© 2018 IJSRST | Volume 4 | Issue 2 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X
Themed Section: Science and Technology

The Synthesis of Graphene as Fast and Considerable Removal of Dye Pollutant from Aqueous Solution

K. M. Sarode, D. R. Patil[*]
Nanomaterial Research Laboratory, R.C. Patel ACS College, Shirpur, Maharashtra, India

ABSTRACT

In the present study, the graphene nanosheets (RGO) were synthesized via improved Hummer's method followed by chemical reduction in hydrazine hydrate. The reduction of graphene oxide (GO) to graphene by gelatin was confirmed by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy and UV-Vis absorption spectroscopy. The application of the RGO materials as an adsorbent for the removal of the organic dye, methylene blue (MB) from aqueous solutions was investigated. The RGO exhibited excellent removal capabilities for MB (99 %) due to adsorption through strong π-π stacking and anion-cation interactions as well as the large specific surface area. The results demonstrated that RGO could be applied in treating contaminated natural water.

Keywords : Reduced Graphene Oxide, Methylene Blue; Adsorption.

I. INTRODUCTION

Nowadays, the rapid growth of chemical companies and the release of various types of pollutants into water bodies are recognized as the main causes of environmental pollution [1]. These dye molecules are harmful to human beings and toxic to microorganisms. Many chemical, biological, and physical processes have been investigated including Adsorption, ultra-filtration, biological treatment, oxidation, electrolysis, photocatalytic degradation for removal of organic Contaminates from water [2-8]. Among these techniques, adsorption process is considered to be economic and efficient approach for the removal of organic compounds from wastewater [9].

Recently, carbonaceous materials such as carbon nanotubes (CNTs), activated carbon, porous carbon, graphene have always attracted attention because of their large specific surface area, chemical stability, abundant pore size distribution [10-12]. As Compared to other carbonaceous materials, the advantage of graphene is the selective adsorption ability to those aromatic compounds with benzene rings through strong π−π interaction [12]. Hence, graphene is expected to be a promising adsorbent for the removal of aromatic compounds in water treatment.

Herein, the graphene nanosheet (RGO) was synthesized via improved Hummer's method followed by chemical reduction in hydrazine hydrate. The dye adsorption capability of the RGO materials was evaluated by the degradation of MB in aqueous solution. Results show that the RGO materials are an ideal candidate for the adsorption of organic dyes from waste water.

II. EXPERIMENTAL

Synthesis of RGO Nanosheets

The Graphene oxide (GO) was synthesized according to the previous literature [13]. Then, the GO was reduced by hydrazine hydrate in the presence of aqueous medium [14]. In brief, 600 mg of GO was loaded in 600 ml water and dispersed in an ultrasonic bath cleaner until it became clear with no visible particulate matter. Then, Hydrazine hydrate (6 ml) was mixed to the solution and heated in oil bath at 100 °C under water cooled condenser for 24 h. The resulting RGO as a black solid was isolated by filtration over a medium fritted glass funnel, washed with water and methanol alternately and dry at 50 °C.

Dye Adsorption Experiments

The initial and final concentrations of MB solutions were determined by the UV-Vis absorbance spectrometer. 50 ml of the MB solutions (12 mg L^{-1}) were mixed with an appropriate amount of RGO powder and stirred for 60 min in a room temperature. The mixtures of the RGO and dye were separated first by filtration and then by a centrifugation.

The removal efficiency of the MB dye was calculated according to Eq. (1):

Removal efficiency (%) = $(C_0 - C_e)/C_0 \times 100$ (1)

Where C_0 and C_e are the initial and equilibrium concentration of MB dye solutions, respectively.

Recycling Test

The adsorption stability of the RGO materials was investigated by recycling the material through 4 separate MB adsorption experiments. In a typical experiment, 60 ml of an aqueous MB (12 mg L^{-1}) Solution was mixed with 40 mg of RGO powder and stirred for 1 h at room temperature. The mixtures of the RGO and dye were separated first by filtration and then by a centrifugation. The resulting RGO was washed with 15% HCl, water and methanol alternately. Then, the RGO washed materials was then used in the second absorption experiment. This process was repeated for the fourth absorption experiment.

