Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Highly-branched Triple-chain Surfactant Mediated Electrochemical Exfoliation of Graphite to obtain Graphene Oxide: Colloidal Behaviour and Application in Water Treatment

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Supplementary Information

^{1}H NMR Spectroscopy

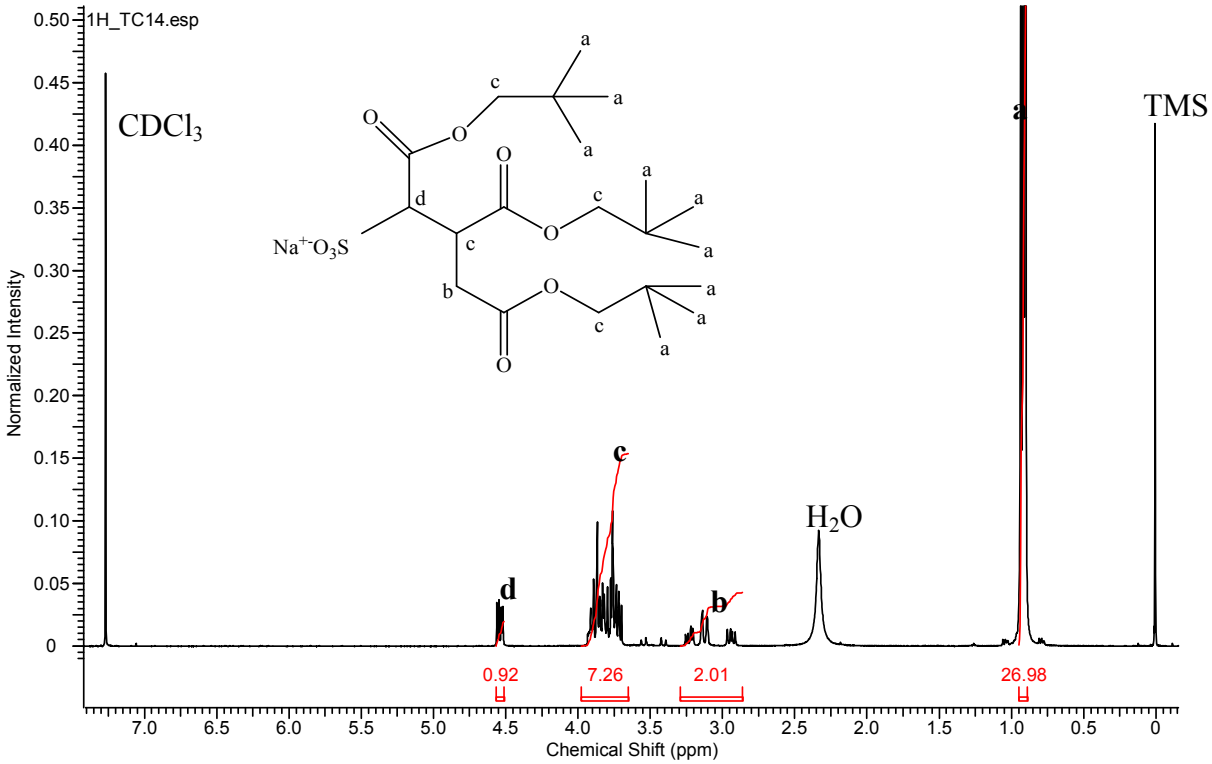

Fig. S1 ^{1}H NMR spectrum for surfactant TC14. The solvent is $CDCl_3$.

