Electronic Supplementary Information (ESI)

MOF derived porous carbon-Fe_3O_4 nanocomposite as a high performance, recyclable environmental superadsorbent

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ESI-I

Experimental Section

Materials and instruments:

For MOF synthesis $FeCl_3.6H_2O$ (97%) and Benzene Dicarboxylic acid (98%) were procured from Sigma Aldrich, and Dimethyl Formamide (GR) was procured from Merck. All the chemicals were used directly without further purification.

Various Characterization techniques such as X-ray diffraction (XRD, Philips X'Pert PRO), UV-Visible spectroscopy (JASCO V-570 spectrophotometer), High-Resolution Transmission Electron Microscopy (HR-TEM, FEI Tecnai 300), BET surface area measurements (Quantachrome Quadrasorb automatic volumetric instrument), Scanning electron microscopy (SEM) with Energy-dispersive x-ray spectroscopy (EDX) (FEI Quanta 200 3D) were used for the determination of various properties. Magnetism measurements were performed on SQUID-VSM magnetometer (Quantum Design).

Preparation of Fe-Metal Organic Framework and Fe_3O_4-Carbon Composite:

Fe-BDC Metal organic framework was prepared as per the previous report.[1] In the typical procedure, a solution of $FeCl_3$ (1mmol, Sigma Aldrich, 98%) and Terephthalic acid (1mmol, 1,4-BDC; Aldrich, 98%) in 5 ml Dimethyl Formamide (Merck, 99%) was reacted in a 23 ml Teflon-liner steel autoclave at a temperature 150°C for 2 hours. After cooling down to room temperature a yellow precipitate was obtained. This was separated by centrifugation at 6000 rpm for 5 minutes. The same procedure was performed repeatedly for bulk synthesis. To remove the solvent, 1 gm of the powder was suspended into 500 ml water and kept for a day. It was then centrifuged in water and dried in vacuum at 60°C for 24 hours. To obtain the Fe_3O_4-carbon composite systems, the MOF was annealed in a tube furnace under argon atmosphere at different temperatures. The MOF was put into the furnace in a ceramic boat and slowly heated (rate 5°C/min) at a temperature of 500°C and 600°C in separate experiments for three hours and then cooled to room temperature.

ESI-II

Characterization of the Fe containing Metal Organic Framework (MOF)

X-Ray Diffraction Pattern of the MOF

The XRD doublets of our metal organic framework at 2θ= 9.29° and 9.69° match with the similar peaks of MIL-53. [1] The XRD peak of our MOF at 2θ = 10.84° corresponds to a similar peak of MIL-88 B.[2]

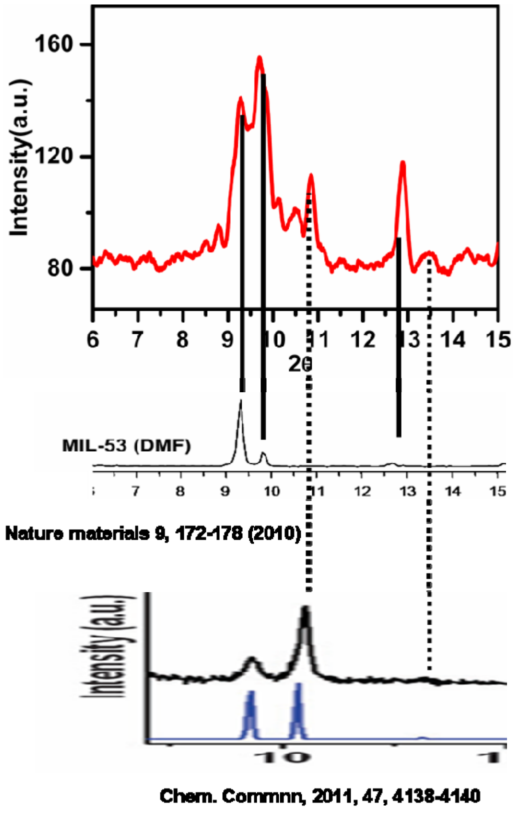

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Figure S1. XRD of the Fe-MOF

This XRD pattern in addition to the SEM images shown later indicate that the Fe-containing MOF in our case is MIL-53 along with an admixture of the polymorph MIL-88B.