Material Characterizations

The morphology and microstructure of the samples were characterized by scanning electron microscopy (SEM, Model JSM-760F), transmission electron microscopy (TEM, JEOL-2010), and Raman spectra (excitation wavelength of 514.5 nm). UV-Vis absorption spectroscopy (shimadzu)

III. RESULTS AND DISCUSSION

The synthesized RGO was characterized by visual, physical and chemical methods. The changes in the color of solution are a good indicator of GO reduction in aqueous solution [15, 16]. The yellow-brown GO solution before reaction (Figure 1a) turned to a black dispersion after it had been heated for 24 h at the desired temperature (100°C), which indicates the successful conversion of GO to RGO (Figure 1b).

Figure 1. Photographic images of (a) GO solution and (b) RGO solution

FESEM &TEM images showed that the RGO material consists of thin, randomly aggregated, crumpled sheets closely associated with each other and forming a disordered solid (Figure 2).

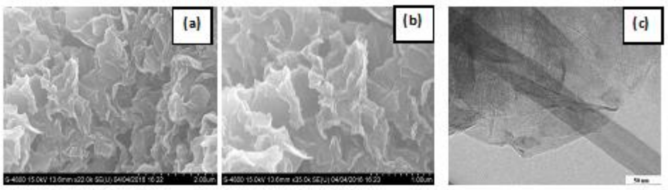
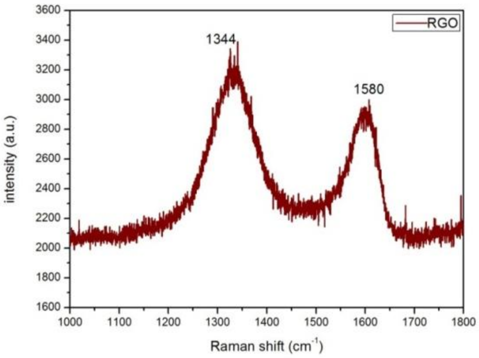
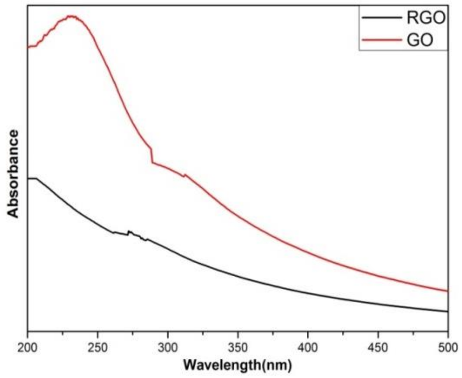


Figure 2. SEM images of RGO (a and b) and TEM images of RGO (c).

Raman spectroscopy was commonly used to monitor structural changes during the oxidation (GO) and reduction Processes of RGO. Fig. 3(a) shows Raman data for the 532 nm laser excitation. Raman spectroscopy shows the presence of characteristic peaks of RGO. The Raman spectrum of RGO displays the characteristic D-band (1344 cm^{-1}) and G-band (1580 cm^{-1}). The relative intensity of the D to G bands (ratio I_D/I_G) is therefore an indication of the graphene quality [17]. The calculated I_D/I_G value of the RGO has been much increased from 0.88 for GO to 1.29 for RGO due to the elimination of defects [18].



(a)



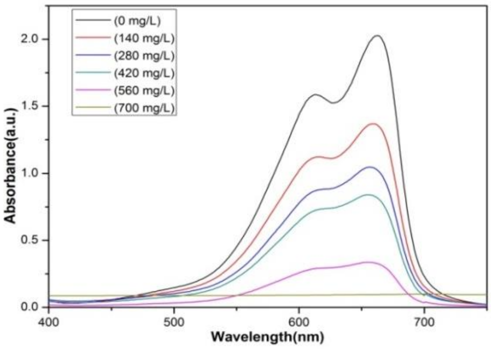
(b)

Figure 3. (a) Raman spectroscopy images of RGO and (b) UV-Vis absorption spectroscopy images of RGO**.**

