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Short Communication Open Access

Sonochemically Synthesized Beta-Cyclodextrin Functionalized Graphene Oxide and its Efficient Role in Adsorption of Water Soluble Brilliant Green Dye

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Abstract

In this short communication, we report a novel and inexpensive approach to synthesize Beta-Cyclodextrin functionalized Graphene Oxide (GOCD) which has been fabricated for the adsorption of water soluble organic dyes from aqueous solution. The adsorbent GOCD has been synthesized using facile sonochemical route and accordingly characterized using techniques such FTIR, TGA, RAMAN and TEM respectively. Brilliant green dye (BG), a cationic, water soluble dye, commonly used as green pigment in textile/dye printing technology, is a highly toxic compound and consequently GOCD has been employed for its removal before recyclability of the waste water. The adsorption study of BG onto GOCD is investigated using UV-vis absorption spectroscopy. The exploration established the fact that the as-synthesized material GOCD has appreciable capability in dye removal and therefore possesses significant roles in waste water treatment technology.

Keywords: Graphene functionalization; Beta-cyclodextrin; Dye adsorption; Brilliant green dye; Toxicity; Water treatment technique

Beta-Cyclodextrin Functionalized Graphene Oxide

Textile and Dye Printing industries are one of the major water consuming and water polluting sources, discharging and contaminating water resources with large amount of water soluble dyes as industrial effluents on a daily basis. These waste waters essentially require proper treatment before being discharged to the environment. These dyes are generally stable to external factors like light, temperature and their partial degradation can lead to more toxic components that may result in inducing serious pollution [1]. Even the presence of extremely low concentrations of dyes in effluent is highly undesirable, as it can impose acute and/or chronic effects on exposed organisms. These dyes often affect the absorption and reflection of sunlight through water, reduce oxygen solubility and threaten the photosynthetic activity of algae and aquatic plants. Even they reduce the bacteria efficiencies that assist in biological degradation of water impurities and consequently disturb the food chain, ecosystem [2]. These serious reasons make the effective elimination of reactive dyes from effluents of textile industries very important step before release into the environment.

The brilliant green dye, ammonium 4-(p-diethylamino)-alpha-(phenylbenzylidene) ($C_{27}H_{34}N_2O_4S$) used in the current investigation is triphenyl nitrogen containing cationic dye [3]. The chemical structure of the brilliant green dye has also been given in Figure 1. Brilliant green is chemically described as with λ_{max} of 625 nm in water, and molecular weight of 482 g mol^{-1}. The use of brilliant green (BG) dye has been banned in many countries due to its carcinogenic nature. It is widely used as a dye to color synthetic fibers and silk biological stain, dermatological agent, veterinary medicine, and as an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus. It is considered highly toxic for humans and animals because it can cause permanent injury to eyes. Its' high concentration also irritates respiratory tract, gastrointestinal tract, along with nausea, vomiting and diarrhea in human beings. Consequently water contaminated with BG requires proper treatment before its recycling [4].

Carbon-based materials like activated carbons, polymers, CNTs have been extensively explored for removal of organic dye pollutants [5-8]. More recently, graphene functionalized materials such as graphene oxide, reduced graphene oxide as well as nanocomposites of graphene materials have also emerged as a promising group of adsorbent for the removal of various environmental pollutants from waste effluents [9-13]. This is because of their good chemical stability, large surface area, structural diversity, low density, cost-effectiveness and suitability for large scale production. Additionally, the negative charges in the GO sheets due to various oxygen-rich functional groups (i.e., carboxy, carbonyl, hydroxyl groups) allow additional strong electrostatic interactions with cationic dye molecules. However, GO sheets exhibit a high dispersibility in water, which prevents the efficient separation of dye-adsorbed GO sheets from an aqueous environment [14,15]. Therefore, various GO-based composites, functionalized systems have been adsorbent materials have been recently developed to facilitate the separation of dye-adsorbed GO sheets from aqueous solutions [16-20] to reduce its dispersing nature without destroying its dye adsorption effectiveness. Recent works by Akhavan et al. exhibited $ZnFe_2O_4$/reduced graphene oxide (rGO) composites for magnetic separation application [21]. However, presence of inorganic material hybrids always leaves behind a high propensity of metal ion toxicity and accordingly requires genuine consideration for more eco-friendly graphene based composite materials for water treatment purposes.

