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Supporting Information

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Adsorption of Pesticides**

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**Supporting Information S1.** Detailed synthetic procedure for the preparation of GO and RGO.

### Preoxidation of Graphite

The reactions were carried out in a 250 mL beaker. 25 mL of concentrated H<sub>2</sub>SO<sub>4</sub>, 5 g of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 5 g of P<sub>2</sub>O<sub>5</sub> were added to the reactor and heated to 90 °C with constant stirring. After complete dissolution of the reactants, the temperature of the reaction was decreased to 80 °C. 6 g of graphite powder were then added slowly to the reactor. Bubbling was observed initially and it subsided over a period of 30 min. Temperature of the reaction mixture was maintained at 80 °C for 5 h. Subsequently, heating was stopped and the mixture was diluted with 1 L of deionized water (DW) and left undisturbed overnight. The resultant solution was then filtered and washed to remove excess acid. The solid product was dried in air overnight.

### **Oxidation to Graphite Oxide (GO)**

Pre-oxidized graphite was added to 230 mL of concentrated H<sub>2</sub>SO<sub>4</sub> maintained under ice bath condition and stirred. 15 g of KMnO<sub>4</sub> was then added to the mixture keeping the reaction temperature below 10 °C. After complete addition of KMnO<sub>4</sub>, the temperature was raised to 35 °C and the reaction was continued for 2 h. Subsequently, 1 L of DW was added carefully keeping the temperature below 50 °C. The reaction mixture was stirred for 2 h and then 1.5 L of DW and 25 mL of 30% H<sub>2</sub>O<sub>2</sub> were added. The mixture was kept at room temperature for 24 h and the supernatant was carefully decanted. The settled dispersion was centrifuged and washed with 10% HCl followed by distilled water. This was repeated several times. The resultant solid was dried and 2% (w/w) dispersion was prepared in DW. This dispersion was put for dialysis for 3 weeks to remove all the impurities like salts and acid. Then the dispersion was diluted to 0.1% (w/w).

### **Reduction of GO to RGO**

The reduction was carried out hydrothermally as well as by chemical reduction using hydrazine. Hydrothermal reduction was carried out in the following manner. GO was

sonicated for 45 min. (CREST TRU-SWEEP 27D, 50 Hz) to exfoliate the suspension completely and centrifuged at 5000 rpm to remove the unexfoliated GO. About 25 mL of the purified exfoliated GO solution (0.05 wt%) was transferred to a teflon-lined hydrothermal reaction vessel and heated at 180 °C for 6 h. After 6 h, the vessel was cooled to room temperature. A black precipitate of RGO settles at the bottom which was redispersed in DW by mild sonication.

For chemical reduction, about 8.1 mL of the purified exfoliated GO solution was diluted to 90 mL using DW. Into this solution, 45 µL of hydrazine solution (35 wt% in water) was added and stirred for one min. To the above mixture, 315 µL of ammonia solution (28 wt% in water) was added and the whole solution was stirred well for five min. After three steps, the mixture was kept at 90 °C without stirring for 2 h. Then, the solution was put for dialysis against 0.5 % ammonia for 2 days to remove excess hydrazine, which may be present in the solution. Dialysis was repeated against DW for two weeks to remove all the residual contaminants that may be present in the reaction mixture.

Because of the similarities in structure, both will be termed as purified reduced graphene oxide sheets (RGO) in the text.

**Table S2.** Water quality characteristics of the groundwater used in this study.

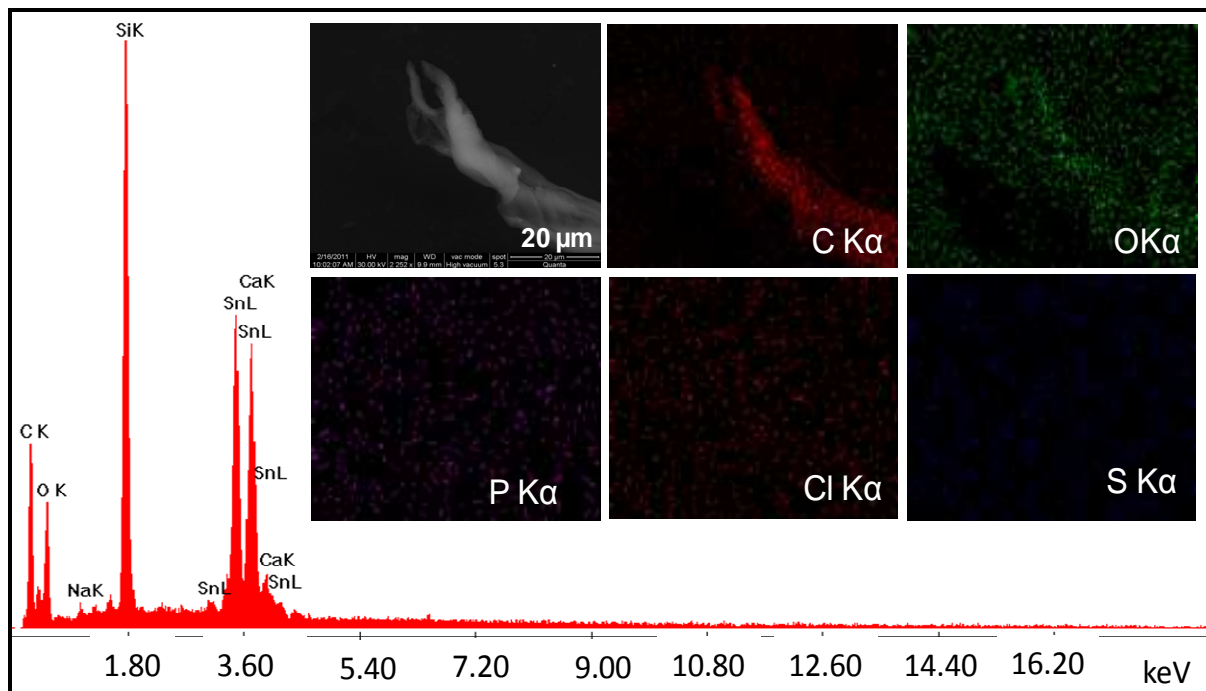
Parameters	Concentration [mg L <sup>-1</sup> ]*
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pH @ 25°C	7.4 (±0.2)
Total alkalinity (as CaCO <sub>3</sub> )	326
Total hardness (as CaCO <sub>3</sub> )	465
Conductivity @ 25°C	1226 µmhos/cm
Organic carbon	<0.5
Total dissolved solids	762
Calcium (as Ca)	113
Magnesium (as Mg)	44
Sulfate (as SO <sub>4</sub> <sup>2-</sup> )	80
Chloride (as Cl <sup>1-</sup> )	96
Phosphate (as PO <sub>4</sub> <sup>3-</sup> )	<0.02
Iron (as Fe)	<0.03
Nitrate (as NO <sub>3</sub> <sup>-</sup> )	50.31
Turbidity (as NTU)	0.1 NTU
Silica (as SiO <sub>2</sub> )	43.72
Manganese	< 0.01

