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Supplementary Information

Kinetics of degradation of sulfur mustard and sarin simulants on HKUST-1 metal organic framework

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Experimental

Materials

Copper (II) nitrate hemipentahydrate, benzene-1,3,5-tricarboxylic acid, N,N-dimethyl formamide (DMF), ethanol, dichloromethane and CEES, were purchased from Sigma–Aldrich chemicals Pvt. Ltd. CEPS and DECNP was purchased from Alfa-Aesar, DEClP, Bis(trimethylsilyl) trifluoro acetamide was bought from Acros Organics . All the chemicals were used without further purification.

Synthesis of HKUST-1

HKUST-1 was prepared by solvothermal method. In this context, benzene-1,3,5-tricarboxylic acid (5.0g, 24 mmol) and copper(II) nitrate hemipentahydrate (10.0 g, 43 mmol) were stirred for 15 min in 250 mL of solvent consisting of equal parts DMF, ethanol and deionized water in a 1-L wide mouth Schott Duran glass jar. The jar was tightly capped and placed in oven at 85°C for 20 h to yield small octahedral crystals. After decanting the hot mother liquor and rinsing with DMF, the product was immersed in dichloromethane for 3 d, during this period the activation solvent was decanted and freshly replenished three times. The solvent was removed under vacuum at170 °C for 8 h, yielding the porous material.

Characterization of HKUST-1

N_2 adsorption–desorption isotherms were measured at 77 K on a Quantachrome Autosorb-1C, USA. The samples were first outgassed under dynamic vacuum (10^{-2}Torr) for 8 h and then allowed to cool to room temperature. The surface area was calculated from the Brunauer-Emmett-Teller method (BET) and micropore volume from the Dubinin- Radushkevich (DR)

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equation. Scanning electron microscopic (SEM) analysis was performed on FEI ESEM Quanta 400 instrument coupled with EDAX, USA equipped with ion sputter JEOL, JFC 1100 coating unit. SEM images were taken after degassing the samples under a vacuum to remove most of the adsorbed guest molecules. The X-ray powder diffraction (XRD) was performed on a Philips XRD PW 3020. Cu Kα radiation (λ = 0.154 nm) was the light source used with applied voltage of 40 KV and current of 40 mA. Subsequently, thermograms were recorded in nitrogen atmosphere on TGA-2950, TA instruments, USA and the Fourier transform infrared spectroscopic (FTIR) data was acquired on Perkin-Elmer FT-IR 1720X, USA.

Reaction procedure and kinetics of degradation of toxicants

50 mg MOF was spiked with 40μL carbon tetrachloride containing 5μL of CEES, CEPS and 40μL chloroform containing 5μL of DEClP and DECNP (incipient volume) in glass tubes separately under ambient conditions and agitated for 5 min in vortex mixer for the homogeneous distribution of toxicants over MOF. These tubes containing reaction mixture were allowed to stand at room temperature and each tube was taken out for kinetics studies at regular intervals of time. For kinetics of degradation, residual toxicants were extracted in carbon tetrachloride/ chloroform and the solutions were subjected to GC/FID (gas chromatograph coupled with flame ionization detector) analysis using split less injection technique. GC spectra were obtained periodically to monitor the reaction in-situ. All gas chromatographic analyses were performed in programming mode from 40 to 250 °C at a rate of 10°C /min to determine the amount of remaining toxicants on a Chemito 8610 gas chromatograph equipped with BP-5 column (5% phenyl methyl silicon capillary column of 30m. length, 0.3 mm internal diameter). The detector and injection port were maintained at 280 and 220 °C respectively. In order to study the kinetics of degradation of toxicants on MOF, residual amount of toxicants i.e., log (a-x) on Y-axis was

plotted against reaction time, t on X-axis. Where ‘a’ is the initial concentration and ‘x’ is the degraded amount. Rate constant (k) was calculated using the slope of the straight line and half life ($t_{1/2}$) by 0.693/k. Effect of coadsorbed moisture on the degradation of sulfur mustard and sarin simulants was also studied by adding 10 µL of water to the MOF prior to the reaction with the toxicants. Thereafter, extracting the residual toxicant after 20 min as stated in the reaction procedure.

