Supporting Information

Chitosan-Graphene Oxide Hydrogels with Embedded Magnetic Iron Oxide Nanoparticles for Dye Removal

Nirbhai Singh,[†] Sk Riyajuddin,[‡] Kaushik Ghosh,[‡] Surinder K. Mehta[†] and Abhijit Dan*[,†]

[†]Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University – Chandigarh, Sector – 14, Chandigarh – 160014, India

[‡]Institute of Nano Science & Technology, Sector- 64, Phase X, Mohali – 160062, India

Corresponding author

*Email: abhijit@pu.ac.in (A. Dan)

Synthesis of Graphene Oxide (GO). The GO was synthesized by oxidation of graphite powder using modified Hummer's method.[1,2] Briefly, 1 gm of graphite powder was added in 20 mL cold H_2SO_4 (98%). Subsequently, 0.5 gm of $NaNO_3$ was mixed and the solution was stirred for an hour. Then, 3 gm of $KMnO_4$ was added very slowly to the solution. The temperature of reaction mixture was maintained within the range of 15 – 20 ^oC. The solution was kept on stirring for another 2 hours, after which, 46 mL distilled water was added slowly at 35 ^oC with constant stirring. The reaction was allowed to continue for 15 minute at 98 ^oC. At the end, the reaction mixture was diluted with 140 mL distilled water with subsequent addition of 2.5 mL H_2O_2 (30%). The color of the solution turned yellow-brown. The resulting product was washed with distilled water and ethanol (three times) by centrifugation. Finally, the sample was dried at 60^oC in an oven.

XRD calculation:

The diameter of the particles can be determined using Debye Scherrer equation,

$D = \frac{k\lambda}{\beta cos\theta}$

k = Dimensionless shape factor (value 0.94)

β = Full Width at Half Maximum (FWHM)

λ = x-rays wavelength (1.54 A^o)

θ = Bragg's angle (in degree)

Table S1. Average particle size of the materials obtained from Scherrer's Equation

Sample	Particle Size (nm)
Bare IO	23.6
CSIO	11.1
CSGOIO	8.1

Determination of Crosslinking Density of the Hydrogel Nanocomposite:

The molecular weight, M_c of the polymer chain between two neighboring crosslinks was calculated from Flory-Rehner equation[3] (S1) as follows:

$$M_c = - d_p V_m \varphi^{\frac{1}{3}} [\ln(1 - \varphi) + \varphi + \chi\varphi^2]^{-1} \quad \text{(S1)}$$

where, V_m is the molar volume of the swelling agent (18.1 cm^3/mol for water), χ is the Flory-Huggins interaction parameter and ϕ is the volume fraction of the cross-linked polymer in the swollen gel polymer.

The value of φ of the polymer in the swollen state can be calculated by using equation (S2):

$$\varphi = \left[\left(\frac{d_p}{d_s}\right)\left(\frac{w_f - w_o}{w_o}\right) + 1\right]^{-1} \quad \text{(S2)}$$

where, d_p and d_s, are the density of polymer and solvent in g/cm^3, respectively, w_o and w_f are the weight of the hydrogel composite before and after swelling, respectively.

The value of χ can be calculated experimentally from the temperature coefficient of volume fraction ($\frac{d\varphi}{dT}$) using equation (S3):

$$\chi = \left[\varphi(1 - \varphi)^{-1} + N\ln(1 - \varphi) + N\varphi\right]\left[2\varphi - \varphi^2 N - \varphi^2 T^{-1}\left(\frac{d\varphi}{dT}\right)^{-1}\right]^{-1} \quad \text{(S3)}$$

where, $N = \left(\frac{\varphi^{\frac{2}{3}}}{3} - \frac{2}{3}\right)\left(\varphi^{\frac{1}{3}} - \frac{2}{3}\varphi\right)^{-1}$ and $\left(\frac{d\varphi}{dT}\right)$ is the slope obtained by plotting the volume fraction data versus temperature (K). For this purpose swelling experiments were conducted at 303, 313 and 323K.