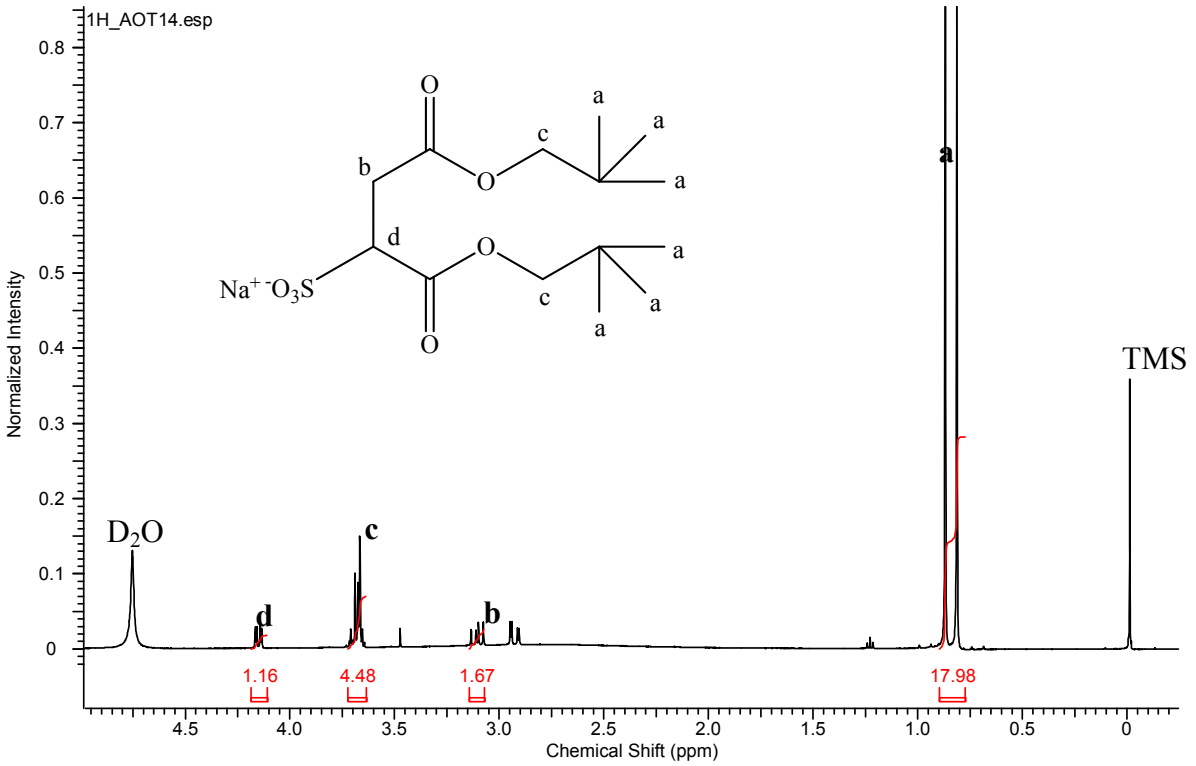

Fig. S2 ^{1}H NMR spectrum for surfactant AOT14. The solvent is D_2O.

Table S1

Comparison of expected and experimental ^{1}H NMR peak integrals for surfactant TC14. Labels a to d represent the environment of each proton set in the surfactant.

Molecular fragment	Identified Proton	Chemical Shift	Relative NMR Integrals	
			Experimental	Expected
CH_3-C-	a	0.85 - 0.97	26.98	27.00
C-CH_2-C=O	b	2.87 – 3.29	2.01	2.00
C-CH_2-O-	c	3.65 – 3.96	7.26	6.00
C-CH-C=O				1.00
C-CH-C=O	d	4.52 – 4.58	0.92	1.00

^{1}H NMR (500MHz, $CDCl_3$, TMS), (δ_H/ppm): 0.85 – 0.97 (a, m, 27H), 2.87 – 3.29 (b, m, 2H), 3.65 – 3.96 (c, m, 7H), 4.52 – 4.58 (d, m, 1H)

Table S2

Comparison of expected and experimental ^{1}H NMR peak integrals for surfactant AOT14. Labels a to d represent the environment of each proton set in the surfactant.

Molecular fragment	Identified Proton	Chemical Shift	Relative NMR Integrals	
			Experimental	Theoretical
CH_3-C-	a	0.77 – 0.90	17.98	18.00
O=C-CH_2-C-S	b	3.07 – 3.14	1.67	2.00
C-CH_2-O-	c	3.64 – 3.72	4.48	4.00
C-CH-C=O	d	4.11 – 4.18	1.16	1.00

^{1}H NMR (500MHz, $CDCl_3$, TMS), (δ_H/ppm): 0.77 – 0.90 (a, m, 18H), 3.07 – 3.14 (b, m, 2H), 3.64 – 3.72 (c, m, 4H), 4.11 – 4.18 (d, m, 1H)

