

# Synthesis and characterization of graphene oxide sheets integrated with gold nanoparticles and their applications for adsorptive removal and catalytic reduction of water contaminants

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## Materials

Graphite powder (99.9%), sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , 99.5%), gold (III) chloride tri hydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 99.9%) were purchased from sigma-aldrich. Malachite green (MG, 90%) and ethyl violet (EV, 90%) dye and the aromatic pollutant 2-nitroaniline (2-NA, 98%) were purchased from Aldrich chemicals and used without further purification. Sodium borohydride ( $\text{NaBH}_4$ , 98%) powder was purchased from sigma-aldrich. Double distilled water (DDW) was used for cleansing of apparatus and solution preparation.

## Synthesis of GO-Au nanocomposites

Firstly, GO was prepared from graphite powder by using modified hummers method as reported in the previous literature. Briefly, 30 mg of GO was dispersed in 50 ml of DDW in an ultrasonication bath for 1 hour to exfoliate the GO sheets. Then 10 ml of 10 mM  $\text{HAuCl}_4$  solution was added into GO solution and kept on stirring for 30 min in order to promote the interaction of gold ions with GO sheets. Next, 10 ml of sodium citrate solution was added under magnetic stirring and the temperature was increased to 80 °C. The reaction mixture was heated at this temperature for 1 hour for the formation of Au nanoparticles on GO sheet. At the end of reaction time, the prepared nanocomposite was separated from reaction medium by centrifugation. The obtained nanocomposite was re-dispersed in DDW and centrifuged again and this process was repeated many times to remove the unreacted species attached with the prepared GO-Au nanocomposite. Finally, nanocomposite was dried in an oven at 60 °C for 12 hours.

## Adsorption experiment

The efficiency of GO and GO-Au nanocomposite as an adsorbent was studied by batch method. Effects of pH, initial concentration of dyes, and temperature were studied. The adsorbed amount was calculated from the following equation.

$$q_t = (C_o - C_t) V/m \quad (1)$$

Where,  $C_o$  and  $C_t$  are the liquid phase concentrations ( $\mu\text{M}$ ) of aqueous solution of dye at zero time and  $t$  time, respectively.  $V$  is the volume of solution (L) and  $m$  is the mass of adsorbent (g).

First of all, adsorption capacity of GO was studied by using its 0.005 g as adsorbent in 10  $\mu\text{M}$ , 50 ml aqueous solution of each of MG and EV dye. The solutions were stirred at stirring speed of 100 rpm. The temperature of the adsorption medium was maintained at 30 °C with the help temperature controlled oil bath. After every three minutes, almost 2 ml of the sample was withdrawn from reaction mixture, measured its absorbance and added back into the reaction medium. The adsorption process was continued for 45 minutes.

To study the effect of pH, 5  $\mu\text{M}$  aqueous solutions of MG and EV were used. To adjust pH, 50 ml of each of MG and EV (with initial concentration of 5  $\mu\text{M}$ ) was taken in separate conical flasks. Aqueous solutions of 0.1 M HCl and 0.1M NaOH were used to adjust pH in acidic and basic ranges, respectively. Once the pH was adjusted, 5 mg of GO-Au nanocomposite was added in each solution as adsorbent and the solutions were stirred at stirring speed of 100 rpm in temperature controlled water bath. After predetermined time intervals, 2 ml of sample was taken out from reaction mixture, measured its absorbance and added the sample back into the reaction mixture. The adsorbed amount ( $q_t$  in mg/g) of each dye was calculated from equation (1). The effect of initial concentration of dyes was investigated by conducting adsorption experiments with different initial concentrations of MG and EV. For each dye, aqueous solutions with four different initial concentrations; 3, 5, 7, and 10  $\mu\text{M}$  were prepared. A 50 ml solution of each concentration was taken in conical flask and 5 mg of GO-Au nanocomposite was added in it as adsorbent. The adsorption was allowed to occur at constant stirring speed of 100 rpm in temperature controlled water bath. The effect of different amounts of adsorbent was also investigated by using different amounts of adsorbents; 3, 5, and 7 mg for 50 ml solution of each dye with initial concentration of 5  $\mu\text{M}$ . Finally, the effect of temperature was studied by conducting adsorption experiments at 25, 30, 35, 40 and 45 °C. At each temperature, adsorption

experiment was conducted with 5  $\mu\text{M}$ , 50 ml aqueous solution of each of MB and EV using 5 mg of GO-Au as adsorbent. The adsorption mixture was stirred at 100 rpm for 45 minutes. The amount of dye adsorbed was calculated from the difference in absorbance of adsorbate solution before and after adsorption process. To study the adsorption kinetics, 50 ml, 7  $\mu\text{M}$  solutions of each dye were taken in separate conical flasks and 5 mg of adsorbent was added in each flask and solutions were stirred at a stirring speed of 100 rpm at room temperature. Aliquots of 2 ml were taken out after every three minutes for the first fifteen minutes and then after every 6 minutes for rest of 20 minutes. After measuring the absorbance of sample, the samples were added back to the reaction medium. The obtained adsorption data was treated with pseudo first order and pseudo second order kinetics models.