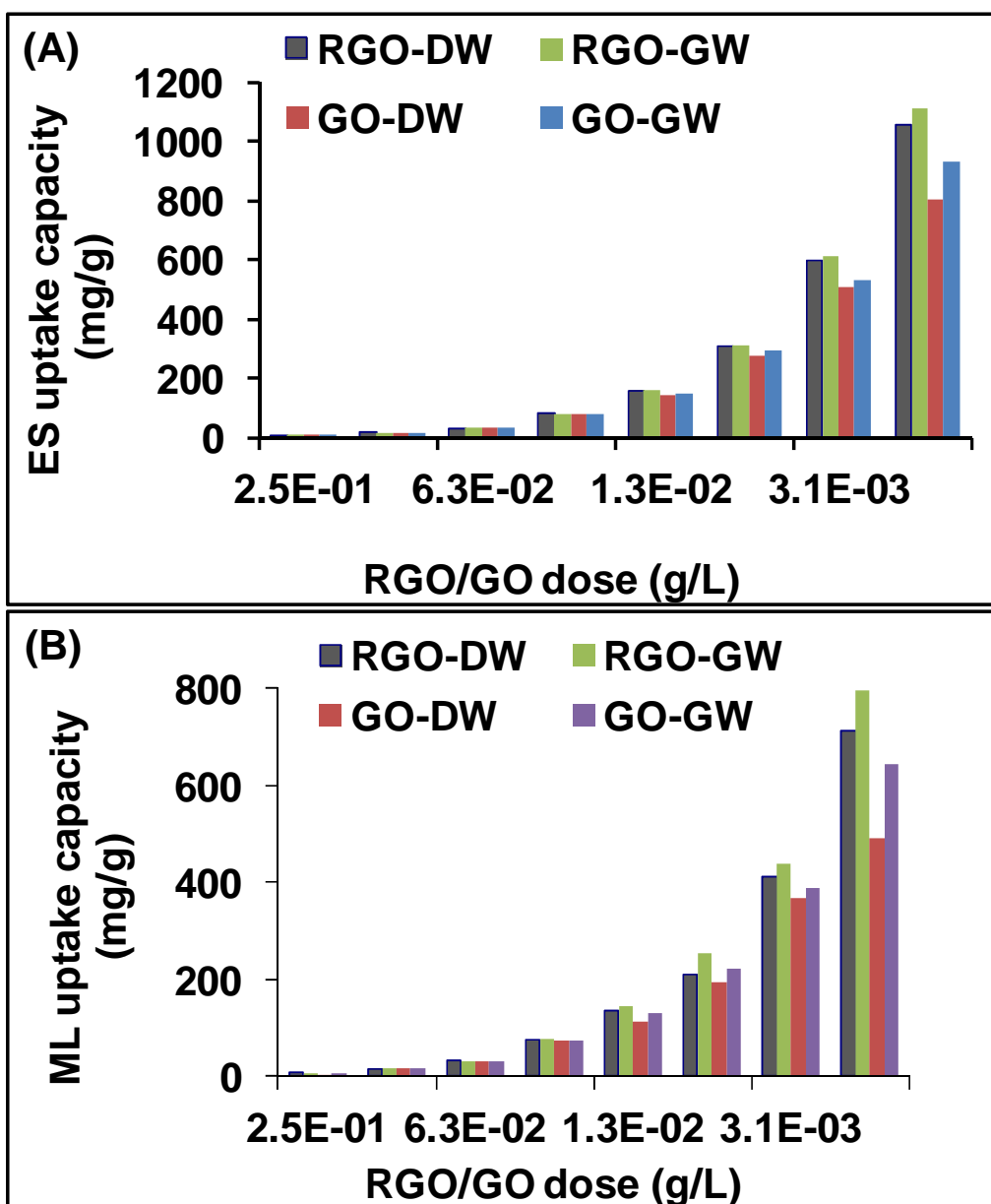
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\*All parameters are expressed in mg L<sup>-1</sup>, except turbidity, pH and conductivity.

