

1 Grape extract assisted green synthesis of reduced graphene oxide 2 for water treatment application

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15 16 **Abstract**

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18 Grapes (*Vitis Vinifera*) extract was explored as a “green reducing agent” for the preparation
19 of reduced graphene oxide (RGO) from graphene oxide (GO). The effect of reduction time on
20 physical, chemical and optical properties of the RGO was also investigated. Synthesized RGO
21 samples exhibited excellent activity as an adsorbent for the removal of organic dye. Proposed
22 synthesis is environmental friendly, cost effective and seems promising for the large scale
23 production of RGO.
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25 **Keywords:** Carbon materials, X-ray techniques, green synthesis, reduced graphene oxide,
26 grapes extract
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32 **1. Introduction**

33 Graphene, owing to its exotic physical and electrical properties has led the recent advances in
34 material sciences and is finding its way into various fields including electronics, biomedical,
35 environment and engineering [1]. Chemical reduction of graphene oxide (GO) is one of the
36 highly explored synthesis approaches for the graphene preparation. The synthesis approach
37 involves oxidation of graphite via Hummers method followed by chemical reduction using
38 harsh chemical reducing agents e.g., hydrazine [2] and NaBH₄ [3]. The involvement of
39 hazardous chemical reducing agents in the second step is a major drawback and ongoing
40 efforts are there to find environment friendly and safe green reducing agents.
41 Environmentally benign reducing agents such as ascorbic acid [4], sugar [5], amino acids [6]
42 and plant extracts [7, 8] have recently been utilized for the reduction of GO to reduced
43 graphene oxide (RGO). Plant extracts are attractive alternatives to the toxic chemical
44 reducing agents as these are easily available, comparatively cheap and environmental
45 friendly.

46 Grapes (*Vitis vinifera*) extract is a rich source of phytochemicals e.g., polyphenols,
47 flavonoids and catechins, which are capable of reducing gold and silver salts to their metallic
48 form [9]. Apart from preparation of metal nanoparticles, grapes extract has also shown
49 remarkable performance as a reducing agent for the selective reduction of ketone [10] and
50 nitro compounds [11]. These reports confirm that grapes extract holds immense potential as a
51 reducing agent. The phytochemicals present in the grapes extract are of great medicinal value
52 and also environmentally benign, which makes these an attractive alternative to the
53 conventional toxic reducing agents.

54 **2. Experimental**

55 Graphite LR was procured from Alfa Aesar. Fresh grapes were purchased from local
56 market. De-ionized water was used in the preparation of all the solutions.

57 Graphene oxide was prepared using modified Hummers method [12-14]. Typically, 1
58 gm of graphite and 23 ml of concentrated H₂SO₄ were taken in a conical flask and the
59 reaction mixture was placed on an ice bath. About 3 g of KMnO₄ was slowly added to the
60 reaction mixture under constant stirring at temperatures of 0-5°C and was further stirred for
61 another 30 minutes. The flask was then transferred on a hot plate with a preset temperature of

62 35°C, and kept for 1 hour. After completion of heating period, 46 ml of de-ionized water was
63 added to the reaction mixture followed by vigorous stirring. As obtained reaction mixture was
64 then further heated on a boiling water bath for 30 minutes. 10 ml of 30% H₂O₂ was added to
65 the reaction mixture to stop the reaction, followed by addition of 140 ml of de-ionized water.
66 Yellow colour graphene oxide was obtained which was filtered and washed repeatedly using
67 10% HCl followed by de-ionized water and ethanol.

68 40 gm grapes were crushed and transferred in to a round bottom flask containing 100
69 ml de-ionized water. As prepared reaction mixture was heated up to boiling and allowed to
70 boil for 10 minutes. After completion of heating the reaction mixture was allowed to cool
71 down to room temperature and filtered to obtain a red colour extract. 30 mg GO was added to
72 the 50 ml extract and stirred vigorously in order to disperse the GO uniformly throughout the
73 extract. 180 µl aqueous NH₃ solution was added to the above reaction mixture, which
74 changed the colour of it from red to dark green. Reaction mixture was placed on an oil bath
75 and heated at 95°C for different time intervals (1, 3 and 6 hours) with a water condenser to
76 avoid the evaporation of water. After completion of heating periods, the RGO samples were
77 filtered, washed and dried in an air oven at 70°C.

78 UV-Vis spectra aqueous dispersion of GO and RGO samples were recorded using
79 UV-Vis spectroscopy (Thermo Scientific Evolution 201). X-ray analysis was performed
80 using Rigaku miniflux X-ray diffractometer (XRD). Morphology and structure of RGO was
81 investigated using transmission electron microscope (TEM, TECNAI G²20 S-TWIN).

