

Simultaneous dehalogenation and removal of persistent halocarbon pesticides from water using graphene nanocomposites: A case study of lindane

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Contents:

Number	Description	Page number
S1	Preparation of GO and RGO	2-4
S2	TEM image of RGO@Ag with varying silver ion concentration	5
S3	XPS spectrum of RGO@Ag composite	6
S4	SEM-EDAX of RGO@Ag	7
S5	XPS spectrum of RGO@Ag after reaction with lindane	8
S6	GC-ECD data of lindane	9
S7	GC trace of lindane and the isomers	10

S8	GC-MS spectrum of lindane and the degraded product	11
S9	GC-MS of three different isomers of TCBs	12
S10	MS2 of the peak of the degraded product, trichlorobenzenes	13
S11	Raman spectrum of the product	14
S12	UV/Vis spectrum of silver nanoparticles	15
S13	UV/Vis spectrum showing degradation capacity of lindane with other adsorbents	16,17
S14	UV/Vis spectrum and comparison for the removal efficiency of lindane with different adsorbents	18
S15	Silver nanoparticle concentration towards the degradation of lindane	19,20
S16	Effect of tap water and 100 ppm of NaCl solution	21
S17	Reuse of RGO@Ag composite	22

Supporting Information 1

S1: Preparation of GO and RGO

Graphene oxide (GO) was synthesized from graphite powder (purchased from R. K. Scientific) based on the Modified Hummers' method. Approximately 2 g of graphite powder was taken and pre-oxidized in a hot solution (temperature maintained around 80-90 °C) of concentrated H₂SO₄ (~ 12 mL) containing K₂S₂O₈ (4 g) and P₂O₅ (4 g) for 6 h. A dark blue mixture was formed which was then cooled to room temperature. About 300 mL distilled water was added carefully and slowly to the mixture. It was filtered using a Whatmann No. 40 filter paper and kept for drying overnight in a hot air oven at 55-60 °C. This pre-oxidized graphite powder (2 g) was added to 100 mL of cold H₂SO₄ at 0 °C (temperature maintained

by an ice bath), to which 12 g of KMnO_4 was added slowly under continuous stirring, making sure that the temperature of the reaction media never crossed $5\text{ }^\circ\text{C}$. The solution was further stirred for 2 h at room temperature and 200 mL of distilled water was added slowly. Care was taken, as the reaction is exothermic. To the mixture, 560 mL of distilled water was added and the reaction was stopped with the addition of 10 mL H_2O_2 (30 %). The resulting bright yellow solution was kept undisturbed overnight. The product was decanted, washed with HCl (1:10) twice and then suspended in water via sonication. Unexfoliated GO was removed by centrifugation at 10000 rpm for 20 min and then suspended in distilled water (1 g in 200 mL of water i.e. 0.5 wt % of GO). The resulting brown dispersion was extensively dialyzed to remove the residual metal ions and to neutralize the pH. The resulting 0.5 wt % of GO (stock solution) was stored in glass bottles for further use.

About 2 ml of GO was taken in a beaker and diluted to 100 mL with distilled water. The solution was heated to $80\text{ }^\circ\text{C}$ and to it 60 μL of NH_3 and 35 μL of hydrazine were added with continuous stirring for 5 min. Stirrer was switched off and the solution was kept at $80\text{ }^\circ\text{C}$ for 2 h. The resulting black colored dispersion was reduced graphene oxide (RGO). This RGO (0.01 wt %) was dialyzed and kept as the stock solution.

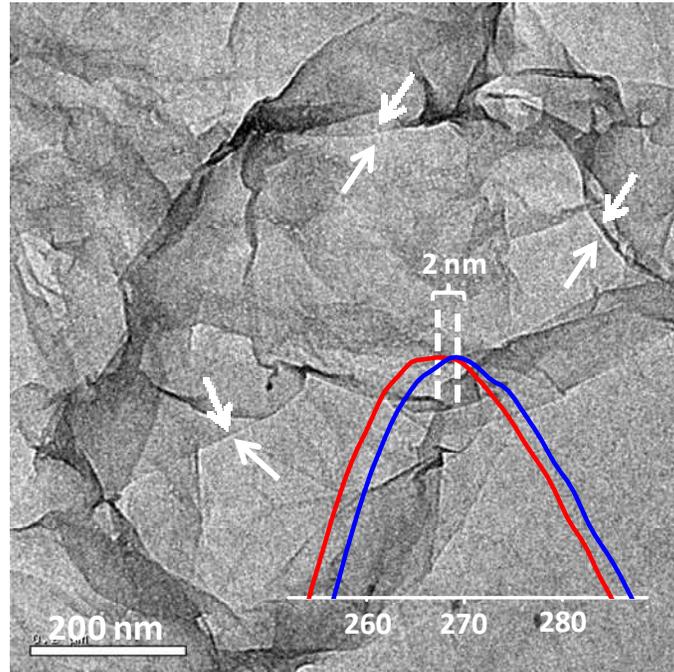


Figure S1: HRTEM image of RGO. Nanometer thick folding of the sheets can be seen. Scale bar is 200 nm. The inset shows an expanded view of the crest of the UV-Vis spectrum shown in Figure 1 (main text), indicating a shift in the graphene peak.

