ultrasonic treatment [21, 22]. In the last route, both oxidation and exfoliation occur in the presence of highly acidic conditions as found in the Brodie-Staudenmaier-Hummers synthesis method. It can be seen that in all these paths, the structural properties of graphene oxide depends upon the degree of oxidation [23]. During the last century, the three major methods are proposed by Brodie, [24] Staudenmaier [25] and Hummers [26] respectively. In these basic synthetic methods, several modifications have been imposed by several researchers to improve the quality and yield of the product like Tour’s group method, [27] free-water oxidation methods, like Sun method [28], Peng method [29], 4-Steps method [30], etc. However, the furtherance of the removal study by using GO was carried out by using modified graphene oxide such as carboxylic group, alcoholic group, and epoxy modified GO. In these modified GO, different functional groups are highly decorated on the layer of graphene and if the targeted group concentration is lacking then the adsorption of heavy metal is negative. Zijie Li et al. have synthesized GO maximum sorption efficiency for U (VI) was 299 mg/g at pH 4 and Wang et al. have synthesized functionalized GO maximum sorption efficiency 398.4 mg.g$^{-1}$ at pH 6 [31, 32]. Nowadays, water pollution by heavy metals is more problems for living organisms. Thus, the removal of heavy metals in municipal wastewater and also in industrial areas like nuclear power plants, metallurgical industries, oil refinery industries, etc draws attention by several researchers. The heavy metal toxicity issue is truly globalized and has affected many areas. Therefore, in the current context, the approach has been made for the removal of heavy metals from water samples with high efficiency and by using low-cost material like GO. Thus, in the present investigation GO and COOH-GO were synthesized, characterized & used for removal of U(VI) in the water sample.

2. Experimental section
2.1. Reagents and materials used
Graphite fine powder (60 mesh, approx. size 250 µm) and NaNO$_3$ (99%) were purchased from LobaChemie Pvt. Ltd. were used as received. KMnO$_4$ (>98.5%), Monochloroacetic acid (>99.0%), NaOH (>97%), H$_2$O$_2$ (30%), H$_2$SO$_4$ (98%) and HCl (35%) were purchased from Sigma Aldrich (Mumbai, India). Standard stock solutions of uranium 100µg/mL (1 lakh ppb) in 2-5% nitric acid (AccuStandard, USA) and all the chemicals and reagents were prepared with millipore deionized (DI) water obtained from Merck Millipore water purifier. The pH was measured with a digital pHep® (Hanna instruments, USA). Uranium analysis was carried out by using LF 2a LED fluorimeter (Quantalase Inc. India).

2.2. Synthesis of GO
GO was synthesized according to modified Hummers method by using graphite fine powder [33-35]. Graphite fine powder (4 gm) has been taken in a beaker (1000 ml) and was put on a magnetic stirrer for 1 hour at 300 rpm and then slowly added 480 ml of concentrated sulphuric acid followed by 0.5g of sodium nitrate under stirring. Then the solution mixture was cooled to 20°C by putting it in an ice bath. Further, 24g of KMnO$_4$ was added to the mixture solution under stirring and was stirred overnight at 35°C. Afterwards, 40 ml of H$_2$O$_2$ in 500 ml ice was added to the above prepared solution slowly to obtain a bright yellow colour precipitate. The precipitate was washed by using 0.5 M HCl to
remove Mn$^{2+}$ & further purified by washing repeatedly with millipore water under centrifugation at 4000 rpm until pH of washings becomes neutral. Further, the obtained black coloured GO was ultrasonicated for 1 h and was dried overnight at 45°C.

2.3. Synthesis of COOH-GO

COOH-GO was synthesized by reduction of -OH groups of GO to -COOH group [36, 37]. In this method, 0.05 g of prepared GO was taken in 50 ml millipore water and sonicated for 50 minutes. Further, 1.2 g of monochloroacetic acid and 1 g of sodium hydroxide was added to the GO solution and then sonicated for 4 hours. Then COOH-GO solution was neutralised with 0.5 M HCl solution and was purified by repeated washing with millipore water under centrifugation at 2000 rpm until the washings becomes neutral [35]. Finally, the obtained COOH-GO was dried overnight at 45°C.

2.4. Characterization of graphite, GO and COOH-GO

Electronic spectra of Graphite, GO and COOH-GO was recorded on a double beam UV-Visible spectrometer in the range from 200-900 nm (LABTRONICS MODE LT-2900). The different-different functional groups were confirmed by FTIR by using Cary 630 in the range from 400-4000 cm$^{-1}$ (Agilent Technologies, UK). The morphological studies were carried out by SEM (SEM Zeiss EVO 18, USA). The X-ray diffractograms were recorded by PANalytical, XPERT-PRO by using CuKαradiation. Raman Spectra were recorded by Research India (RIAR-0403, Raman Spectrometer RIRAMAN532, India). The zeta potential was measured on a Zetasizer Nano (MALVERN, UK).