82 20 mg RGO-6hrs was added to the 100 ml malachite green solution (5 ppm). A fixed
83 volume of the dye solution was taken out after regular time intervals and centrifuged for the
84 removal of RGO. Absorbance for all extracted dye samples was recorded at 617 nm.
85 Removal percentage was estimated by using the following formula [15].

86 Removal percentage = $(A_0 - A_t) / A_0 \times 100$ (1)

87 Where A₀ is the initial absorbance of dye and A_t is absorbance after a time interval 't'. The
88 adsorption amount q_t was calculated using following equation [16]:

89 $q_t = [(C_0 - C_t) V] / m$ (2) ~~16~~

90 Where q_t is the amount of adsorbed dye per gram of the adsorbent (mg/g), C_0 and C_t are the
91 concentrations of the MG solution (mg/L) at the initial and adsorption time t , respectively. V
92 is the volume of the MG solution (L) and m is the mass of the adsorbent (g) used.

93 3. Results and discussion

94 The UV-Vis spectrum of GO (Fig. 1a) exhibits a peak at 230 nm and a shoulder peak
95 at 300 nm. The peak at 230 nm can be corresponded to π - π^* transitions of aromatic C=C,
96 while the shoulder peak originates from n - π^* transition of the C=O bonds [17]. The
97 absorption spectra of RGO samples (Fig. 1b) exhibit a single peak around 270 nm. This red
98 shift in the absorption spectrum from 230 to 270 nm points towards the restoration of sp^2
99 hybridized carbon network due to removal of the oxygen bearing functional groups. An
100 increase in the absorbance around 600 nm on increasing the reduction time from 1 to 6hrs has
101 also been observed (Fig. 1b).

102 The FTIR spectrum of GO (Fig.1c) comprises of a broad peak at 3180 cm^{-1} and a
103 sharp peak at 1615 cm^{-1} , which can be ascribed to stretching and deformation vibrations,
104 respectively of physically adsorbed water. Peaks at 1715 , 1360 and 1040 cm^{-1} can be
105 corresponded to C=O, COO^- and C-O stretching vibrations, respectively. However, with the
106 increase in the reduction time the intensity of these peaks reduced significantly and after 6 hrs
107 of reaction time, most of the peaks assigned to oxygen containing groups almost disappeared
108 (Fig.1c), confirming the efficient reduction of GO by the grapes extract.

109 The XRD-diffraction pattern of graphite exhibits one sharp basal reflection peak at 2θ
110 value of 26° (d-spacing of 0.357 nm) corresponding to (002) plane (Fig. 2a). Oxidation of
111 graphite to graphene oxide results in a shift in this peak towards lower 2θ value 10.4° (d-
112 spacing 0.850 nm). This large increase in the d-spacing indicates the intercalation of water
113 molecules as well as formation of oxygen containing functional groups in between the
114 graphite layers. In the case of RGO-6hrs sample, the sharp peak at 10.4° disappeared,
115 however, a broad peak at approximately similar same 2θ value can still be observed
116 suggesting the presence of residual oxygen functionalities in the sample. Simultaneously, sa
117 new another new broad peak, centred at 23.7° , was also observed can also be seen indicative
118 of the formation of few layered graphene structure indicating formation of few layers of
119 graphene [18, 19]. The transmission electron microscopy TEM image of RGO-6hrs sample
120 shows that the sample consists of aggregated and wrinkled few layers of graphene. These

121 wrinkles and corrugations endow thermodynamic stability to the two-dimensional graphene
122 sheets.

123 | For dye absorption experiments, 20 mg RGO was utilized to treat 100 ml malachite
124 green solution (5 ppm). A sharp decrease in the absorbance for the initial 5 minutes indicates
125 that most of the dye was removed in first 5 minutes (Fig. 3). Graph plotted between removal
126 percentage and time (Fig. 3 inset) shows that for all the samples (GO, RGO-1hr, RGO-3hrs
127 | and RGO-6hrs) most of the dye has been removed in first 10 minutes, -after which the wards
128 adsorption process achieved equilibrium. The order of removal percentage in the first 10
129 minutes for all the samples was found to be following:

130 GO <RGO-6hrs <RGO-1hr~RGO-3hrs

131 | The removal percentage of the GO was found to be lowest as compared to compare to the
132 RGO-1hr, RGO-3hrs and RGO-6hrs samples. We believe that ~~the~~ reason behind the lowest
133 removal percentage for the GO might be the presence of trace amount of GO which leftover
134 in the dye solution after centrifugation.