Surfactant-assisted exfoliated graphene oxide preparation

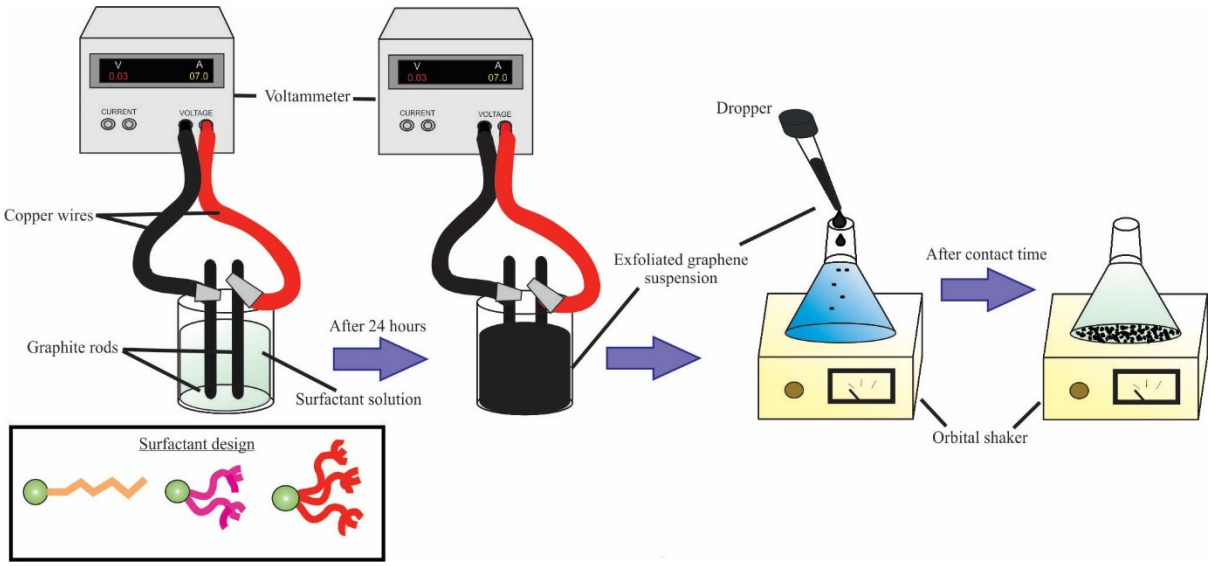

Fig. S3 The procedure for the preparation of surfactant-assisted exfoliated graphene oxides.

Table S3

Compositions employed for exfoliation process and methylene blue adsorption studies.

Surfactant (0.05M in 50 mL deionized water)	Mass of graphite rods before exfoliation (g)	Mass of graphite rods after exfoliation (g)	Total of graphene in suspension (mg/mL)	Volume of exfoliated suspension used for adsorption studies (mL)	Initial concentration of MB (mg/L)						Total of solution for adsorption studies (mL)
					Volume of MB (mL)			Total of deionized water added (mL)			
					5	10	15	5	10	15	
TC14	40.850	40.433	8.340	0.600	0.250	0.500	0.750	24.150	23.900	23.650	25
AOT14	40.770	40.670	2.000	2.500	0.250	0.500	0.750	22.250	22.000	21.750	25
SDS	40.760	40.687	1.460	3.400	0.250	0.500	0.750	21.350	21.100	20.850	25

Adsorption study

Table S4 Isotherms and calculated kinetic models for methylene blue adsorption using sEGO

Sample	Langmuir isotherm				Freundlich isotherm			Pseudo first order			Pseudo second order		
	K_L (L/mg)	Q_0 (mg/g)	R^2	R_L	K_F (mg/g)	n	R^2	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg.min)	q_e (mg/g)	R^2
TC14 sEGO	0.39	2.46	0.99	0.15	0.30	0.11	0.89	8.5×10^{-4}	0.68	0.63	0.01	13.41	1.00
AOT14 sEGO	0.31	1.43	0.91	0.18	0.74	0.07	0.85	6.1×10^{-4}	0.69	0.46	0.08	10.31	1.00
SDS sEGO	0.24	0.61	1.00	0.22	1.12	0.04	0.97	7.0×10^{-4}	0.78	0.59	0.05	5.61	1.00