Cyclodextrin molecules are cyclic oligosaccharides composed of six to twelve α-Dglucopyranose monomers, connected at 1 and 4 carbon atoms. Cyclodextrins with six to eight αD-glucopyranose units are assigned as α-, β- and γ-Cyclodextrins respectively [22]. Among these various types of cyclodextrins, α-cyclodextrins are not suitable for many

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dyes and drugs primarily due to small cavity size while γ-cyclodextrins are very expensive. Contrastingly, βCyclodextrin (β-CD) is widely used because of easy availability and appropriate cavity size for hosting a wide range of guest molecules [23]. In general, the special characteristic of cyclodextrins embraces comprehensive study as supramolecular hosts, ability to form inclusion complex with various organic molecules through non-covalent host-guest interaction with the interior cavity providing hydrophobic environment to trap a less-polar pollutants, and surfaces containing hydroxyl groups adhering polar guests.

Accordingly, one would expect that β-cyclodextrin-functionalized graphene oxide (GOCD) shall definitely open up new environmental friendly routes for successful waste water treatment techniques. The study would also simultaneously visualize the new knowledge window for host-guest inclusion complex exploring the types of bonding that would alter the photochemical and photophysical properties of the guest molecules in that inclusion environment.

In the present study, GOCD was successfully prepared using facile sonochemical technique and was characterized by Fourier Transformed Infrared Spectrometry (FTIR), Thermogravimetric analysis (TGA) and Transmission Electron Microscopy (TEM) respectively. Then, the adsorption performance of GO-CD for BG solution was investigated by UV-vis spectrophotometer: JASCO model V-630 at room temperature (~27°C) and the experimental data was analyzed. The cause for high adsorption efficiency of GOCD for BG has been explained too.

In the preparation of GOCD, at first graphene oxide (GO, 250 mgL^{-1}) pre-synthesized according to modified Hummers method [24,25], was taken and thoroughly suspended in water and subsequently mixed with Beta-Cyclodextrin (β-CD, 4 gL^{-1}). After stirring for half-an-hour to obtain a homogeneous solution, the mixture was added with 10 ml aqueous ammonia (1:1, v/v) and then the resultant solution was ultrasonicated for 4 hrs. The ensuing black suspension was centrifuged and repeatedly washed with distilled water till all unreacted components were eliminated. The so-obtained semi-solid mass was dried around 90°C and subjected to following characterization techniques like FTIR, TGA, TEM. Fourier Transform Infrared (FTIR) spectra were obtained in solid state using KBr pellets in Perkin Elmer Spectrum 100 FTIR Spectrometer. Thermogravimetric analyses (TGA) of samples were carried out in SDT600 under dinitrogen gas atmosphere at a heating rate of 10°C/min. The morphologies of the samples were studied by depositing drop-coated samples (from acetone suspension) onto carbon-coated copper grids, and subsequently characterized by Transmission electron microscopy (TEM, JEOL).

The FT-IR spectra of samples β-CD, GO and GO-CD are shown in Figure 2A. It is found that the FT-IR spectrum of GO (green curve) has typical characteristics peaks — stretching of hydroxyl group at 3450 cm^{-1}, >C=O (1735 cm^{-1}), aromatic >C=C< (1622 cm^{-1}), carboxy C–O (1414 cm^{-1}), epoxy C–O (1228 cm^{-1}), and alkoxy C–O (1116 cm^{-1}) respectively; the obtained results are well in agreement with literature [26]. The FT-IR spectrum of pure β-CD (magenta curve) exhibits ring vibrations at 578, 708, 756, and 943 cm^{-1}, the coupled C—O—C stretching/O—H bending vibrations at 1156 cm^{-1}, the coupled C—O/C—C stretching/O—H bending vibrations at 1030 and 1079 cm^{-1}, $-CH_2-$ stretching vibrations at 2925 cm^{-1}, C—H/O—H bending vibrations at 1416 cm^{-1}, and O—H stretching vibrations at 3429 cm^{-1} respectively [26]. For GOCD sample, the spectrum (blue curve) shows stretching vibrations having features of both GO and β-CD with slightly peak shifts. This clearly confirms that CD molecules are attached to the surface of GO sheets. Since β-CD and GO contain multiple OH groups, the formation of strong hydrogen bonding between them is strongly supported, which is in accordance with the above FTIR data and also supporting literature reports [26,27].

