Supporting Information

Surface tailored graphene oxide paper: An efficient filter for dye pollutants

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Experimental section

Graphene oxide (GO) synthesis

GO was synthesized by modified Hummers method using graphite powder as the precursor. In the synthesis process, 1 gm of graphite, 61.86 g of H_2SO_4, and 0.7578 g of $NaNO_3$ are mixed and stirred at 520 *rpm* in a beaker on an ice bath. Then, 0.5048 g of $KMnO_4$ (99% pure) was constantly added over a duration of 1 h. The cooling of the solution is continued for 2 h and the mixture was kept with gentle stirring at 290 *rpm* for 5 days. The mixture of GO thus obtained is added to 100 ml of H_2SO_4 (5 wt% aqueous solution) for about 1 h aided by stirring and the mixture is further stirred for 2 h. 3 gm of 30 wt% H_2O_2 aqueous solution was added to the above mixture and the resultant mixture was again stirred for 2 h. In order to remove the oxidant ions, especially manganese ions, the final solution was purified by centrifugation for almost 15 times at 5000 rpm for 5 min by adding H_2SO_4 (3 wt%) aqueous solution and H_2O_2 (0.5 wt%) aqueous solution. This step is repeated just by changing the liquid with DI (de-ionized) water. Finally we get a highly dispersed solution of GO.