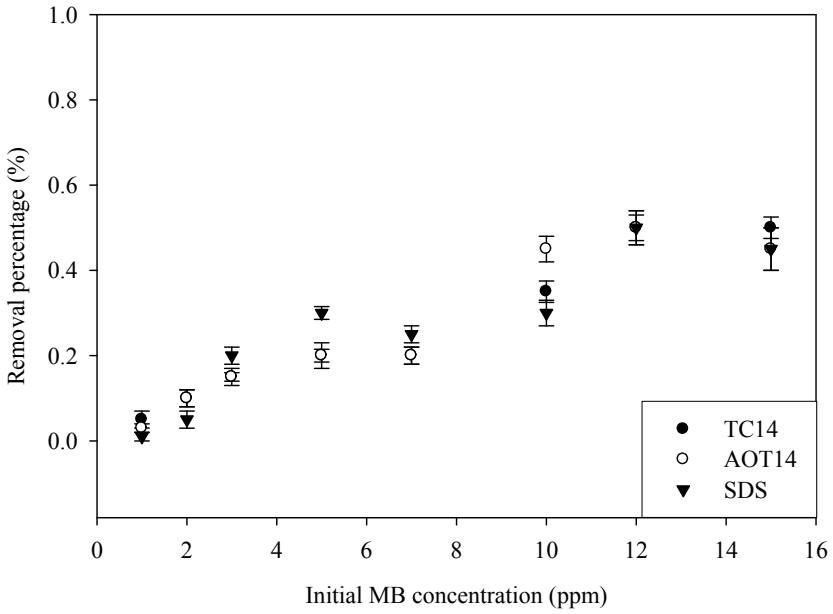

Fig. S4. Removal of TC14, AOT14 and SDS at various initial MB concentrations at 22.5°C and pH7 after 24 hours of contact time.

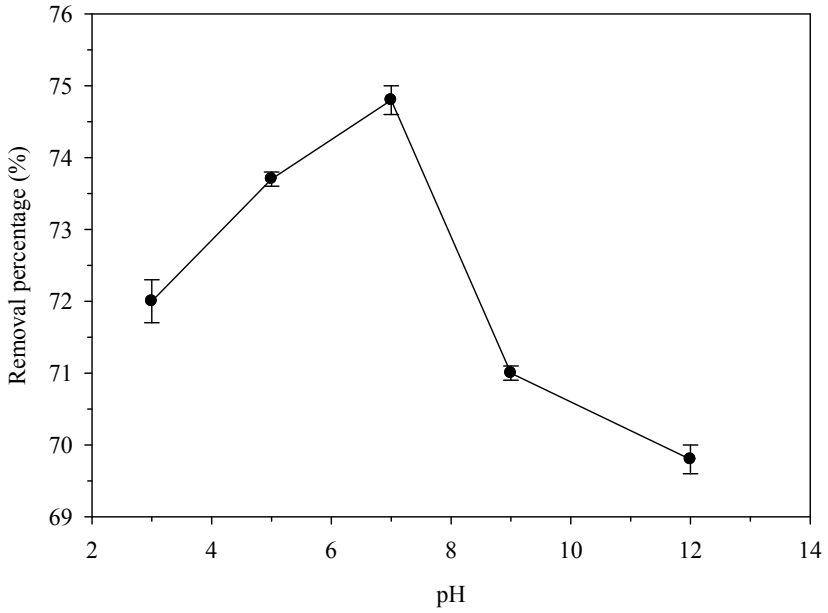

Fig. S5. Optimization of colloidal environment pH for adsorption studies using 5mg SDS sEGO in 15ppm MB at 22.5°C.