Reusability of HKUST-1

The reusability of HKUST-1 was checked by recovering the MOF after completion of the kinetics study from every cycle. The insoluble MOF was treated with the methanol and agitated for 5 min in vortex mixer to remove every portion of the unreacted toxicant adsorbed on the HKUST-1. This process was repeated for 5 times thereafter, the MOF was filtered out, dried and reused without further purification for the second run. The procedure was repeated and the efficiency of the MOF was checked up to the 4th cycle.

Identification of reaction products

In order to investigate the reaction products 50 mg of toxicants exposed HKUST-1 MOF were extracted after 2 h of reaction with 5.0mL of methanol in well-stopped test tubes. The reaction mixtures were centrifuged and transferred to another tube. This process was repeated for five times. Then the extracts were then purged with nitrogen gas to concentrate the extracted reaction products and were silylated by bis-(trimethylsilyl) trifluoroacetamide and analyzed by GC/MS (gas chromatograph coupled with mass spectrometer) instrumental techniques. GC/MS (6890N GC coupled with 5973 inert MS detector) of Agilent Technologies, USA was used for characterization of reaction products. It was equipped with HP-5MS column of 30m×0.25mm×0.25m dimensions. Temperature programming [50 °C (2min hold) to 280 °C (10

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min hold) at 10°C/min] with split injection technique (10:1) was used to perform the study. Injection port and GC/MS interface, MS source and quadruple analyzer were kept at 280 ºC, 230 ºC and 150 ºC, respectively.

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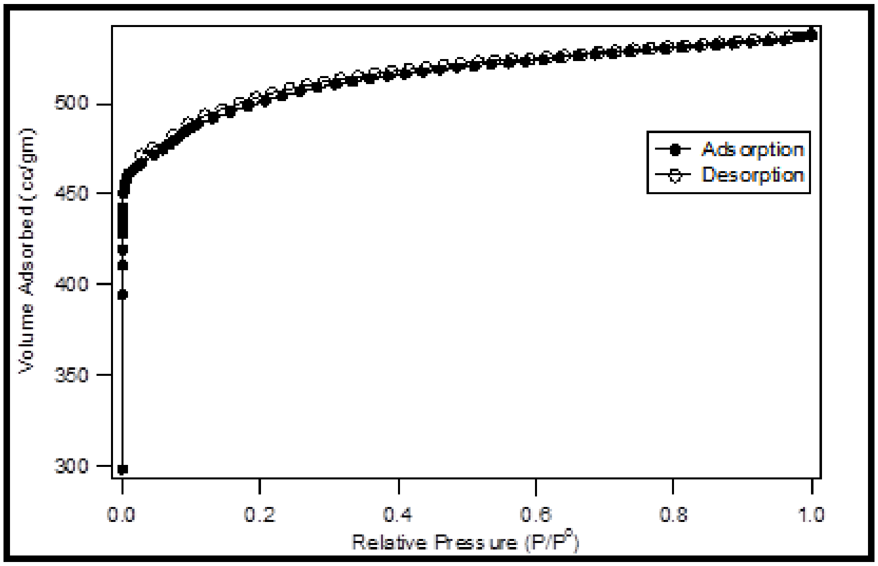