Supporting Information 2

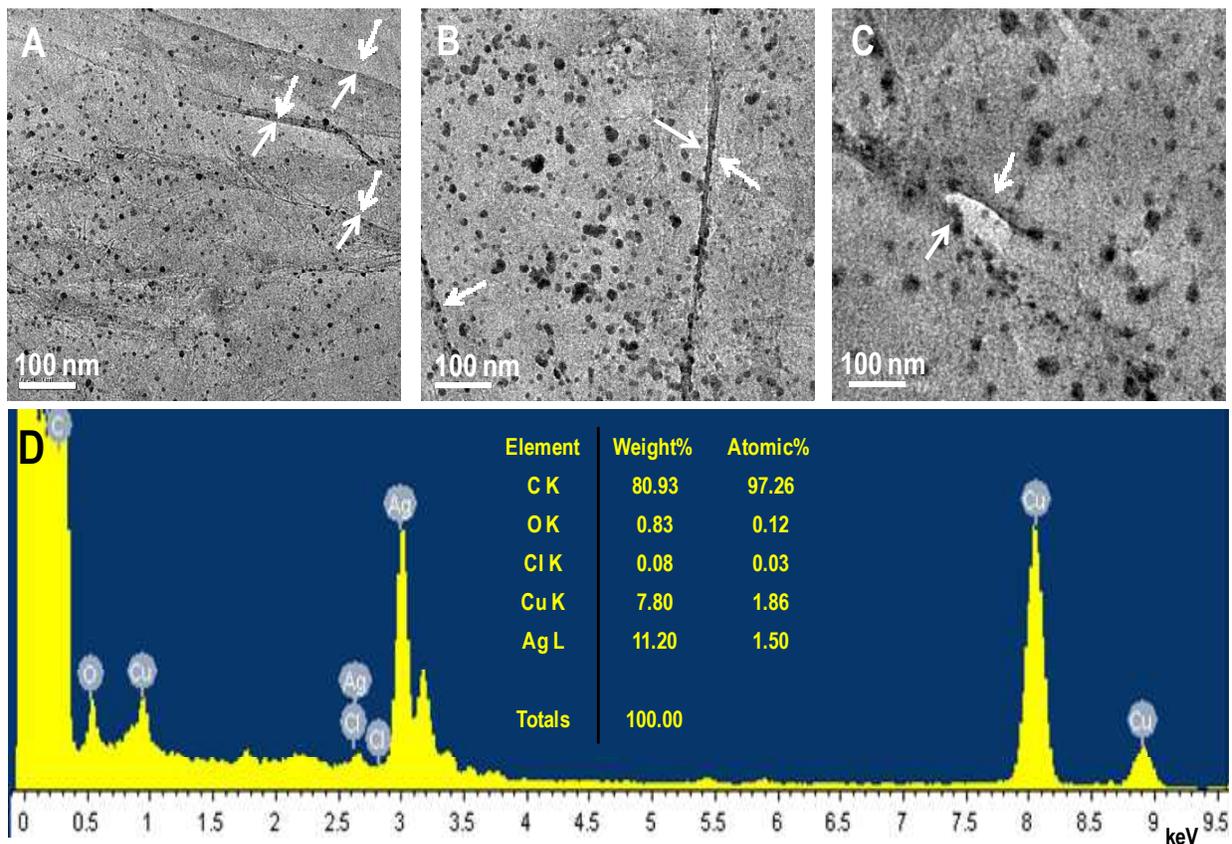


Figure S2: TEM image of RGO@Ag with varying silver ion concentration A) 0.01, B) 0.05 and C) 0.1 mM, respectively, yielding NPs of the size 5, 20 and 50 nm, respectively. D) HRTEM-EDAX spectrum of RGO@Ag.

Here, we have taken three different concentrations (0.01, 0.05 and 0.1 mM, respectively) of AgNO_3 and 25 mL of 0.01 % RGO was added to them separately. It is quite evident from the HRTEM images that with the increase of silver ion concentration (AgNO_3) during the preparation of the composite, the size of the silver nanoparticles formed on the graphene sheets increased. The sizes of silver nanoparticles formed over graphene sheet were 5, 10, and 50 nm for the concentration of 0.01, 0.05 and 0.1 mM, respectively.

Supporting Information 3

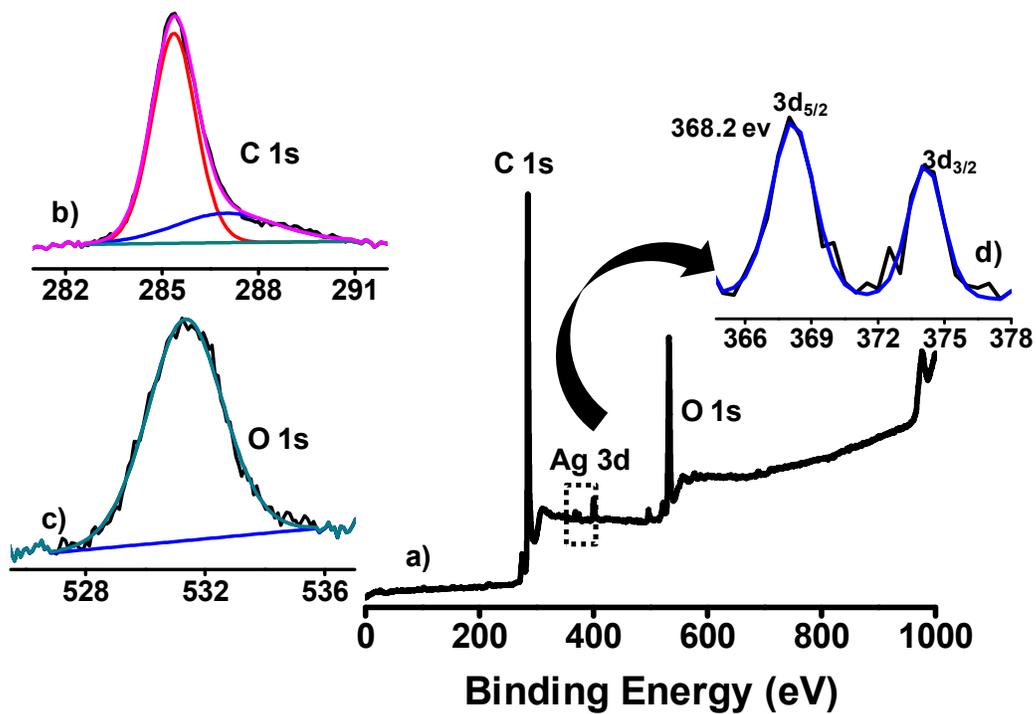


Figure S3: a) XPS survey spectrum of RGO@Ag composite showing the presence of silver, carbon and oxygen. Deconvoluted XPS spectrum of b) carbon, c) oxygen and d) silver.