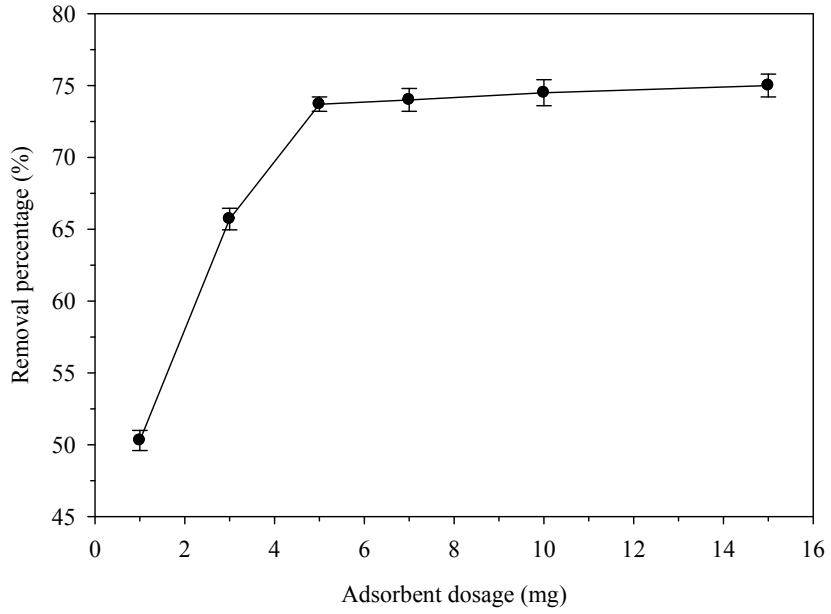

Fig. S6. Optimization of exfoliated sEGO mass for adsorption studies using SDS sEGO in 15 ppm MB at 22.5°C.

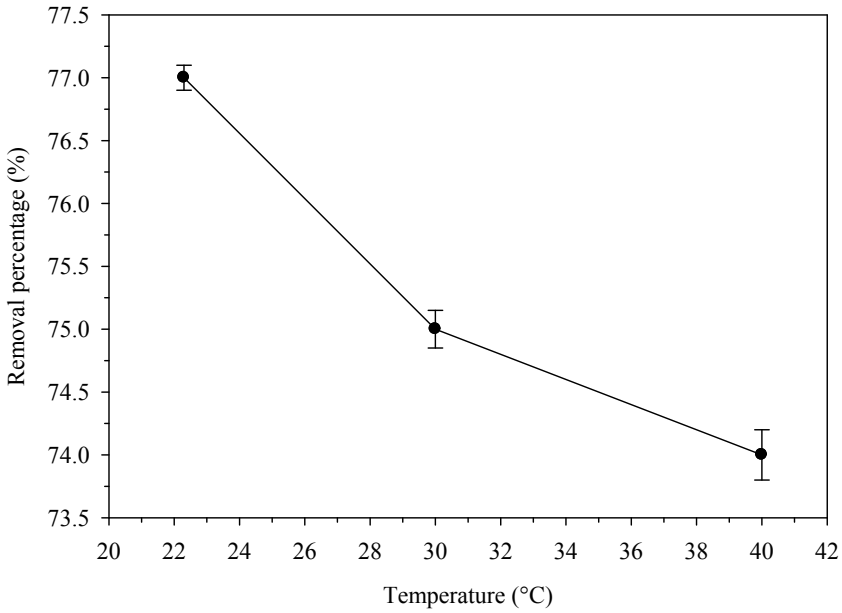

Fig. S7. Optimization of temperature for adsorption studies using SDS sEGO.

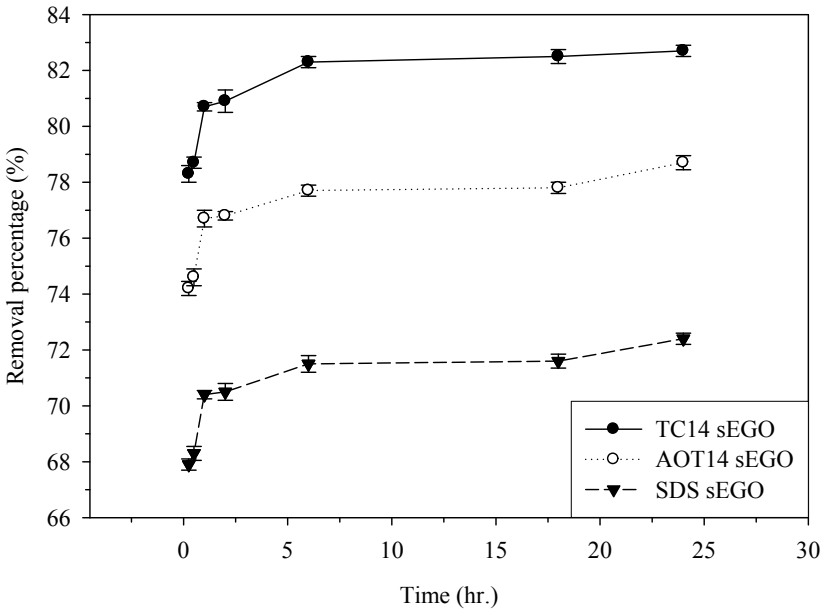

Fig. S8. Effect of initial dye concentration and contact time for adsorption studies on MB removal at 22.5°C.