The crosslink density, ρ of the polymer network was determined from equation (S4):

$$\rho = \frac{d_p}{M_c} \quad \text{(S4)}$$

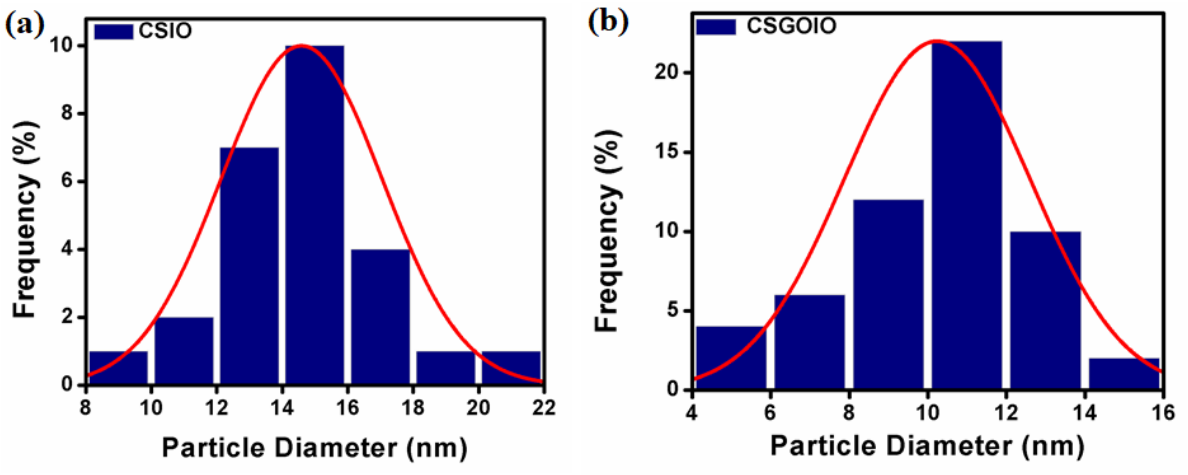

Figure S1. Particle size distribution obtained from TEM images of (a) CSIO and (b) CSGOIO.

Table S2. Detailed porosity properties of CSIO, CSGOIO-12.5 and CSGOIO-50 obtained from BET and the BJH methods.

Sample	BET surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Average pore diameter (nm)
CSIO	1.35	0.0021	6.36
CSGOIO-12.5	22.37	0.0181	3.24
CSGOIO-50	25.83	0.0198	3.07

