

## **Supplementary Information**

### **Effective Photocatalytic Dechlorination of 2,4-Dichlorophenol by A Novel Graphene Encapsulated ZnO/Co<sub>3</sub>O<sub>4</sub> Core-shell Hybrid under Visible Light**

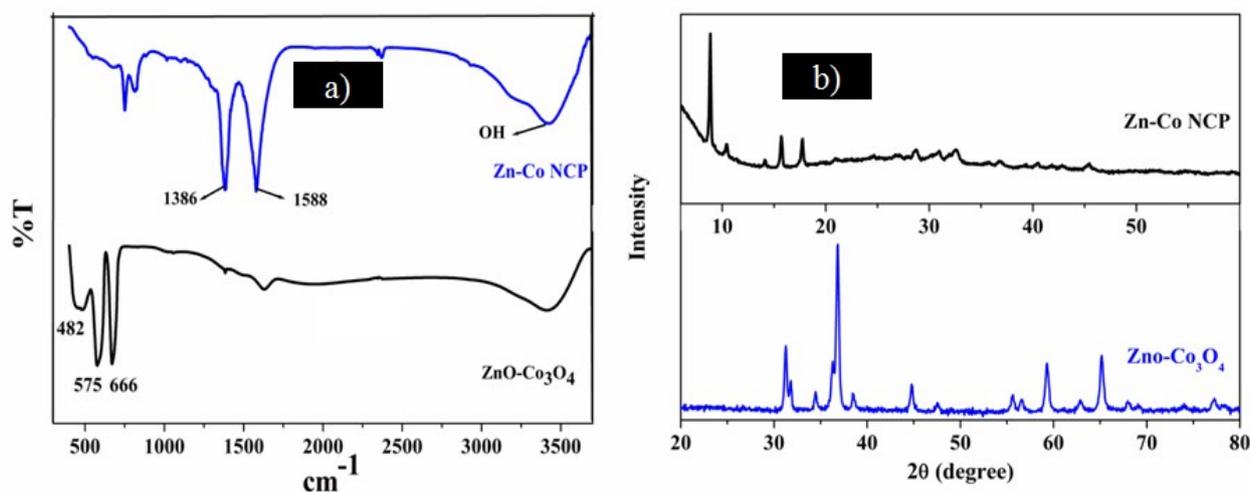
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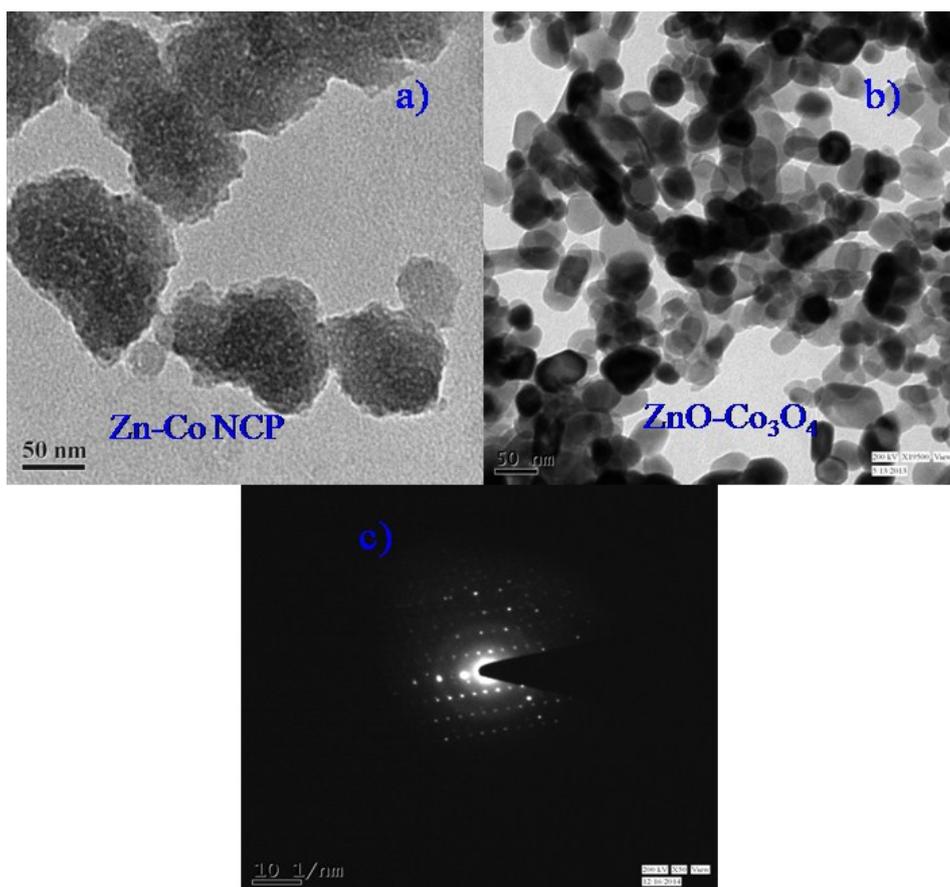
#### **Instrumentation**