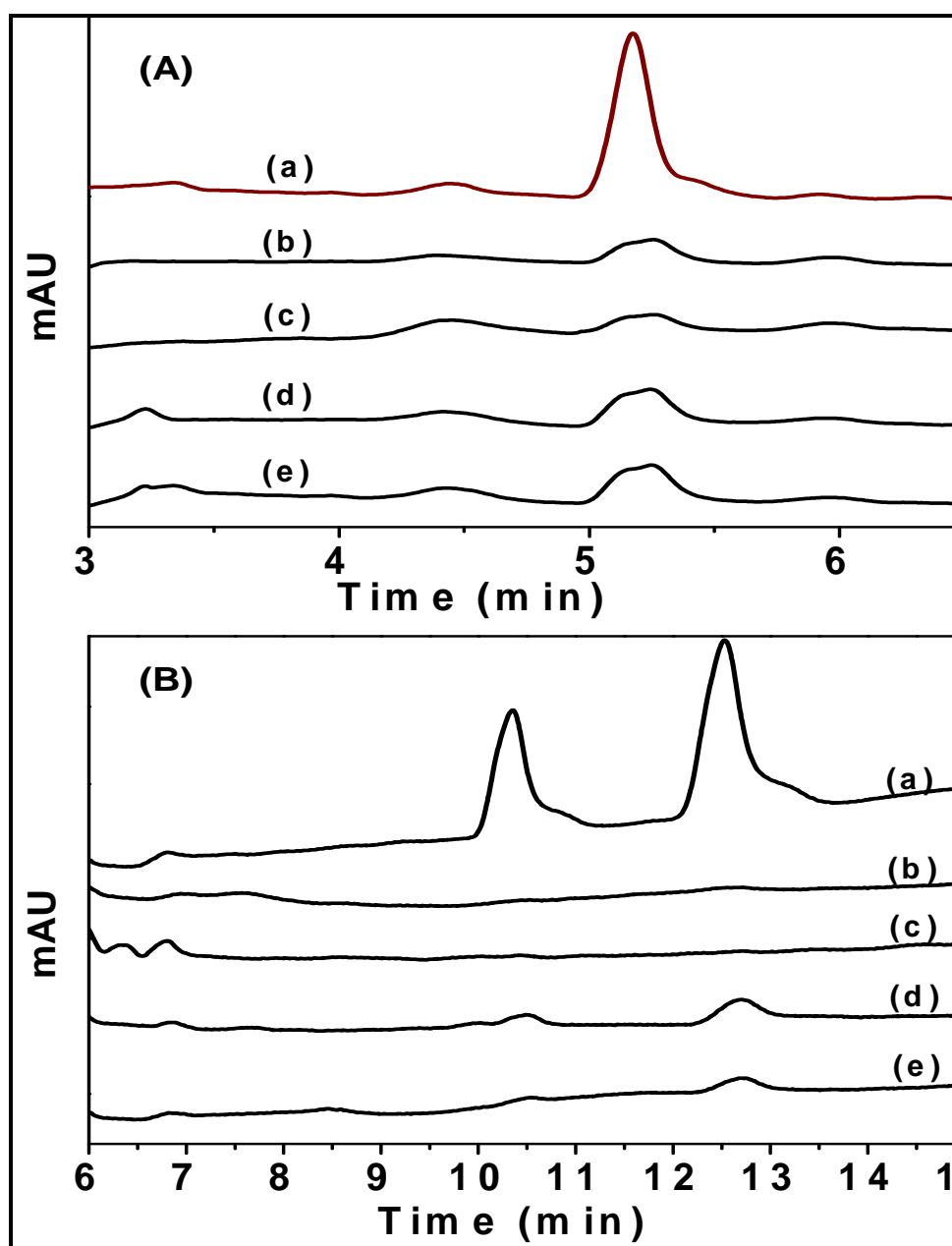


**Figure S3.** EDAX spectrum of the RGO. Inset shows the EDAX images of various elements along with a SEM image of RGO. Si and Sn are due to the conducting glass substrate used.