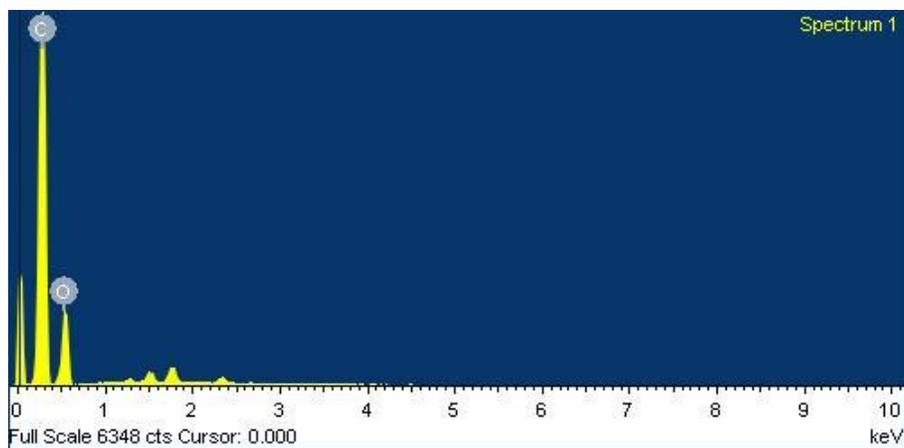
Fig. S1. A representative EDS spectrum of the graphene oxide paper.
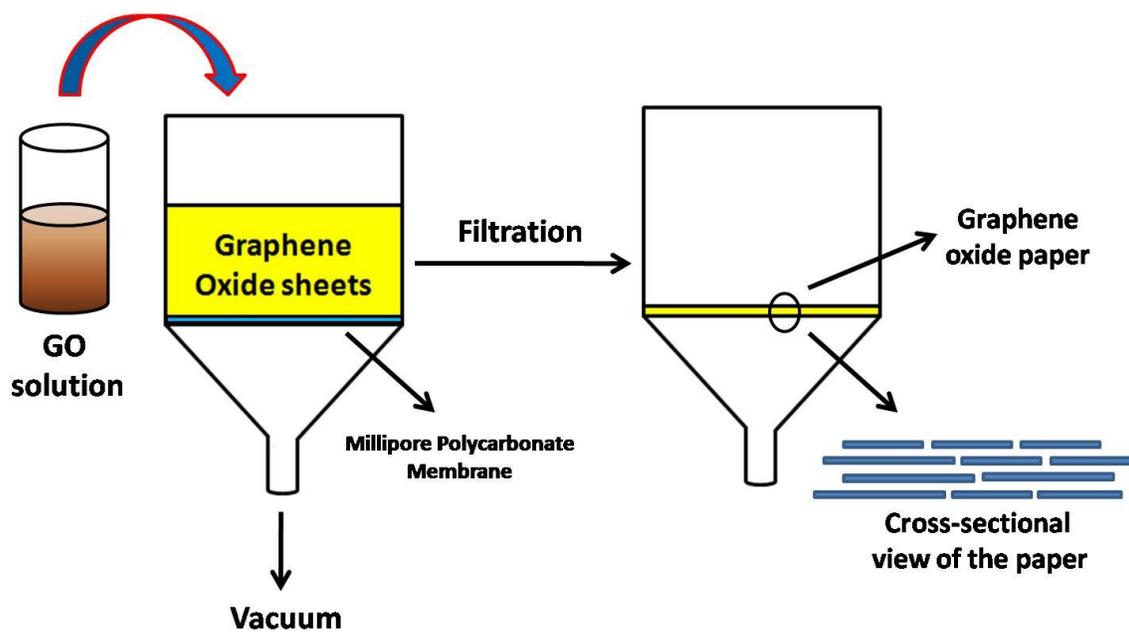
Fig. S2. Schematic explanation of the graphene oxide membrane fabrication
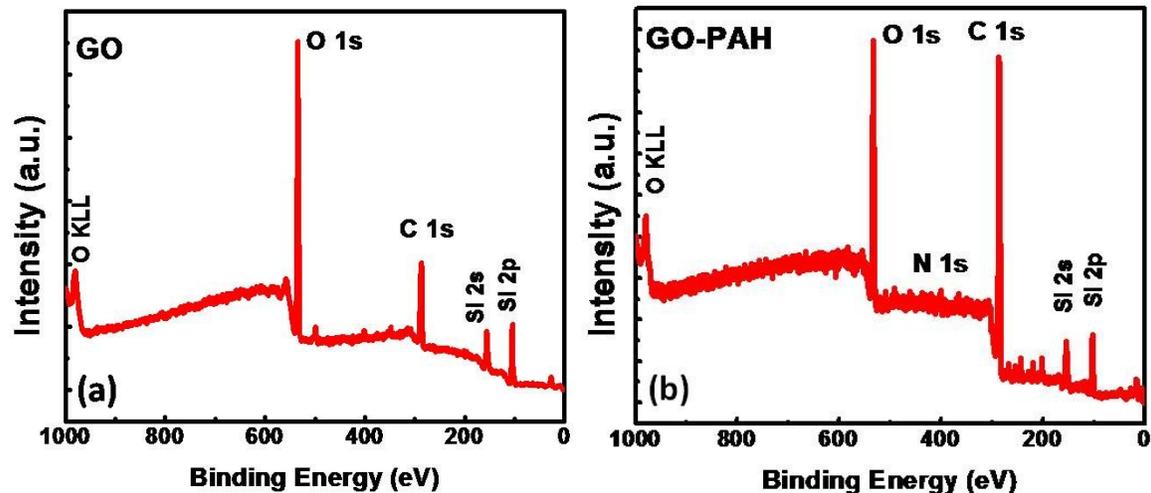
Fig. S3. Wide region XPS spectra of (a) graphene oxide (GO) and (b) PAH-modified graphene oxide (GO-PAH) samples.
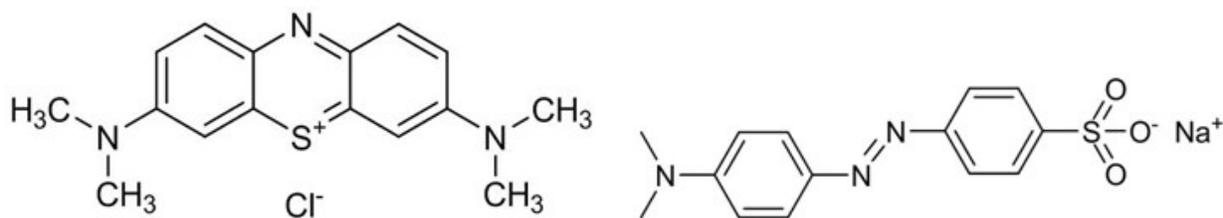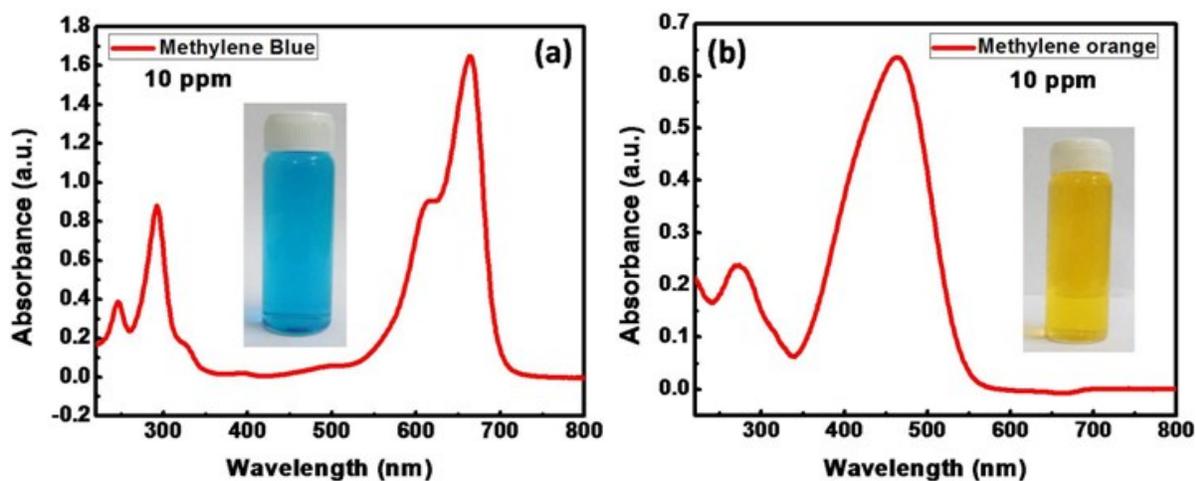
Fig. S4. shows the UV-Vis spectra of (a) Methylene blue (b) Methylene orange with the chemical structure.
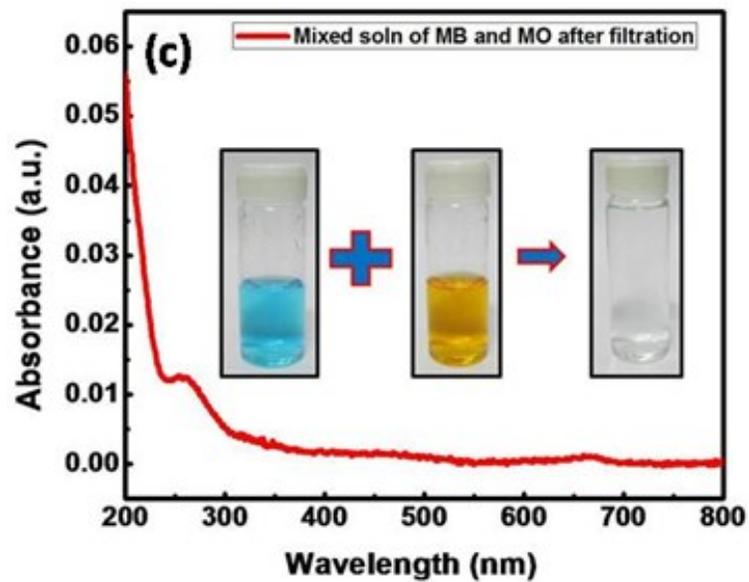