Supporting Information 4

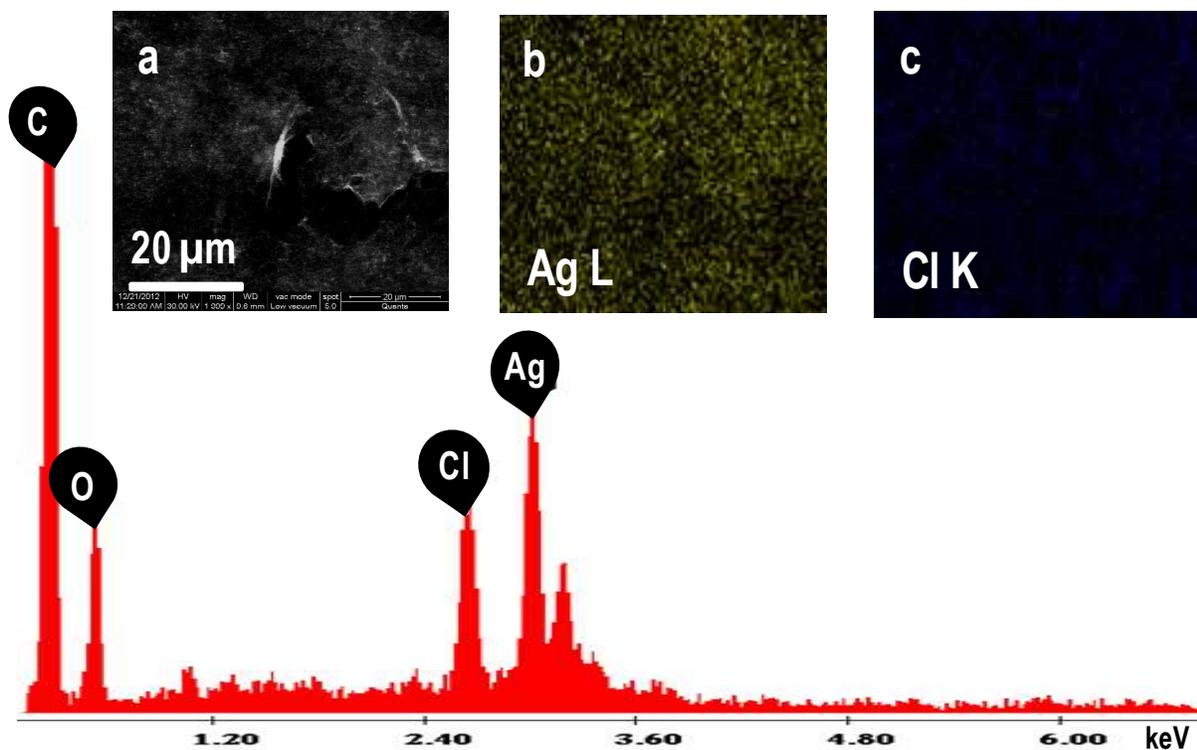


Figure S4: SEM-EDAX spectrum of the image a in the inset. a) SEM image of RGO@Ag after the reaction. b & c) Elemental mapping of the image 'a' showing the presence of silver and chlorine, respectively. The scale bar is the same in a, b and c.

Supporting Information 5

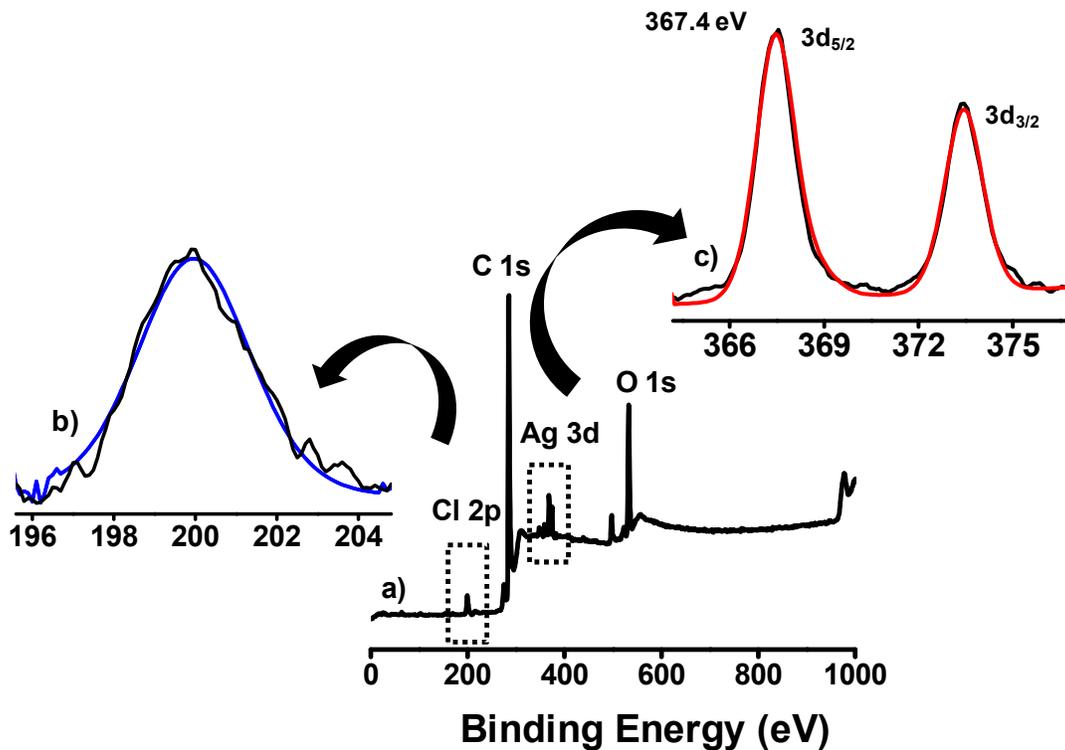


Figure S5: a) XPS survey spectrum of RGO@Ag composite after the reaction with lindane showing the presence of silver, chlorine carbon and oxygen. Deconvoluted XPS spectrum of b) chlorine and c) silver.

Supporting Information 6

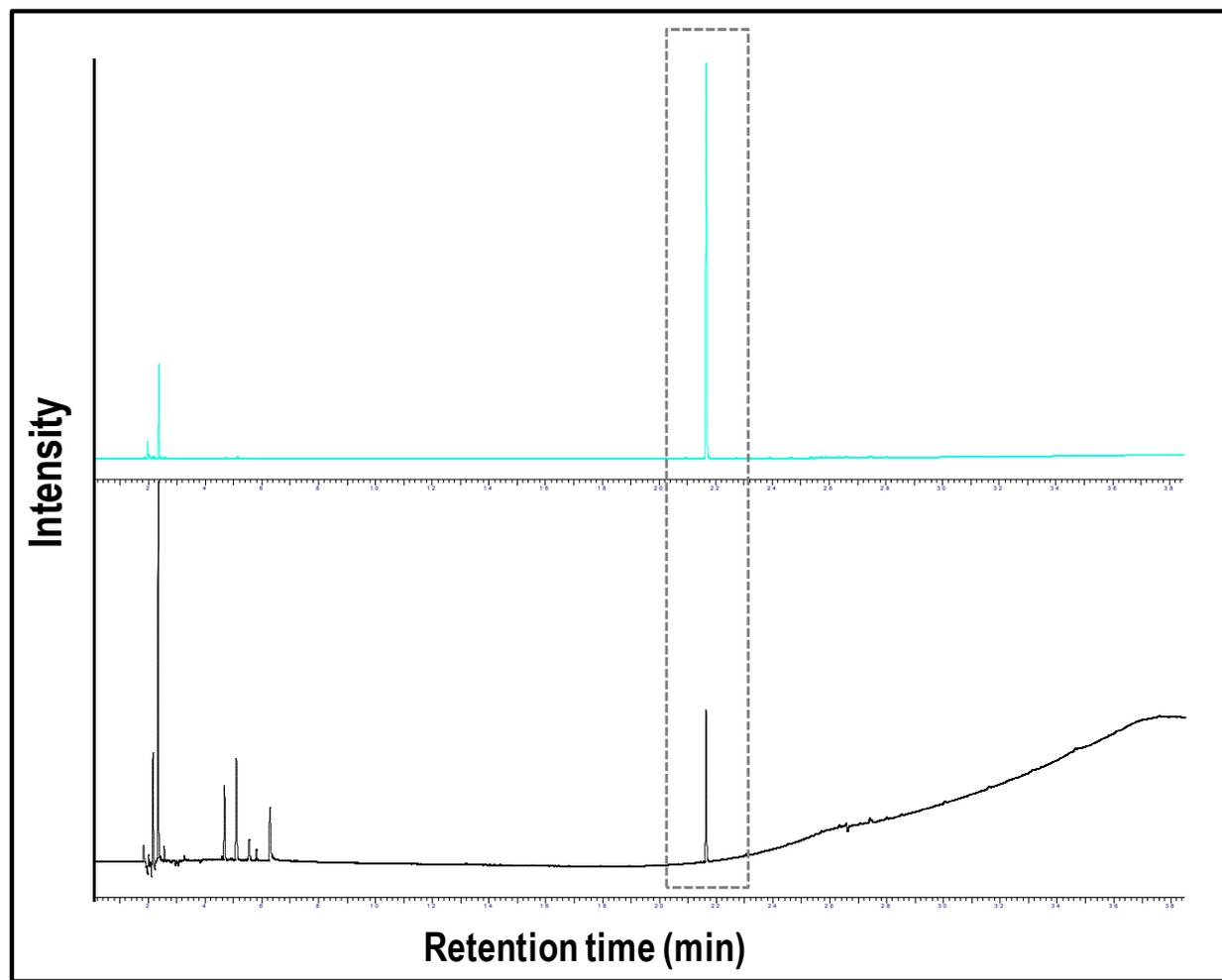


Figure S6: GC-ECD data of lindane (light blue trace) and the degraded product (black trace) after 5 min of reaction (note that in this case, lindane was initially dissolved in hexane and spiked). The dotted box corresponds to the peak of lindane.