Fig.S1 N_2 adsorption–desorption isotherm of HKUST-1

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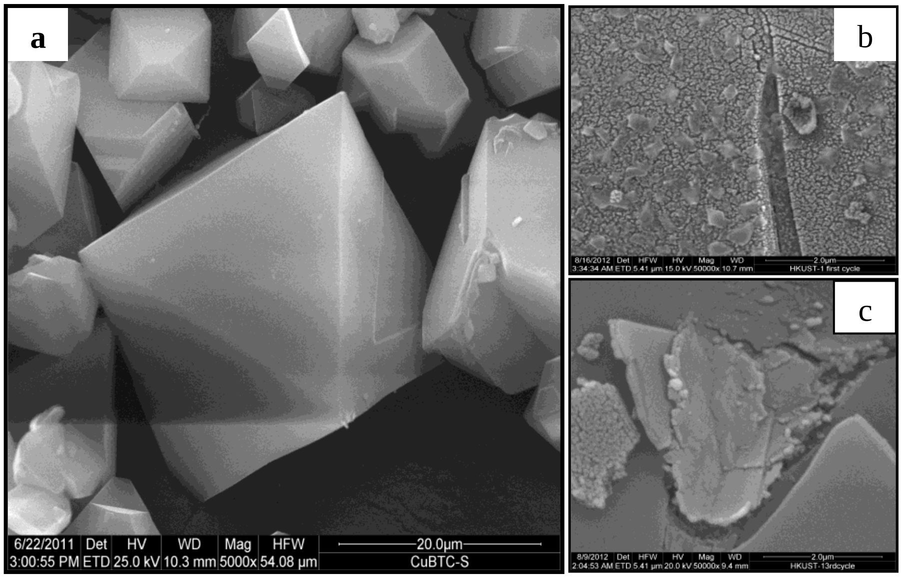

Fig.S2 SEM images of HKUST-1

(a) as synthesized HKUST-1, (b)After 1st cycle exposed with CEES,

(c) after 3rd cycle exposed with CEES

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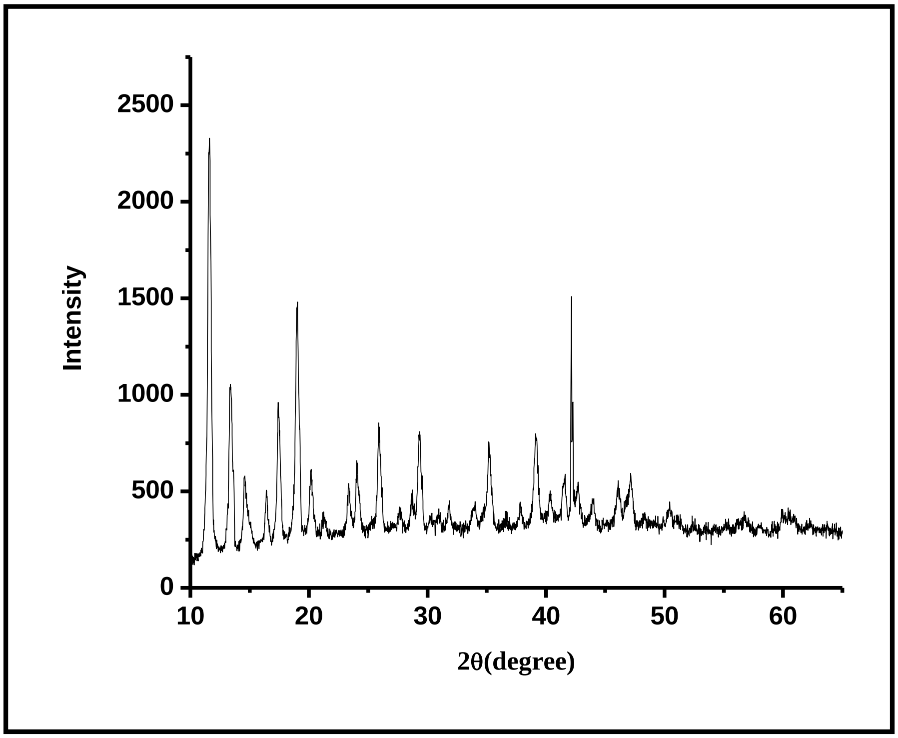