Fig. S5. The UV-Vis spectra of the mixture of methylene Blue and methylene orange after filtration through the stacking structure of GO membrane and PAH modified GO paper.
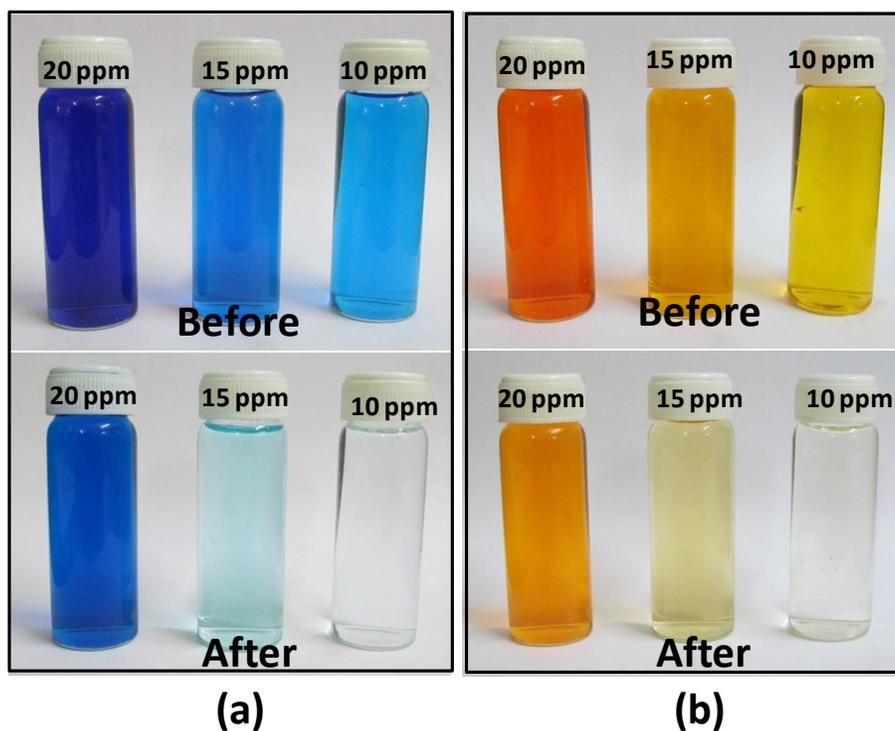
Fig. S6. Concentration dependent filtration of MB and MO through GO membrane (15mgl/ml GO) and PAH modified GO membrane (30 mg/ml GO-PAH).
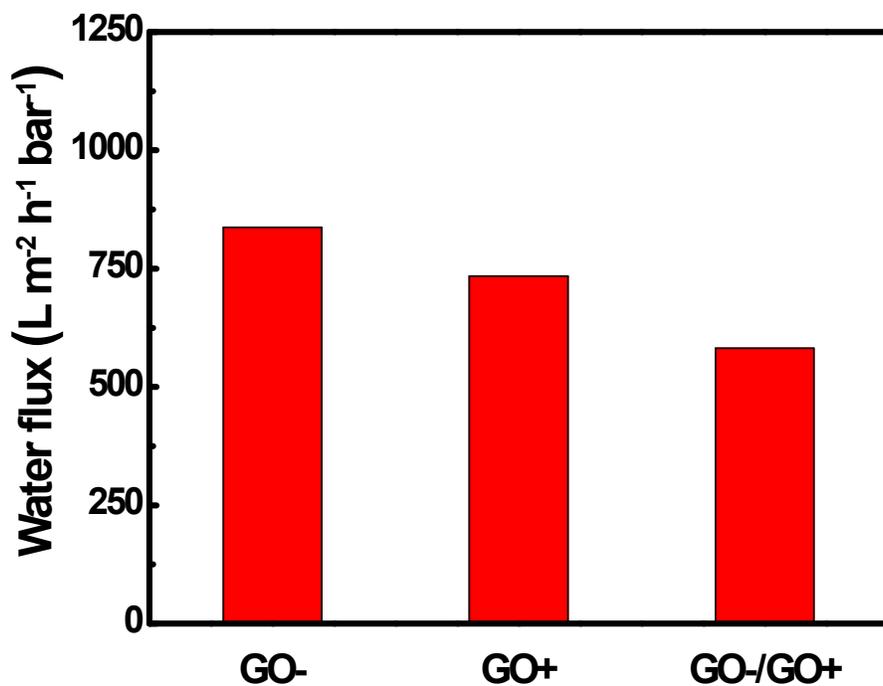
Fig. S7. Water fluxes through the GO-, GO+ membrane and stacking of GO-/GO+ membranes.
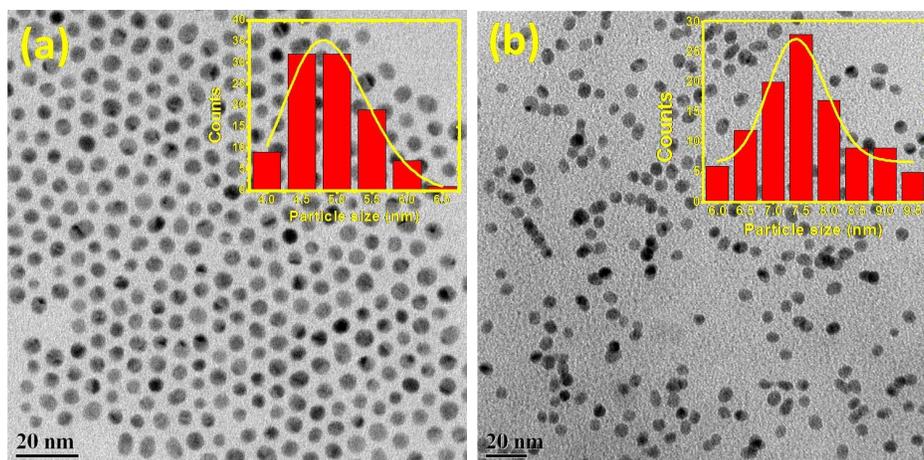
Fig. S8. HRTEM images of the AuNPs of (a) 5 nm and (b) 7 nm. The inset shows the particle size distribution.
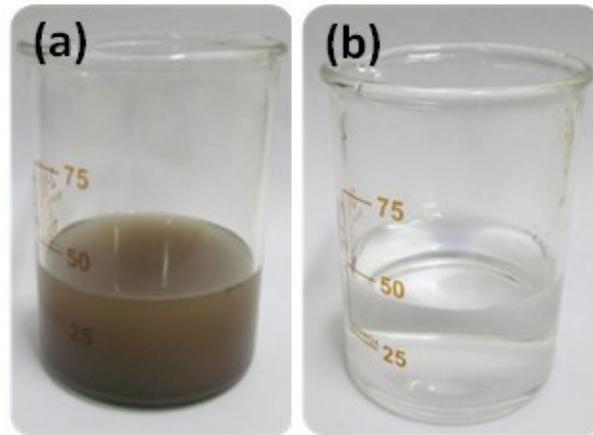