135 Pseudo second order kinetic was applied in order to analyze the kinetic data, which can be
136 defined using following equation:

$$137 \quad t/q_t = 1/(K_2q_e^2) + t/q_e \quad (3) [16]$$

138 Where q_t and q_e are the amounts of adsorbed malachite green on the adsorbent (g/mg) at time
139 t and at equilibrium respectively, and K_2 is the pseudo-second order rate constant ($\text{gmg}^{-1}\text{min}^{-1}$).
140 Fig.S2 shows the graph between q_t and time, it can be seen from the graph that in the
141 initial 5 minutes adsorption is fast and afterward the rate of the adsorption has been reduced
142 and achieved equilibrium. Fig.S3 depicts graph showing values of the t/q_t plotted as a
143 function of time. The value of correlation coefficient (R^2) is around 0.999 for all the samples
144 suggesting suitability of second order kinetics model for explaining adsorption kinetics of
145 MG dye on GO and RGO samples.

146 4. Conclusions

147 An environmental benign, economical and facile synthesis approach for the preparation of
148 reduced graphene oxide has been demonstrated. Aqueous extract of grapes (*Vitis Vinifera*)
149 has been successfully utilized for the reduction of GO. An increase in the reduction time
150 increased the extent of reduction also. Owing to the ease of availability of grapes worldwide,
151 the developed synthesis methodology can be adopted for the large scale production of RGO.

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201 **Figure captions**

202 Figure 1 (a) UV-Vis spectrum of GO and real pictures of GO and RGO aqueous suspension
203 (Inset) (b) UV-Vis spectra of RGO samples (c) FTIR spectra of GO and RGO samples.

204 Figure 2 (a) XRD of Graphite, GO and RGO-6hrs (b) TEM image of RGO-6hrs sample

205 Figure 3 Removal of Malachite green dye using RGO-6hrs sample and graph showing change
206 in the removal percentage with time for GO, RGO-1hr, RGO-3hrs and RGO-6hrs samples
207 (Inset)