Fig.S3 Powder XRD spectrum of HKUST-1

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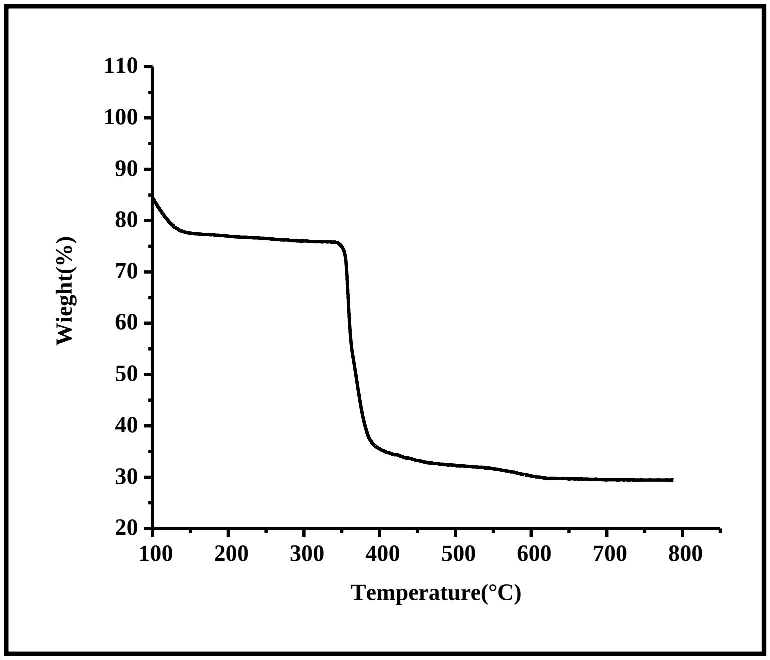

Fig.S4 Thermogram of HKUST-1

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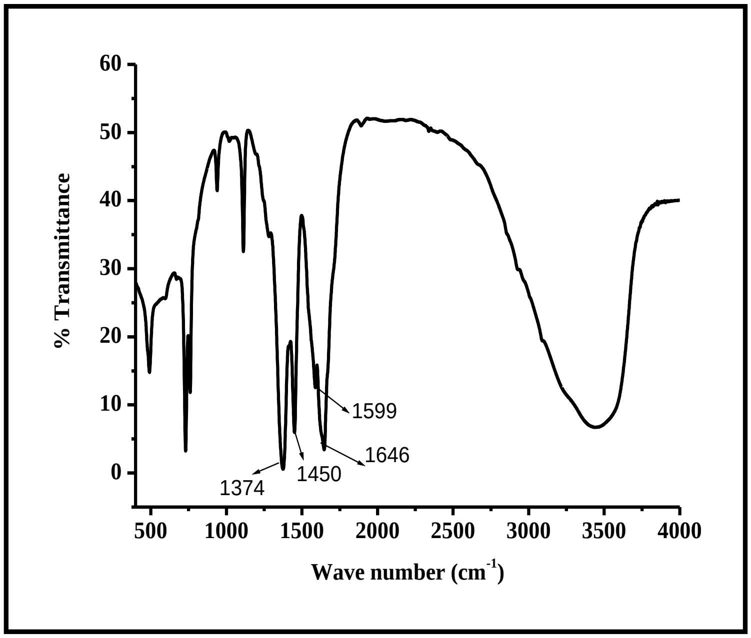