### **Desorption studies**

Desorption study is very significant as the regeneration of adsorbent governs its commercial accomplishment. Desorption of both the dyes was studied in two different mediums; ethanol and 0.1M HCl. The GO-Au nanocomposite accumulated with MG or EV dye was separated from adsorption medium, washed with water and placed in 50 ml of ethanol or 50 ml of 0.1M HCl. Desorption of dyes was allowed to occur for 30 minutes with constant stirring at stirring speed of 100 rpm. The amount of each dye desorbed was measured from the concentration of that dye in the desorption medium. The concentrations of dyes in desorption medium was calculated in terms of absorbance measurement by UV-Vis spectrophotometer.

### **Catalytic test**

The catalytic performance of prepared GO-Au nanocomposite was investigated by using it as a catalyst for the reduction of 2-NA. In a typical run, to a 50 ml, 0.5 mM aqueous solution of 2-NA containing 0.1g of  $\text{NaBH}_4$  as reducing agent, 5 mg of GO-Au nanocomposite was added as catalyst to initiate the reaction. During the reaction, about 1ml sample was withdrawn from the reaction mixture after specific time intervals and their absorption spectra were by UV-Visible spectrophotometer. The decrease in absorption intensities for the nitro compound was monitored at 410 nm and the corresponding reduction rate constants at different initial amount of catalyst were calculated. The reduction reaction was carried out at three different temperatures to investigate the effect of temperature and to calculate the activation energy of the reduction

reaction. The reusability of the catalyst was studied by using the same catalyst for 3 times in the reduction process. After every run, the catalyst was separated from the reaction mixture, washed with DDW and used again.

## **Characterization**

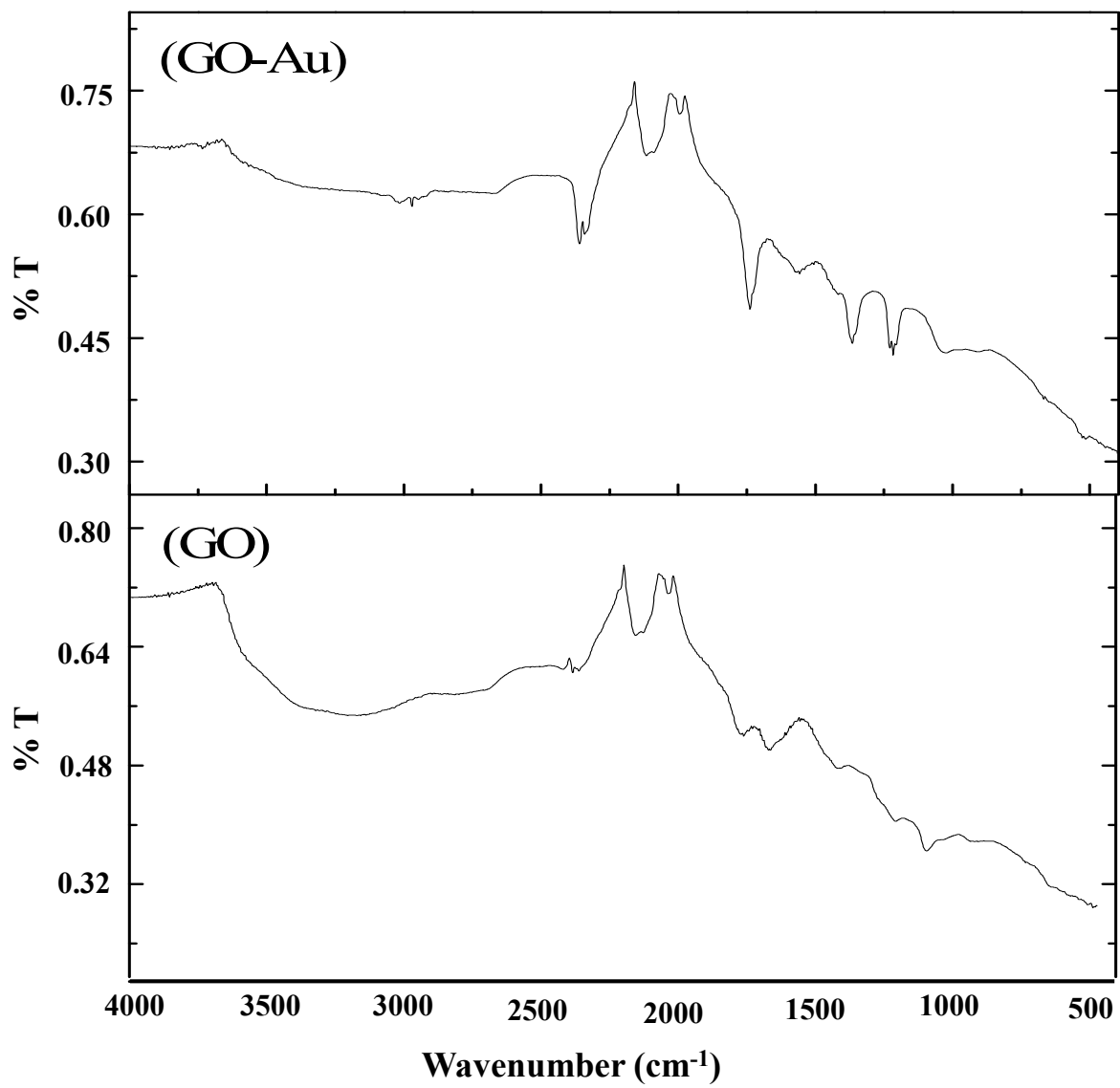
Following techniques have been employed in this work for the characterization of synthesized material. For phase identification, XRD pattern of GO-Au nanocomposite was recorded with Shimadzu XRD-6000 (Cu K $\alpha$  radiation  $\lambda=0.154\text{nm}$ ) in  $2\theta$  range from  $5^\circ$  to  $80^\circ$  at a scan rate of  $8^\circ \text{ min}^{-1}$ . To study the morphology and particle size of the prepared nanocomposite FE-SEM image was recorded with FESEM-Hitachi S4800 scanning electron microscope. For SEM images, samples of GO and GO-Au were prepared by placing a 1 cm-diameter drop of dilute GO suspension on a  $1 \times 1$  cm section of silicon wafer by a carbon tap and allowing the solvent to evaporate. The wafer was then attached to an aluminum sample holder with conductive carbon adhesive. The samples were coated with 2-3 nm of iridium to ensure good conductivity. Elemental analysis was carried out with EDX attached to FE-SEM. Sample used for SEM was simultaneously used for recording EDX spectra. TEM Hitachi Tecnai G20 was used to take TEM image of Au nanoparticles integrated on GO sheet. For TEM, GO-Au sample was first sonicated in methanol for 30 minutes then a diluted drop of that sample was placed on carbon grid, dried overnight, and then TEM image was recorded. Thermogravimetric analysis (TGA) was performed by Mettler toledo thermogravimetric analyser under a nitrogen atmosphere and heating rate of  $10^\circ \text{C min}^{-1}$ . UV-Vis spectra were recorded by UV-1700 UV-vis spectrophotometer (Shimadzu) to monitor the adsorption of dyes and catalytic reduction of dyes and nitro compounds in their aqueous solutions. FT-IR spectra of nanocomposite and dye loaded nanocomposite were performed using FT-IR spectrometer [Brooker tensor II, Germany in the range of  $4000\text{-}600 \text{ cm}^{-1}$ ]. For recording FT-IR spectra, sample were first dried and obtained in powder form. Dried powder form of samples was used to record FT-IR spectra.