Powdered X-ray Diffraction (PXRD) was measured by Bruker APEX-2 diffractometer. Fourier Transform Infra Red spectra (FT-IR) were carried out with a Perkin-Elmer FT-IR spectrophotometer RXI. The X-ray Photoelectron Spectroscopy (XPS) was performed by Specs (German). Thermogravimetric Analysis (TGA) was analysed on Perkin-Elmer instrument, Pyris Diamond TG/DTA with Al<sub>2</sub>O<sub>3</sub> crucible. Transmission Electron Microscopy (TEM) and High Resolution TEM (HRTEM) were performed with JEOL JEM2010 electron microscope operating at 200 kV. Energy Dispersive X-ray (EDX) measurement was carried out with FEI TECNAI-G2-20S-TWIN (USA). BET surface area and N<sub>2</sub> sorption isotherms (77K) were carried out by Quantachrome Autosorb-1 instrument. Photoluminescence spectra were recorded by F-7000 FL Spectrophotometer. The photodegradation of 2,4-DCP were measured by UV- 1601, Shimadzu spectrophotometer and high performance liquid chromatography (HPLC, Thermo Fisher Scientific Dionex UltiMate 3000). The HPLC were consisted of a UV/Vis Diode Array Detector and a reversed-phase Acclaim Polar Advantage-II column (3 μm, 120 Å, 3 ×150 mm). The chromatographic conditions were: 80: 20 for

mobile phase (V) acetonitrile: water, 0.3 mL min<sup>-1</sup> for the flow rate of mobile phase, 20 μL for the injection volume, 30 °C for column temperature and the detection wavelengths for 2,4-DCP and its degradation products *o*-chlorophenol (*o*-CP), *p*-chlorophenol (*p*-CP) and phenol were 285 nm, 274 nm, 280 nm and 270 nm, respectively. The GCMS study of the photo-degraded products was carried out using a Thermo Scientific Trace 1300 gas chromatograph and ISQ Single Quadrupole MS system.

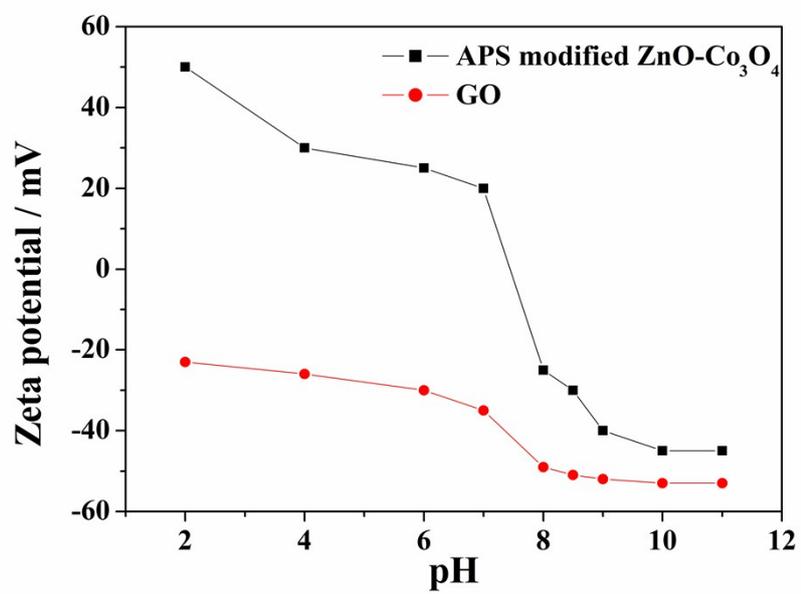


**Figure S1** a) FT-IR spectra and b) PXRD pattern of the synthesized Zn-Co NCP precursor and synthesized ZnO-Co<sub>3</sub>O<sub>4</sub> heteronanostructure after calcination of Zn-Co NCP at 550 °C.