Functionalization of GO to form GOCD can be circuitously asserted by comparing their relative thermal stabilities. Consequently, thermogravimetric analyses of GO and GO-CD samples were carried out and compared by TGA profiles shown in Figure 2B. It is evident that GO decomposes in three steps: the initial weight loss at around 180°C relates to the loss of physically adsorbed gases and loosely bound water molecules. The second step observed centered around 270°C is due to the loss of oxygen-containing groups while the third step involving loss above 400°C relates to loss of an unstable carbon remaining in the structure and the pyrolysis of oxygen functional groups in the main structure to yield CO and CO_2 [26,28,29]. The GO-CD shows characteristic of greater instability compared to GO. The initial weight loss is around 100°C with higher degree of weight loss around second step observed around 200-400°C- due less loss of oxygen-containing groups on being covalently bonded to β-CD molecules as well as from GO, resulting in decomposition of the composite. From the above observation, the % β-CD in GOCD calculated to be ~50% which shows much higher loading compared to available reports [9,26]. This also brings out the superiority of adopting sonochemical route over conventional thermal-stirring route as available in the literature Therefore, the above thermal study assets that GOCD is thermally less stable than GO under similar conditions which may be attributed to loss of cohesive interaction between GO sheets as a result of functionalization with β-CD during its transformation to GO-CD.

Raman spectroscopy is a good technique to characterize the structure and quality of graphene systems. We compared the Raman spectra of both GO with GOCD to further explore the extent of interactions between GO and CD in the GOCD sample, shown in Figure 2C. Generally the G band (~ 1575 cm^{-1}) and the D band (~ 1352 cm^{-1}) intensities and positions provide significant information about the defects, disorder and doping levels present in the graphene systems [26,30]. In GO, the G band (~ 1595 cm^{-1}) which is assigned to E_{2g} phonon of sp^2 C atoms, is broadened and shifted to higher frequency while the D band (~ 1342 cm^{-1}) assigned to breathing mode of κ–point phonons of A_{1g} symmetry, slightly shifts to lower frequency with increased intensity [30]; with the band intensity (D/G) ratio close to 0.957 which indicates presence of substantial amount of defects being introduced here as a result of oxidation and chemical exfoliation of graphite. In GOCD, the D/G bands' intensity ratio value further increases and approaches to

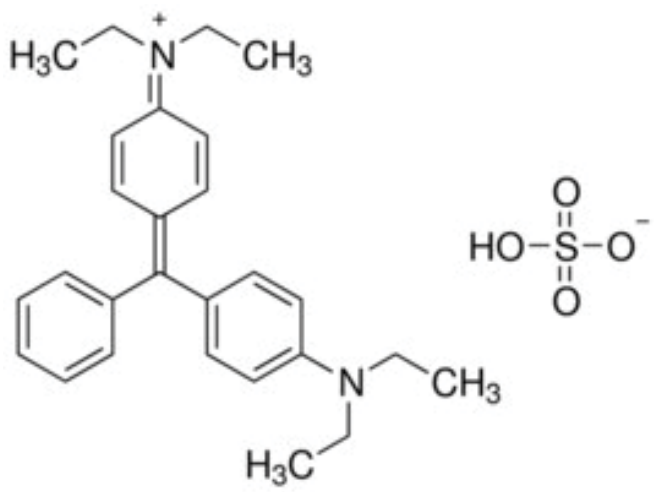

Figure 1: Chemical structure of brilliant green dye.