Fig.S5 FT-IR spectrum of HKUST-1

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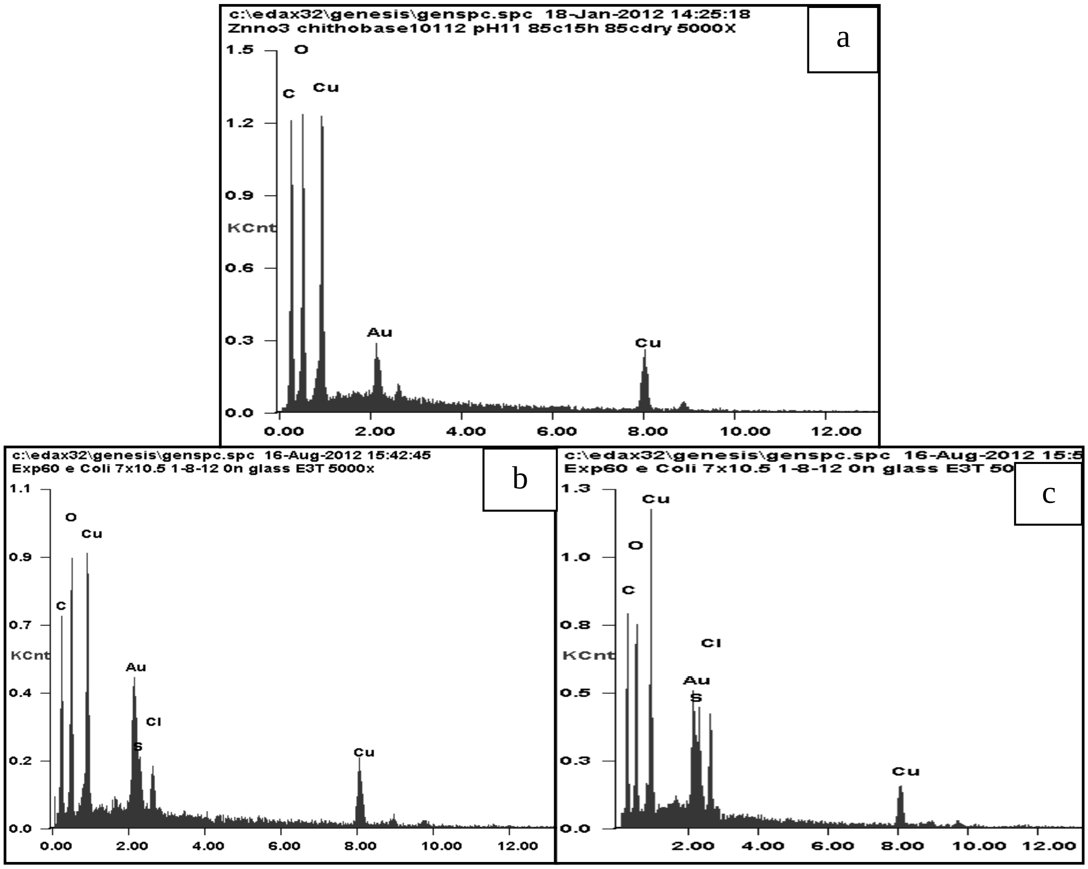

Fig.S6 EDAX spectra of HKUST-1

(a) As synthesized HKUST-1, (b) After 1st cycle exposed with CEES,

(c) After 3rd cycle exposed with CEES

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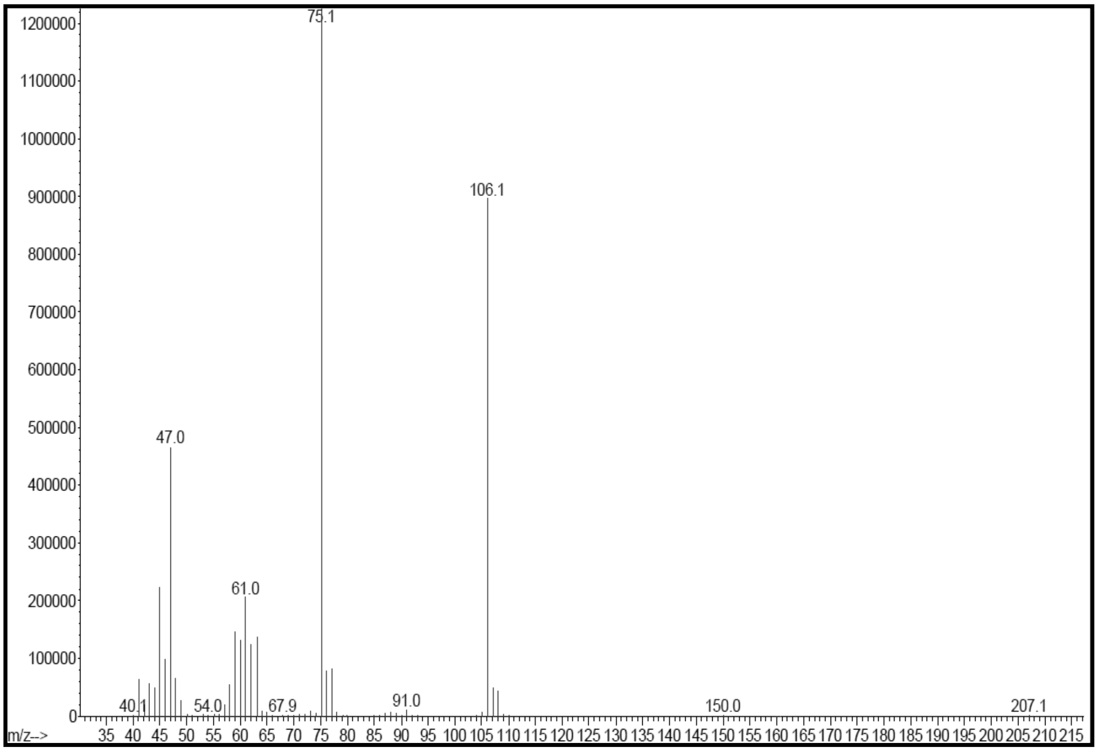