**Supporting Table T1:** Thermodynamic parameters for the adsorption of malachite green and ethyl violet on graphene oxide-gold nanocomposite. [ $\Delta G$  = Gibbs free energy change,  $\Delta H$  = enthalpy change,  $\Delta S$  = entropy change, Reaction conditions; Aqueous solution 5  $\mu\text{M}$  EV or 5  $\mu\text{M}$  MG = 50 ml, graphene oxide-gold nanocomposite adsorbent = 5 mg, 100 rpm].

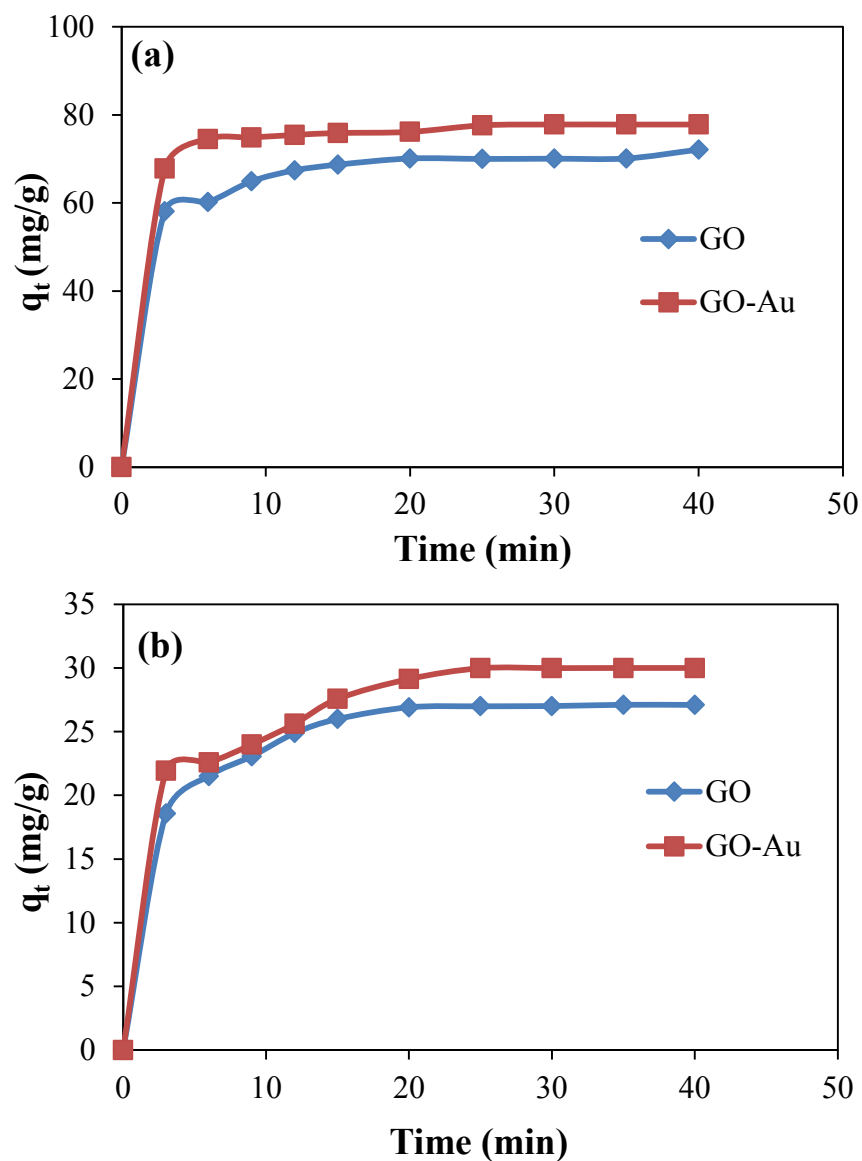
<b>Dyes</b>	<b><math>-\Delta G</math> (kJ/mol)</b>					<b><math>\Delta H</math> (J/mol)</b>	<b><math>\Delta S</math> (J/mol.K)</b>
	298K	303K	308K	313K	318K		
malachite green	9.7	10	10.79	11.09	11.6	17.60	91.77
ethyl violet	6.8	7.24	7.45	7.93	8.18	15.07	73.12