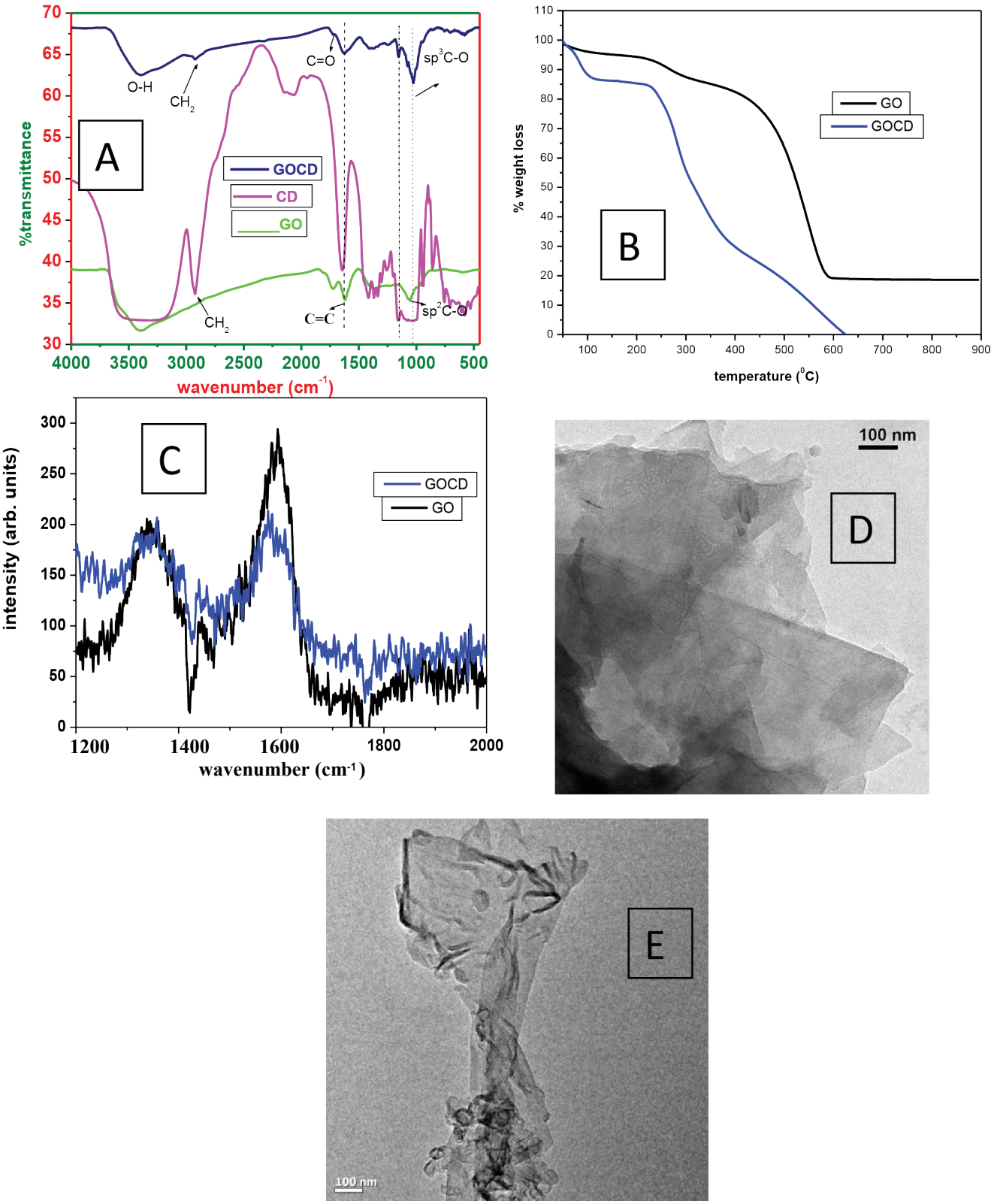

Figure 2: (A) FTIR spectra of GO, β-CD and GOCD samples; (B) TGA profiles of GO and GOCD samples; (C) Raman spectra of GO and GOCD samples; (D) and (E) TEM images of GO sample and wrinkled sheets in GOCD sample respectively.

value of 0.998, which signifies that functionalization of GO with β-CD has additionally introduced significant defects and disorders in the GO sheets, reducing the average sp^2 domain size in the GOCD sample compared to pristine GO, which is possible only when βCD molecules are in strong interactions with GO surfaces. Thus the above results further asserts the fact that β-CD are covalently linked with the GO sheets in GOCD system.