Supporting Information 7

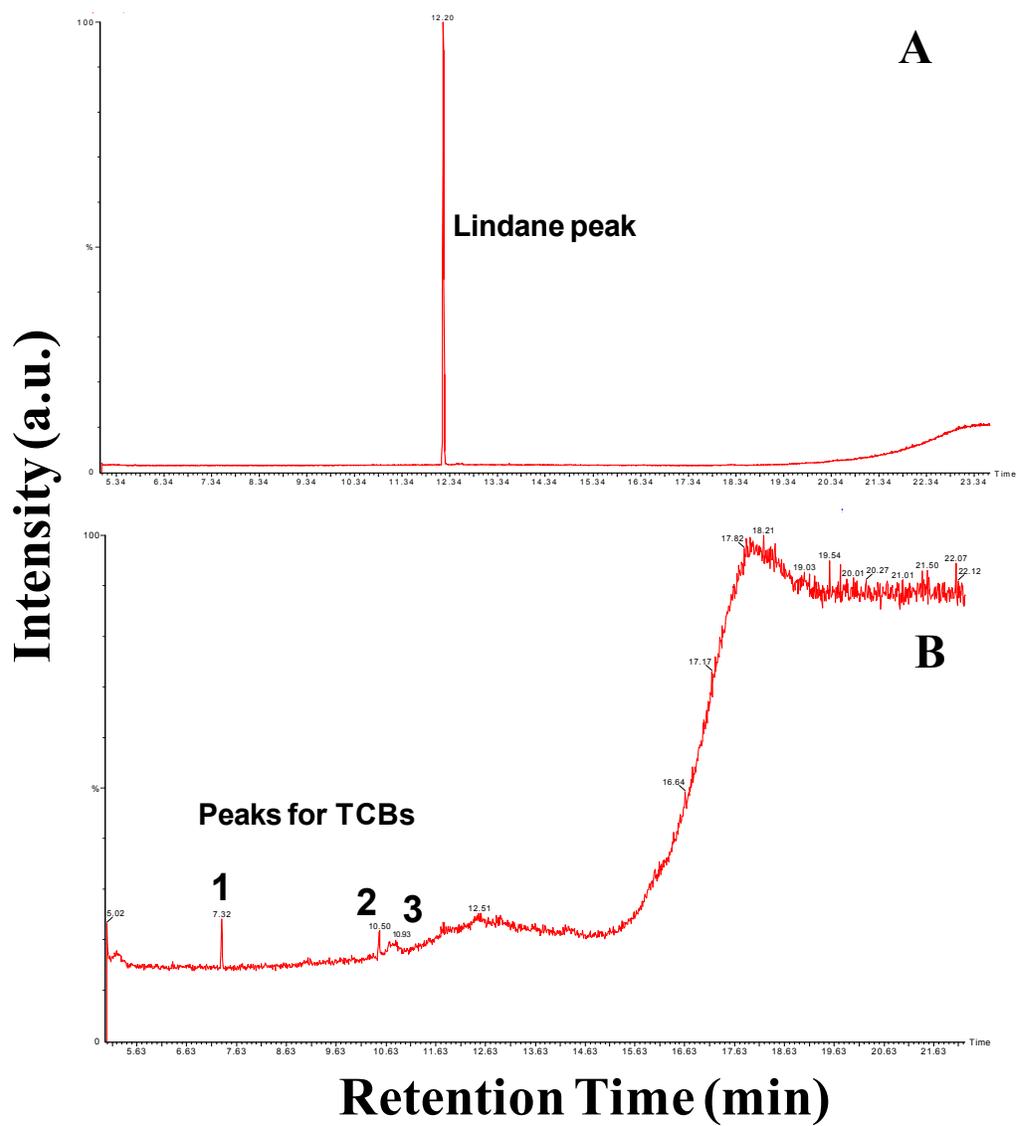


Figure S7: GC-MS trace of A) lindane and B) the isomers of TCB. (1, 2 and 3 are the peaks for TCB).

The GC traces of Figure 2 in the main text give different retention time for lindane and the products, as the parameters are different..

