Supplementary data

Immobilized graphene-based composite from asphalt: Facile synthesis and application in water purification

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Supplementary data 1

Methods and Materials

Materials

The carbon source used for the preparation of graphene, asphalt, was procured from the local market of Chennai, India. Toluene (industrial grade) was purchased from Rankem Chemicals Pvt. Ltd., India. CP (HPLC assay 99.9%) and Rhodamine 6G chloride (R6G, $C_{27}H_{29}ClN_2O_3$) were obtained from Sigma Aldrich. Standard sand collected from Ennore, Tamilnadu was initially treated with 0.1 M nitric acid to remove impurities. Subsequently the sand was washed extensively with deionized water and dried at 100 ± 3 °C. This purified sand was sieved to obtain particles of desired size. All chemicals were used as received without additional purification. All solutions and suspensions were prepared using deionized water, unless otherwise mentioned.

In-situ synthesis of graphene-sand composite (GSC)

Asphalt was initially dissolved in toluene at a solid to solvent ratio of 1:10. The dispersed asphalt was then mixed with sand particles of size ranging from 200-500 micrometers. The carbon loading on the sand particles was varied by changing the sand to asphalt ratio. The samples were then dried in a hot air oven at 90 ± 3 °C under constant stirring for about 5 h. The dried sample was then transferred to a muffle furnace and subjected to heat treatment. The furnace was programmed as follows: a) temperature was increased from 30 to 250 °C in 30 min. b) held at 250 °C for an hour, c) again increased to 400 °C in next 1 h and d) finally held at 400 °C for next 4 h. It was then cooled to room temperature, just by switching off the power and without any control on the cooling rate. The optimum temperature was 400 ± 5 °C, which was established after several iterations. The stable carbon coating on the sand surface was evident from the characteristic black color of the sample. The pre-weighed material was then soaked in concentrated sulfuric

acid for about 30 min and filtered, washed several times with deionized water until the pH of the wash-water reaches that of the input water. The composite was then dried at 110 ^{o}C for further use. The sample was again weighed to check any weight gain or loss. This material is termed as graphene sand composite (GSC). The carbon loading (wt%) was calculated from thermo-gravimetric analysis (TGA) (Supplementary data Fig. S2).

Batch adsorption experiments

Batch experiments were carried out to evaluate the pollutant uptake capacity of the composite in 25 mL conical flasks. Calculated amount of adsorbent was added to 10 mL of the water spiked with the target pollutant (R6G or CP) and placed on a shaker at room temperature (30±2 ^{o}C). The solid-liquid separation was done by filtration. The filtrate was analyzed to quantify the target molecule R6G in the aqueous phase by UV/Vis spectrophotometer based on the absorbance at 527 nm. Analysis of CP was carried out at a wavelength of 297 nm. The effect of particle size, contact time, and adsorbent dose were evaluated by varying the parameters in the appropriate window. Except kinetics, all other studies were conducted by batch equilibration method. Control samples were kept in all the cases to assess the natural attenuation of the target molecule. All the experiments were conducted in duplicate and the average values are reported.

Fixed-bed column experiments

Continuous removal of the R6G was studied in fixed-bed columns made of transparent glass with a length of 500 mm and an internal diameter of 18 mm. The columns were packed with the adsorbent to a depth of 3 cm and operated in down-flow mode at a feed flow rate of 2.3 mL/min. The performance of the column was evaluated as a function of time at room temperature. The initial R6G concentration was maintained at 1 mg/L. The residual concentration of the effluent samples were analysed as a function of time.

The R6G loaded adsorbents were regenerated *in-situ* in the columns using acetone as the eluent. The regenerant was passed through the column bed with the same flow rate of adsorption cycle. Nearly 42 bed

volumes of acetone were passed through the column in down-flow mode and followed by purging with hot air. The column was then washed to check the pollutant concentration in the wash-water. The spent regenerant and back washed water were collected and analysed for eluted concentrations of the pollutant as function of time.