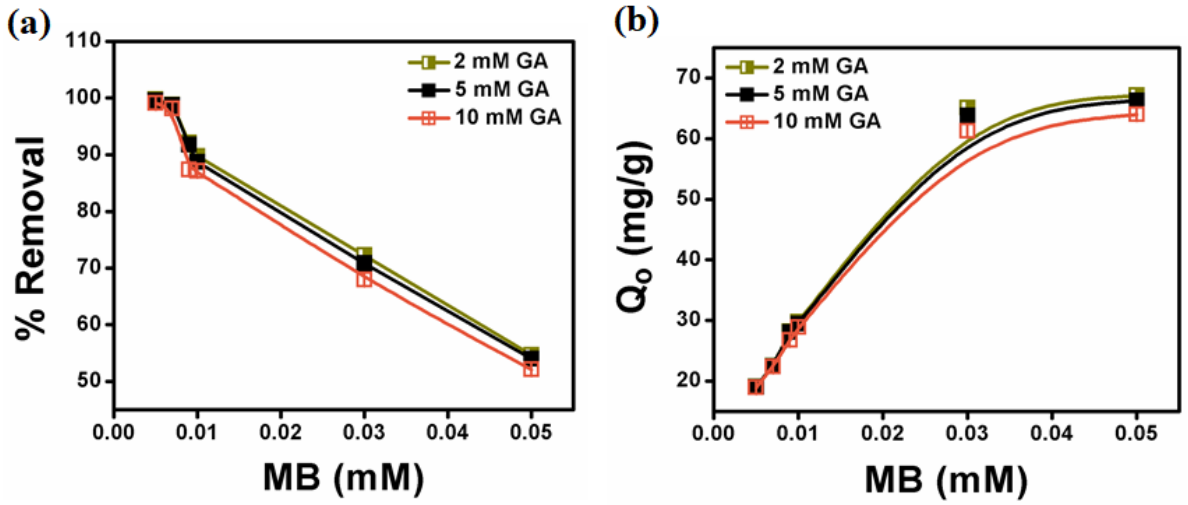

Figure S2. Effect of cross linker dosage (GA) on MB adsorption onto CSGOIO-50: (a) % of dye removal and (b) adsorption capacity. [Initial MB concentration 0.005 – 0.05 mM, adsorbent dosage 0.2 mg/mL, contact time 300 min, pH = 7.4, temperature 298 K].

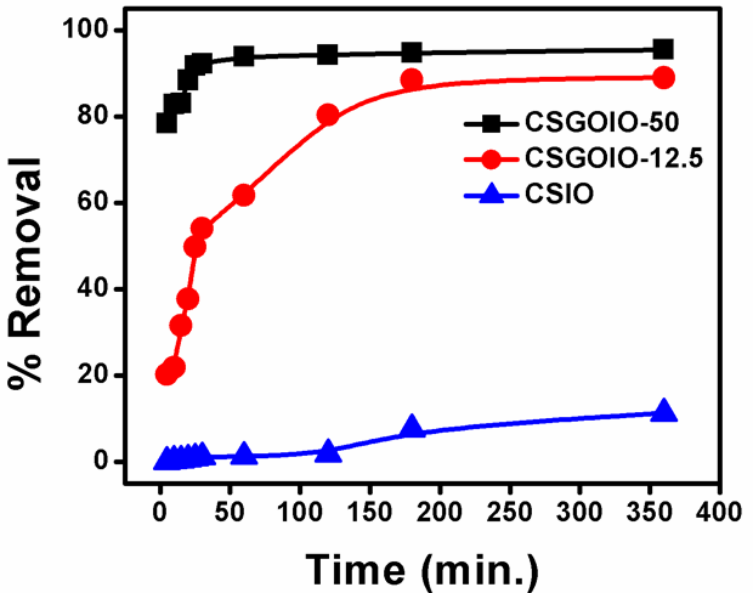

Figure S3. % removal of MB by CSIO, CSGOIO-12.5 and CSGOIO-50 as a function of contact time. [Initial MB concentration 0.05 mM, adsorbent dosage 2 mg/mL, contact time 5 – 360 min, pH = 7.4, temperature 298 K].

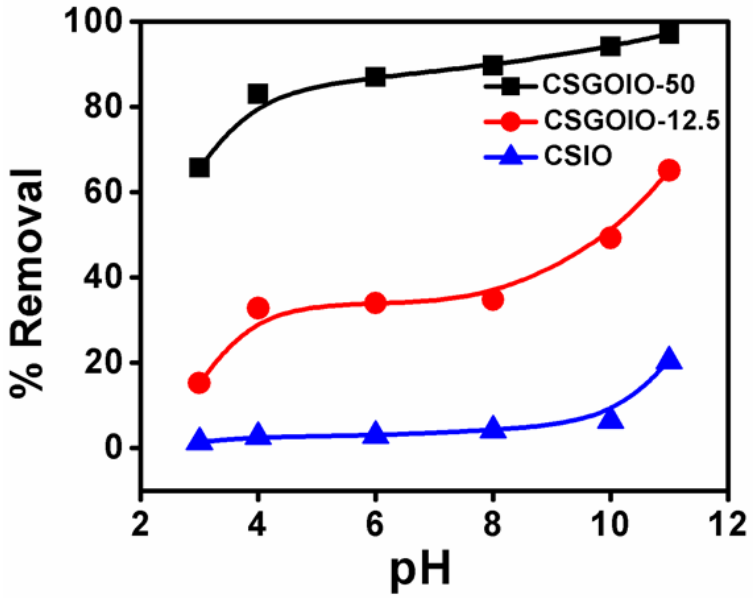

Figure S4. % removal of MB by CSIO, CSGOIO-12.5 and CSGOIO-50 at different pH of the solutions. [Initial MB concentration 0.05 mM, adsorbent dosage 0.6 mg/mL, contact time 300 min, pH = 3–11, temperature 298 K].