Magnetization Data of the Fe-MOF

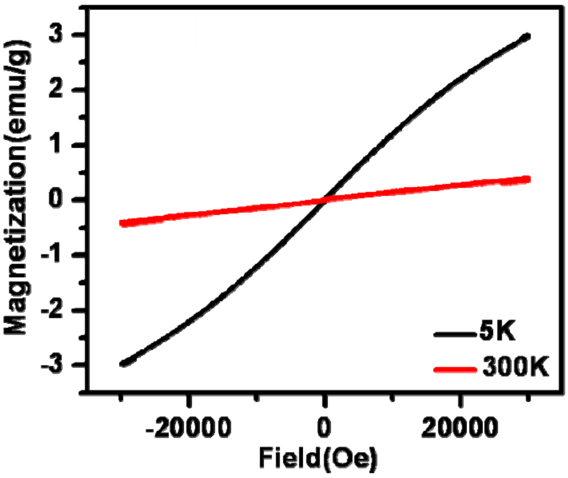

Figure S2. Magnetization curve of the Fe-MOF

The above curves show that the MOF exhibits paramagnetism at room temperature, as expected for non-interacting Fe^{3+} ions (the valence state being established by Mössbauer spectroscopy, shown later), while weak canted ferromagnetism appears at extremely temperature.

Mossbauer Spectroscopy

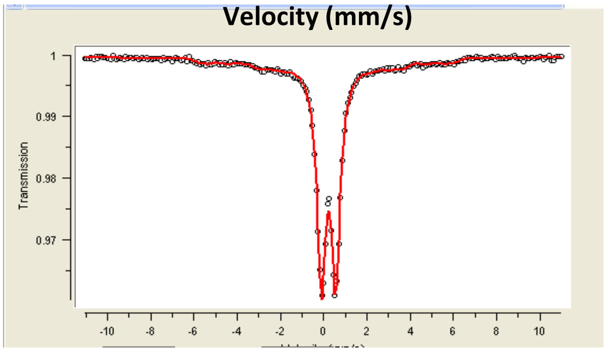

Figure S3. Mössbauer data of the Fe-MOF

The Mössbauer spectrum for the MOF shown above reflects a quadrupole split (QS) doublet. The isomer shift is 0.373 +/- 0.038 mm/s which corresponds to Fe ions in 3+ (ferric) state[3] and the QS is -0.183 +/- 0.075 mm/s.

Inductive Coupled Plasma (ICP) Analysis

ICP analysis of the Fe-MOF shows that the % Fe content in the MOF is 19.8 %, which is close to the value of 21.9 expected for this MOF. [6]

Elemental Analysis (C, H, N analysis)

Quantitative elemental analysis was performed for the Fe-MOF. The carbon and hydrogen contents are : C: 38.5 %, and H: 2.85%. These are close to the expected values for the said MOF.

FTIR Spectroscopy

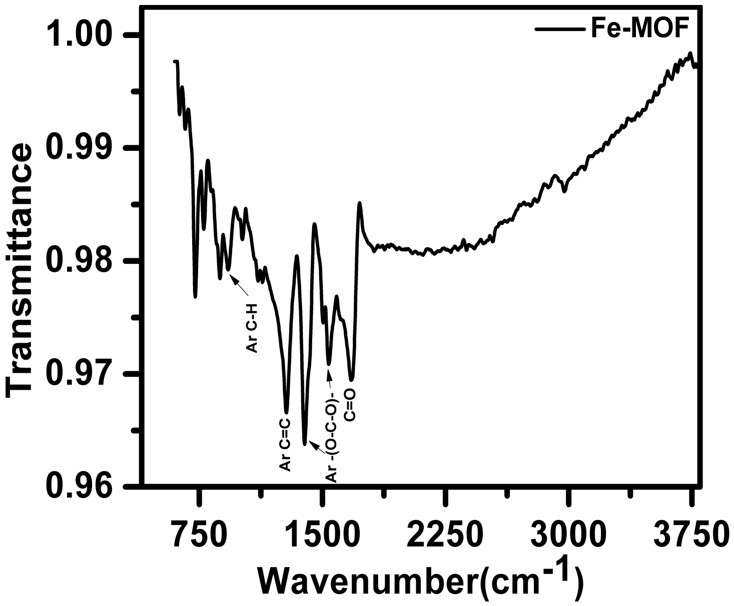

Figure S4. FTIR spectra of the prepared Fe-MOF

The Infrared spectrum of the MOF clearly shows the presence of the vibrational bands corresponding to the -(O-C-O)- groups around 1530 cm^{-1} and 1390 cm^{-1} which confirm the presence of the dicarboxylate within the compound.