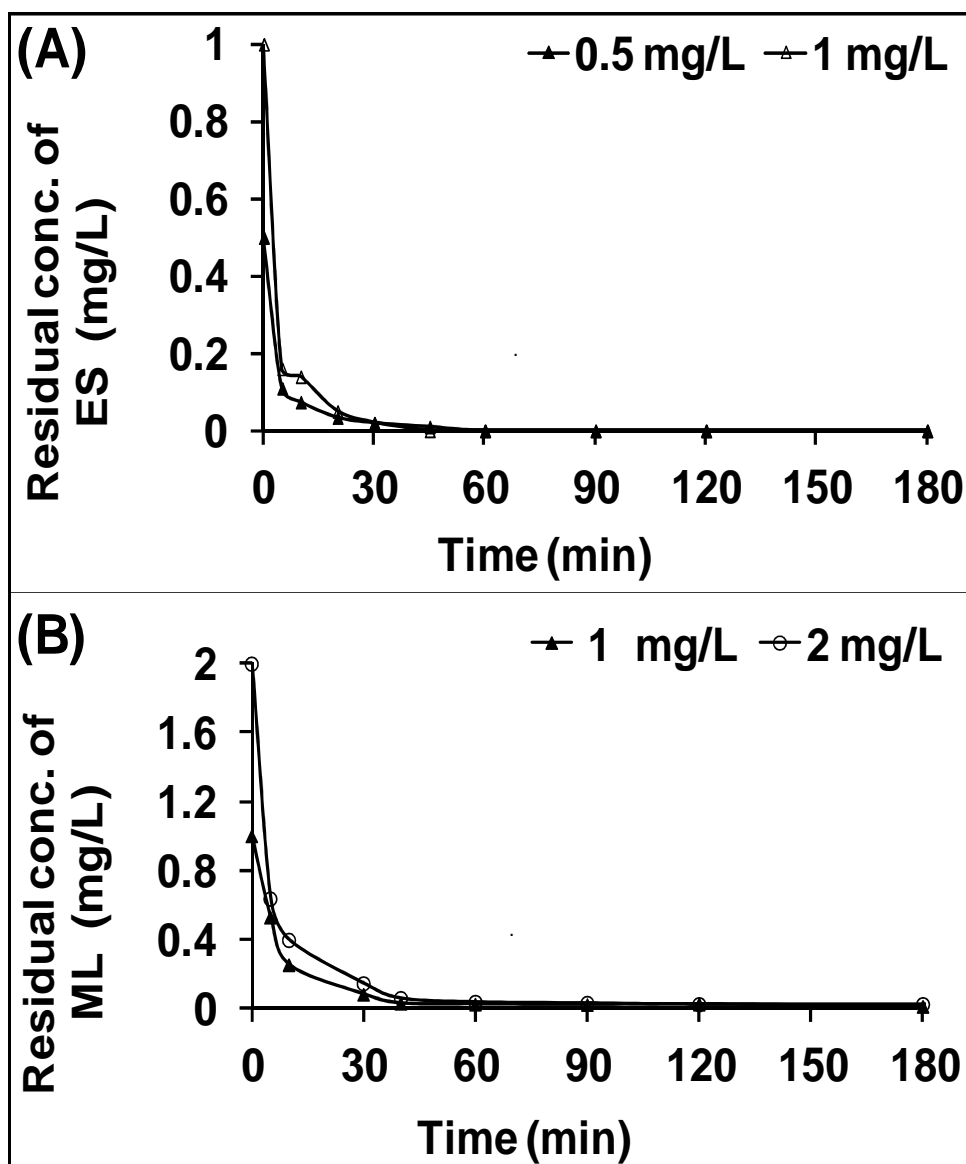




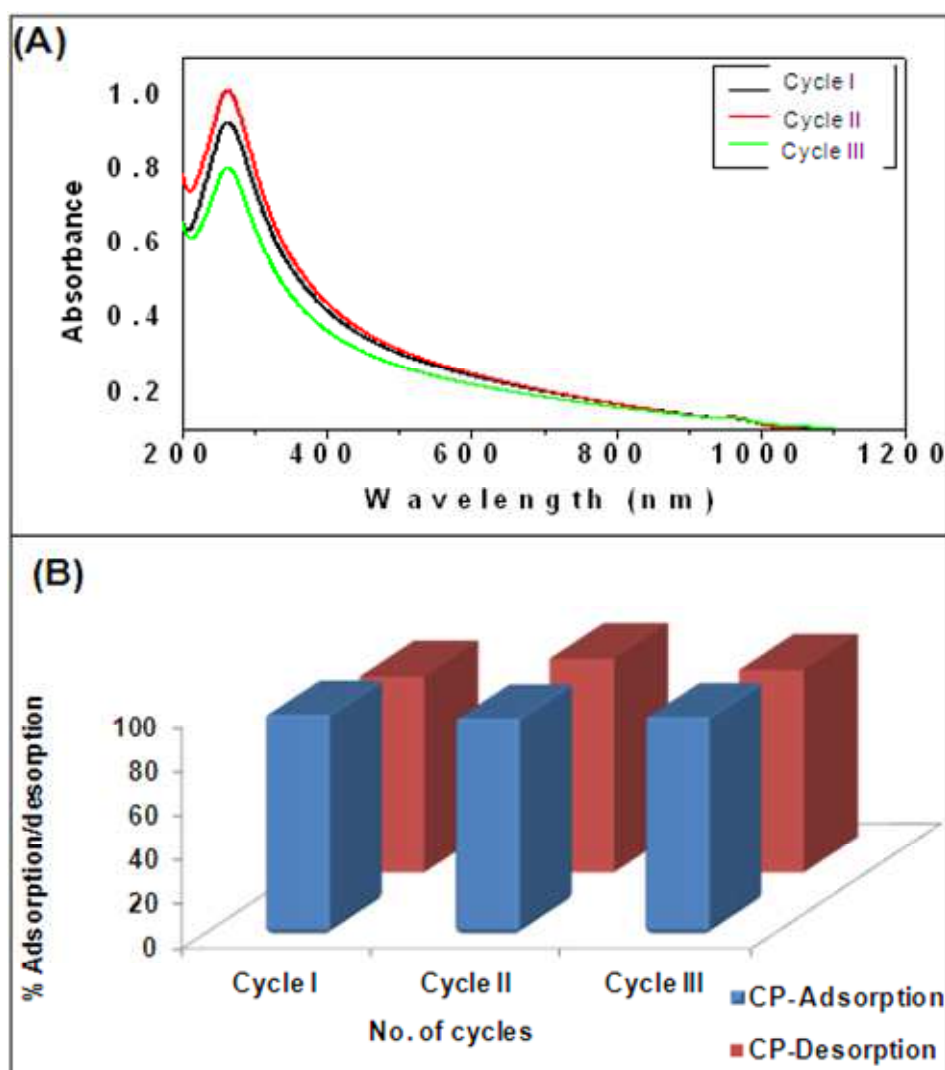
**Figure S4.** Adsorption of (A) ES, and (B) ML as a function of RGO and GO dose. Initial concentration of the solute =  $2 \text{ mg L}^{-1}$ ;  $\text{pH} = 7 \pm 0.2$ ; temperature =  $30 \pm 2 \text{ }^\circ\text{C}$ .