Instrumentation

UV/Vis spectra were measured using a Perkin-Elmer Lambda 25 UV/Vis spectrophotometer. Raman spectra were collected using a confocal Raman spectroscope (WiTec GmbH CRM 200). High-resolution transmission electron microscopy (HRTEM) of the samples was carried out using a JEOL 3010 microscope with a UHR pole piece. X-ray photoelectron spectroscopy (XPS) measurements were done with Omicron ESCA Probe spectrometer with unmonochromatized Mg K_α X-rays (h_γ = 1253.6 eV). The energy resolution of the spectrometer was set at 0.1 eV at pass energy of 20 eV. Binding energy was corrected with respect to C 1s at 284.5 eV. Surface morphology, elemental analysis and elemental mapping studies were carried out using scanning electron microscopy (SEM) equipped with energy dispersive analysis of X-rays (EDAX). SEM measurements used indium doped tin oxide (ITO plate), presence of Si and Sn in the images is expected. For mass analyses, an Applied Biosystems Voyager DE Pro LDI-MS instrument was used. A pulsed nitrogen laser of 337 nm was used for desorption/ionization.

Mechanism of formation of graphenic material from asphalt

The mechanism behind the formation of graphenic material is not fully understood. However, Raman and XPS evaluation suggested the loss of organic functionalities from asphalt during the process. TGA also indicated a weight loss during the process. Asphalt mainly consists of highly condensed polycyclic aromatic hydrocarbons. It is considered as a colloidal mixture with the chief component being asphaltene. Asphaltene is composed of nitrogen, oxygen and sulfur (as functional groups or adsorbates) in addition to carbon and hydrogen. Asphaltene is highly soluble in toluene. In our process, asphalt was first dissolved in toluene and hence chief fraction in the solution is asphaltene. The carbon functionalities are highly

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susceptible to thermal decomposition above 300 ^{0}C [1, 2]. Hence, based on the prevailing knowledge and Raman, XPS and TGA results obtained in the study, it is proposed that at elevated temperatures, asphaltene will lose the impurities (the functional groups) and will form unfunctionalized carbon. This carbon, in presence of a solid substrate (sand particle), is believed to combine and form the graphenic materials. The substrate not being single crystalline, the formation can start from different places in different orientation. This leads to the formation of large number of structural defects in the films formed.

Supplementary data 2
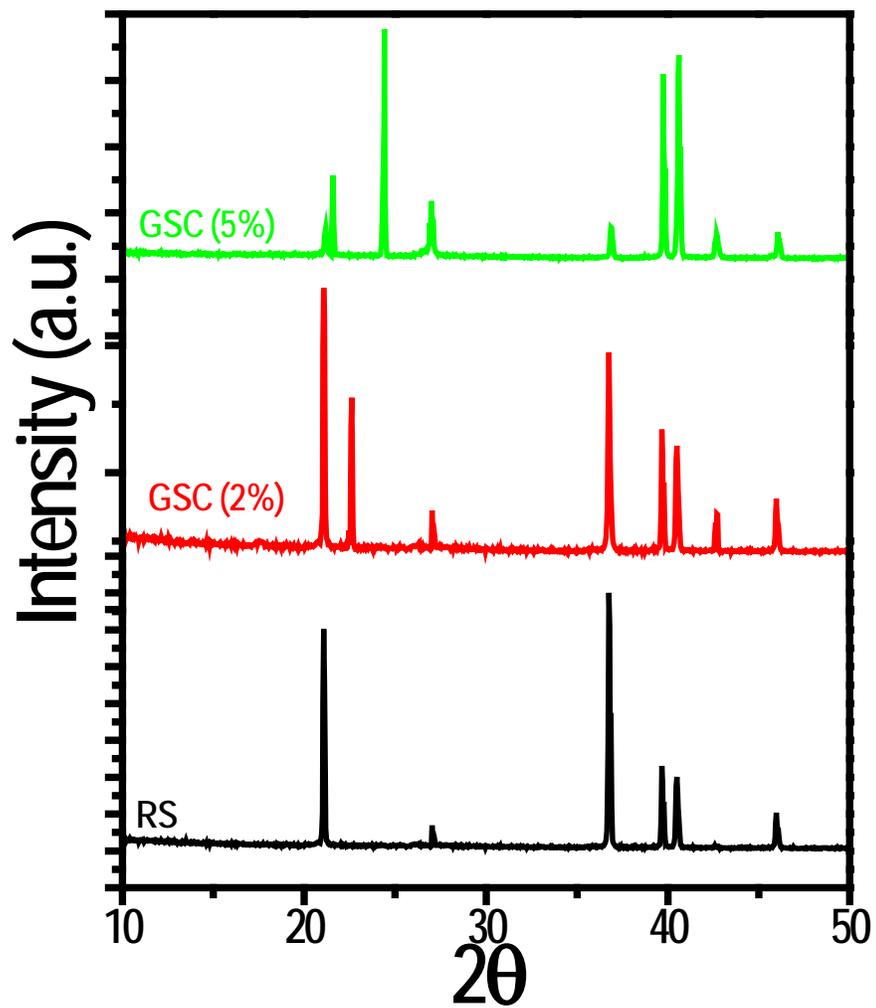
Fig S2: *XRD data of bare sand (silica) and GSC at different graphenic carbon loading (2 and 5 wt%).*