Fig. S9. The photo of the sewage water (a) before and (b) after filtering through the graphene paper.
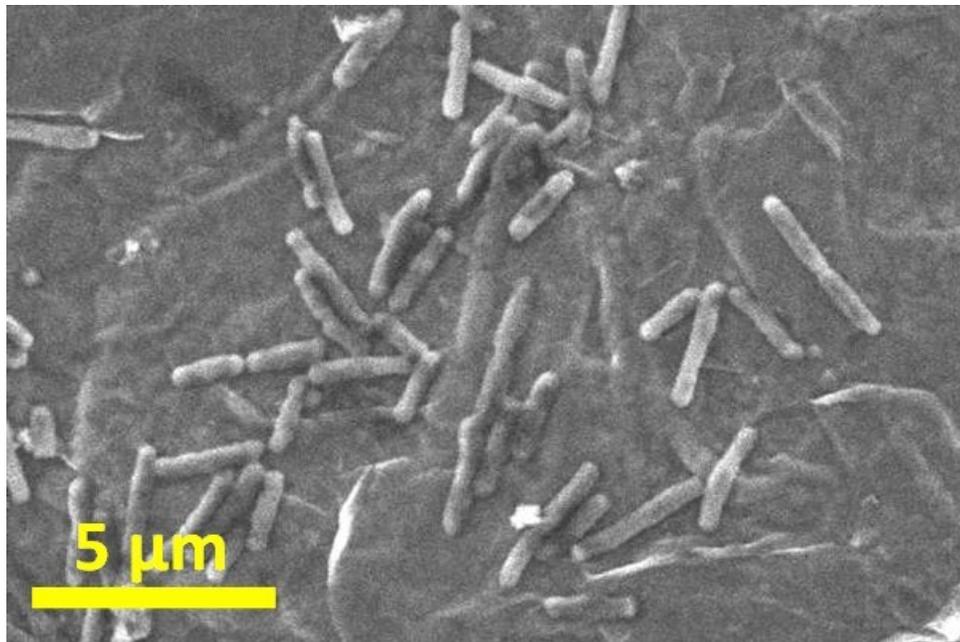
Fig. S10. Removing of the *Escherichia coli* (E-Coli) bacteria through the GO filter paper. The image shows the E-Coli bacteria on the surface of the GO paper. *Escherichia coli* is a rod-shaped bacterium found in the human gut which can cause severe food poisoning and Urinary Tract Infection (UTI).
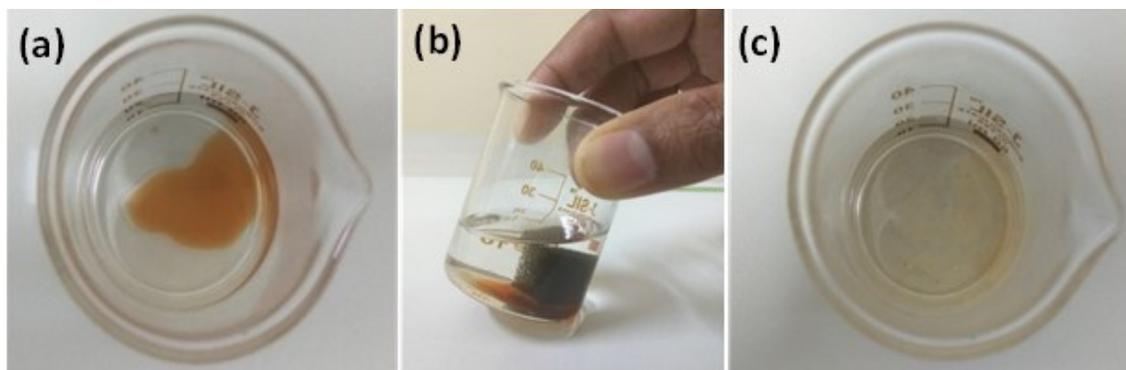
Fig. S11. The photo of the oil spill removed from water with a GO hybrid sponge (a) oil in water (b) GO sponge dipped in the oil spill water (c) GO sponge was removed after oil absorption.