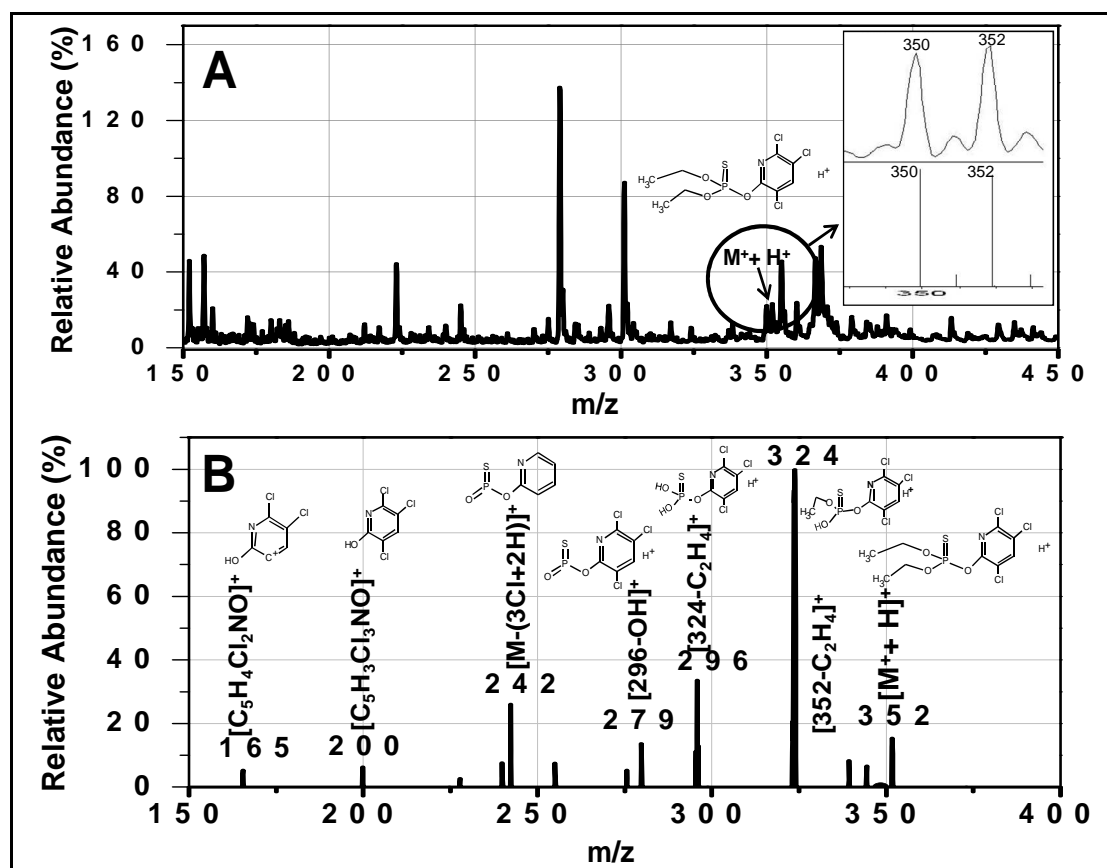
**Figure S5.** HPLC traces of (A) ML, and (B) ES. (a) The spectra show the initial concentrations of the pesticides. (b) and (c) show residual pesticide concentration after contact with RGO dispersed in DW and GW, respectively; (d) and (e) show residual pesticide concentration after contact with GO dispersed in DW and GW, respectively. Initial conc. of the pesticide =  $2 \text{ mg L}^{-1}$ ; pH = nearly neutral; temperature =  $30 \pm 2 \text{ }^{\circ}\text{C}$ ; GW- represent pesticide spiked in groundwater; DW- represent pesticide spiked in deionized water.