Fig.S7 Mass spectrum of HEES

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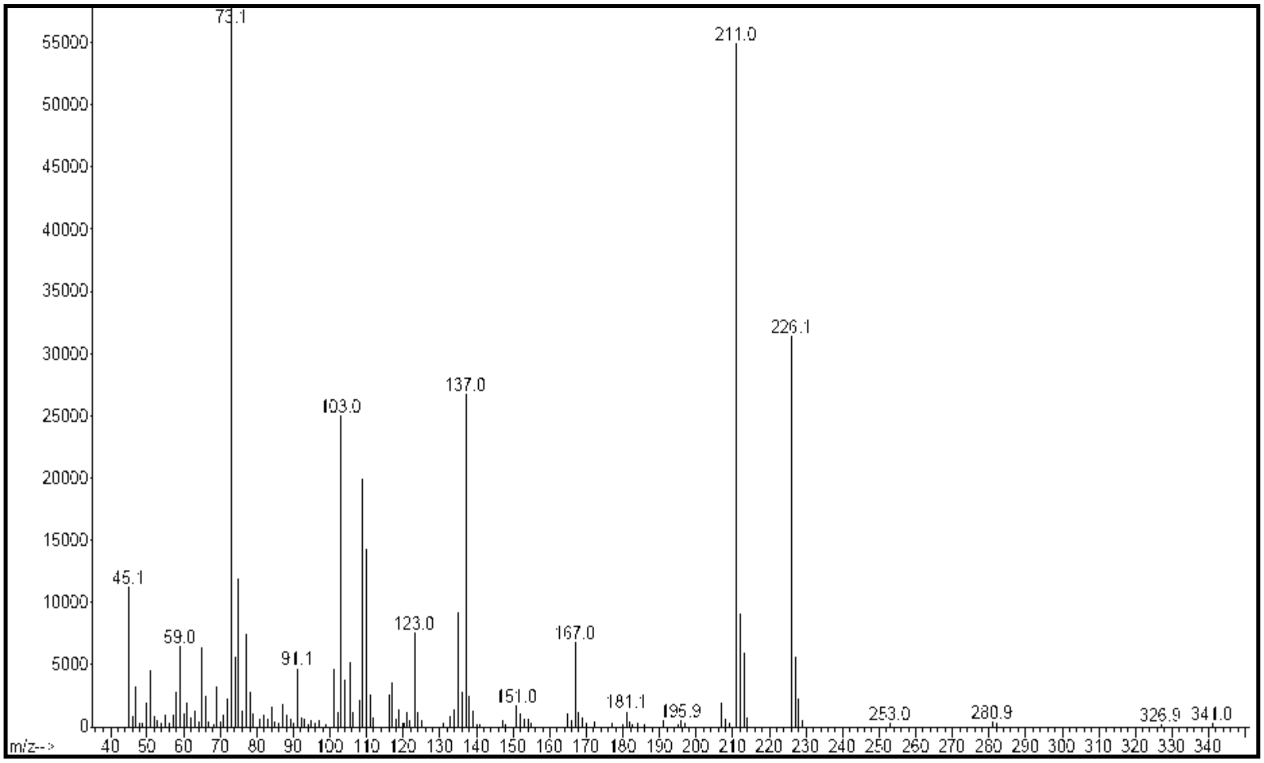