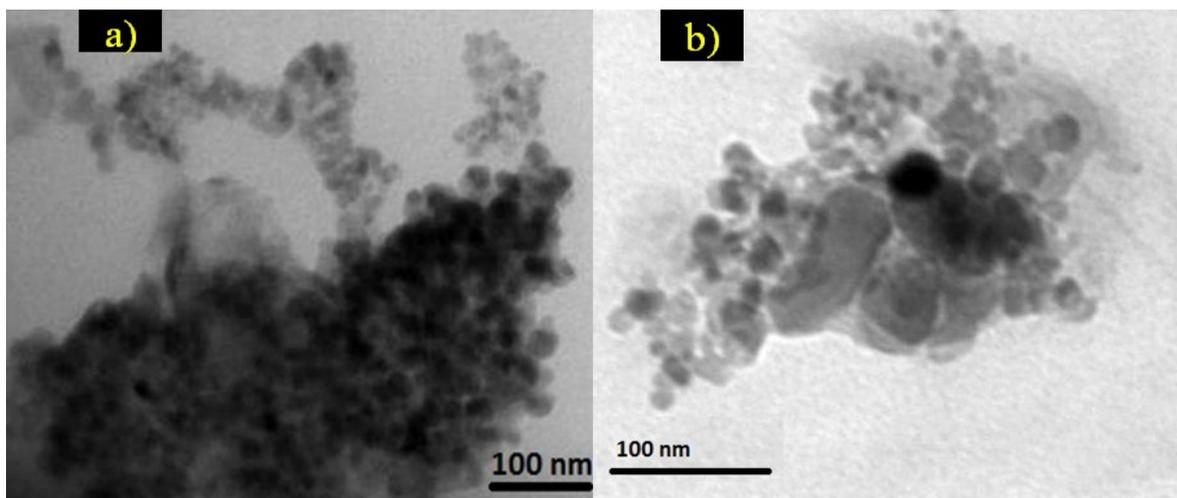


**Figure S2.** TEM image of the prepared a) Zn-Co NCPs, b) ZnO-Co<sub>3</sub>O<sub>4</sub> nanostructures prepared from Zn-Co NCPs after calcinations and c) SAED pattern of prepared ZnO-Co<sub>3</sub>O<sub>4</sub> heteronanostructures.

The average size of the Zn-Co NCP and corresponding derived ZnO-Co<sub>3</sub>O<sub>4</sub> heteronanostructures are ~60 nm and ~25-40 nm. The SAED pattern indicates high crystalline nature of the ZnO-Co<sub>3</sub>O<sub>4</sub>.



**Figure S3.** Zeta potentials of APS-modified ZnO-Co<sub>3</sub>O<sub>4</sub> and GO in aqueous solution at different pH values.



**Figure S4.** TEM image of the GE/ZnO/Co<sub>3</sub>O<sub>4</sub> core-shell hybrid.

The TEM shows the ZnO-Co<sub>3</sub>O<sub>4</sub> is wrapped by thin graphene shells.