<u>Supplementary data 3</u>
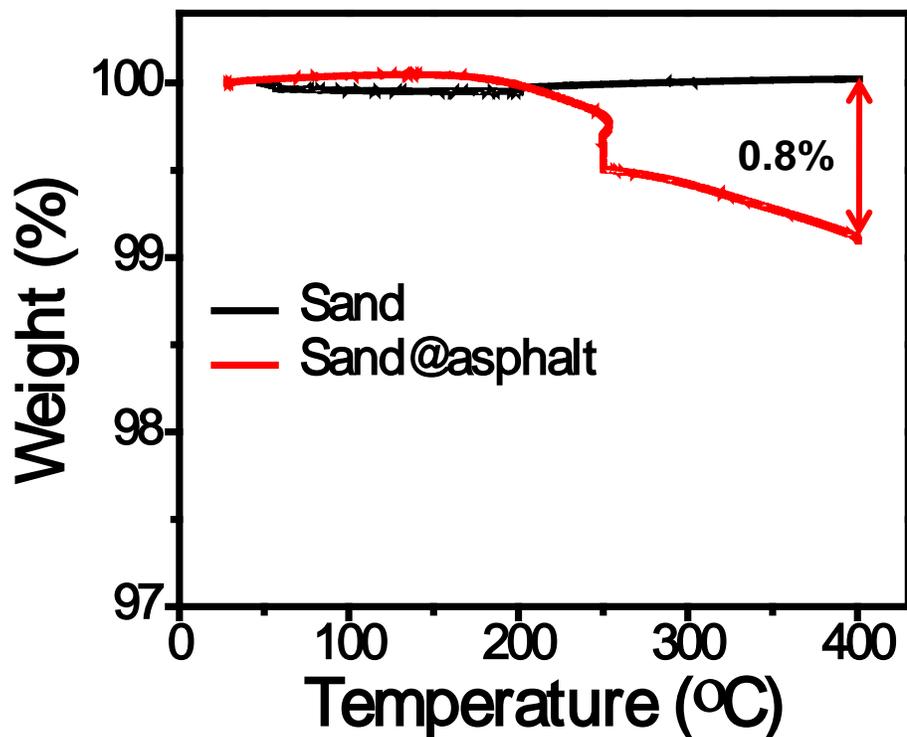
Fig. S3: TGA of sand and asphalt coated sand (2 wt%), showing weight loss of 0.8 wt%. Temperature was programmed as given in text. The initial loading is based on calculation. The temperature was not ramped above 400 ^0C as the auto-ignition temperature in air is above this value. However, heating up to 750 ^oC in N_2 atmosphere did not increase the adsorption capacity.