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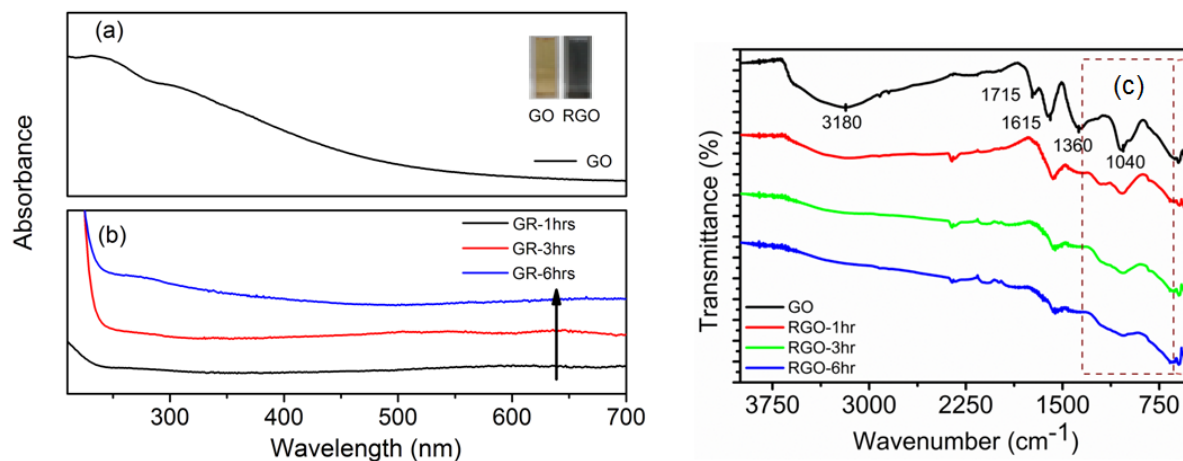
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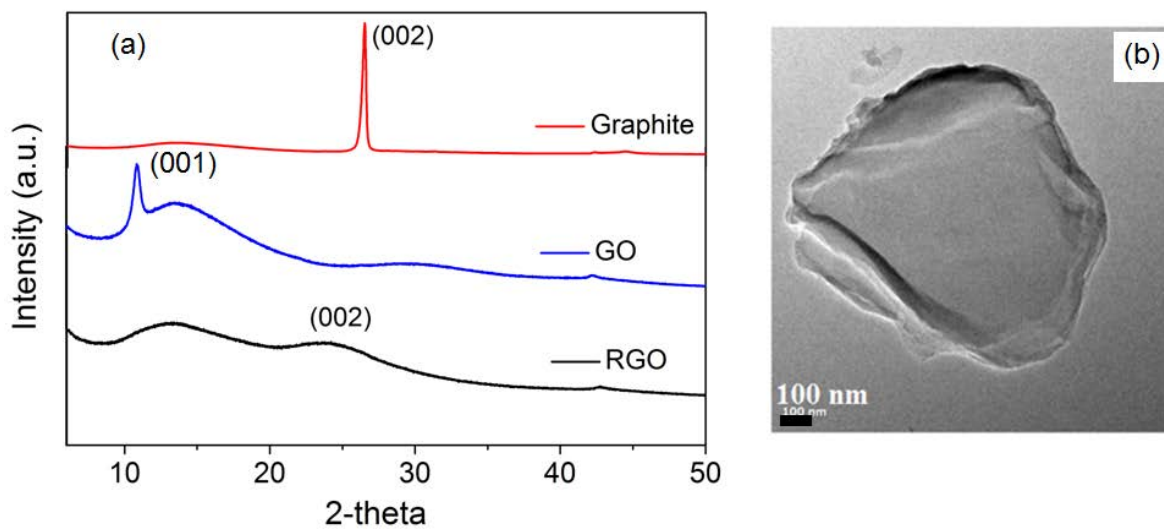
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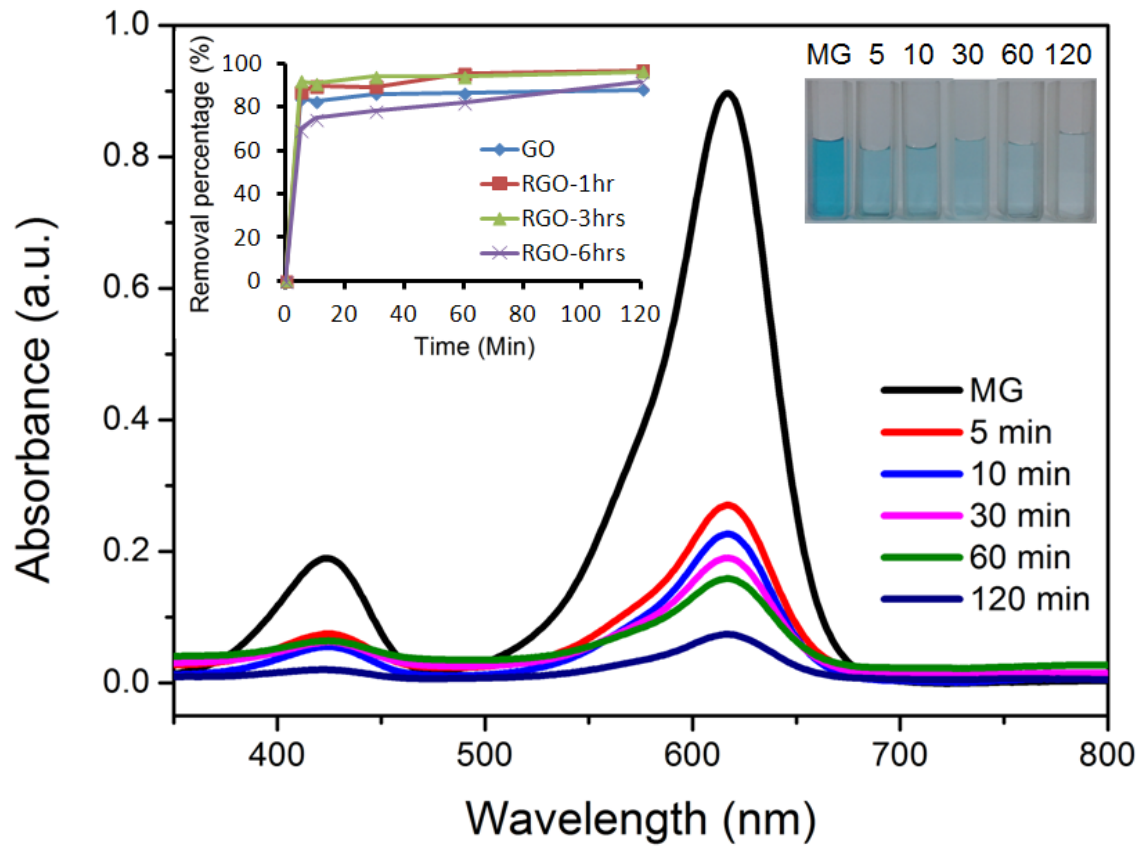
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Figure 4 (a) XRD of Graphite, GO and RGO-6hrs (b) TEM image of RGO-6hrs sample



250

251 Figure 5 Removal of Malachite green dye using RGO-6hrs sample and graph showing change
 252 in the removal percentage with time for GO, RGO-1hr, RGO-3hrs and RGO-6hrs samples
 253 (Inset)