Fig. S8 Mass spectrum of HEPS

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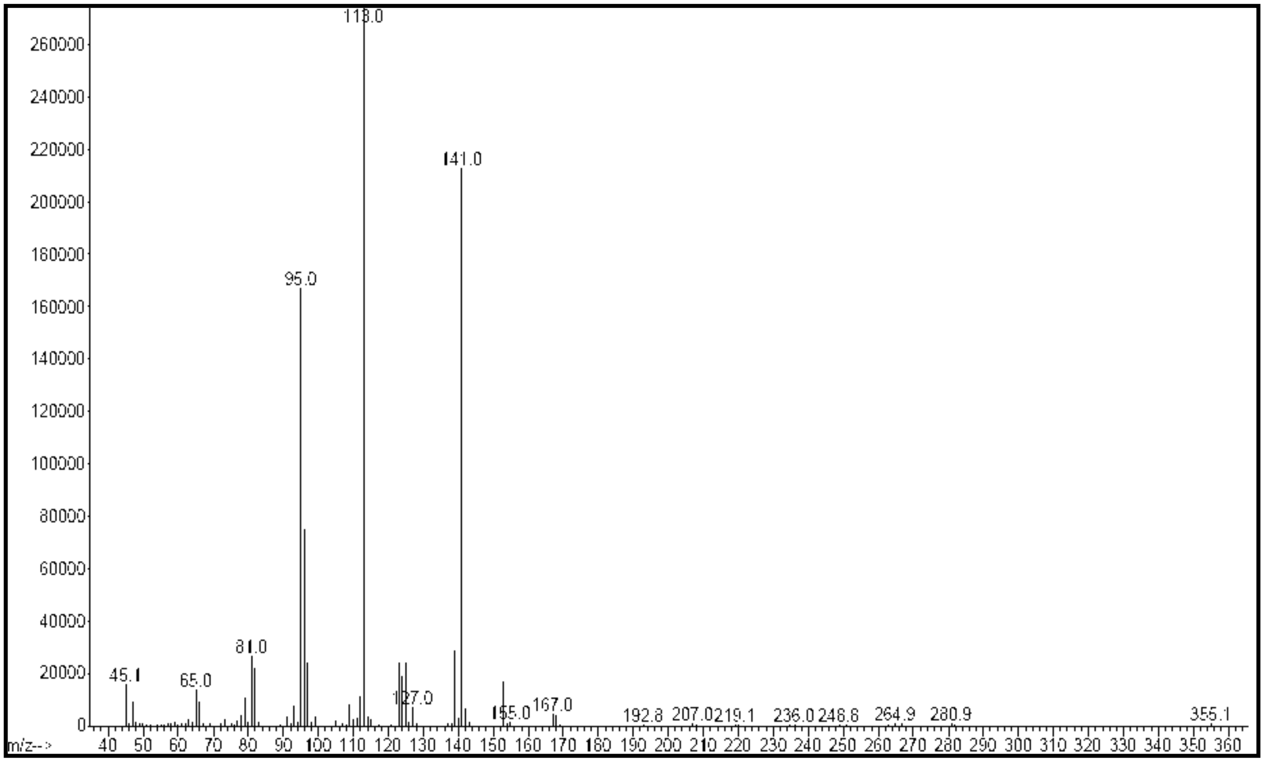

Fig.S9 Mass spectrum of DEP