**Supporting Table T2:** Kinetic parameters for the adsorption of malachite green and ethyl violet on to the GO-Au nanocomposite. [ $k_1$  = rate constant for pseudo first-order kinetics,  $k_2$  = rate constant for pseudo-second order constant,  $q_e$  = amount of adsorbate adsorbed at equilibrium condition,  $R^2$  = coefficient of determination, Reaction conditions; Aqueous solution 7  $\mu$ M EV or 7  $\mu$ M MG = 50 ml, GO-Au nanocomposite adsorbent = 5 mg, 100 rpm, 30 °C].

Kinetics	Parameters	Dyes	
		Malachite green	Ethyl violet
<b>Pseudo-first order Model</b>	$k_1$ ( $\text{min}^{-1}$ )	0.1766	0.116
	$q_e$ (mg/g)	16.71	17.29
	$R^2$	0.7924	0.9506
<b>Pseudo-second order Model</b>	$k_2$ (g/mg min)	0.0356	0.0054
	$q_e$ (mg/g)	50.76	20.12
	$R^2$	0.9945	0.9943

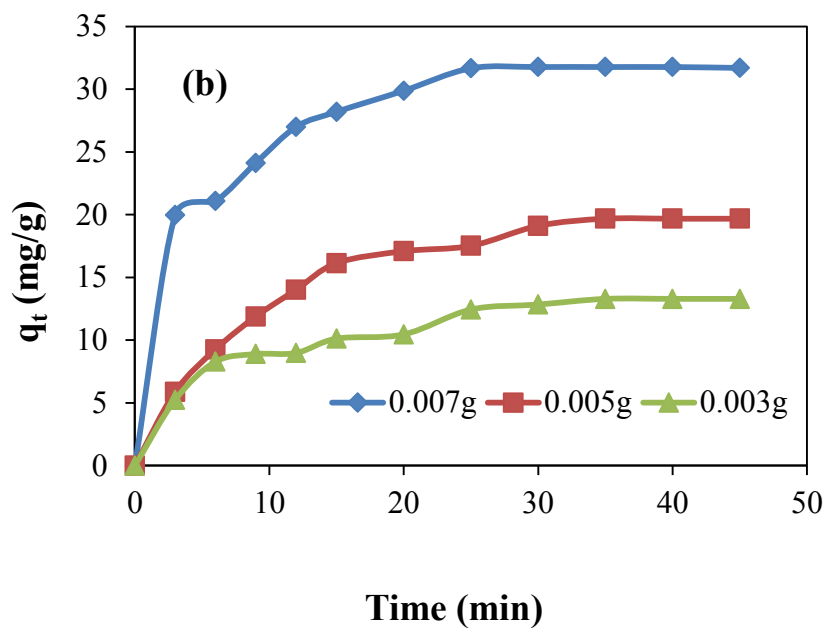
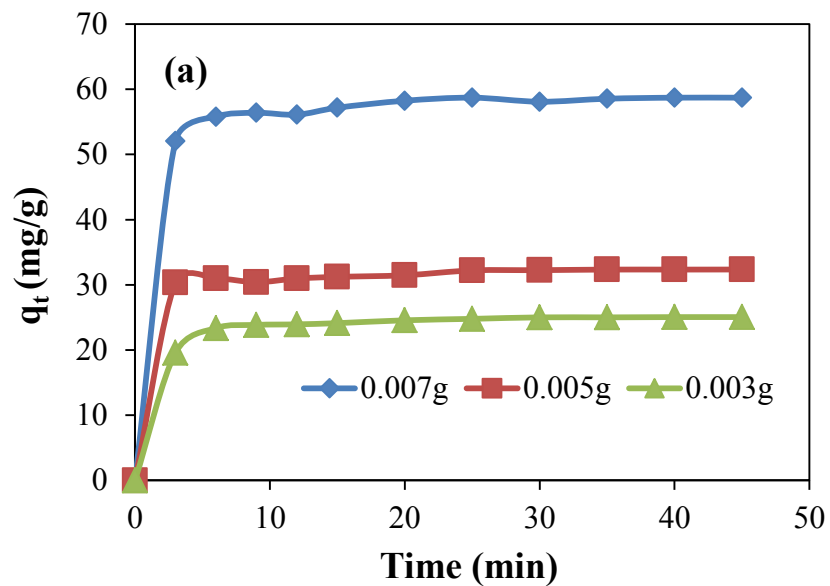