To investigate the morphology of the GO and GOCD samples, TEM studies were carried out as shown in Figures 2D and 2E respectively. We found that in the GOCD sample, the sheets are more crumpled than that in GO, which is invariably possible due to functionalization of GO to GOCD. The supramolecular inclusion complex forming ability of β-CD promoted its application in dye removal techniques [31-33]. We have explored that β-CD and GO have synergistic action on adsorption of dyes which has been reported elsewhere [34]. Accordingly, the adsorption experiments were conducted following the procedure in which the initial concentrations of BG (100 ml, 100 μM) was treated with GOCD (solid, 35 mg) and at certain time intervals (10, 20, 30, 40, 60, 90, 120, 150, 180 and 240 min), 5 mL aliquot was taken out of the 100 mL solution and processed with ultracentrifugation and then subjected to UV-vis absorption spectroscopy to measure the concentration of free dye BG at 625 nm wavelength in the supernatant solution and calculate the adsorption efficiency of the adsorbent therefrom. Figure 3A shows the UV-vis absorption spectra of neat/blank BG in aqueous medium, with max wavelength absorption centered at 625 nm. The absorption measurements were repeated at definite time intervals and observed that there was insignificant change in spectral characteristics as well as in concentration with time which signifies the fact that neat BG aqueous solution is stable in the time range of adsorption study. Figure 3B shows the variation of absorbance after addition of adsorbent GOCD to the BG aqueous solution. It is observed that just after 10 minutes of addition of the adsorbent, the absorbance of the supernatant liquid was drastically lowered, yielding a very light green solution, which gained more transparency with time. Figure 3C shows the variation of absorbance of BG in the supernatant liquid with time. It was found that the removal rate of GOCD is 91.21% which is appreciable higher compared to other available adsorbents [9]. Thus, in this case, dye removal can be done in a simpler technique, with very low concentration of adsorbent and fast removal rate, which makes it a potential adsorbent in the waste water treatment processes in the near future. To understand the adsorption mechanism of dye onto adsorbent, three kinetic models, pseudo-first-order (3), pseudo-second order (4), Elovich equations (5), were employed stated as follows [9]:

$$\ln(q_e \sim q_t) = \ln q_e - k_1 t \quad (3)$$

Where, q_t is the amount of dye adsorbed on adsorbent at different time (mgg^{-1}); k_1 is the adsorption rate constant (min^{-1}).

$$t/q_t = (1/k_2 q_e^2) + (t/q_e) \quad (4)$$

Where, k_2 is the pseudo-second-order rate constant ($g\ mg^{-1}\ min^{-1}$)