Supplementary data 4
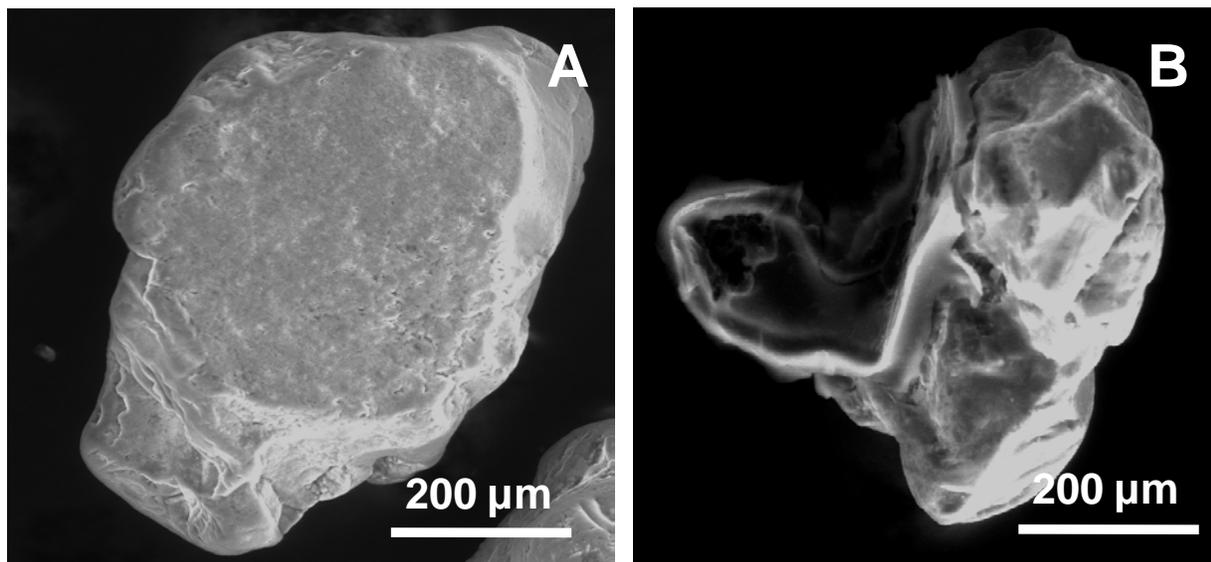
Fig. S4: SEM images of A) virgin-sand showing that the surface is plain and B) sand coated with graphene, where the surface is rougher and sheet-like structures can be seen.
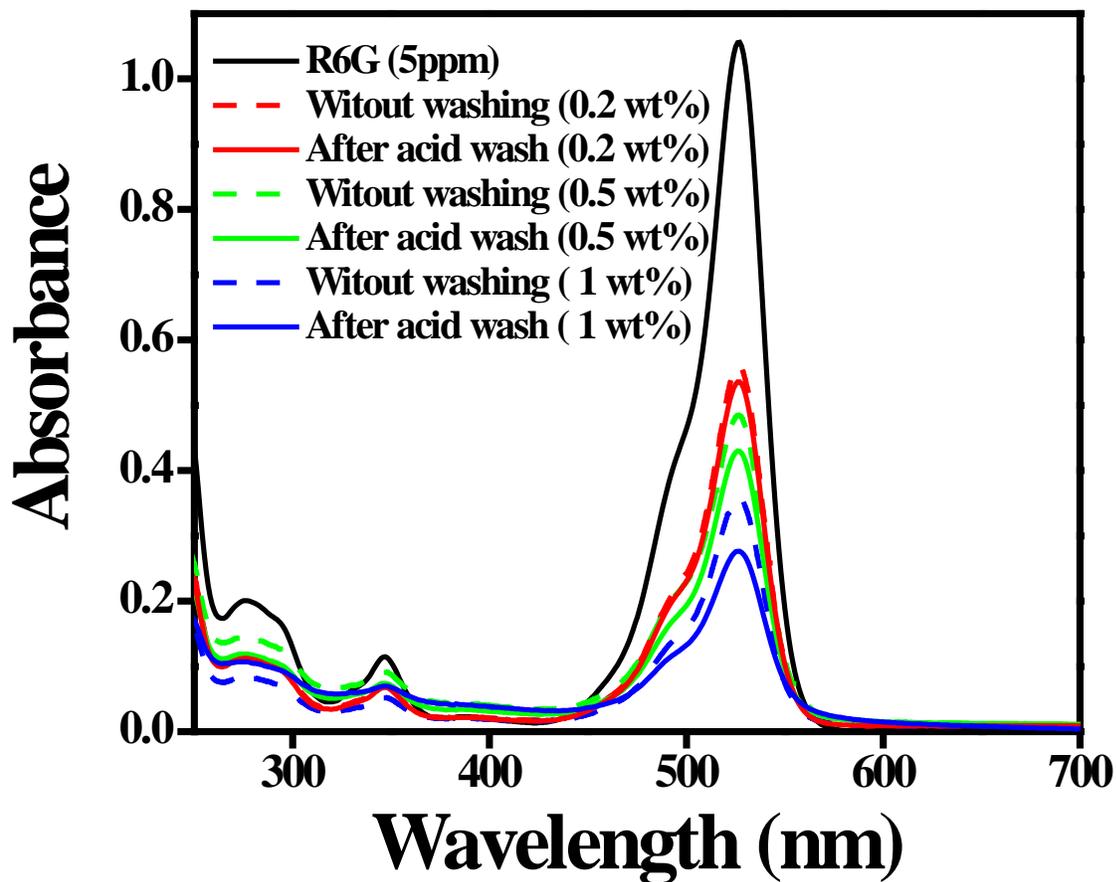
Supplementary data 5