**Supporting Figure S1:** Fourier transform infra-red spectra of graphene oxide and graphene oxide-gold nanocomposite.

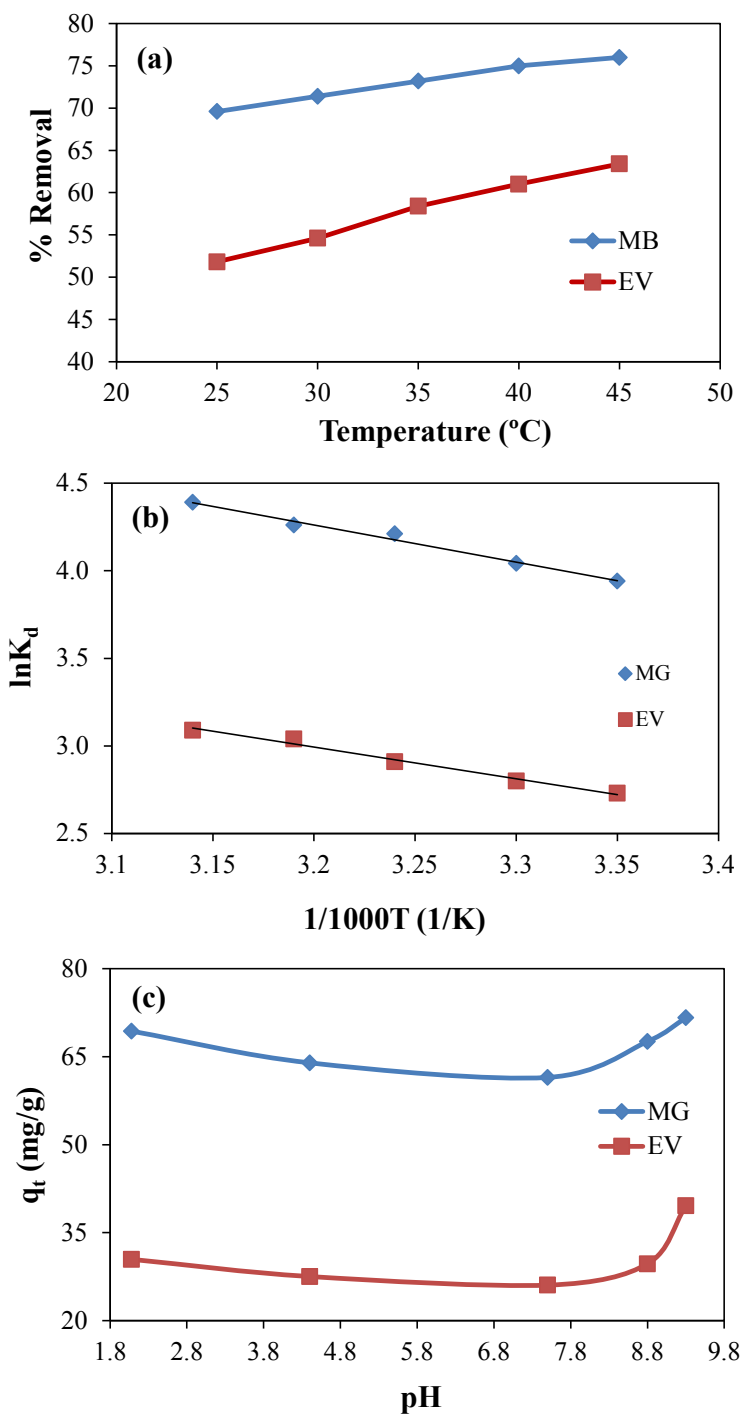


**Supporting Figure S2.** Comparative graphs for the adsorption of (a) malachite green, and (b) ethyl violet on graphene oxide and graphene oxide-gold nanocomposite. Reaction conditions; adsorbent = 0.005 g, 10  $\mu$ M aqueous solution of each dye = 50 ml, 100 rpm, 25  $^{\circ}$ C.