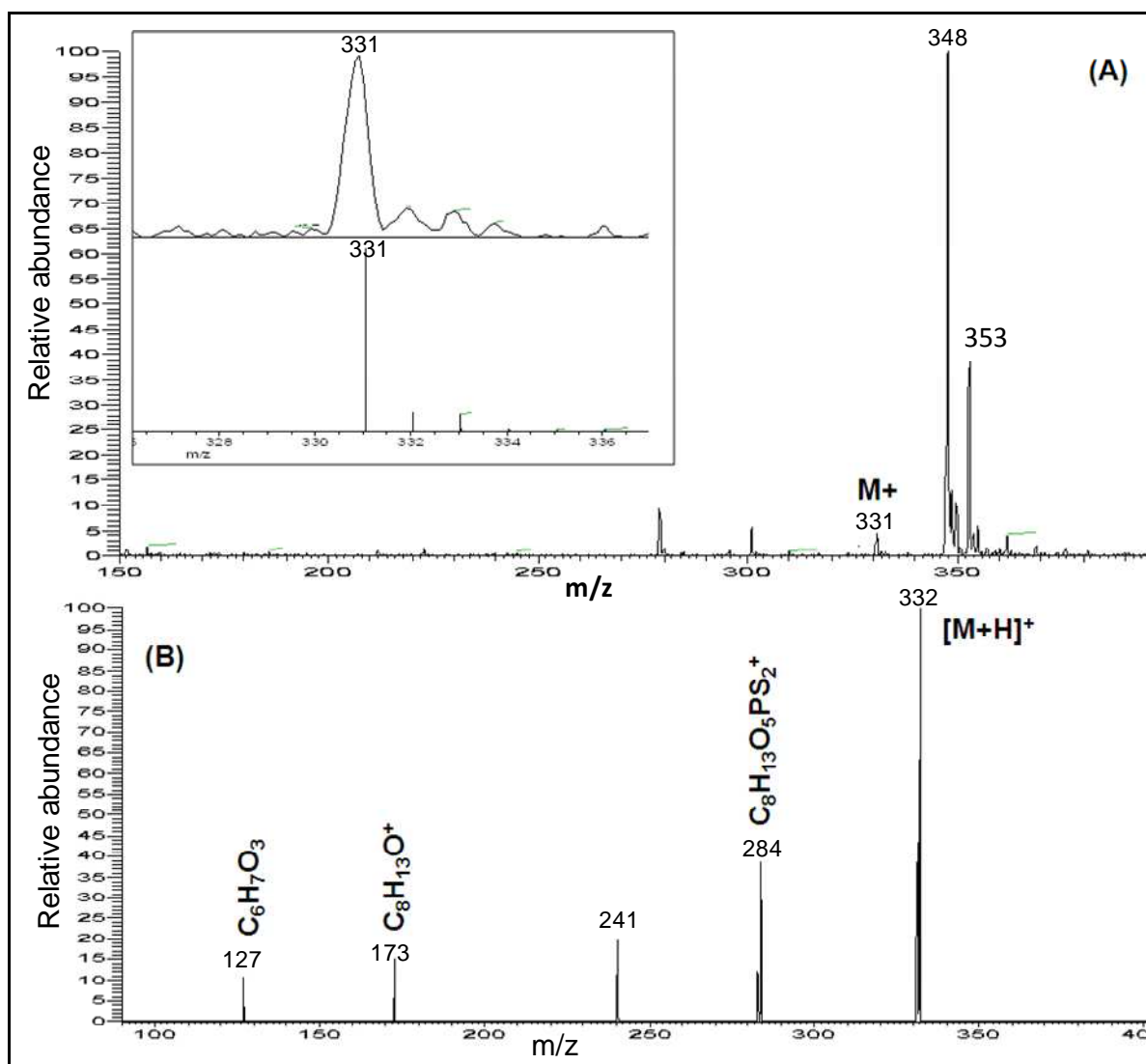
**Figure S6.** Time dependent removal of (A) ES and (B) ML by RGO. Initial concentrations of the ES and ML are shown in the inset of A and B, respectively.



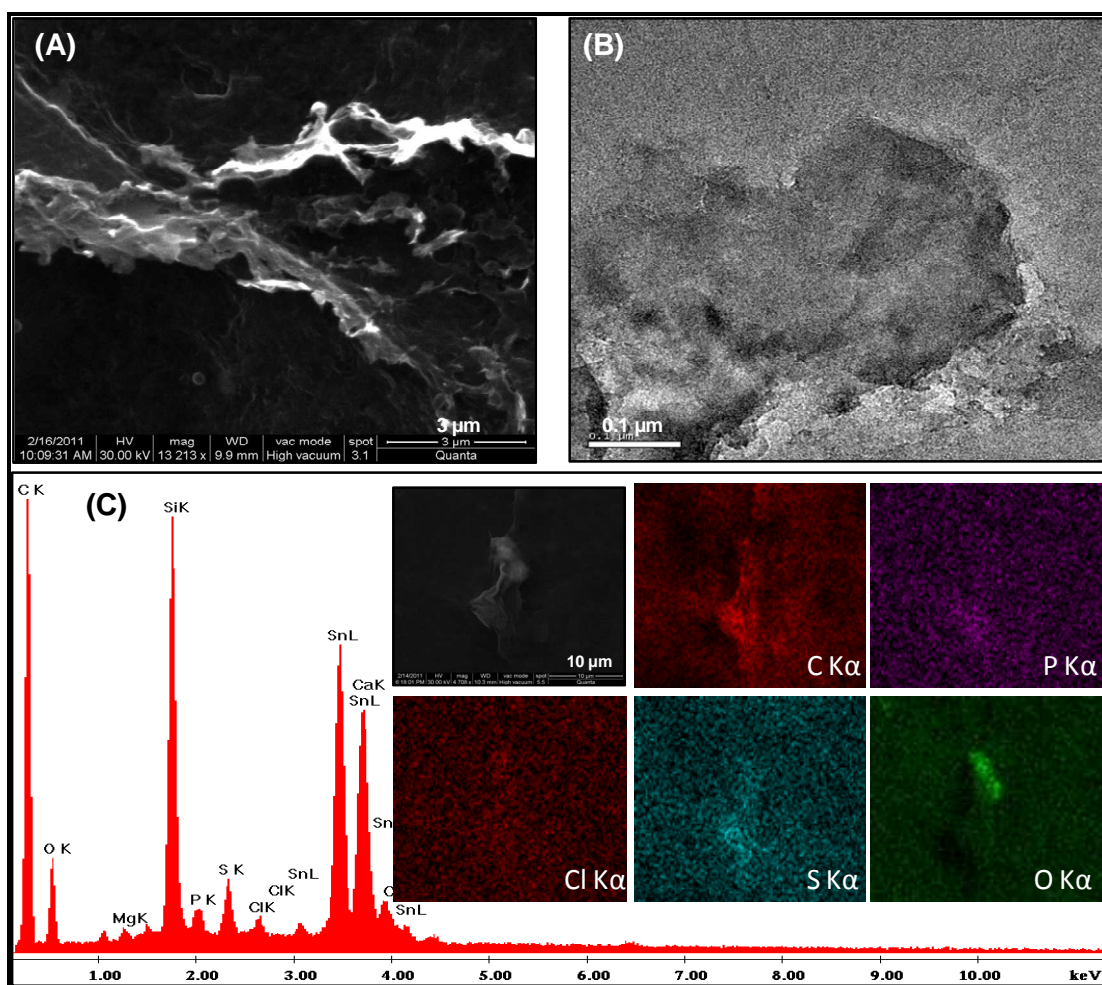
**Figure S7.** (A) UV/Vis spectra of RGO recorded at the end of each adsorption-desorption cycle. (B) Performance comparison of RGO for three consecutive cycles of adsorption/desorption process. RGO dose = 0.01%; Initial concentration of CP = 2 mg L<sup>-1</sup>; Temperature = 30±2 °C.