Theoretical Background:

1. Adsorption analysis:

On the basis of known dye concentration, we could calculate the average ε from *Beer's* law,

$$A = \varepsilon\, b\, C$$

where, A is absorbance, ε (L mg^{-1} cm^{-1}) is the molar absorptivity, b (cm) is 1, C (mg L^{-1}) is the concentration of dye samples.

Then, from the recorded A, known average ε, and b we could calculate C_t

The amount of dyes attached onto GOs was calculated according to the mass balance equation as

Adsorption capacity, $\qquad\qquad q_t = V\,(C_o - C_e)/W$

where, q_t is the amount of dyes absorbed on GOs (mg/g) at the fixed time intervals; C_0 and C_e are the initial and liquid-phase concentration of dyes (mg L^{-1}); V (L) is the employed dyes volume; and W (g) is the weight of the used 3D GOs.

Removal Efficiency, $\qquad\qquad E = (C_o - C_e)/\,C_o$

The calculation was done by measuring the maximum absorbance of the two dyes (at $\lambda = 464$ nm for MO and at $\lambda = 665$ nm for MB).

To calculate C_e we need to calculate ε from the from Beer's law $A = \varepsilon\, b\, C$, where $b = 1$ cm

2. Adsorption Isotherms:

The most common sorption models were used to fit the experimental data are: Langmuir[1], Freundlich[1] and Tempkin isotherms[2].

(i). Langmuir isotherm

The langmuir isotherm assumes a surface with homogenous binding sites, equivalent sorption energies and no interaction between adsorbed species.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}k_L}$$

Where q_{max} and K_L represents the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

A plot of C_e/q_e versus C_e gives a straight line with q_{max} and K_L determined from the intercept and the slope respectively.

The separation factor or equilibrium parameter, R_L is used to determine the feasibility of adsorption in a given concentration range over adsorbent and it is evaluated from the equation

$$R_L = \frac{1}{1 + K_L C_0}$$

Where K_L is the Langmuir adsorption constant (1/mg) and C_0 is the initial dye concentration.

Ho and McKay[3] established that

    (1) $0 < R_L < 1$ for favorable adsorption

    (2) $R_L > 1$ for unfavorable condition

(3) $R_L = 1$ for linear adsorption

(4) $R_L = 0$ for irreversible adsorption

(ii) Freundlich isotherm

The freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies

$$\ln q_e = \ln k_f + \left(\frac{1}{n}\right)\ln C_e$$

Where k_f (L/g) and n are freudlich constants related to adsorption capacity and adsorption intensity respectively.

A linear plot of ln q_e vs ln C_e confirms the validity of the Freundlich isotherm.

(iii) Tempkin isotherm

The third model is the Tempkin isotherm and is represented by the following equation:

$$q_e = Bln(k_t) + Bln(C_e)$$

Where k_t is the equilibrium binding constant and corresponds to the maximum binding energy and B is constant related to the heat of adsorption.