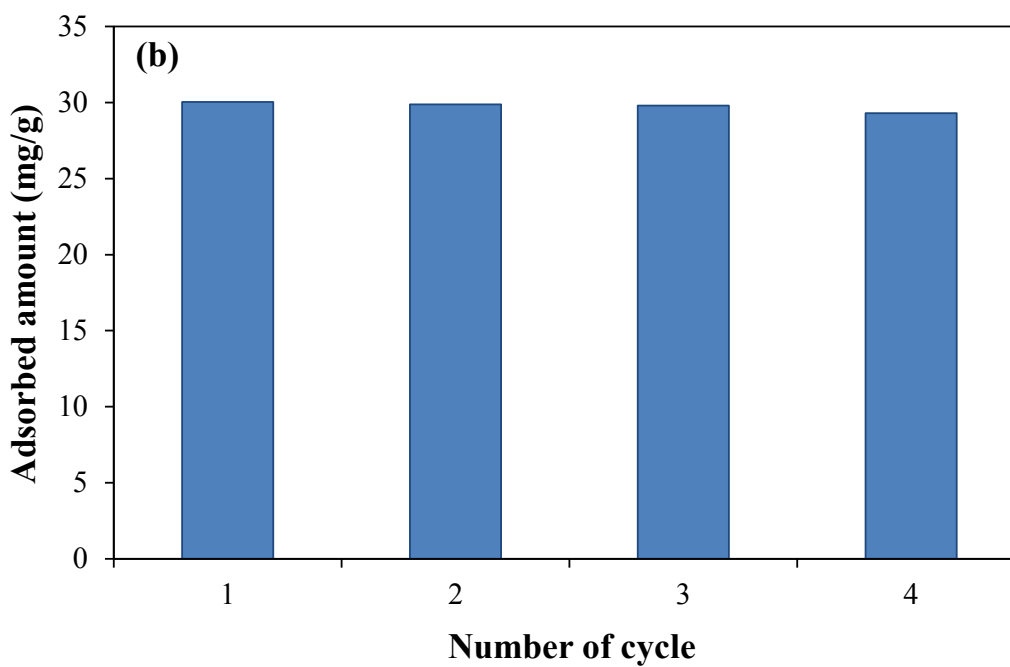
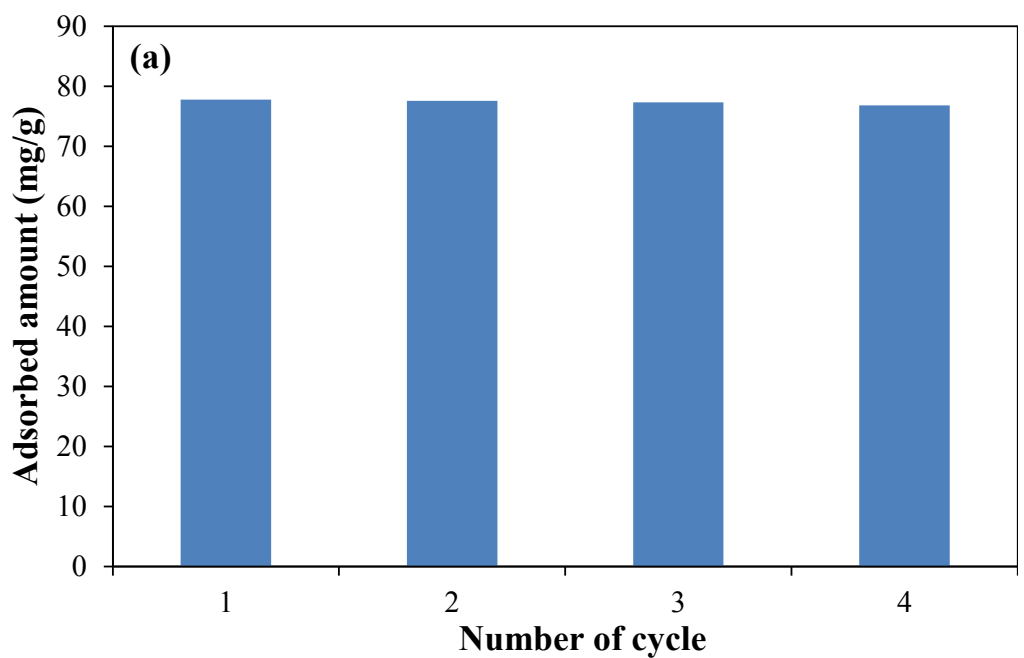