ESI- III

Characterization of the MOF annealed composites

Thermogravimetric analysis

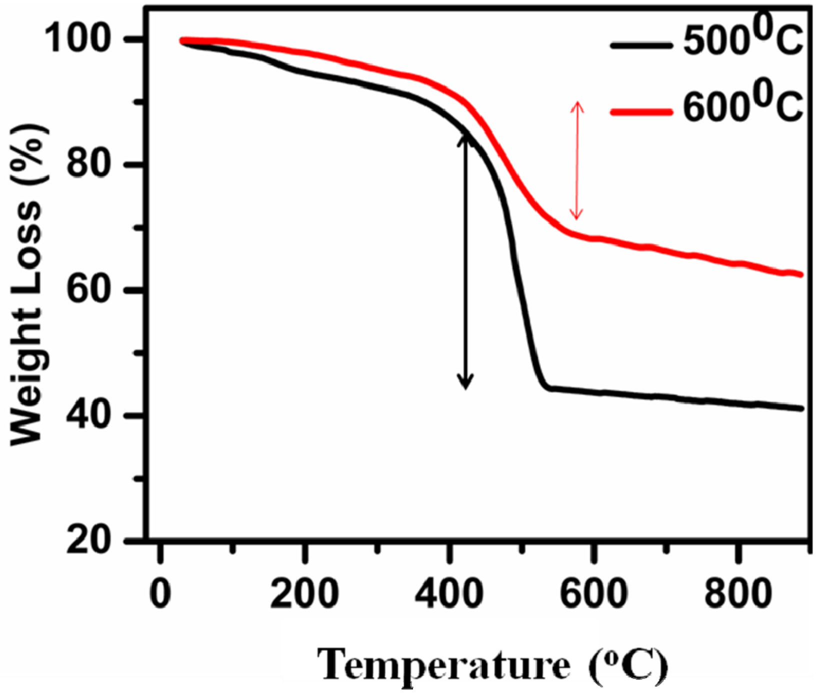

Fig S5. Thermogravimetric Analysis (TGA) of composites

Thermo gravimetric analysis of the two composites was done in air at a heating rate of 10^0C per minute and the data are shown in the above figure. In the TGA data we can identify the sharp loss of weight in the temperature region of ~ 450^0C-520°C which can be attributed to the removal of carbon as CO_2 by the oxidation in the presence of air. The loss in 500°C case composite is almost twice as higher as the 600^0C composite case, implying that the amount of carbon is almost double in the 500°C case, which is consistent with XPS data.

Mossbauer Spectroscopy

The typical Mössbauer spectrum of the iron-oxide-carbon nanocomposite appears as shown in Figure S6 and the corresponding fitted hyperfine interaction parameters are given in Table T1. The hyperfine interaction parameters clearly show that the main phase component is Fe_3O_4 (magnetite) with Fe in 3+ and 2+ states in the expected proportion. These parameters are distinctly different than those for maghemite of gamma-Fe_2O_3 phase; hence presence of magnetite phase in our case can be equivocally established. There is a central component which most possibly reflects the interface phase between carbon and Fe_3O_4 in the composite.