A linear plot was obtained when Q_e was plotted against *ln C_e*
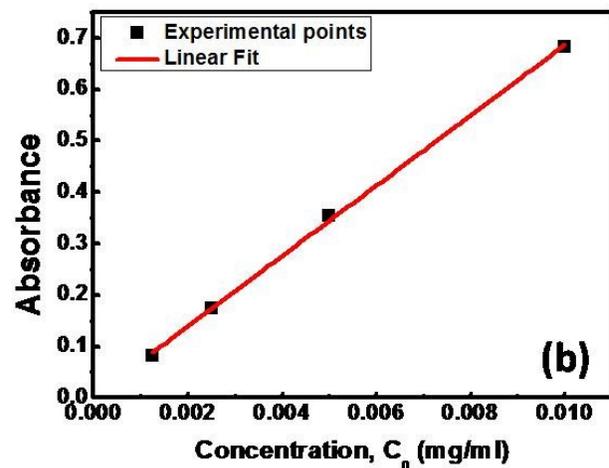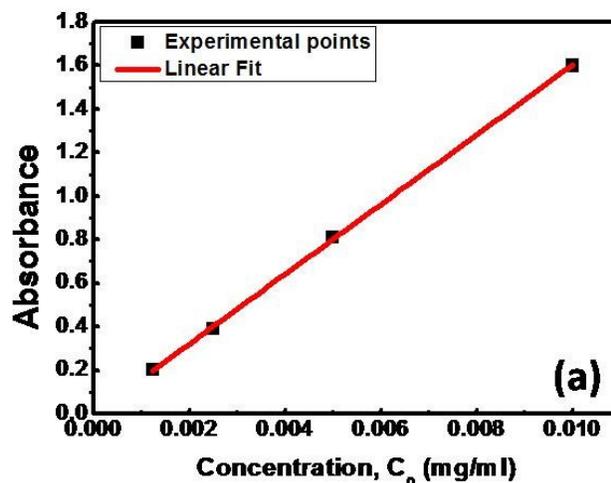
Fig S12. Calibration curve for (a) Methylene blue (MB), (b) Methylene orange.
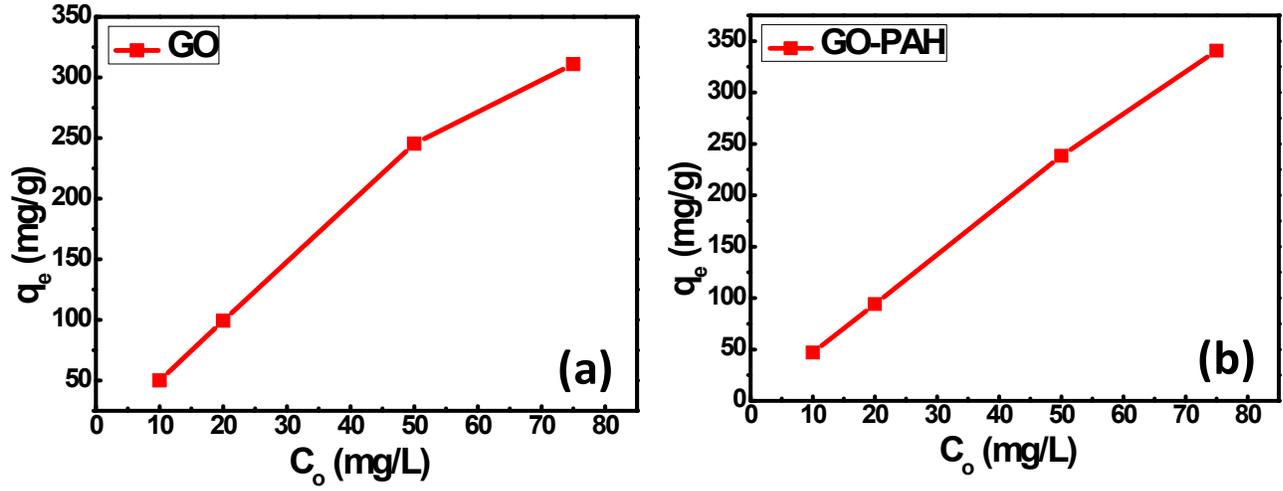
Fig S13. The isotherm was obtained at initial concentration range of 10-75 mg/L. The sorption capacity attained 311 mg/g (for GO) and 340 mg/g (GO-PAH) at an initial concentration of 75 mg/L.
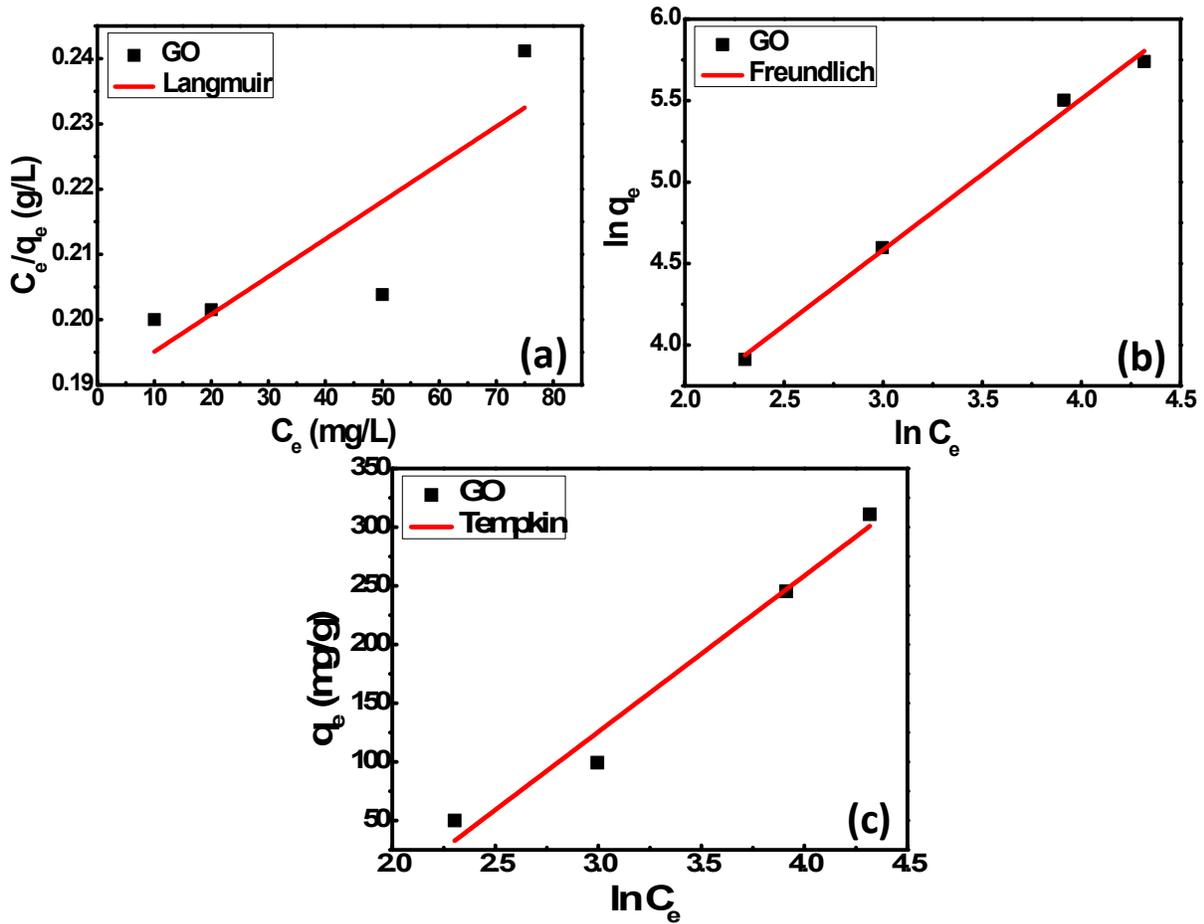