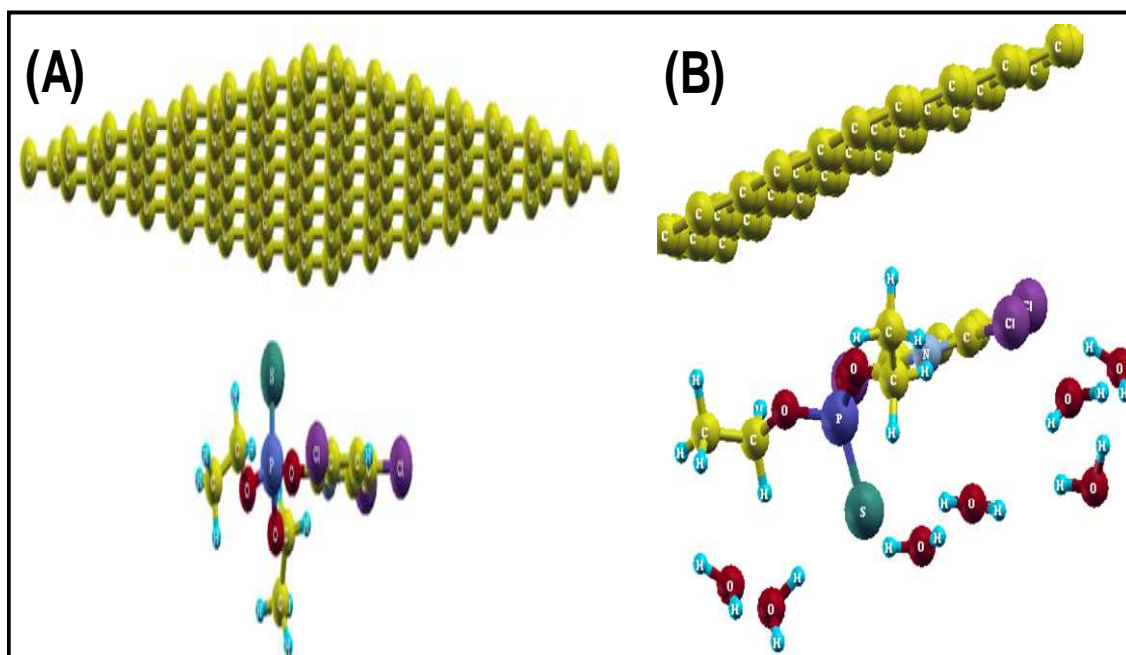
**Figure S8.** (A) Positive ion DESI mass spectrum of CP on a glass plate. (B) MS/MS analysis of m/z 352. Inset of A shows an expanded view of the molecular ion peak and its comparison with the theoretical isotope pattern.



**Figure S9.** (A) Positive ion DESI mass spectrum of ML on RGO. Inset of A shows the experimental (a) and its comparison with the theoretical isotope pattern (b) of the molecular ion peak of ML. (B) MS/MS analysis of the molecular peak at m/z 331.



**Figure S10.** (A) SEM (B) TEM and (C) EDAX spectrum of RGO after adsorption of ML. Inset of C shows the corresponding SEM image and elemental maps derived from the X-ray intensities.



**Figure S11.** Relaxed structure of (A) G-CP and (B) G-CP-W complexes.

**Table S12.** Binding energies of thermodynamically most stable configurations of both binary (P, W-G) and the ternary (W-G-P) complexes. The values clearly indicate that ternary complexes are more favorable than the binary.

Pesticide [P]	No. of water molecules [n]	System	Binding energy [kJ mol <sup>-1</sup> ]
ES	6	P-G	33
		W-P	-203
		Ternary	-218
CP	6	P-G	32
		W-P	-95
		Ternary	-181
ML	6	P-G	-3
		W-P	-98