Fig. 4A and B show the SEM images of GSC with 0.2 % loading, where the surface is rougher than the pristine sand. When the loading reached 0.5%, careful observation showed more prominent surface changes. The surface looked rougher compared 0.2% loading (Fig. 4C and D). At 1% loading, a clear sheet-like structure was visible (Fig. 4E and F). Fig. 4F shows a closer view (higher magnification) of a GSC particle with 1% loading. We can see a sheet covering the surface of sand. The outward appearance (color) of the sand also changed as the loading increased. The color turned more intense as the loading increased (Fig. 4G).

Supplementary data 6
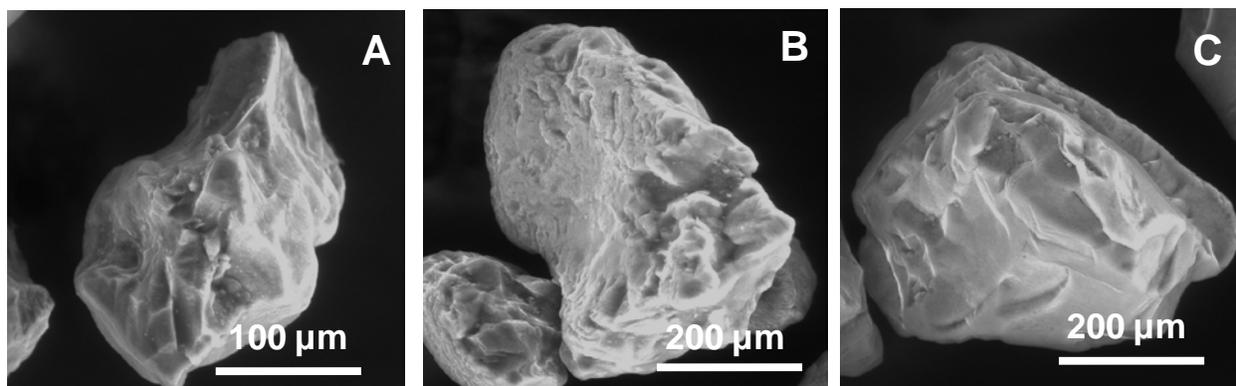
Fig. S6: *SEM images of GSC with different sand particle sizes. A) Less than 0.2 mm, B) between 0.2-0.3 mm and C) more than 0.3 mm having 0.5% carbon loading.*

Fig. S7: UV/Vis spectrum showing an increase in efficiency of GSC after acid wash for different carbon loading.

Supplementary data 8

Video 1: Removal of Coca-cola. Bed depth was 6 cm and no special care was taken for controlling the flow-rate in this clip.

Supplementary data 9

Pseudo-first-order equation: $q_t = q_e \left(1 - e^{-k_1 t}\right)$ (1)

Pseudo- second-order equation: $\dfrac{q_e^2 k_2 t}{1 + q_e k_2 t}$ (2)

