

# STUDY ON THE INFLUENCE OF AQUEOUS PHYTOEXTRACT IN THE REDUCTION OF GRAPHENE OXIDE

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**Abstract-** In this work, Graphene Oxide (GO) was synthesized by treating graphite powder with  $KMnO_4$  and a mixture of concentrated  $H_2SO_4$  and  $H_3PO_4$ . The experiment is carried out at room temperature without  $NaNO_3$ . The effects of reaction parameters such as reaction time, reaction temperature and amount of  $KMnO_4$  on the degree of oxidation of graphite powder to graphene oxide were studied. The results showed that treating graphite powder with  $KMnO_4$  at  $40^\circ C$  for 12 h resulted in better degree of oxidation. The reduction of the synthesized graphene oxide (GO) by phytoextract was investigated using aqueous peel extract of orange (*Citrus sinensis*). The prepared GO and phytoextract reduced GO (RGO) were characterized by ultraviolet-visible spectroscopy & Fourier transform infrared analyses to provide a clear indication of the removal of oxygen-containing groups from the graphene and the formation of RGO. The extent of reduction was determined from elemental analysis.

**Index Terms-** Graphite, GO, rGO, modified hummers method, phytoextract, *Citrus sinensis*, UV-Vis Spectroscopy, FTIR

## I. INTRODUCTION

Graphene has attracted fabulous research interest in energy-storage techniques. It has great mechanical strength, large specific area and high electrical conductivity. Graphene is a one atom thick structure of  $sp^2$  bonded carbon atoms. Chemical method is the prominent method of producing graphene based materials in large quantity [1]. However, the well-known chemical synthesis methods such as Brodie method [2], Staudenmaier method [3] and Hummer's method [4] were hazardous and toxic since  $ClO_2$  and  $NO_2$  evolves during the process. The Tour method (improved green synthesis method) is the one that is relatively safe (environmental friendly) [5]. In addition, the final yield is much higher than the former methods. This method describes that GO is synthesized by treating graphite powder with  $H_3PO_4$ ,  $H_2SO_4$  and high quantity of  $KMnO_4$ . However, influence of quantity of  $KMnO_4$ , reaction time, and the temperature on graphite oxide preparation was not clear.

From literature, it is clear that various phytochemicals, obtained from different natural sources like leaves, peels or other parts of plants are used as reducing agents for the preparation of different metal nanoparticles like  $Ag(0)$  and  $Au(0)$ . It is also reported that leaves of *Mesua ferrea* Linn., and peel of orange have tremendous potential for reduction [6],[7].

orange peel is one of the waste materials throughout the world. *C. esculenta* leaves, *M. ferrea* Linn. leaves and orange peel extract mainly contain pectins, flavonoids, ascorbic acid, apigenin, luteolin and various other flavones which have high tendency to get oxidized. Generally, these types of phytochemicals are converted to the corresponding quinone forms in the presence of reactive oxygen. Therefore these phytoextracts have sufficient potential to reduce the oxygen containing group of GO.

In this work, graphene oxide was prepared by easy, cost effective and convenient method via treating graphite powder with  $KMnO_4$  and a 9:1 mixture of concentrated  $H_2SO_4$  and  $H_3PO_4$  as oxidants. To optimize the oxidation level, the effects of  $KMnO_4$ , reaction time and reaction temperature were studied. The prepared powder is then reduced using a green and useful phytoextract from orange peel. The extent of reduction of the graphene oxide is verified by UV-Vis spectroscopy and FTIR.

## II. EXPERIMENTAL

### Chemicals Used

Graphite flakes, Concentrated sulphuric acid (98%), hydrogen peroxide ( $H_2O_2$ , 30%) concentrated hydrochloric acid (30%) and Potassium permanganate ( $KMnO_4$ ) were purchased from Merck, India and were used as received, without further purification. The orange peel were collected from local area.

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In addition to that *Colocasia esculenta* and *M. ferrea* Linn. are abundant in different countries, whereas

### Synthesis Of Graphite Oxide

In the synthesis of graphite oxide a mixture of 96 ml of concentrated  $\text{H}_2\text{SO}_4$  and 10.7 ml of concentrated  $\text{H}_3\text{PO}_4$  (9:1) Volume ratio was prepared. The mixture of these acids were poured slowly into the mixture of 0.6 g graphite powder and 4.8g Potassium Permanganate (1:8) in a beaker under stirring with glass rod and was continued for 12 Hours with a magnetic stirrer. Then the mixture was added into 250 ml of de-ionized water to stop the reaction. Following that 15ml of  $\text{H}_2\text{O}_2$  was added into the mixture. The addition of  $\text{H}_2\text{O}_2$  resulted in yellow colour, indicating high level of oxidation. The solution was then filtered to remove metal ions using filter paper and funnel. A yellow paste was produced. The paste was washed with 5% HCl aqueous solution using centrifuge until  $\text{SO}_4$  was removed completely. The removal of  $\text{SO}_4$  was detected by the addition of Barium chloride where the presence of sulphate ion ( $\text{SO}_4$ ) showed a white precipitate when barium chloride was added to the supernatant. The supernatant was decanted away and the remaining solid material was collected. Then the mixture was washed multiple times with de-ionized water using centrifuge until the pH of the supernatant was neutral. Finally the material was dried at  $50^\circ\text{C}$  for 24 hrs and a brown black sample was obtained.

### Preparation of phytoextract

The orange peel collected were washed separately with water then grounded using a domestic blender followed by stirring for about 20 min in 50 mL of water at  $50^\circ\text{C}$ . The aqueous extract was filtered under ambient conditions.