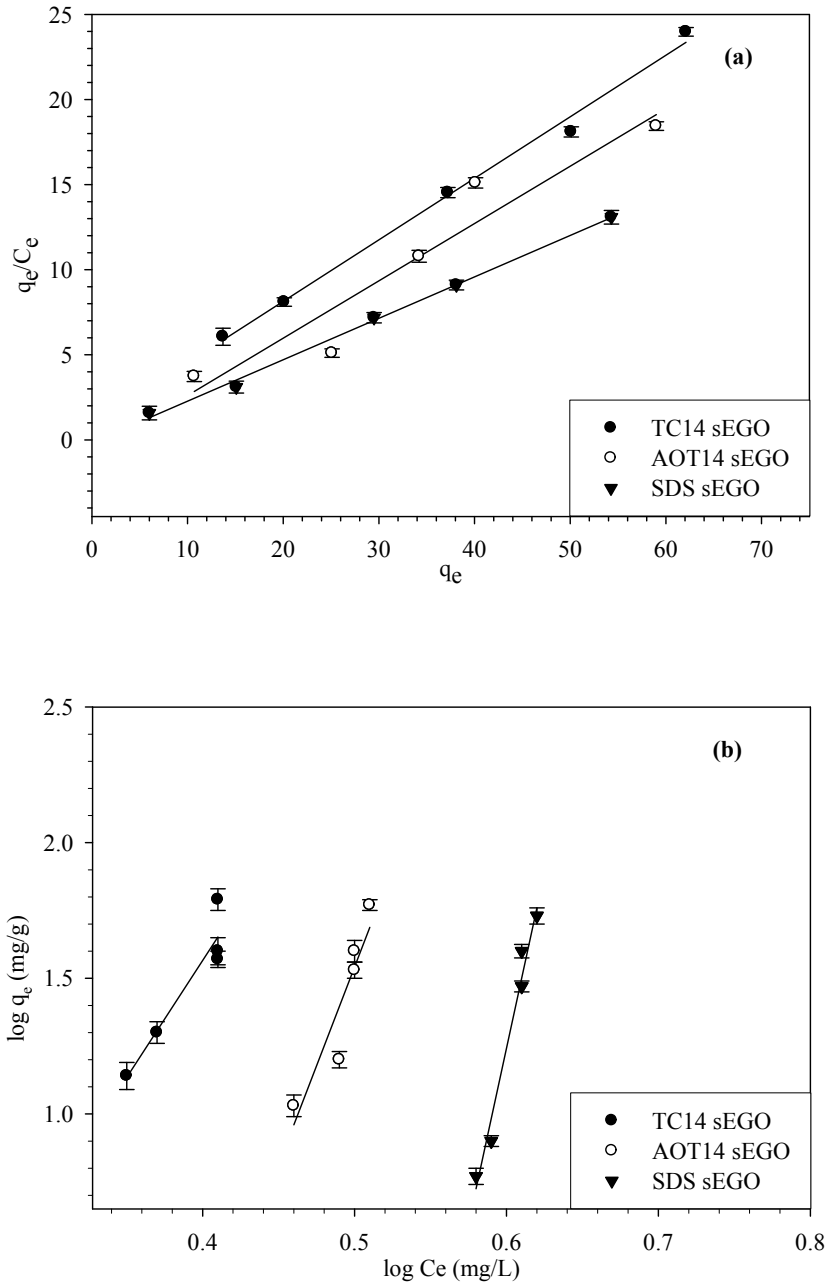

Fig. S9. Langmuir adsorption isotherm (a) and Freundlich model plot (b) for the adsorption of MB by the different surfactant exfoliated graphene oxides at 22.5°C.