Where q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively (mg/g). k_1 is the rate constant of pseudo-first-order adsorption (L/min) and k_2 is the rate constant of pseudo-second order adsorption (g/mg min). The estimated value of k_1 and k_2 are 0.02 /min and 0.019 mg/g min, respectively.
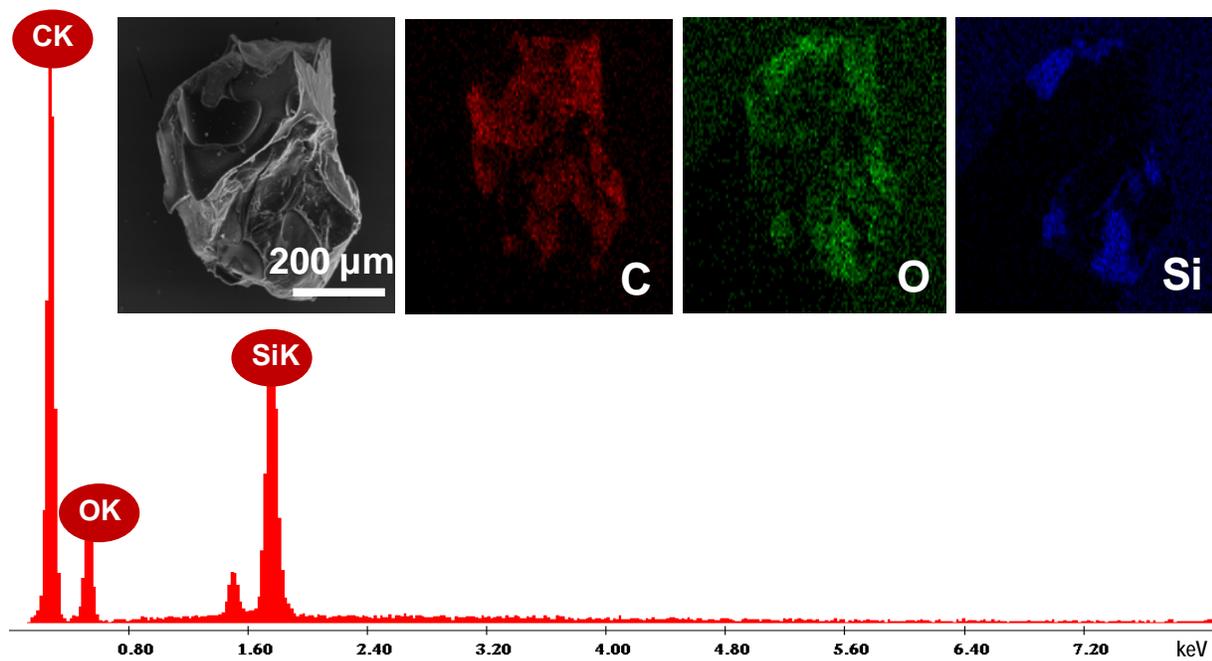
Supplementary data 10
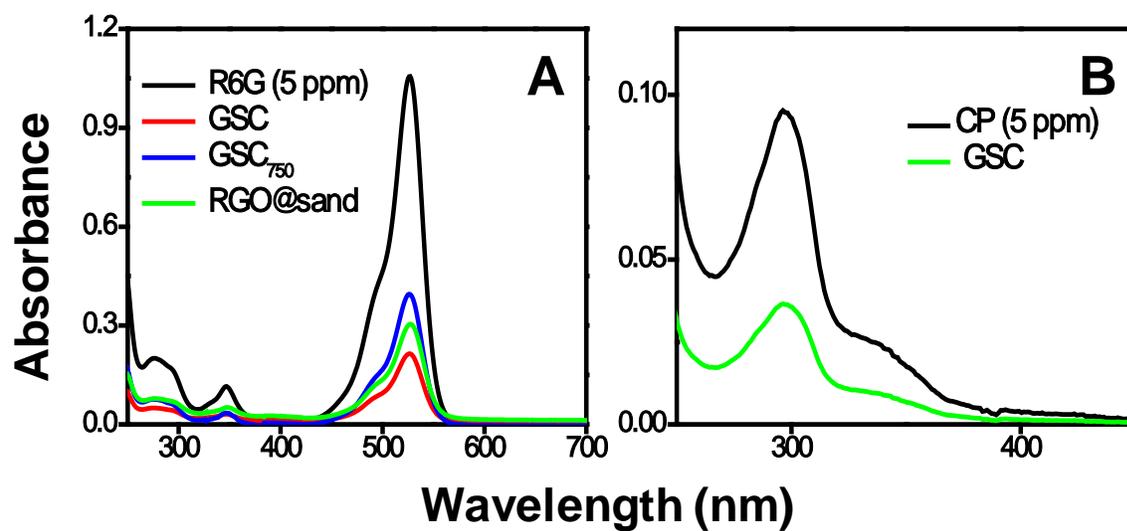
Fig. S10: UV/Vis spectrum showing A) removal of R6G with different graphenic materials as the adsorbent.

B) Removal of CP with GSC.

Fig. S11: SEM-EDAX of CP adsorbed GSC after regeneration. P, Cl and S are absent.