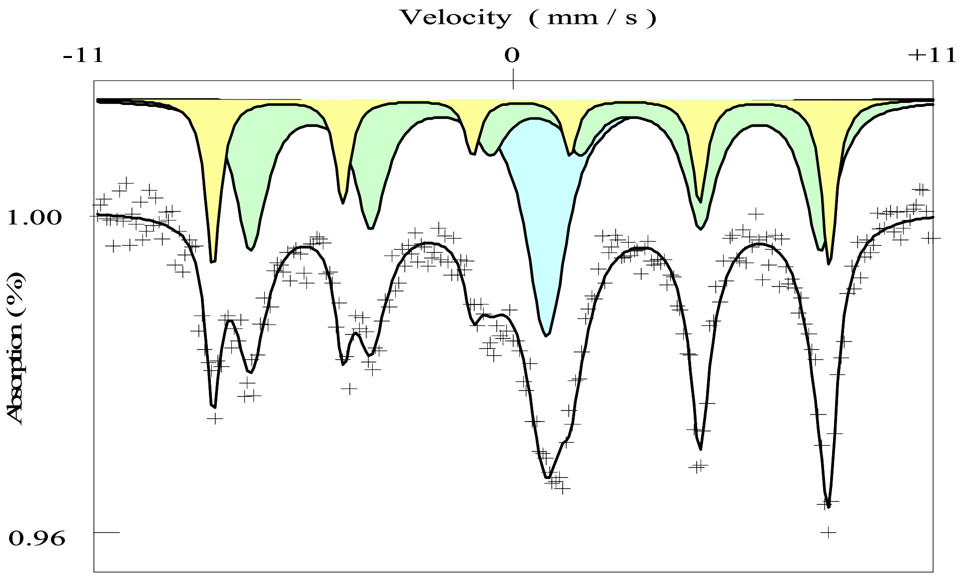

Figure S6: Mössbauer spectrum of the iron-oxide-carbon nanocomposite

Spectrum	IS (mm/s)	Γ/2 (mm/s)	Δ (mm/s)	H (T)	Area (%)	phase
E110711	0,273 ± 0,012	0,237 ± 0,021	0	49.7 ± 0.1	25	Fe3O4
	0,648 ± 0,018	0,497 ± 0,032	0	46.0 ±0.1	51	Fe3O4
	0,928 ± 0,021	0,632 ± 0,033	0	-	24	Fe-C

Table T1: Mössbauer spectrum of the iron-oxide-carbon nanocomposite

Optical Spectroscopy

The optical spectroscopy data for pure magnetite and iron oxide-carbon nanocomposite are presented in figure S7. These data clearly show that our composite has Fe_3O_4 (magnetite) and not gamma-Fe2O3. The main signature of the presence of mixed valent Fe_3O_4 is the absorption encountered over the wavenumber range. This is absent in single 3+ valence gamma-

Fe_2O_3 compound if present. [4, 5]

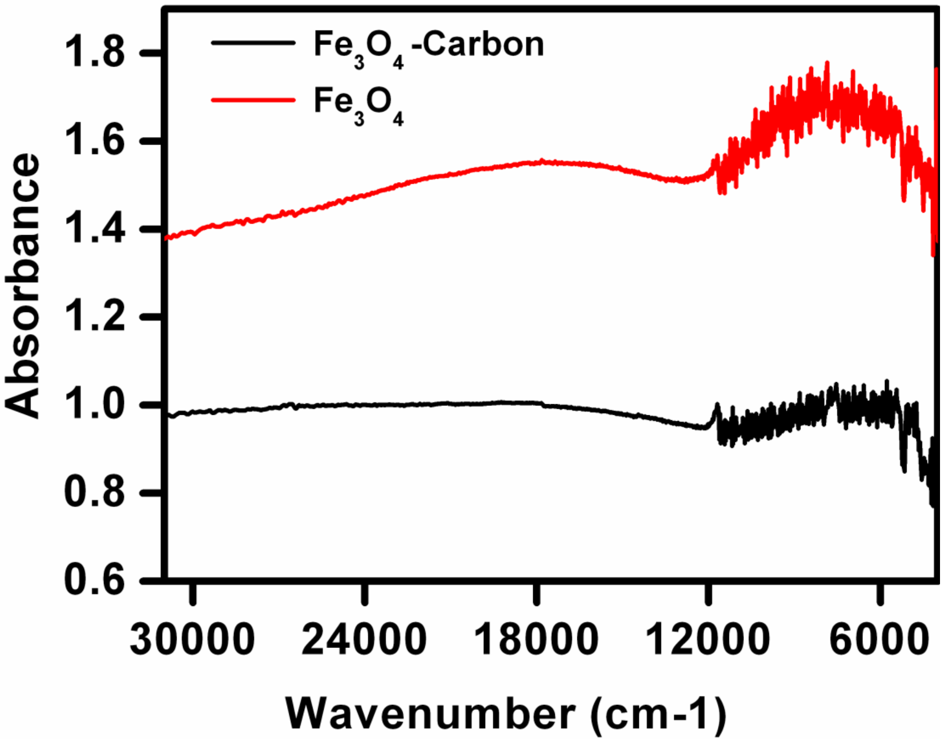

Figure S7: UV-Vis-NIR optical absorption data for magnetite and iron-oxide-carbon nanocomposite