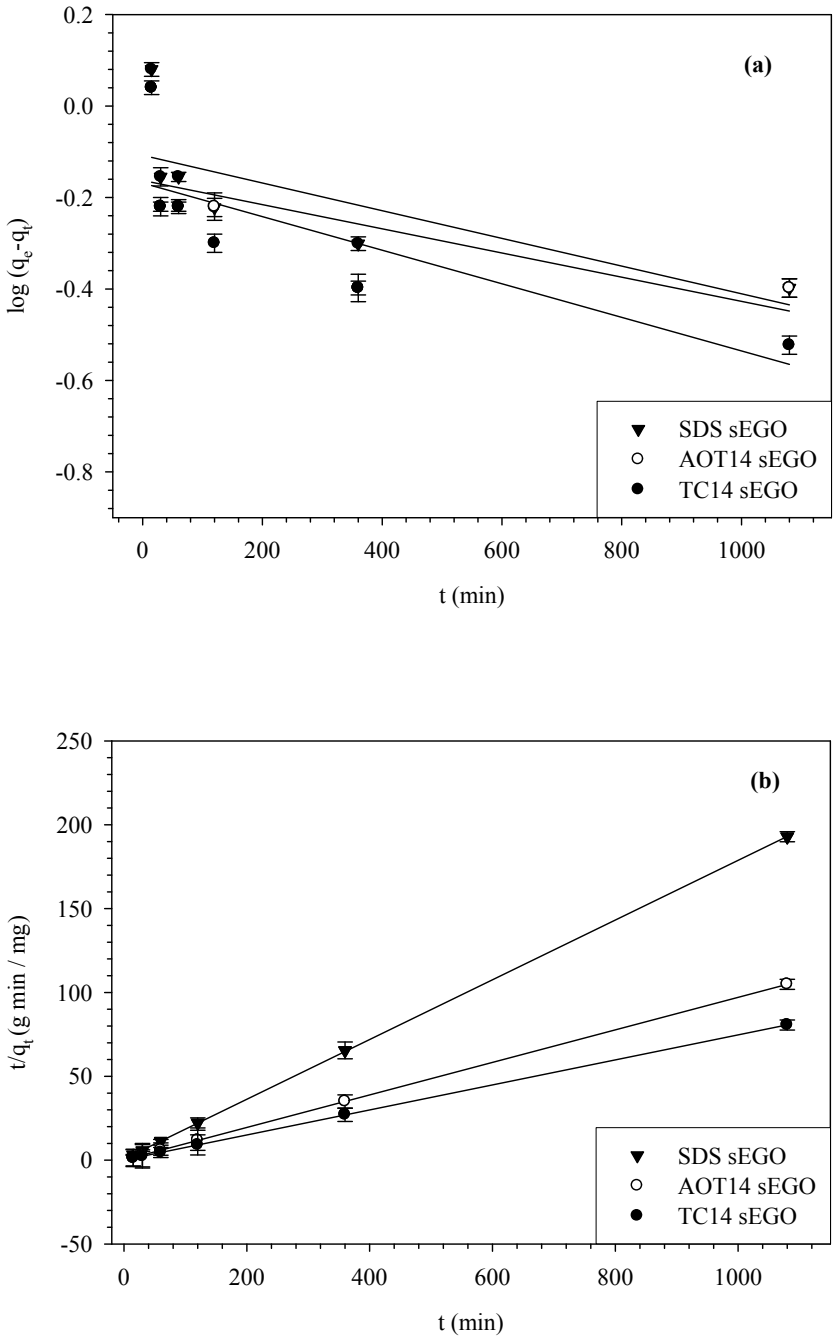

Fig. S10. The pseudo first-order model (a) and the pseudo second-order model (b) for the adsorption of MB by the different surfactant exfoliated graphene oxides at 22.5°C.

Zeta-potential measurement

Table S5

Zeta potentials along with the degree of branching and numbers of methyl groups in the surfactants.

Sample	Zeta (ζ)-potential (mV)		No of surfactant tails	No of terminal methyl ($-CH_3$) groups on each surfactant tail
	Prior washing	After washing		
sEGO	-20 ± 1[a]	-	-	-
TC14 sEGO	-46 ± 1	-46 ± 3	3	3
TC14 sEGO (below cmc)	-30 ± 1	-30 ± 1	3	3
AOT14 sEGO	-29 ± 1	-29 ± 3	2	3
SDS sEGO	-21 ± 1	-21 ± 3	1	1

[a] Data collected by Zhang et al. [1]