Supporting Information 8

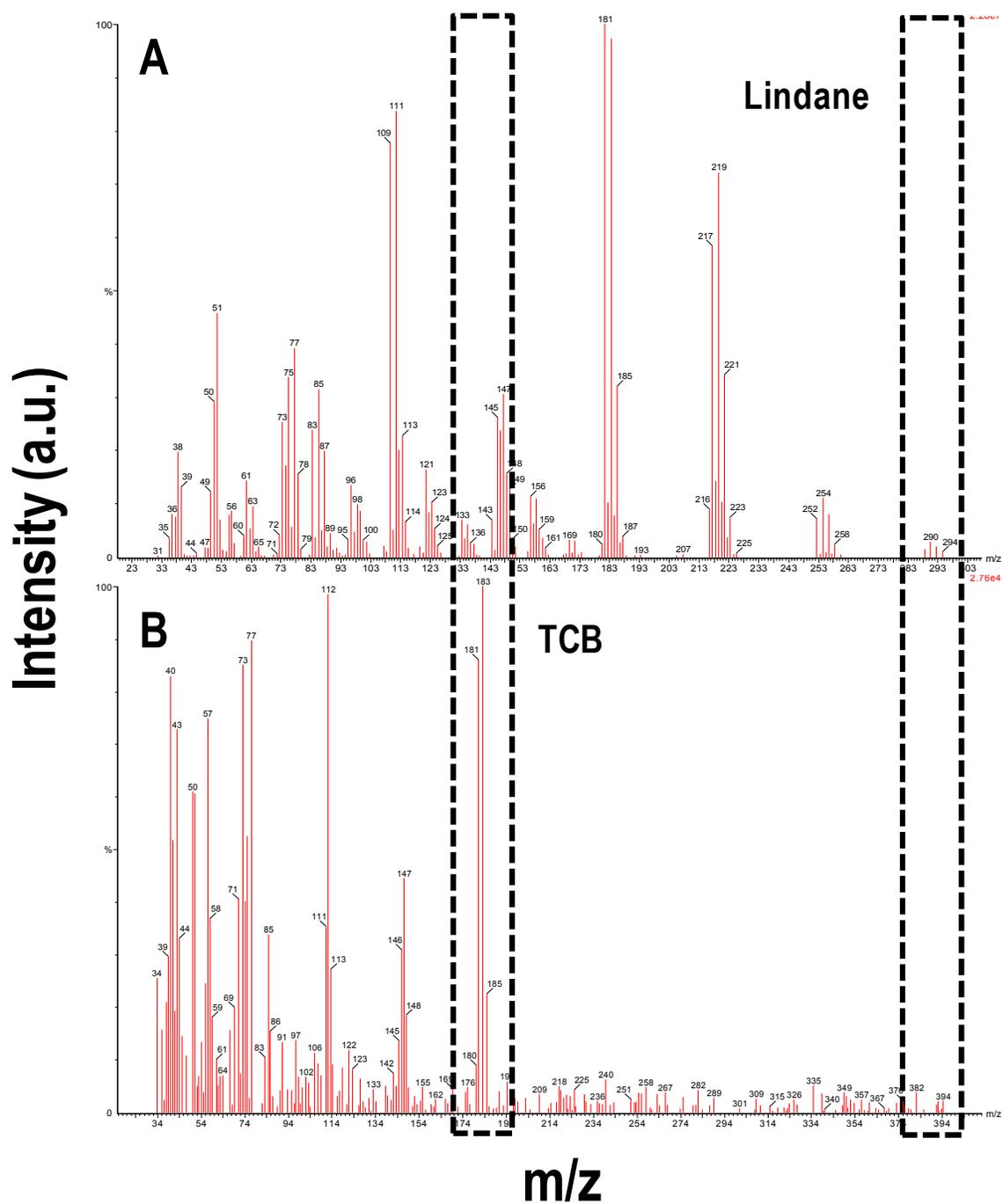


Figure S8: GC-MS spectrum of A) lindane and B) the degraded product appearing at a retention time of 7.32 min in Figure S5B.

Supporting Information 9

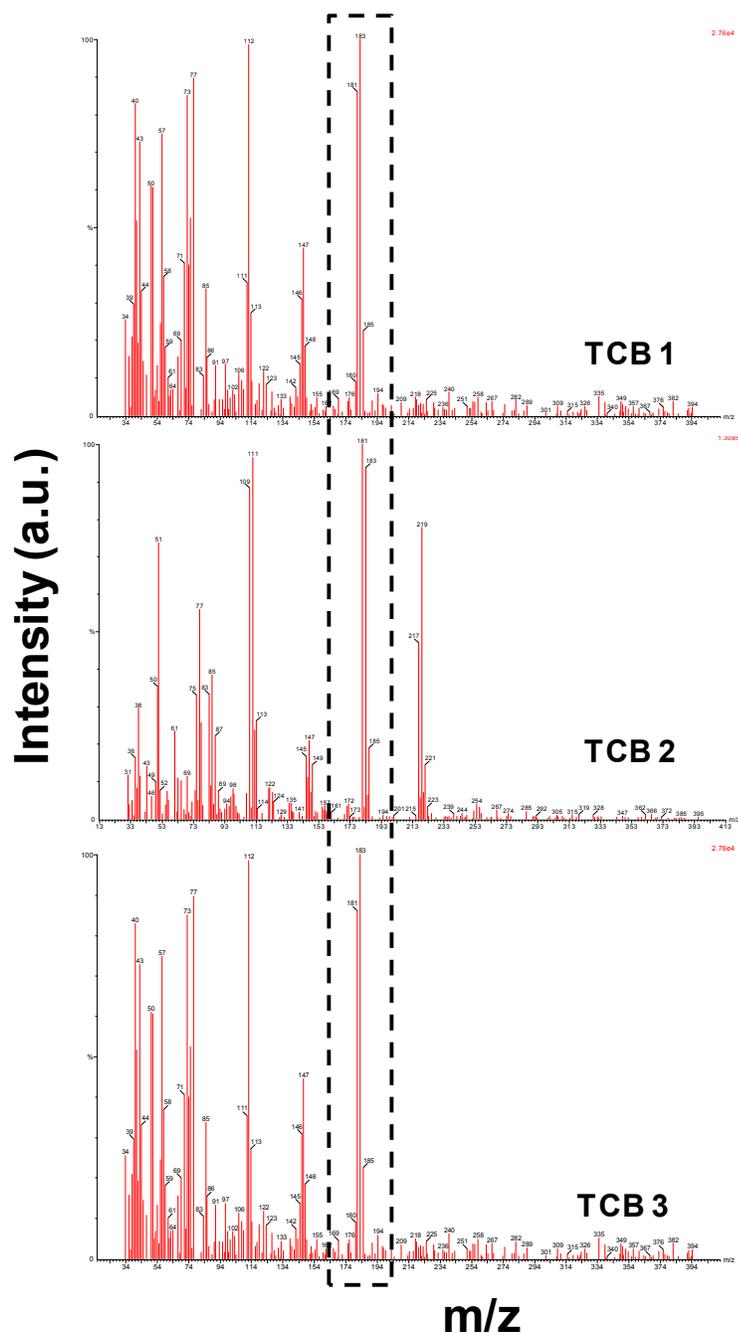


Figure S9: GC-MS of three different isomers of TCB marked as 1, 2, and 3 in Figure S5B.