Fig. S14. (a) Langmuir isotherm model, (b) Freundlich isotherm model, (c) Tempkin isotherm model for adsorption of MB on GO- paper.
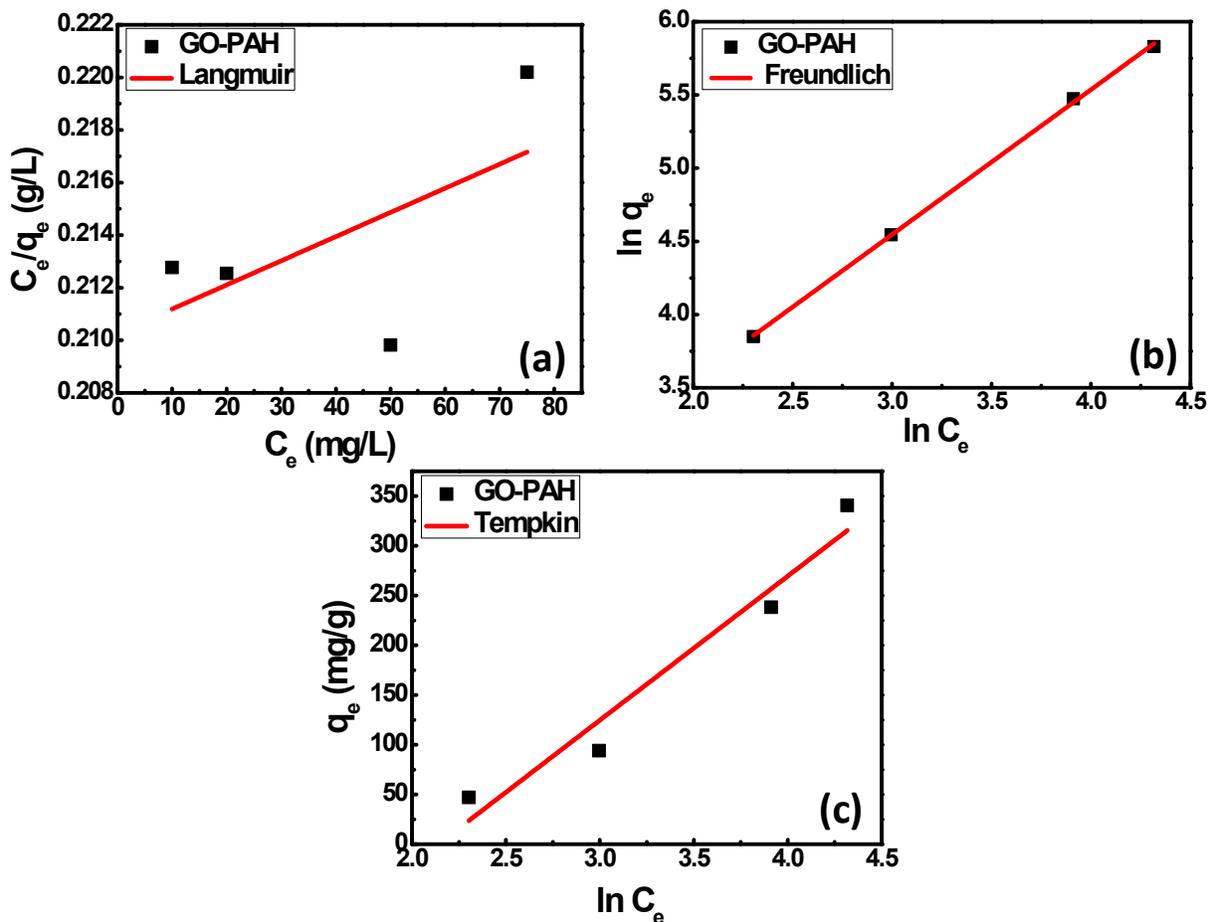
Fig. S15. (a) Langmuir isotherm model, (b) Freundlich isotherm model, (c) Tempkin isotherm model for adsorption of MO on GO+ paper.

References:

1. I. Lagmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 1918, **40**, 1361-1403.
2. M. J. Tempkin, Kinetics of Ammonia Synthesis on Promoted Iron Catalysts, *Acta Physiochim.* 1940, **12**, 217-222.
3. Y. S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Ehg. J.,* 1998, **70**, 115-124.