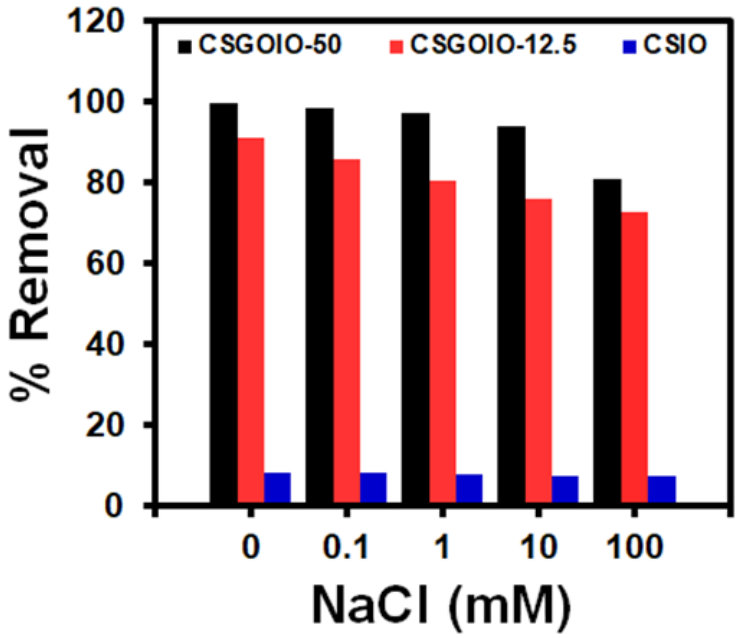

Figure S5. % removal of MB by CSIO, CSGOIO-12.5 and CSGOIO-50 at different ionic strength of the solutions. [Initial MB concentration 0.05 mM, adsorbent dosage 0.6 mg/mL, contact time 300 min, pH = 7.4, temperature 298 K].

Table S3. Thermodynamics parameters for the adsorption of MB onto CSIO, CSGOIO-12.5 and CSGOIO-50 at different temperatures.

Adsorbents	Temperature (K)	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})
CSIO	298	-0.25		
	318	-0.89	+9.23	+0.031
	338	-1.53		
CSGOIO-12.5	298	-1.85		
	318	-2.34	+5.46	+0.024
	338	-2.83		
CSGOIO-50	298	-5.39		
	318	-6.28	+7.84	+0.044
	338	-7.17		