Supporting Information 10

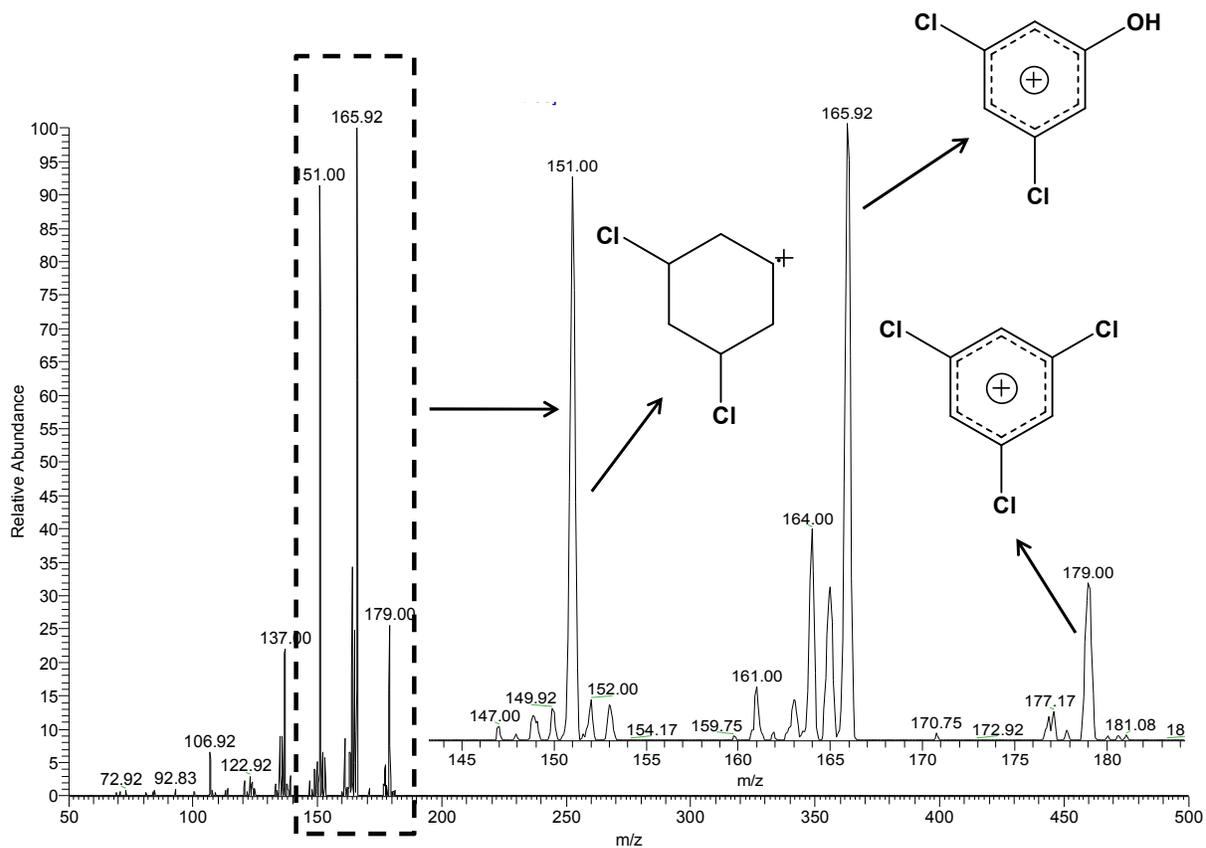


Figure S10: MS2 of the peak of the degraded product, trichlorobenzenes (m/z 180) at collision energy 60 (in instrument unit) measured using ESI MS. Please note that there are isomeric structures for TCBS, only one isomer is shown here.

Supporting Information 11

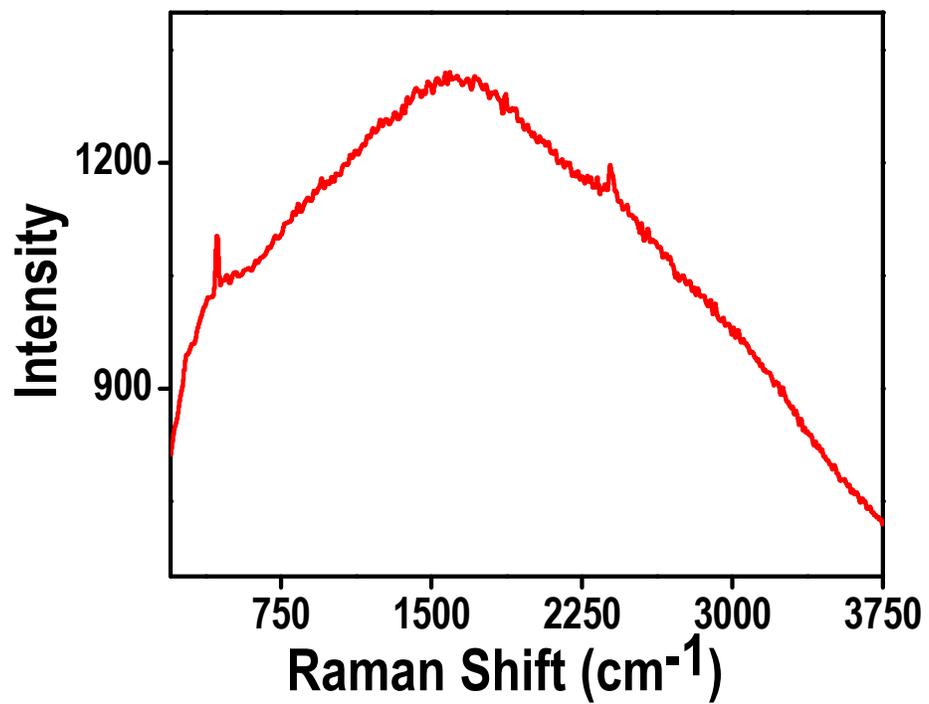


Figure S11: Raman spectrum of the product (trichlorobenzenes), showing the luminescence background.

Supporting Information 12

Preparation of citrate capped silver nanoparticles: Calculated amount of AgNO_3 was dissolved in 50 mL water such that the final concentration of silver in the solution was 5 mM. To the solution, sodium citrate was added and the mixture was heated for 30 min at 80 °C till the color of the solution changed to brown. This brown colored solution was kept for cooling at room temperature for an hour. This was the stock solution for silver nanoparticles (5 mM), which was characterized using UV/Vis spectroscopy and HRTEM. UV/Vis spectrum gives characteristic peaks corresponding to Ag NPs (peak maximum around 420 nm) and TEM image shows that the particle size is around 50 nm. Silver nanoparticles formed by this method are polydisperse.

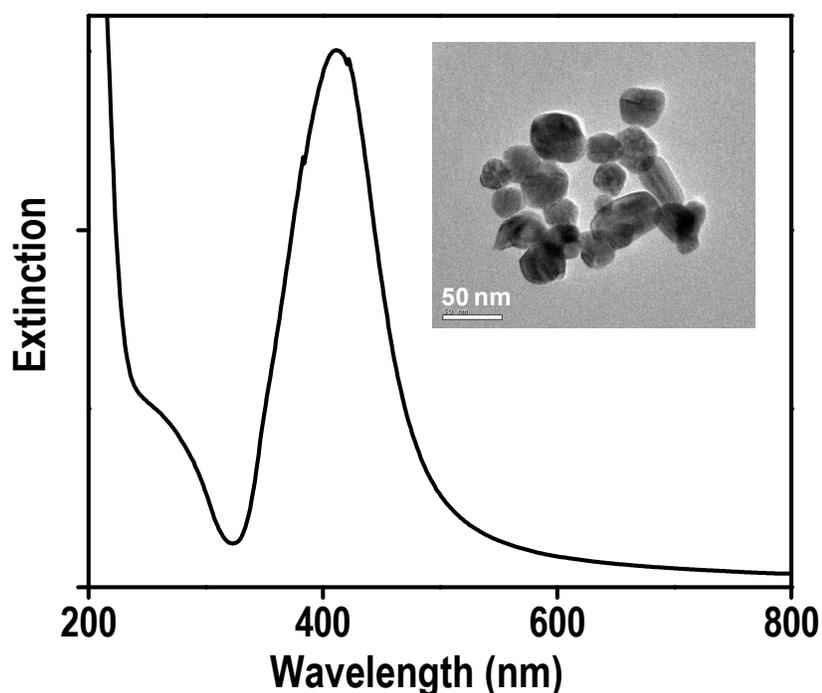


Figure S12: UV/Vis spectrum of silver nanoparticles and the inset shows a typical TEM image of the particles.