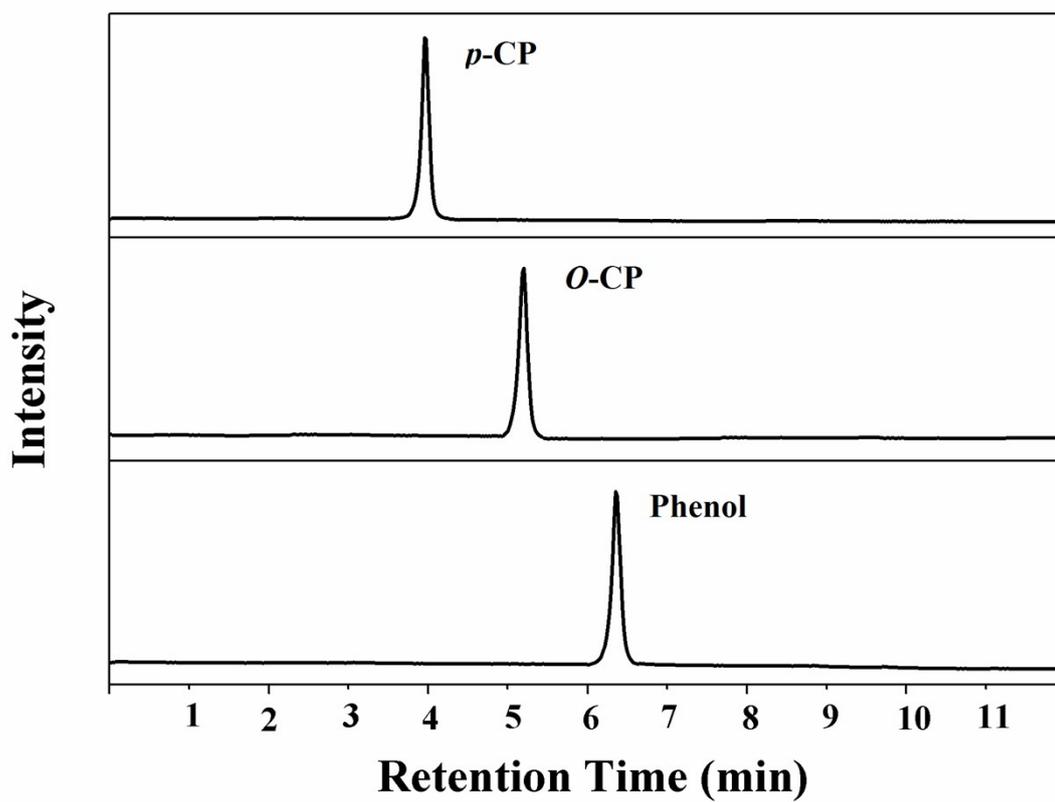
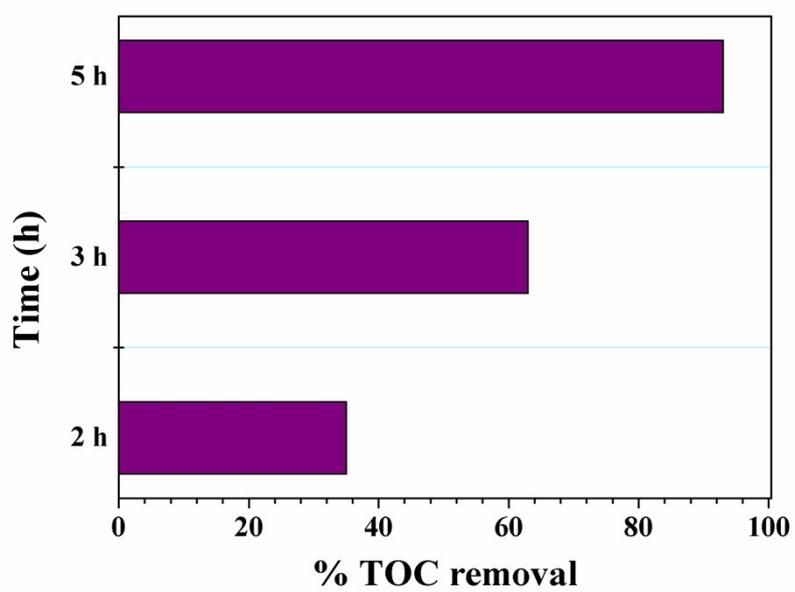
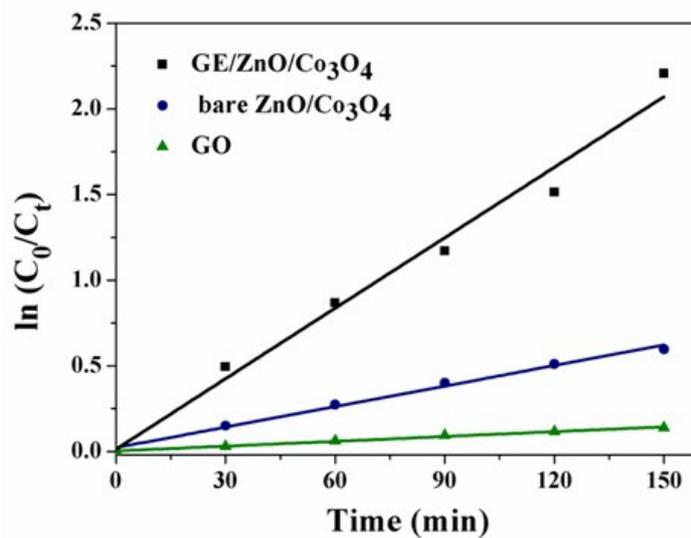