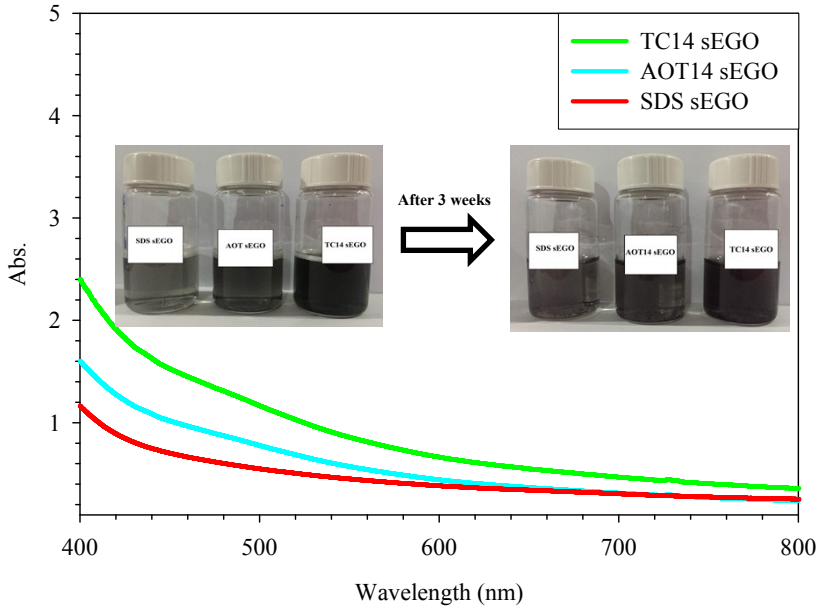

Fig. S11. UV Visible spectrum of TC14 sEGO, AOT14 sEGO and SDS sEGO, inset is the photograph of the sEGO suspension after exfoliation and after 3 weeks.

SANS data model fitting in SAS View

The scattering intensity I(Q) is proportional to the product of two dimensionless functions, one describing particle size and shape (form factor, P(*Q,r*)) and one describing interparticle interactions (structure factor, S(*Q*)), where the particle radius is denoted as *r*.

$$I(\mathrm{Q}) \propto \mathrm{P}(\mathrm{Q}, r)\mathrm{S}(\mathrm{Q}) \qquad \text{(Eq. S1)}$$

The 'reduced' (instrument-independent) SANS data were fitted to different models using the SasView interactive fitting program (http://www.sasview.org/).

Known parameters, such as scattering length densities, dielectric constants, volume fractions, and temperature, were fixed at constant values. Other parameters, such as *r*, were then optimized by the program until a minimum value of χ^2 was obtained. The equations for the form factors used are described as below. Further information and references can be found in the associated SasView help documentation.

Sphere model

The scattering from a dispersion of homogeneous smooth spheres is given by Equation S2

$$I(\mathrm{Q}) = \frac{scale}{V}\left[\frac{3\mathrm{V}(\Delta\rho)(\sin(\mathrm{Qr}) - Qr\cos(Qr))}{(Qr)^3}\right]^2 + bkg \qquad \text{(Eq. S2)}$$

where *scale* is the volume fraction, *V* is the volume of the scatterer, Δ*ρ* is the contrast (difference in scattering length density between the scatterer and dispersion medium), and *bkg* is the background level. The scattering length density of the various components are given in Table S6 below.

Ellipsoid model

The form factor for ellipsoid model given by equations S3 to S5

$$\mathrm{P}(\mathrm{Q}, \alpha) = \frac{scale}{\mathrm{V}} f^2(\mathrm{Q}) + bkg \qquad \text{(Eq. S3)}$$

$$f(\mathrm{Q}) = \frac{3(\Delta\rho)V(\sin[Qr(\mathrm{R_a}, \mathrm{R_b}, \alpha)] - Qr\cos[Qr(\mathrm{R_a}, \mathrm{R_b}, \alpha)]}{[Qr(\mathrm{R_a}, \mathrm{R_b}, \alpha)]^3} \qquad \text{(Eq. S4)}$$

$$r(\mathrm{R_a}, \mathrm{R_b}, \alpha) = [\mathrm{R}_b^2 \sin^2 \alpha + \mathrm{R}_b^2 \cos^2 \alpha]^{1/2} \quad \text{(Eq. S5)}$$

Table S6

Scattering length densities (ρ) of the components used in this study

Compounds	**ρ (x 10^{-6} Å^{-2})**
D_2O	6.37
sEGO	7.33
SDS	0.37
AOT14	0.48
TC14	0.85

[1] F. Zhang, S. Li, Q. Zhang, J. Liu, S. Zeng, M. Liu and D. Sun, *J. Mol. Liq.*, 2019, 276, 338–346.