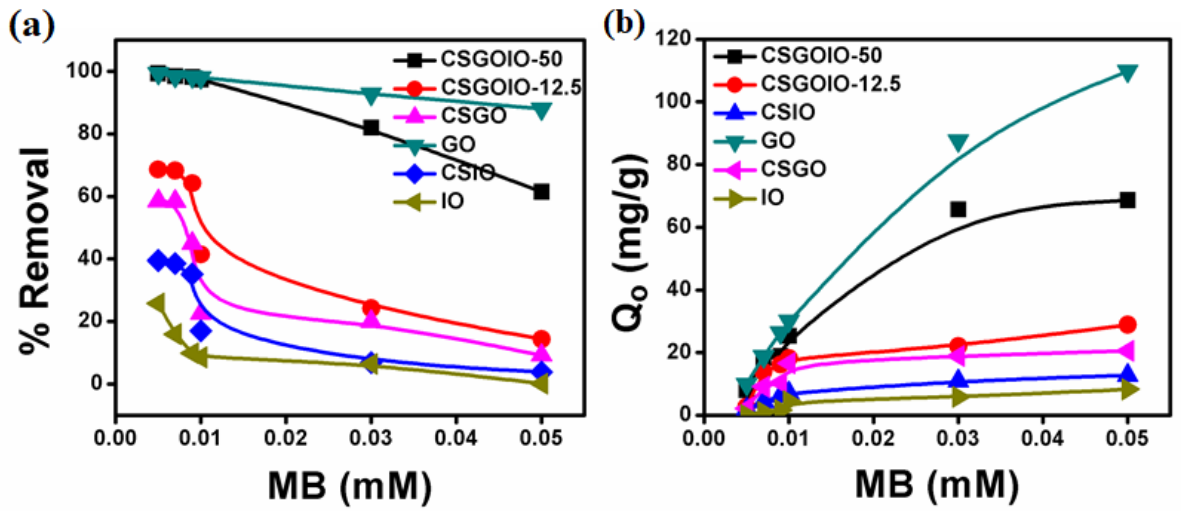

Figure S6. (a) % removal and (b) adsorption capacity of different adsorbents for MB. [Initial MB concentration 0.005 – 0.05 mM, adsorbent dosage 0.2 mg/mL, contact time 300 min, pH = 7.4, temperature 298 K].

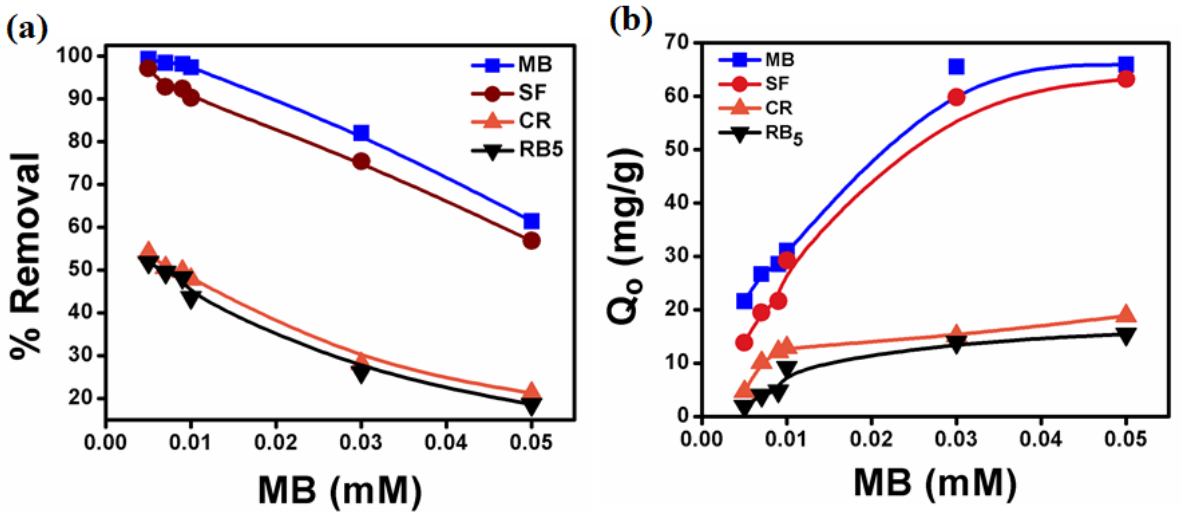

Figure S7. (a) % removal and (b) adsorption capacity of CSGOIO-50 for cationic (MB, SF) and anionic (RB_5, CR) dyes. [Initial MB concentration 0.005 – 0.05 mM, adsorbent dosage 0.2 mg/mL, contact time 300 min, pH = 7.4, temperature 298 K].

References

1. Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339.
2. Dhopte, K. B.; Zambare, R. S.; Patwardhan, A. V.; Nemade, P. R. Role of Graphene Oxide as Heterogeneous Acid Catalyst and Benign Oxidant for Synthesis of Benzimidazoles and Benzothiazoles. *RSC Adv.* **2016**, *6*, 8164–8172.
3. Singh, B.; Singh, B. Influence of graphene-oxide nanosheets impregnation on properties of sterculia gum-polyacrylamide hydrogel formed by radiation induced polymerization. *Int. J. Biol. Macromol.* **2017**, *99*, 699–712.