$$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t \quad (5)$$

Where α is the initial adsorption rate ($mg\ g^{-1}\ min^{-1}$) and β is the

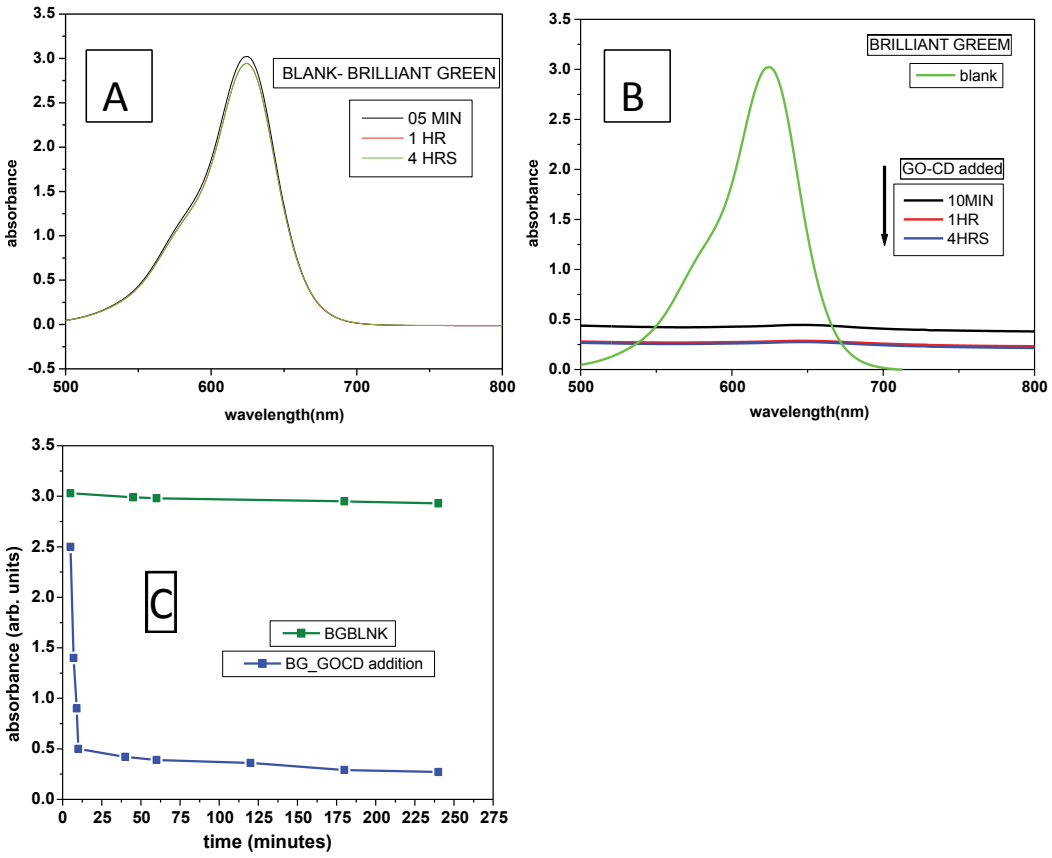

Figure 3: (A) UV-Vis absorption spectra of neat BG dye in aqueous medium with variation in time; (B) UV-Vis absorption spectra of supernatant liquid after GOCD addition with variation in time; (C) variation of absorbance of BG with time in absence and presence of GOCD adsorbent.

desorption constant (g mg^{-1}).

Further, the intra particle diffusion (6) model was considered to understand the process of

adsorption,

$$q_t = k_i t^{1/2} + l \quad (6)$$

where, k_i is the intraparticle diffusion constant and l is the effect of boundary layer thickness.

Accordingly, the above models were applied and found that the pseudo-second-order model best fits of all. Figure 4A represent the plots of variations of $\mathbf{t/q_t}$ versus time (**t**); for adsorption of BG onto adsorbent GOCD. The fitting results for the above equation was calculated and enlisted in the tabular form as inset in the graph**.** The determination coefficients R^2 of the pseudo-first-order (0.884) and Elovich model (0.9604) (not shown) are lower than that of pseudo-second-order rate model (0.995), indicating that the adsorption kinetics, in this case, follows pseudo-second-order model. From the plot, we calculated the value of q_e (the amount of dye adsorbed onto GOCD at equilibrium), was found to be 10.32 mgg^{-1} and the pseudo-second order rate constant was calculated to be 0.0102 gmg^{-1} min^{-1} respectively, quite higher than reported for other adsorbents [9,35,36].

The high removal rate and faster kinetics may be attributed to larger surface area of the GOCD adsorbent being exposed to the dyes in our adsorbent compared to available reports [9,31,32]. This is because of adoption of superior sonochemical synthetic route compared to conventional heating-stirring route which helps in better exfoliation (separation of GO layers) and interpenetration of β-CD molecules in between these GO layers and anchor on the exfoliated GO surfaces. The ultrasound energy produces ultrafast jets near the surface of large GO sheets and cut off then into smaller fragments as indicated from TEM image shown in Figure 4B. Moreover, ultrasonic aid produces local heating and provides necessary activation energy for bond formation between GO and β-CD. The TGA results also depicted higher functionalization of GO with CD compared to that reported in the literature by other synthetic procedures [9,27]. Thus the synergistic effects of both GO (by virtue of its opposite polarity with that of BG dye) and β-CD, (by virtue of hydrophobic interactions between BG and CD) in the material GOCD, accelerates the removal of BG from the medium. Moreover, dispersive nature of GO could be modified by anchoring β-CD, which helped in faster and prompt separation of phases, which is very essential in treatment processes.