Supplementary data 12

m/z= 181

m/z= 79

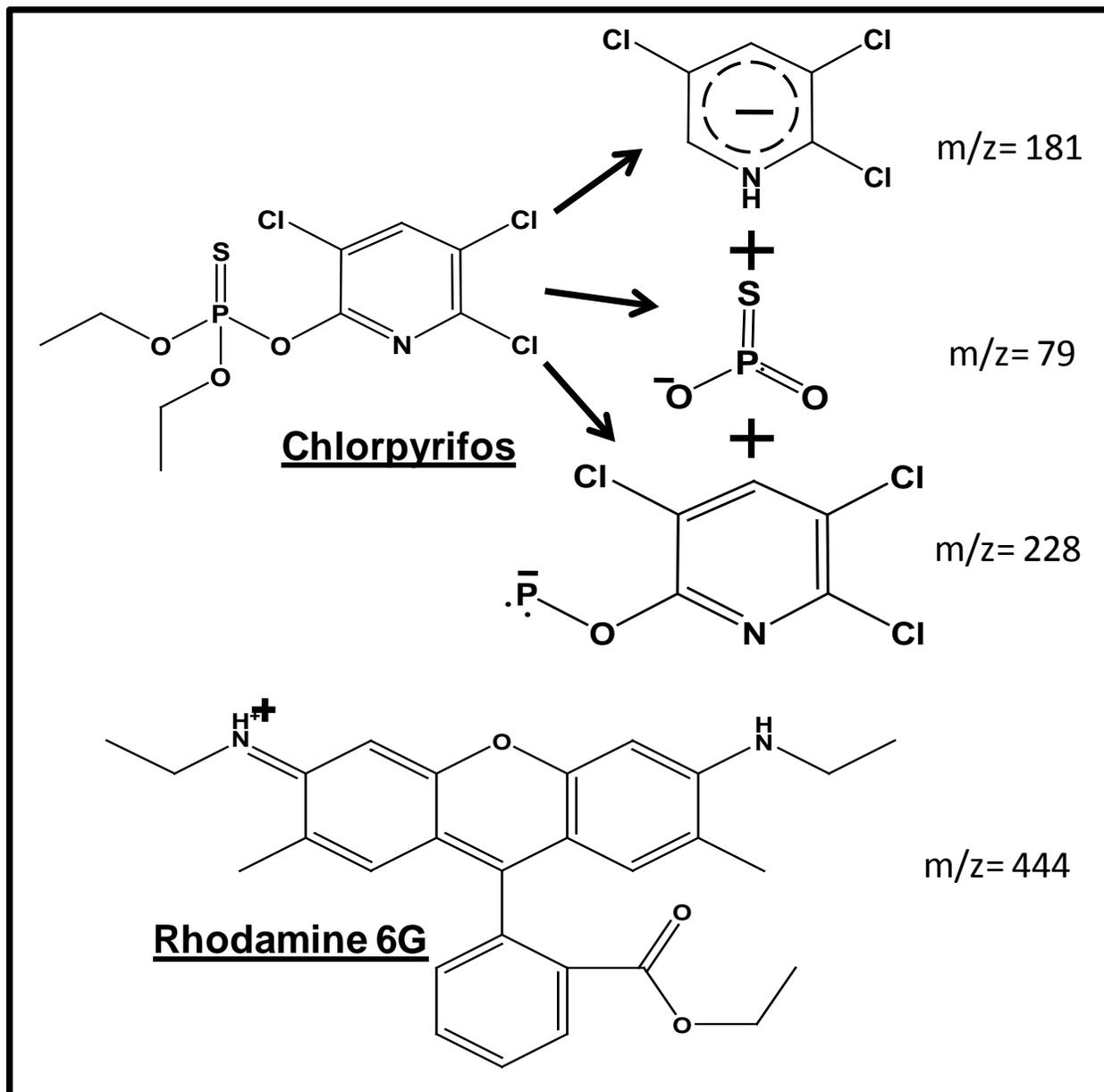m/z= 228

m/z= 444

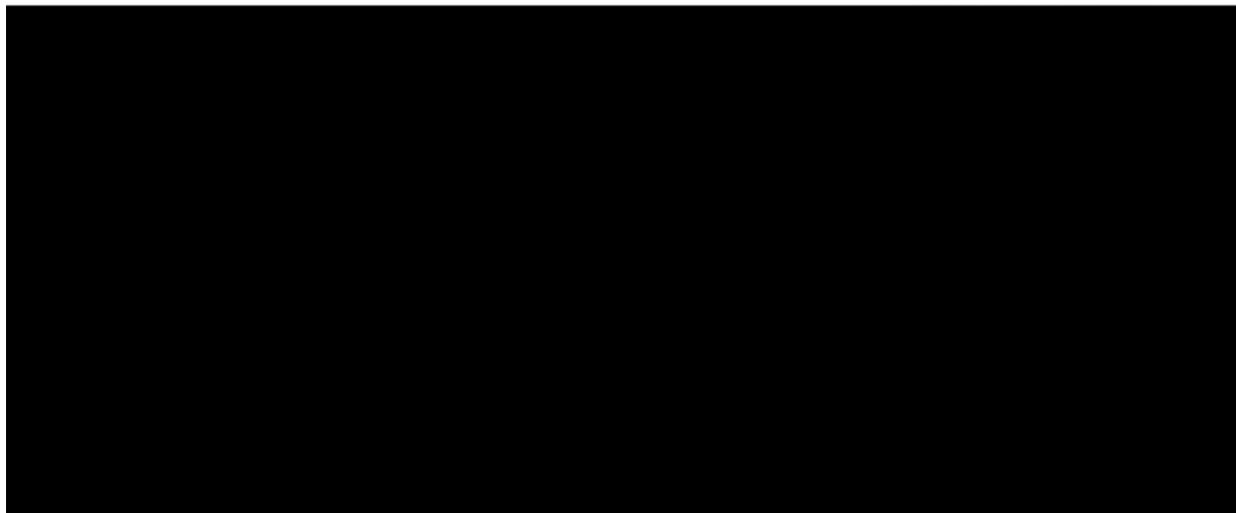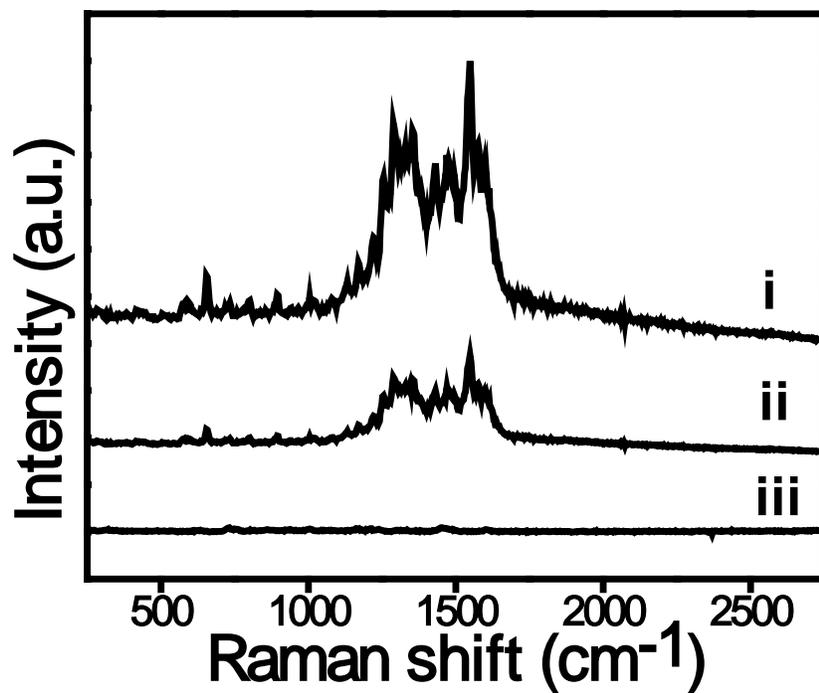**Chlorpyrifos**

Rhodamine 6G

Fig. S12: Common fragments of CP and the molecular ion of R6G.

Supplementary data 13

Fig. S13: *Photographs of a) initial material (GSC), b) R6G adsorbed GSC and c) GSC after regeneration. The color change of the material after adsorption of R6G, from black (a) to reddish (b) can be clearly seen.*

Fig. S14: *SERS of the filtrate after passing different volumes of acetone during regeneration, i) after 10 bed volume, ii) after 20 bed volume and iii) 30 bed volume.*

References:

[1] G. de la Puente, J. J. Pis, J. A. Menendez, P. Grange, Thermal stability of oxygenated functions in activated carbons, J. Anal. Appl. Pyrol. 43 (1997), 125–138.

[2] A. G. Vandeputte, M. F. Reyniers, G. B. Marin, Theoretical study of the thermal decomposition of dimethyl disulfide, J. Phys. Chem. A 114 (2010), 10531-10549.