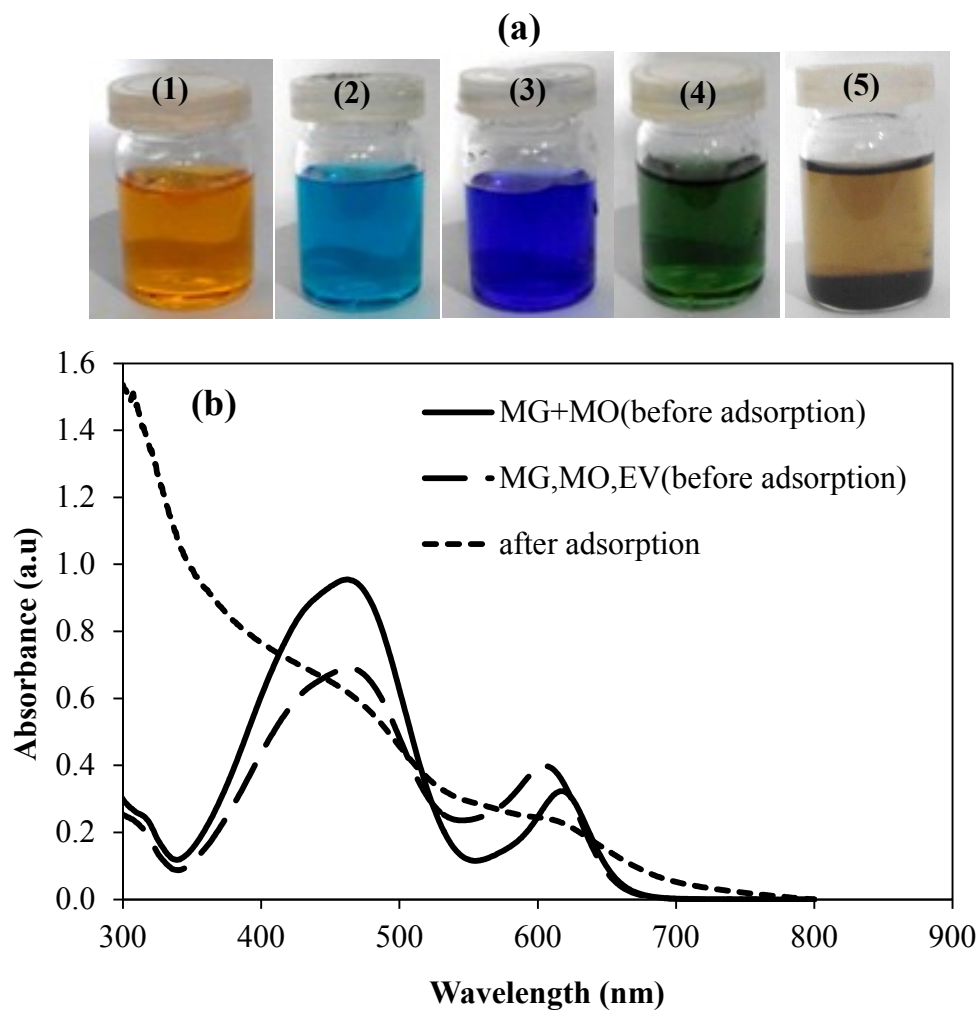
**Supporting Figure S3:** Effect of different amounts of nanocomposite on the adsorbed amount of (a) malachite green and (b) ethyl violet. [ $5\mu\text{M}$  solution of each dye = 50 ml, 100 rpm,  $30\text{ }^\circ\text{C}$  temperature].



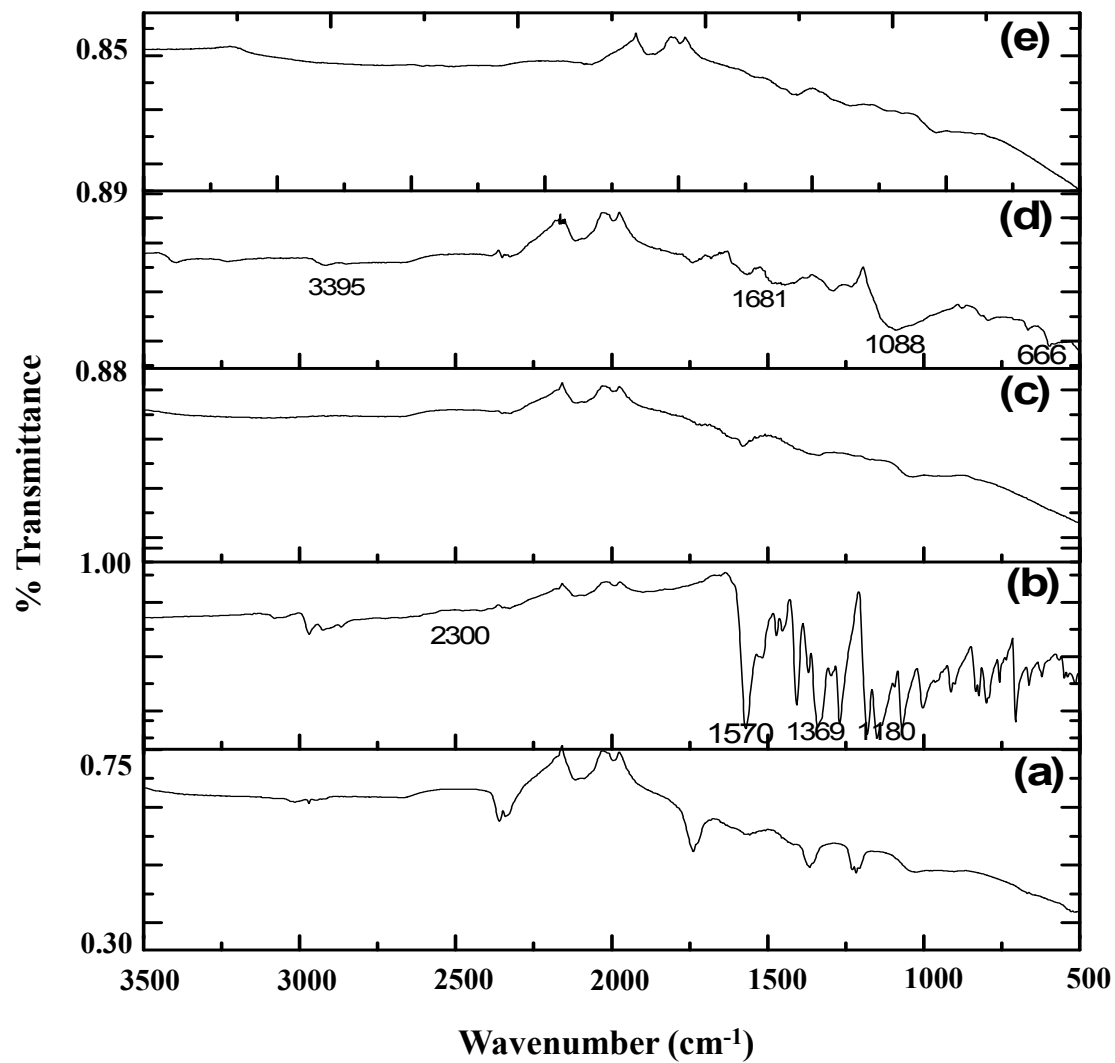
**Supporting Figure S4:** (a) Effect of temperature on the % removal of malachite green and ethyl violet. (b) Van't Hoff plot (c) Effect of pH for the adsorption of malachite green and ethyl violet on graphene-gold nanocomposite at 30 °C. [5 $\mu$ M solution of each dye = 50 ml, 100 rpm, 5 mg graphene-gold nanocomposite adsorbent].