2.5. Batch sorption study for removal of U(VI)

Sorption study for U(VI) was studied in the batch experiment using a 500 ppb standard diluted uranium solution at the desired pH. LED fluorimeter was used for measurement of U(VI) in an aqueous medium. The sorption equilibrium capacity $Q_e$ (mg/g) and percentage removal for U(VI) in aqueous medium were calculated by using equations, $Q_e = [(C_0 - C_e)\times V]/m$ & % of removal of U(VI) = $[(C_0 - C_e)\times 100]/C_0$ respectively; where, $C_e$ is the final concentration after sorption equilibration, $C_0$ is the initial concentration of U (VI) ions in solution (µg/l), V is the volume of the uranium solution (ml) and m is amount of adsorbent (mg).

2.6. Selectivity of studies

The U(VI) removal was investigated in the prepared water sample solution by using sorbent materials COOH-GO, GO and graphite. All experiments were observed at room temperature. The U(VI) ion concentration was measured in filtrate of the sample water solution by LED Fluorimeter. The minimum detection limit of LED Fluorimeter is 0.2 ppb in the water sample.

3. Results and Discussion

3.1. UV-Visible spectra of GO and COOH-GO

UV-Visible spectra were recorded for GO and COOH-GO (Figure 1) and the $\lambda_{max}$ were obtained ~230 nm due to $\pi-\pi^*$ transition of >C=O functional group in GO. A slight shift in the
absorption spectra of COOH-GO was due to increased oxygen domain carboxylic group concentration. The wavelength region 400 to 900 nm is not affected by the absorptions[38].

3.2. FTIR of GO and COOH-GO
The FT-IR spectra were reported in figure 2 for GO and COOH-GO. The FT-IR spectrum for GO contains peaks for hydroxyl (-OH), epoxide (-C-O-C-) and ketonic (>C=O) functional group corresponding to vibrational stretching frequencies around 3420 cm\(^{-1}\), 1245 cm\(^{-1}\) and 1719 cm\(^{-1}\), respectively. The two doublet peak 1719.2cm\(^{-1}\) and 1589.5 cm\(^{-1}\) observed due to keto-enol tautomerism in carboxyl/carbonyl functional groups, as previously reported by Pendolino et al. and Bagri et al. [39, 40] However, in the FT-IR spectrum for COOH-GO signals arises due to the above mentioned functional groups but with a slight shift as the hydroxyl (-OH) groups reduced to carboxylic carbonyl group increased.
3.3. XRD study of GO and COOH-GO

X-ray diffractograms of the GO synthesized above has shown a single broad peak at $2\theta = 9.12^\circ$ (Figure 3(A) and 3 (B)). The inter-planar distance ($d$) of the synthesized GO is 0.969 nm which is comparable to that reported by Jalili et al. [41] Further, the particle size of GO has been calculated as 7.72 nm by using Scherrer equation (Eq.1). It has been calculated that the synthesized GO contains 8 layers.

\[
D_p = \frac{(0.94 \times \lambda)}{\beta \cos\theta} 
\]

Where, $D_p =$ Average size of crystallite, $\lambda =$ X-Ray wavelength, $\theta =$ Bragg diffraction angle, $\beta$ (Full Width Half Maximum) = Line broadening in radians.

The XRD pattern for COOH-functionalized GO has shown no sharp peak and thus it can be concluded that the inclusion of functional groups has introduced disorderness and amorphy leading to a more amorphous FGO.

![Figure 3. (A) X-Ray diffraction peak of graphene oxide](image)

![Figure 3. (B) X-Ray diffraction peak of COOH-GO](image)

3.4. Raman spectra for GO and COOH-GO

Raman spectra of GO &COOH-GO havetwo peaksshown corresponding to G& D band. The G band (~1580 cm$^{-1}$) is due to the ordered structure of sp$^2$ carbon and the D band (~1350 cm$^{-1}$) is due to the presence of sp$^3$ carbon atom which has arisen by the introduction of oxygen-containing functional groups(Figure 4). The intensity were observed for GO ($I_D/I_G = 1.0232$) & COOH-GO ($I_D/I_G = 1.1435$)[42, 43], respectively.
3.5. SEM Study of GO & COOH-GO
The surface morphology of nanomaterials was detected by SEM for graphite powder, GO and COOH-GO (Figure 5). In graphite the flake like structure was observed whereas in GO and COOH-GO have exfoliated porous like structures observed [44].
3.6. Zeta potential measurement of GO and COOH-GO
The colloidal dispersion of Graphite, GO and COOH-GO in DI water was prepared by 30 minutes sonication. The zeta potential for graphite (-21.6 mV), GO (-28.9 mV), COOH-GO (-39.9 mV), 20 ppb of U(VI) solution (-17.1), 100 ppb of U(VI) solution (+3.61) and 200 ppb of U(VI) solution (-7.54) were observed at pH 4.5. Graphite, GO and COOH-GO have shown more negative values corresponding to their negative surface charge. And thus, they can absorb Uranium atoms owing to the fact that the surface charge of COOH-GO is more negative than GO and graphite and thus the removal of U(VI) was investigated practically in the order; COOH-GO > GO > Graphite [45].