To further understand the dye adsorption progress, the intraparticle diffusion model was employed to analyze the diffusion mechanism of MB. The plot of $\mathbf{q_t}$ **vs.** $\mathbf{t^{1/2}}$ shown in Figure 4C, is found to be non-linear throughout the entire time range, indicating that the key step determining MB adsorption onto GOCD is not the

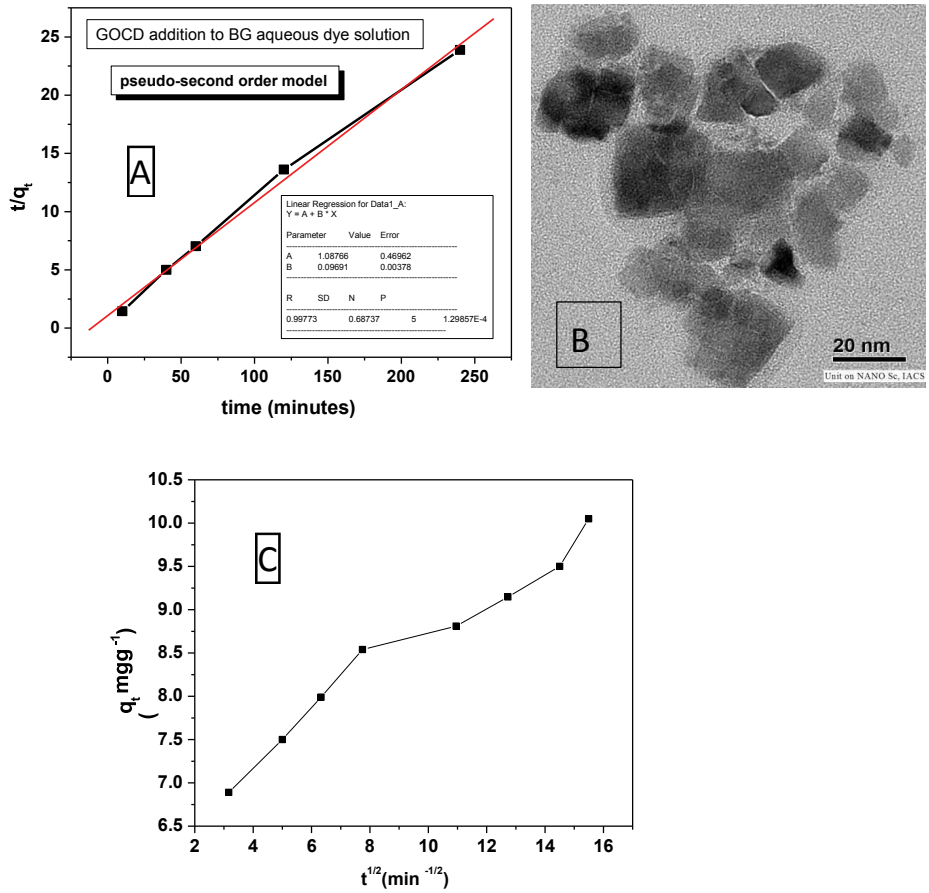

Figure 4: (A) Pseudo-second order model fitting curves; (B) shows TEM image showing ultrasound effect on GO sample; (C) inter-particle diffusion kinetic model applied for adsorption of BG dye onto adsorbent GOCD.

intraparticle diffusion process, in which the dye molecules gradually diffuses from the surface into the adsorbent interior [37]. So, it may be adsorbed superficially which brings up possibilities of recycling of these dyes from the adsorbent. It's worth mentioning that recycling of soluble organic dyes from wastewater not only solves an environmental problem, but also saves reusable resources as well as reduces industrial cost. Hence, we investigated the recycling rate of BG onto GOCD from the BG-GOCD complexes. BG was then recycled from the BG-GOCD residues using absolute alcohol using ultrasound energy for 5 minutes. We reused the recovered GOCD residues for further MB adsorption and on recycling, found that the recycling rate was around 60%, even after 3 times of reuse of GOCD.

Thus, in this work, Beta-Cyclodextrin functionalized Graphene Oxide (GOCD) was successfully prepared by adopting a green, simple and inexpensive sonochemical method. The material was well characterized and its adsorption for brilliant green (BG) dye adsorption was found to follow pseudo-second order kinetics. It exhibited high removal rate and good recyclability which thereby makes it a promising material for the purification of wastewater and recycling of water soluble dyes efficiently.

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