### Reduction of graphene oxide by aqueous phytoextract

In this experiment 60 mg of GO was dispersed in 120 mL of water by sonication for 30 min. Then 10 mL of aqueous phytoextract was added into the solution. The resulting suspension was stirred on a magnetic stirrer either at room temperature or refluxed until the reduction was completed (as confirmed by UV analysis). After reduction, RGO was settled and it was washed with water for several times to remove the unwanted materials.

## III. CHARACTERISATION TECHNIQUES

### 3.1. UV-Vis spectroscopy

UV-Vis spectroscopy was used in detection of the conjugation network and absorption of graphene oxide in acetone and ethanol. Double beam Lamda UV-Vis spectrophotometer (UV -2600 Shimadzu)

was used to obtain the absorption spectra of graphene oxide in acetone and ethanol. The GO and RGO solution samples were scanned for wavelength range from 200 to 800 nm.

### 3.2. FTIR

FTIR (Perkin Elmer, USA) was employed to analyze the presence/absence of functional groups on A- GO and E-GO. A- GO and E-GO samples were prepared using KBr and scanned in the range from  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  to obtain the FTIR spectra.

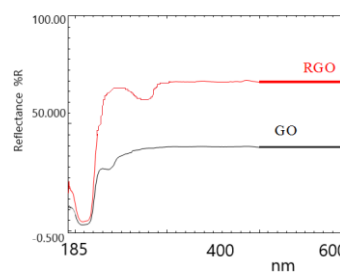


Figure 1. UV-Vis spectrum of graphene oxide samples

From figure 1, it is observed that graphene oxide shows maximum absorption peak at  $\sim 257\text{ nm}$  attributable to  $\pi-\pi^*$  transition of the atomic C-C bonds and shoulder peak at  $\sim 300\text{ nm}$  due to  $n-\pi^*$  transition of aromatic C-C bond [6].

The reduction reaction was monitored by recording the UV-visible absorption spectra of RGO as a function of time. GO shows a maximum absorption peak at  $235\text{ nm}$  which was attributed to the  $p-p^*$  transitions of the aromatic C-C bonds and a weak shoulder at  $300\text{ nm}$  due to  $n-p^*$  transitions of C=O bonds. After complete reduction, a red shift of this characteristic peak was observed at  $294\text{ nm}$  for C synthesis peel aqueous extract reduced GO (RGO) [6]. This indicated that the electronic conjugation was restored (Fig. 1).

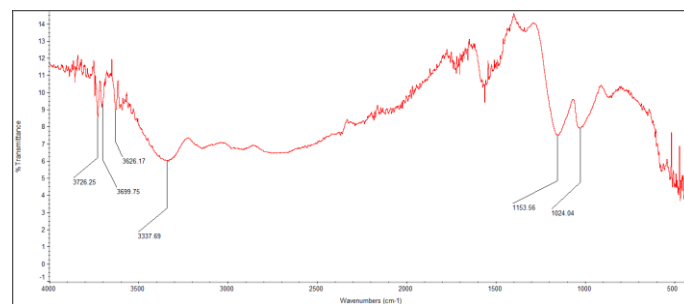


Figure 2.a. FTIR spectra of GO sample

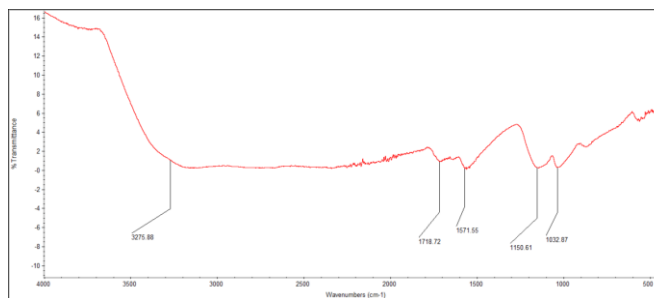


Figure 2.b. FTIR spectra of RGO sample

FTIR spectra of GO and RGO samples are shown in Figure 2.a and 2.b. Investigation of bonding interactions in both samples is carried out by FTIR. The presence of intense bands at  $1718\text{ cm}^{-1}$  (for C=O stretching),  $1150\text{ cm}^{-1}$  (for C–O–C stretching),  $1032\text{ cm}^{-1}$  (for C–O stretching) and a broad band at around  $3275\text{ cm}^{-1}$  for hydroxyl group indicate the presence of oxygen containing moieties such as carbonyl, carboxylic, epoxy and hydroxyl in GO. The removal and weakening of such oxygen-containing groups of GO in the RGO is clearly indicated by disappearance of the bands of C=O stretching, C–O–C stretching, C–O stretching and relative decrease in the intensity of broad band at  $3337\text{ cm}^{-1}$  for the hydroxyl group [10,11,12,14]. From the spectra it was cleared that the used phytoextract have comparable potential to reduce GO.

## V. CONCLUSION

The graphene oxide was synthesized by oxidizing purified natural flake graphite through modified Hummers method. UV-Vis spectrum of Graphene oxide shows maximum absorption peak at  $\sim 257\text{ nm}$  attributable to  $\pi\text{-}\pi^*$  transition of the atomic C-C bonds. And the shoulder peak is at  $\sim 300\text{ nm}$  due to  $n\text{-}\pi^*$  transitions of the aromatic C-C bonds. From FTIR studies, it has been proved that all peaks show the functional group existed in A-GO and E-GO samples. The graphite powder has been successfully oxidized with concentrated acid and  $\text{KMnO}_4$ . In this approach an improved hummer's method is applied to produce graphene oxide, and is different from conventional hummer method of synthesis graphene oxide with  $\text{NaNO}_3$ . It shows that,  $\text{NaNO}_3$  does not affect the synthesis method to produce graphene oxide. Same characteristic of graphen oxide is obtained without using  $\text{NaNO}_3$ . This method can decrease cost and further free toxic gases. Ethanol and acetone were used to perform the liquid medium of GO.

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