XPS of the composites

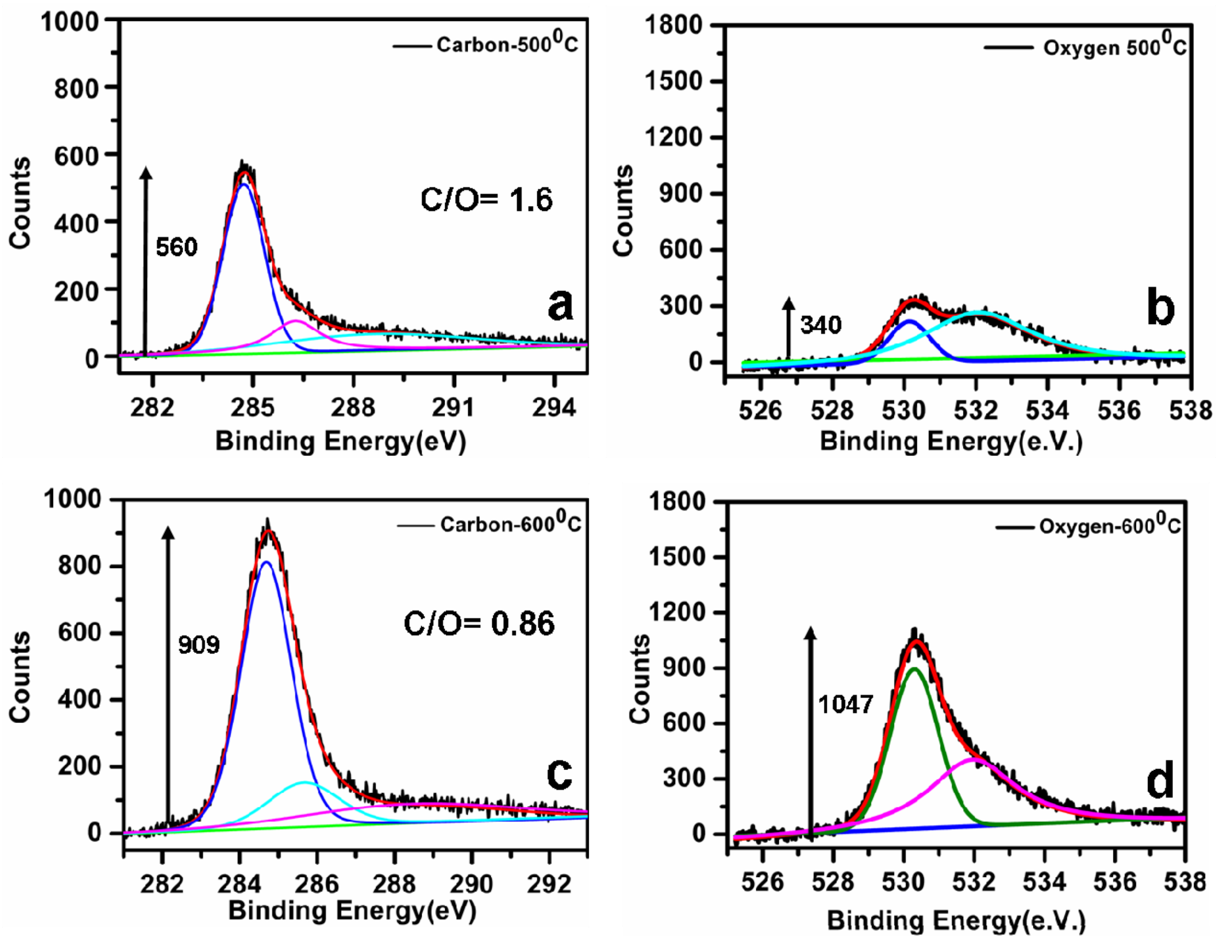

Figure S8. XPS peak of the C-Fe3O4 composites obtained at (a&b): 500^{o}C (c&d): 600^{o}C

XPS data for the composites are shown is the above figure. In Figure S8a (sample pyrolyzed at 500^{0}C) and c (sample pyrolyzed at 600^{0}C), the peaks at 284.7 eV corresponds to the binding energy of the C1s electron of the sp^2-hybridized carbon atom. The oxygen peak at 530.2 eV corresponds to the Fe_3O_4 lattice oxygen and 532.2 eV corresponds to the adsorbed oxygen molecule. The carbon to oxygen ratio (C/O) in the low temperature case is considerably higher (almost double) as compared to the high temperature case, consistent with the TGA result.