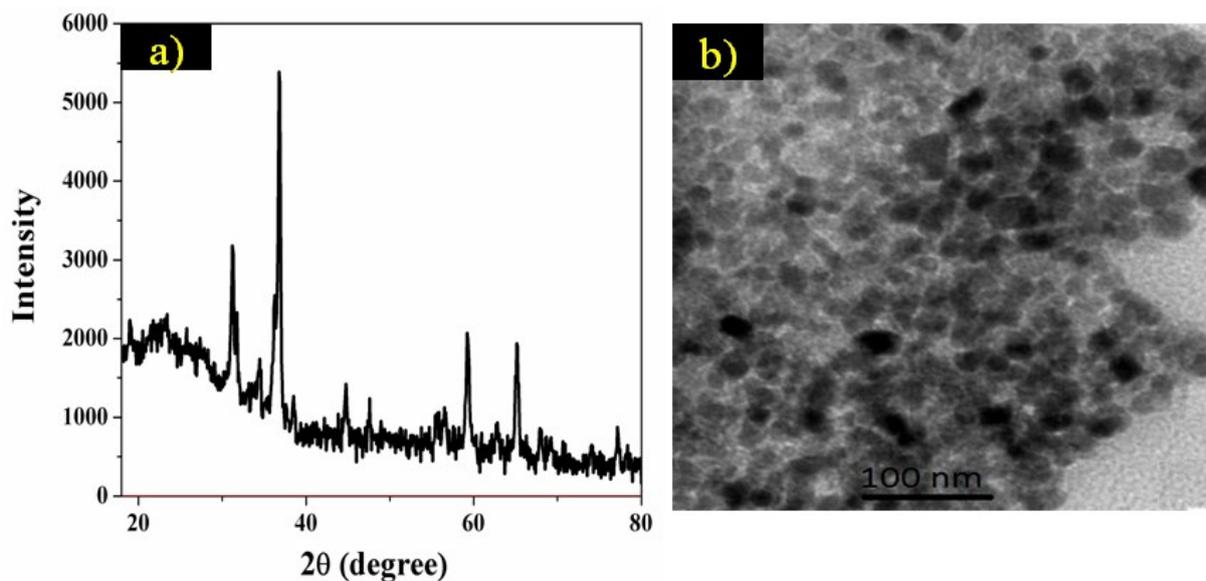
Figure S5. The retention time of the standard substance of *o*-CP, *p*-CP and Phenol.



**Figure S6** TOC removal at different time during photocatalytic mineralization of 2,4-DCP under visible light irradiation in presence of GE/ZnO/Co<sub>3</sub>O<sub>4</sub>.