Supporting Information 13

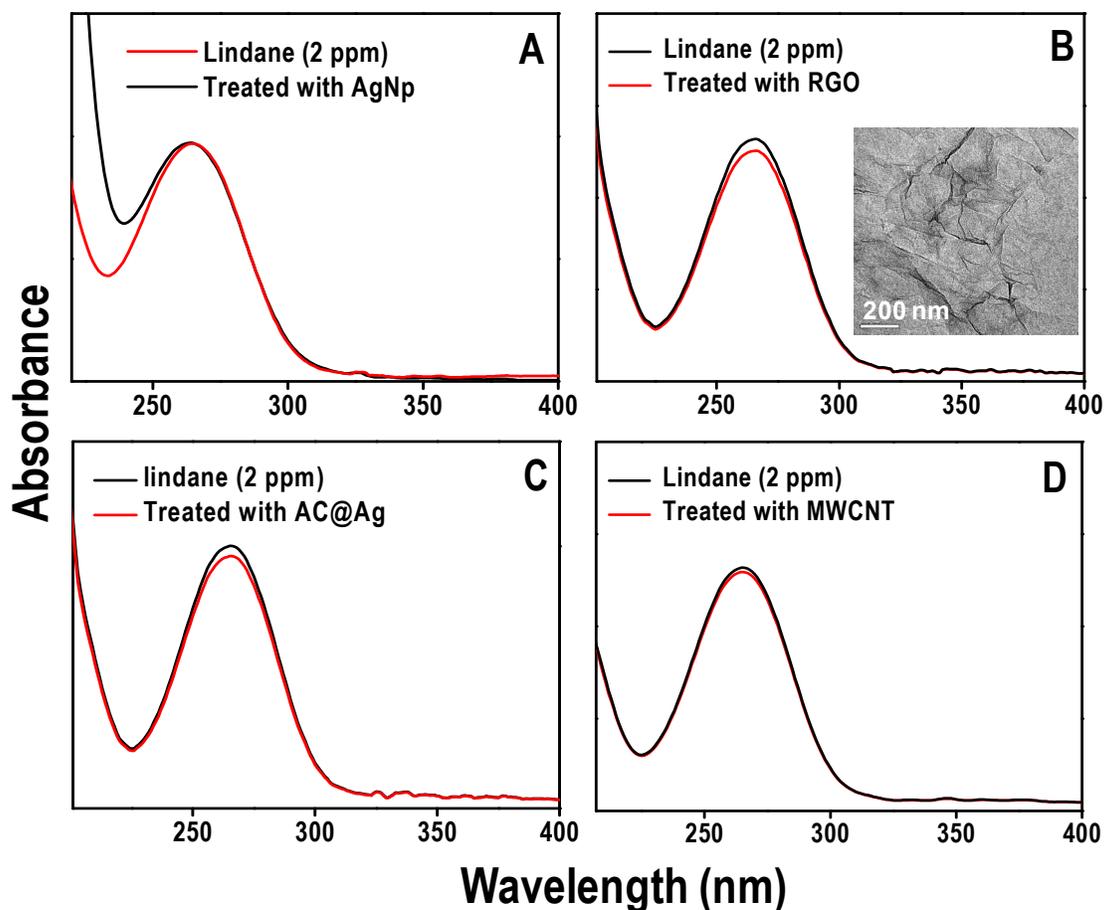


Figure S13: UV/Vis spectrum showing negligible removal/degradation capacity of lindane when treated with A) silver nanoparticles, B) graphene, C) AC@Ag and D) MWCNTs. The inset in Figure B shows the TEM image of graphene.

To test the degradation capacity of lindane with various adsorbents, equal weight of adsorbents were taken (1 mg in 5 mL of water). To each sample, lindane (dissolved in ethanol from stock solution) was spiked, such that final concentration of lindane in the solution was 2 mg/L (ratio of water:ethanol was 500:1 (v/v)). Characterization was done using UV/Vis and the removal percentage was plotted against

adsorbents. The result showed that the composite RGO@Ag was superior than any other adsorbents reported recently.

Preparation of AC@Ag

About 1 mg of AC was taken in 5 mL of DI water and sonicated for 5 min. To it AgNO₃ solution was added such that the final concentration of Ag in the solution was 0.01 wt%. The composite was kept for 24 h, undisturbed. This is referred to as AC@Ag. It was seen that AC does not have the reducing capacity for Ag ions. This was confirmed by ICPMS, the initial and final concentration of Ag was 1.1 ppm and 1.08 ppm, respectively in the solution, which suggest that Ag was not reduced to Ag NP and hence a composite was not formed.

Supporting Information 14

Preparation of elemental silver particles: Calculated amount of AgNO_3 was dissolved in water such that the final silver concentration was 5 mM. To the solution, NaBH_4 was added and heated to 90 °C for an hour, so that reduction of silver takes place. A shiny precipitate was formed on the glass vessel. The precipitate was isolated and dried overnight in vacuum at 50 °C. This precipitate was used as elemental silver with varying concentrations in water. TEM image of this elemental silver was performed but the data were not good as expected due to poor electron beam transmission.

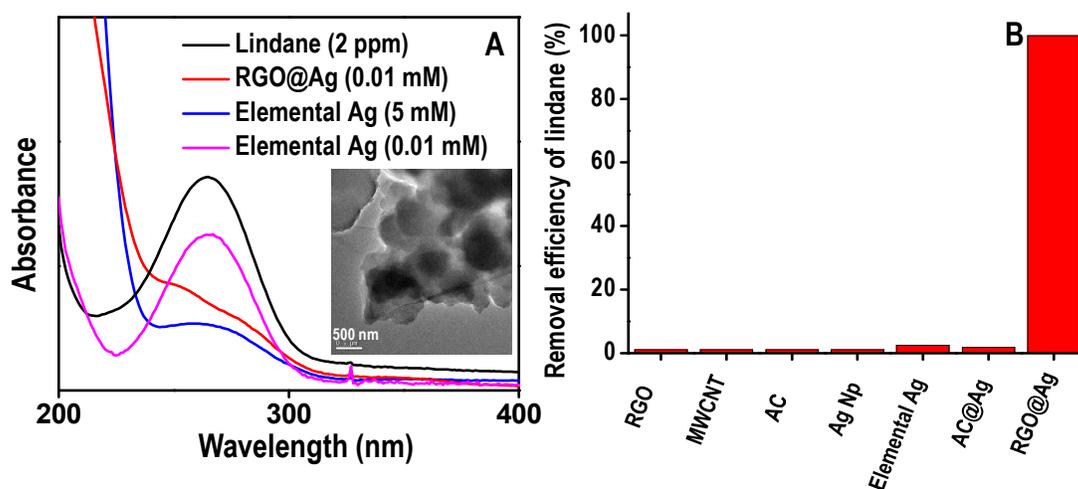


Figure S14: UV/Vis spectrum showing the comparison of the removal capacity of lindane (2 ppm) using the composite and elemental silver (Ag), the values represents the amount of silver used for the degradation reaction. The inset shows a TEM image of the prepared elemental silver. B) Comparison for the removal efficiency of lindane with different adsorbents.