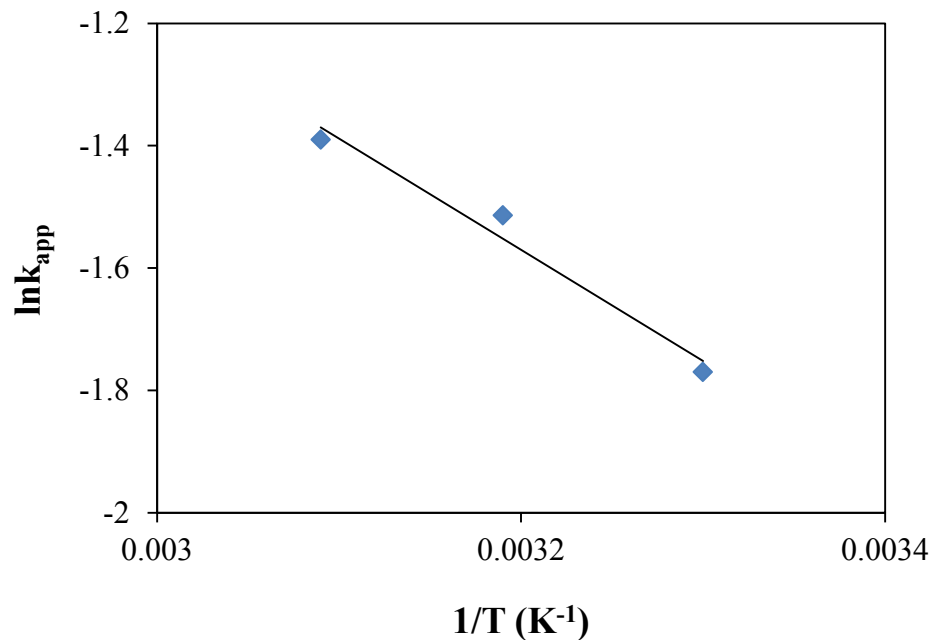
**Supporting Figure S5:** Change in adsorption capacity of graphene oxide-gold nanocomposite for (a) malachite green and (b) ethyl violet in four successive cycles. [ $5 \mu\text{M}$  solution of each dye = 50 ml, adsorbent = 0.005 g, 100 rpm, 30 °C, Desorption medium for malachite green = 0.1M HCl, Desorption medium for ethyl violet = ethanol].



**Supporting Figure S6:** (a) Photographs of aqueous solutions of (1) methyl orange, (2) malachite green, (3) ethyl violet and their mixture (4) before and (5) after adsorption on graphene oxide-gold nanocomposite. (b) Absorption spectra of mixture of methyl orange, malachite green and ethyl violet before and after adsorption.



**Supporting Figure S7:** Fourier transform infra-red spectra of (a) graphene oxide-gold nanocomposite, (b) ethyl violet, (c) graphene oxide-gold nanocomposite containing ethyl violet after adsorption, (d) malachite green, (e) graphene oxide-gold nanocomposite containing malachite green.



**Supporting Figure S8:** Arrhenius plot for the determination of  $E_a$  for the catalytic reduction of 2-Nitroaniline using graphene oxide-gold nanocatalyst. Reaction conditions; 0.5 mM aqueous solution of 2-Nitroaniline = 50 ml,  $\text{NaBH}_4$  = 0.1 g, graphene oxide-gold catalyst = 5 mg, 100 rpm.