BET Adsorption Isotherm and Pore size distribution

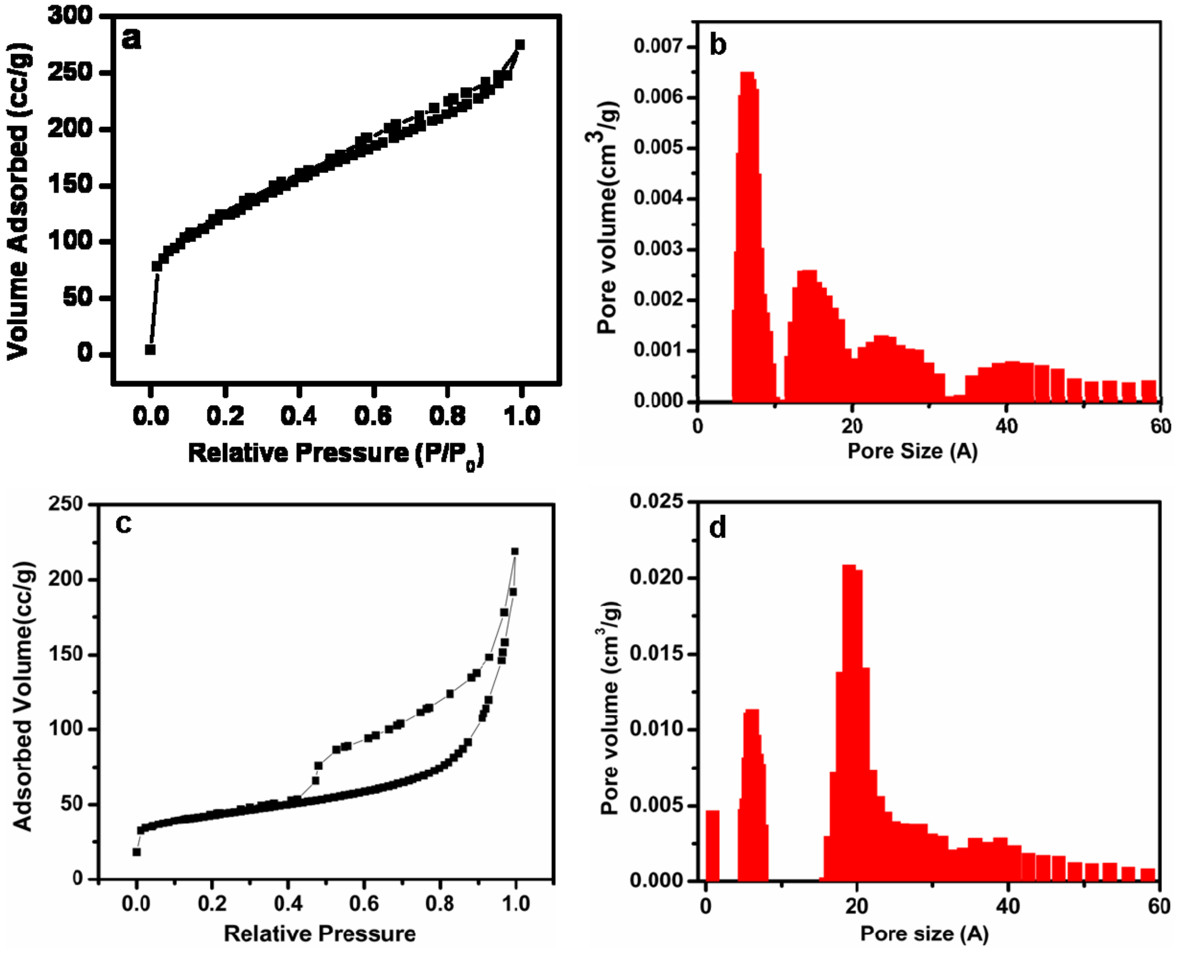

Figure S9. a-b. 500°C composite N2 adsorption isotherm and pore size distribution respectively. c-d. 600°C similar.

The BET nitrogen adsorption isotherm along with the pore size distribution is shown in Figure (S9). Both these cases exhibit type (II) adsorption isotherm. The low temperature (500°C) processed composite shows higher surface area (439 m^2/g) as compared to the high temperature (600°C) processed composite (202 m^2/g). The pore size distribution is also shown for the two composites, where we can clearly see that for the low temperature (500^0C) synthesized case the pore sized is centered around 0.8 nm whereas in the high temperature synthesized (600^0C) case it is centered at 2 nm. High temperature synthesized case also shows better hysteresis than the low temperature annealed case.