3.7. Uranium batch sorption experiment
3.7.1. Effect pH for removal of U(VI)
Removal of heavy metal ions are strongly affected by pH of the solution. In current investigation, the effect of pH for U(VI) removal by COOH-GO, GO and graphite is provided in figure 6. The pH ranges have varied from 2 to 12 pH and pH was adjusted by using 0.01M HCl and 0.01M NaOH. The same kind of sorption trends were observed for sorbent substances such as graphite, GO and COOH-GO [42, 43]. Sorption (%) for U(VI) in pH range 2 to 12 was investigated and it is in the order: COOH-GO > GO > graphite. This investigation suggests that the occurrence of -COOH domain increase removal efficiency of heavy metal such as U(VI). The sorbent material developed electrostatic force of attraction on positively charged U(VI) [42]. In contrast, at higher pH, the amount of U(VI) removal considerably decreased for all three sorbents. The hydrolysed solution of Uranium containing
(UO$_2$)$_3$(OH)$_5$$^{3+}$, UO$_2$(OH)$^+$, (UO$_2$)$_2$(OH)$_2$$^{2+}$ and (UO$_2$)$_2$(OH)$_2$ species results in sorption of U (VI) and thus its removal efficiency [46].

![Figure 6. Effect of pH for removal of U(VI) (Experimental conditions U(VI) conc. = 100 ppb, Mass of sorbent = 10 mg, Volume of sample = 50 mL, pH range 2-12)](image)

3.7.2. Effect of contact time for removal of U(VI)
The sorption activity was observed for time range from 10-140 minute (10, 20, 30, 40, 50, 60, 80, 100, 120 and 140 minutes) for 50 ml sample solution(Figure 7). The conc. of U(VI) solution was 100 ppb and adsorbent dose 10 mg at an optimum pH of 4.5. The percentage removal efficiency of U(VI) sorption increased steadily from 10 and 20 minutes and after that almost no change was observed. The highest removal of U(VI) was found to be 96.2% for COOH-GO, 93.3% for GO and 87.6% for graphite powder. The maximum sorption capacity was achieved by COOH-GO as time gradient increases [42].

![Figure 7. Effect of contact time for removal of U(VI)](image)
(Experimental conditions U(VI) conc. = 100 ppb, Mass of sorbent = 10 mg, Volume of sample = 50 mL & pH = 4.5)

3.7.3. Effect of sorbent dosage for U(VI) removal

The sorption rate of U(VI) increased from 37% to 94% with an increase in dosage of COOH-GO, GO and graphite from 5 to 100 mg. However, the sorption increases steadily when the dosage was varied from 5 to 10 mg and thereafter removal of Uranium slowly increases [Figure 8]. The maximum sorption of ~96% was observed when the adsorbent dosage was 100 mg. The U(VI) sorption result indicates COOH-GO is much better than GO and graphite powder [47]. Thus, 10 mg of sorbent was chosen for further experimentation. The sorption process was performed under a rotatory shaker without sonication treatment.

![Figure 8](image)

**Figure 8.** Effect of contact time for removal of U(VI) (Experimental conditions U(VI) Conc. = 100 ppb, Mass of sorbent = 10 mg, Volume of sample = 50 mL, pH 4.5 & Contact time = 20 minute)

3.7.4. Effect of initial U(VI) concentration on uranium sorption

The effect of initial concentration of U(VI) was also investigated by sorbent materials COOH-GO, GO and graphite by using 10-200 ppb of U(VI) solution (Figure 9) at pH = 4.5, adsorbent dosage = 10 mg and at room temperature. The COOH-GO, GO and graphite was added to U(VI) solution kept on rotator shaker and were shaken for 20 minute. The sorption rate of U(VI) increased gradually from 10-100 ppb and then increased slightly with an increase in U(VI) concentration from 100-200 ppb. The maximum sorption of 93.5% was observed when the concentration of U(VI) was 200 ppb [42].
4. Conclusion

UV-Visible spectra, FT-IR, XRD, Raman and SEM analyses confirmed the formation of GO and COOH-GO. The removal efficiency of U(VI) is highly dependent on pH and contact time. The removal of uranium was found to be more for functionalised GOOH-GO than GO and graphite due to the presence of more oxygen containing domains in COOH-GO. In this study, COOH-GO have the maximum sorption capacity for U(VI) and was found to be 97.2% at pH 4.5 in comparison to GO and graphite. This fact was also verified from zeta potential study. The zeta potential study suggests the highly negative charge for COOH-GO due to carboxyl group on its surface which are responsible for the removal of U(VI).

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