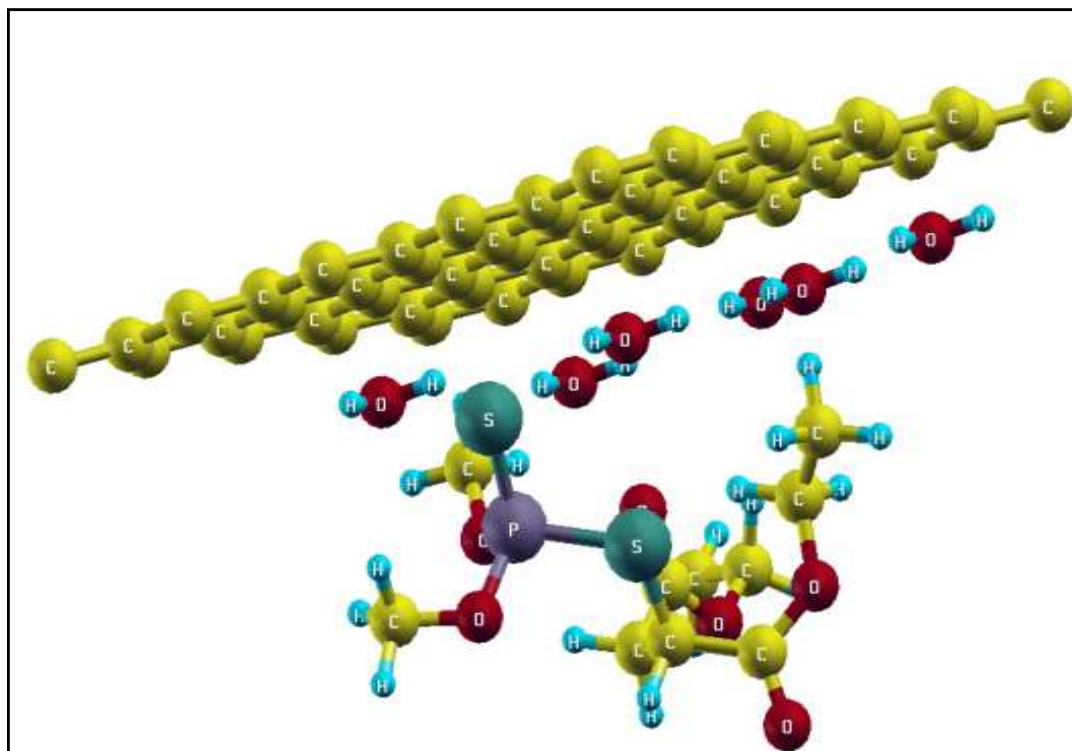


**Table S13.** Adsorption energies of ternary complexes of endosulfan, water and graphene.

System	Configuration [n = 6]	Adsorption Energy [kJ mol <sup>-1</sup> ]	Governing equation
Ternary	G-W-ES	-218	$E_{G-W-P} = E_{Complex} - (E_G + E_P + nE_W)$
	ES-G-W	-21	
	G-ES-W	-184	

G-W-ES: Water sandwiched between graphene and endosulfan; ES-G-W: Graphene sandwiched between endosulfan and water; G-ES-W: endosulfan sandwiched between graphene and water.

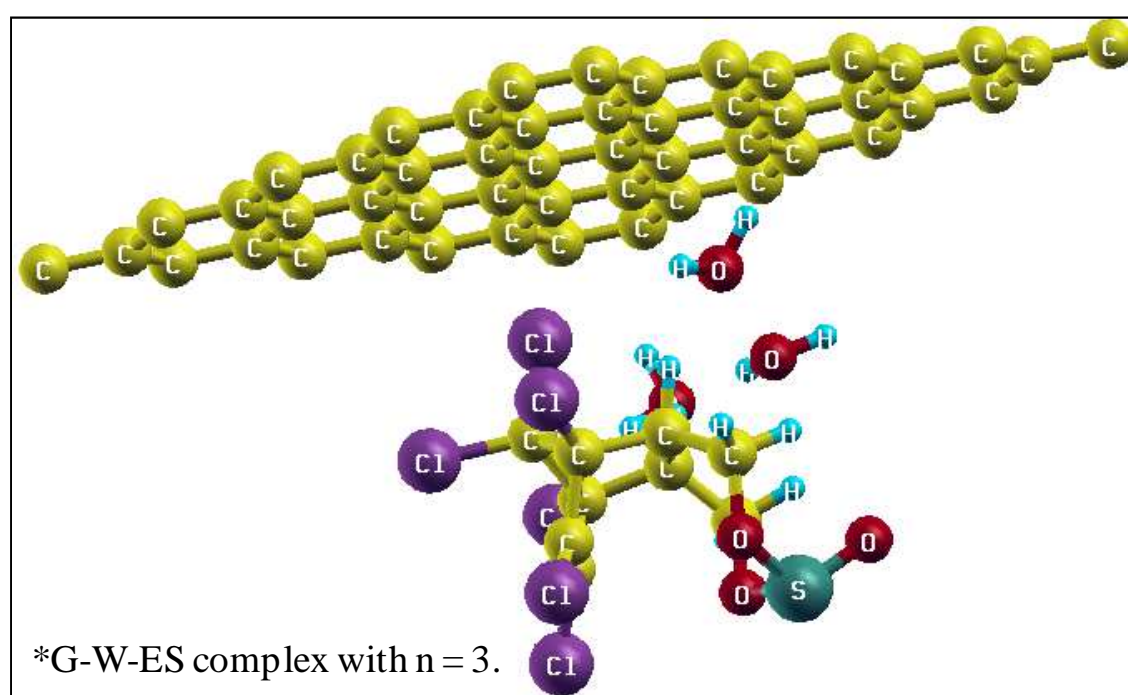
The above values show that G-W-ES complex is most stable when compared to other ternary configurations. Similar things were observed for other two pesticides.



**Figure S14.** Relaxed structure of G-W-ML complex.

**Table S15.** Variation in binding energy as a function of number of water molecules.

System	No. of water molecules [n]	Adsorption energy, $E_{G-W-P}$ [kJ mol <sup>-1</sup> ]	Governing equation
GWES*	3	-62	$E_{G-W-P} = E_{Complex} - (E_G + E_P + nE_W)$
	6	-169	
	12	-471	



**Table S16.** Variation in energies of adsorption of G-W-ES complex as function of concentration of endosulfan (mg g<sup>-1</sup> of C).

System [n=6]	Amount of ES [mg g <sup>-1</sup> of C]	Adsorption energy [kJ mol <sup>-1</sup> ]	Governing equation
G-W-ES	1879	258	$E_{G-W-P} = E_{Complex} - (E_G + E_P + nE_W)$
	1409	146	
	1056	-195	
	697	-217	