ESI IV

Experimental details of Oil/Hydrocarbon, Dye/Phenol adsorption and contact angle measurements

Oil and Hydrocarbon adsorption study:

For oil and hydrocarbon absorbance study, a Petri dish containing water was taken and 2.5 ml of oil or hydrocarbon was added to it. Due to their hydrophobic nature, oil and hydrocarbon float on water surface. 20 mg of hydrophobic (synthesized at 500^{o}C temperature) Fe_3O_4-carbon nanocomposite was then added and the dish was shaken it gently for one time .The composite particles adsorbed the oil or hydrocarbon quickly from the surface of water. The oil adsorbed material was separated by magnetic field using a bar magnet. For recyclability test, the adsorbed oil was removed from the composite by sonication in ethanol, then separated and again washed once with ethanol for 2 minutes under sonication. Finally the composite was collected and kept for drying in an oven at 60 degree celsius.

The adsorption capacity (k) was measured by the formula $k = (M_1\text{-}M) / M$, Where M is the initial weight of the Composite and M1 is the final weight of the composite, the weight measured by an electronic balance. For recyclability, the composite activity was reinvestigated by removing the oil from the composite by sonication and washing. The adsorption capacity was checked for 9 cycles for the oil and the hydrocarbons.

Contact angle measurement:

The wettability of the composite was investigated by contact angle measurements. For this study, we made a film of the composite and put a drop of water (pH=7) on it and then checked the contact angle. We also performed the wettability measurement of the composite for different pH values and checked stability of the compound after 14 hours by contact angle measurement. The recyclability of the composite was also investigated by water contact angle measurement with consecutive adsorbed and desorbed oil fraction from the composite up to 9 cycles.

Miscibility test of the organic hydrocarbons (octane, decane and dodecane) and the oil was carried out by Dynamic contact angle measurements. 5 microlitres of liquid (oil and hydrocarbons) was added as a drop on the composite film. The time taken for miscibility of the drop for each case was recorded.

Dyes and Phenol adsorption:

UV-VIS spectrometer was used to find out the equilibrium concentration of dye adsorbed. In a typical experiment 10 mg of the magnetic nanocomposite was added into 25 ml of the dye and Phenol solution (30 mg L^{-1} for MB and MR dye and 500 mg L^{-1}) and stirred to form the dispersed solution. Time dependence of the UV-Visible spectra was studied after removing the dye solutions at uniform intervals. The equilibrium adsorption isotherm was obtained by adding 8 mg of the composite into 25 ml of different concentrations of the dye and phenol solutions, and stirring until the equilibrium was reached. After reaching equilibrium, the composites were separated by a magnet and the solutions were analyzed by the UV-VIS spectrometer.

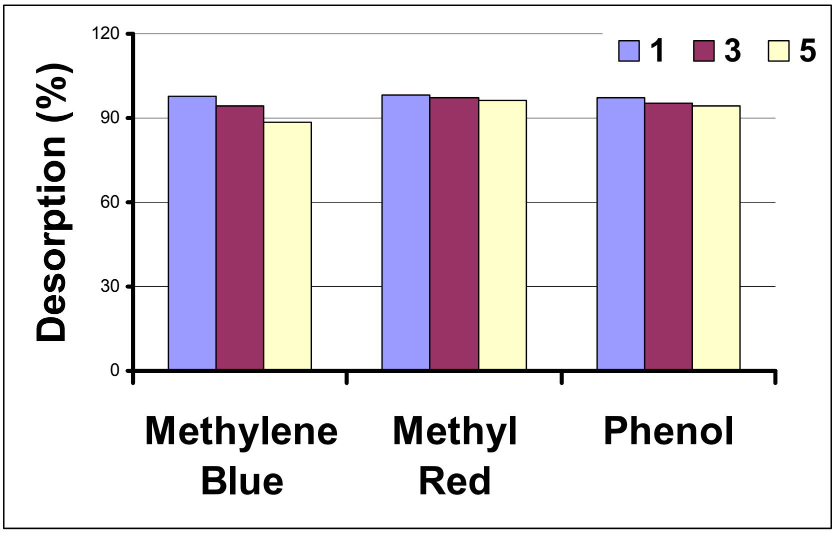

Fig S10. Desorption percentage of the Dyes and Phenol up to 5 cycles

References

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