Supporting Information 15

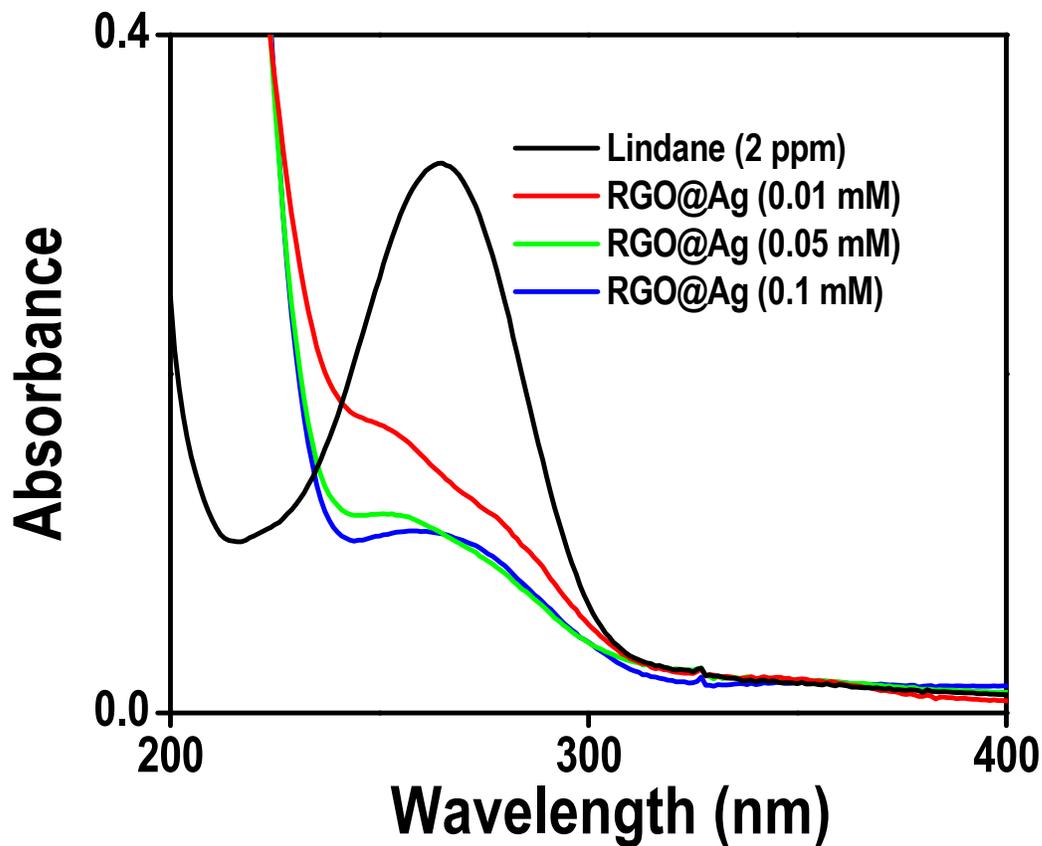


Figure S15: UV/Vis spectrum showing the size dependence of silver nanoparticle on RGO for the degradation of lindane.

Here three different composites, namely, RGO@Ag^I, RGO@Ag^{II}, RGO@Ag^{III} were used to check the efficiency of the composite towards the degradation of lindane which yielded size of 5, 20 and 50 nm of Ag Np on RGO sheet. For this experiment, lindane stock solution (dissolved in hexane) was used such that final concentration of the solution was 5 ppm. It was seen that more the concentration of Ag precursors on RGO, more is the degradation efficiency but the efficiency with respect to mg/g of silver

shows that RGO@Ag^I is much superior to the others. Thus it is concluded that smaller is the size of Np higher is the surface area and hence, higher is the degradation capacity. The data were taken after 15 min.

Supporting Information 16

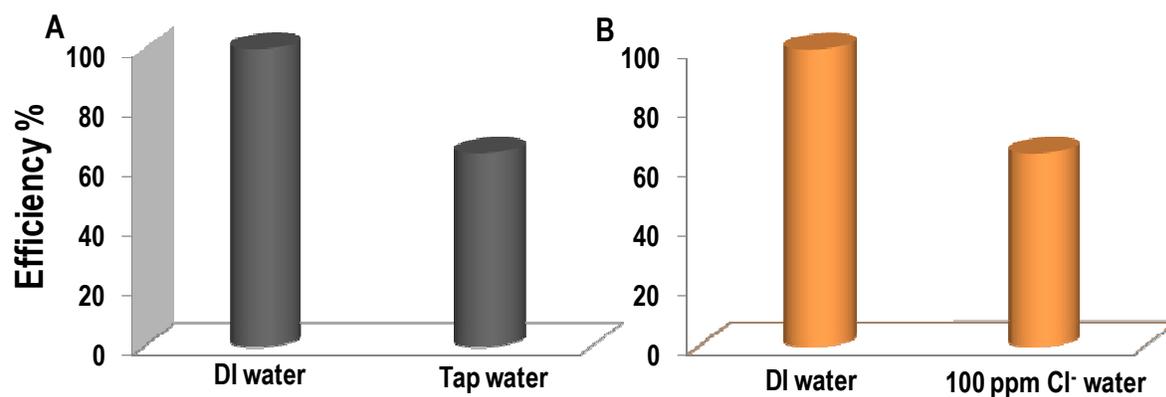


Figure S16: Effect of A) tap water/ground water and B) 100 ppm of NaCl solution (in DI water)_ on the removal efficiency of lindane using RGO@Ag.

Supporting Information 17

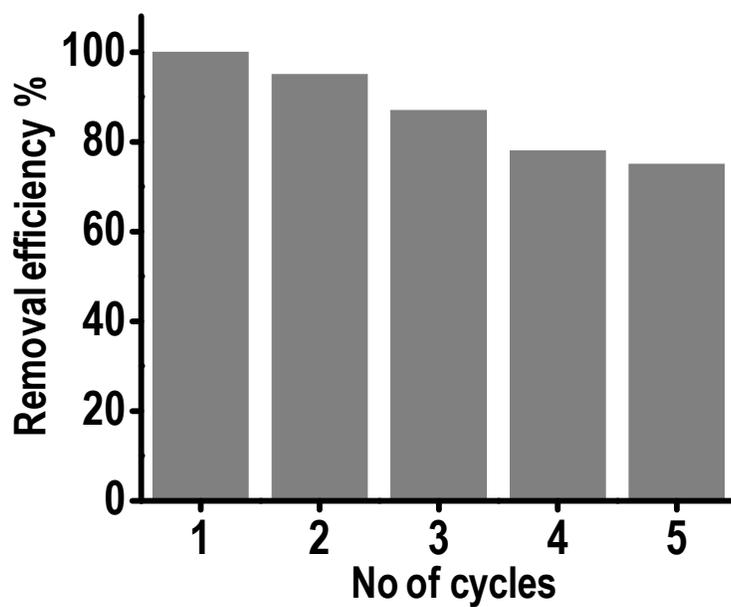


Figure S17: Removal efficiency of lindane by the RGO@Ag composite for multiple cycles, after regeneration.