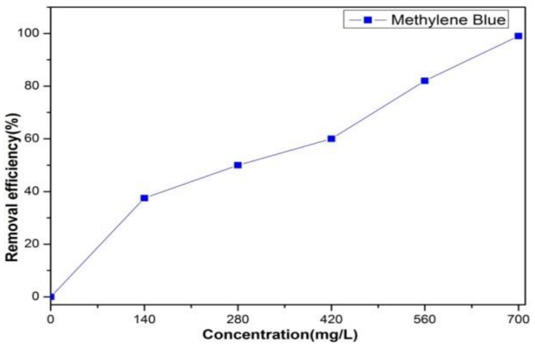
The UV-VIS spectra of GO exhibits a maximum absorption peak at about 232 nm, corresponding to π-π transition of aromatic C-C bonds. Also, the absorption peak around ~300 nm is observed and can be attributed to n →π* transitions of the carbonyl groups(C=O) (Fig. 3(b)). The absorption peak for reduced GO had red shifted to 271 nm. This phenomenon of red shift has been used as a monitoring tool for the reduction of GO.

Adsorption Properties

The adsorption of MB dye onto the RGO was measured by scanning the UV-visible spectra of aqueous solution. As shown in Figure 4(a), the characteristic UV-vis absorption intensity of MB at 664 nm decreased on increasing the concentration of RGO. When the amount of RGO was increased to 700 mg L^{-1}, 99% of MB could be captured within 60 min at room temperature (Figure 4b).



(a)



(b)

Figure 4. The capture of MB (a and b) at different concentrations of RGO.

The excellent rate of adsorptions is attributed to chemical adsorption through anion-cation interactions and strong π-π stacking, as well as the large specific surface area (fig 5) [19]. In more detail, firstly, Aromatic organic molecules are demonstrated to adsorb onto graphene nanosheets primarily through π-π interactions, so the elimination of oxygen-containing functional groups can significantly enhance the interaction between the π system of graphene and the π units of aromatic organic molecules; secondly, the electrostatic attraction between the positively charged amino groups and the negatively charged oxygen-containing surface groups [20].

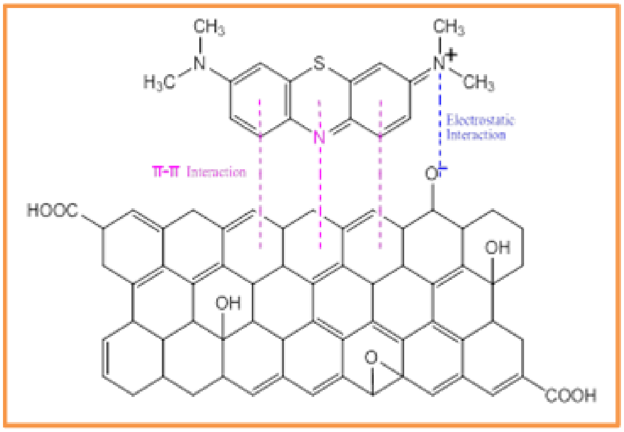


Figure 5. Schemes of interactions between the surface of rGO-based adsorbent and MB dye molcules.

Durability of RGO

Cycling of adsorbents is plays an important role in practical applications, due to economic demands for sustainability. Fig.6 show the RGO exhibit high adsorption capacity for MB dyes after four repeated adsorption and desorption treatments. The high absorbance capacity and recyclability of the RGO indicate that they have potential in industrial applications.

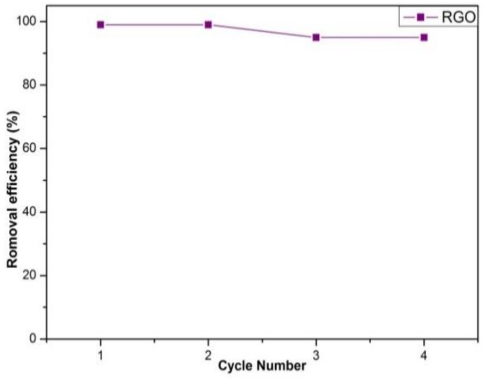


Figure 6. Recycling of RGO for the capture of MB

IV. CONCLUSIONS

In conclusion, the RGO nanosheets were successfully prepared using improved Hummer's method followed by chemical reduction in hydrazine hydrate. The results indicated that the High adsorption capacity of RGO for MB dye was attributed to the strong π-π stacking and electrostatic interaction of anion-cation. The good reusability results demonstrated that RGO would have great potential for the practical application in water purification.

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