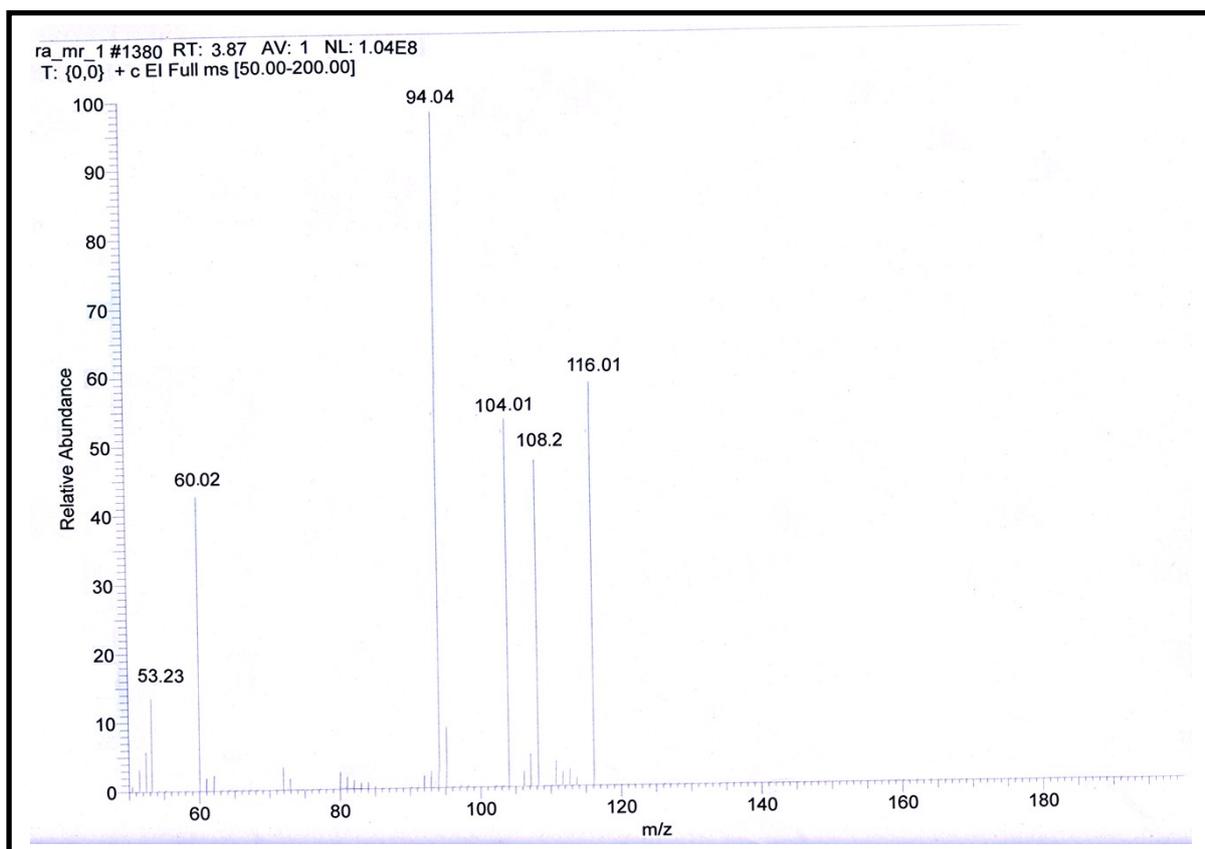


**Figure S7** Plot of  $\ln C_0/C_t$  vs. Time for determination of the rate constant of the GE/ZnO/Co<sub>3</sub>O<sub>4</sub>, GO and bare ZnO/Co<sub>3</sub>O<sub>4</sub> ([2,4-DCP]=20 mg/L, [catalyst]= 1.0 g/L, pH=5.0).



**Figure S8.** a) PXRD pattern and b) TEM image of the GE/ZnO/Co<sub>3</sub>O<sub>4</sub> hybrid after 6<sup>th</sup> cycle of photocatalytic reaction.

The PXRD patterns indicate that there is no remarkable alteration or shift of the peak in the crystal structure of the catalyst after 5<sup>th</sup> cycle of operation, and TEM image of the hybrid shows the ZnO/Co<sub>3</sub>O<sub>4</sub> core still is wrapped by graphene shells and hence no noticeable change in morphology is observed after 5<sup>th</sup> cycle.



**Figure S9.** GC-MS spectrum of the photo-degraded products of 2,4-DCP after 5 h of photocatalytic reaction.

The GC-MS spectrum of the degraded products of 2,4-DCP after 2 h of photocatalytic reaction (Fig. 15, in the manuscript) exhibits the mass peaks of (a) unreacted 2,4-DCP ( $m/z$ , 162.15) and also its fragmented products, like (b) chlorophenols ( $m/z$ , 128.21), (c) phenol ( $m/z$ , 94.04), (d) *p*-benzoquinone ( $m/z$ , 108.2), (e) acetic acid ( $m/z$ , 60.02) and (f) 1,3-butadiene ( $m/z$ , 53.23).

However, the GC-MS spectrum of samples subjected to photodegradation for 5 h (above Fig. S9) show significant degradation of the 2,4-DCP. The mass peaks of phenol ( $m/z$ , 94.04), *p*-benzoquinone ( $m/z$ , 108.2), acetic acid ( $m/z$ , 60.02) and 1,3-butadiene ( $m/z$ , 53.23) are mainly observed in the photo-degraded products of 2,4-DCP after 5 h of reaction, however, the peaks related to 2,4-DCP ( $m/z$ , 162.15) and chlorinated-phenols ( $m/z$ , 128.21) have not been observed.