Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Material

Al-doped magnetite encapsulated in mesoporous carbon: A long-lasting Fenton catalyst for CWPO of phenol in a Fixed-bed reactor at mild conditions

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1. Materials and Methods

1.1 Materials

The following chemicals were used without further purification. Sodium hydroxide (98 %), Phenol (AR), Sucrose (AR), $FeSO_4.7H_2O$ (AR) and $Al(NO_3)_3.9H_2O$ (AR) were obtained from SRL chemicals. Hydrogen peroxide (30 %), Sulfuric acid (97 %), Fumaric acid (99 %), Oxalic acid (99 %), Maleic acid (AR) Methanol (AR) and Ethanol (99.9 %) were purchased from Merck Millipore chemicals. Waste PET bottles (Coke, Pepsi) are collected from Vellore institute of Technology campus. Ultrapure water (18.2 MΩ) was used throughout the experimental synthesis.

1.2 Characterization methods

XRD: The crystallinities size and structure of the catalytic materials were identified by powder X-ray (Cu Kα radiation source) diffraction method. The Panalytical Empyrean Powder Diffractometer equipped with position-sensitive detector X'Celerator fitted with a graphite monochromator, at 40 kV and 30 mA was used for collecting of catalysts XRD patterns. They were analysed with software developed by Crystal Logic. The SBDE ZDS computer search/match program coupled with the ICDD database was used for phases identification. The extent of substitution of Fe^{3+} ions in the magnetite structure for Al^{3+} ions (x value in the composition $Fe(Fe_xAl_{(1-x)})_2O_4$) was calculated by Rietveld refinement by adjusting of the Fe^{3+}/Al^{3+} ratio in the crystalline framework which unit cell is shown in Fig. S1. The selected F^{3+}/Al^{3+} ratio yielded simulated diffractogram profile that fits the recorded one with an accuracy of 100-R<10. The Al-substituted magnetite phase (Fig. S1(b)) resembles magnetite Fe_3O_4 ($Fe(2+)O{\cdot}Fe(3+)_2O_3$ (Fig. S1(a)) with a modified value of lattice parameter **a** of spinel structure. This modification is a result of partial substitution Fe^{3+} ions for Al^{3+} in the crystal lattice of magnetite, yielding the composition $Fe^{2+}(Fe^{3+}{}_xAl^{3+}{}_{(1-x)})_2O_4$ with a spinel structure

(Fig. S1(b)), the simulated XRD patterns of which fit the experimental spectra. Changing of crystalline lattice parameter **a** due to formation of the spinel structure with partial substitution of Fe^{3+} ions in magnetite for Al^{3+} ions, as illustrated in (Fig. S1(b)), changes its crystal lattice parameter **a**, This is reflected by the shift of positions of [311] and [440] peaks maxima in the XRD patterns to higher 2θ values being the experimental basis for Rietveld simulations.[1] Scherrer equation $h = K\lambda/[(B^2 - \beta^2)^{0.5} \cos(2\theta/2)]$ was applied to determine the crystal size, where K = 1.000 is the shape factor, λ = 0.154 nm, β is a correction for instrumental broadening and B is correction for reflection broadening at respective 2θ value. **TGA**: Thermogravimetric analysis was carried out by using TA Q600 SDT instrument for the prepared catalytic materials under nitrogen atmosphere to determine the information about phase transition of the metals (physical phenomena) and decomposition of the catalytic support (chemical phenomena) under inert atmosphere at the heating rate of 5°/min. **BET**: The specific surface area, pore volume, and pore size distribution of the catalytic materials were derived from N_2 adsorption-desorption isotherms by Brunauer-Emmett-Teller (BET) & Barrett-Joyner-Halenda (BJH) methods. The isotherms were recorded at 77k liquid nitrogen temperature using Quantachrome USA, Autosorb IQ, Model-6 instrument. Before the analysis catalytic materials were out-gassed at 300 °C for 12 h under Helium atmosphere. **FE-SEM**: The morphology and elemental composition of the catalytic materials were identified by high resolution Carl Zeiss Supra 55 FE-SEM instrument. **HR-TEM**: Distinctive morphology and STEM-EDX elemental mapping images were acquired by a JEOL JEM-2200FS 200kV TEM at the MEA platform (Université de Montpellier, France) operated at 200 kV and equipped with a 100 mm^2 windowless EDX Silicon Drift Detector from Oxford Instruments (XMax 100 TLE). FEI-Tecnai G2 20 S-TWIN 200kV TEM instrument was also used for imaging. **XPS**: The X-ray photoelectron spectrometer ESCALAB 250 apparatus working at ultrahigh vacuum (1·10-9 bar) with an Al Kα X-ray source and a monochromator was applied for collecting of XPS spectra. Fitting a sum of the single component lines to the experimental data by means of a non-linear least-square curve was used for identification of the spectral components of Fe signals. Cleaning the surface from adsorbed species before recording the XPS spectra was done using the EX05 argon gun system. **TOC**: TOC-L Shimadzu instrument was utilized to determine the total organic carbon present in the water sample before and after the treatment using Non-Purgeable Organic Carbon (NPOC) method. **AAS:** Varian AA240 Atomic Adsorption Spectroscopy instrument was used to detect the leached Fe ions in the solution after the treatment. Inductively Coupled Plasma Optical Emission Spectroscopy **(ICP-OES)** analysis was carried out in AVIO 200 spectrometer (Perkin Elmer) to enumerate the presence of Iron and Aluminium in the catalyst. 100mg of fresh γ-Fe_2O_3/$FeAl_2O_4$@MC catalyst was taken for the digestion process in the acidic environment. Catalyst was mixed with 2.5 ml of concentrated nitric acid and 5 ml of 30%H_2O_2. The obtained solution mixture was digested in microwave oven by raising the temperature to 170˚C for 20 minutes. After cooled down to room temperature the samples were diluted by using 100 ml of Milli-Q water and it was filtered by using metal free pure fibre filter (Stock). Along the line, it was diluted with Milli-Q water to 100 ml by taking 1 ml of filtered stock before to the analysis. Similarly, 70mg of recovered spent catalyst $Fe(Fe_{0.68}Al_{0.32})_2O_4$@MC was digested by the same procedure as described above and diluted to 25ml using Milli-Q water (Stock). Further, 1ml of stock was prepared to 100ml in advance to the analysis. Evaluated the entire amount of Iron and aluminium in the acid digested catalysts by using ICP standard of multi elemental calibrations in a range of 1000 ppm. **UPLC**: Acquity H class UPLC was employed to identify the phenol and organic acid intermediates in the treated water samples. Methanol and water (50:50) used as a mobile phase with 0.2 % phosphoric acid and the flow rate was 0.1 mL/min along with 200 – 800 nm UV absorbance range.

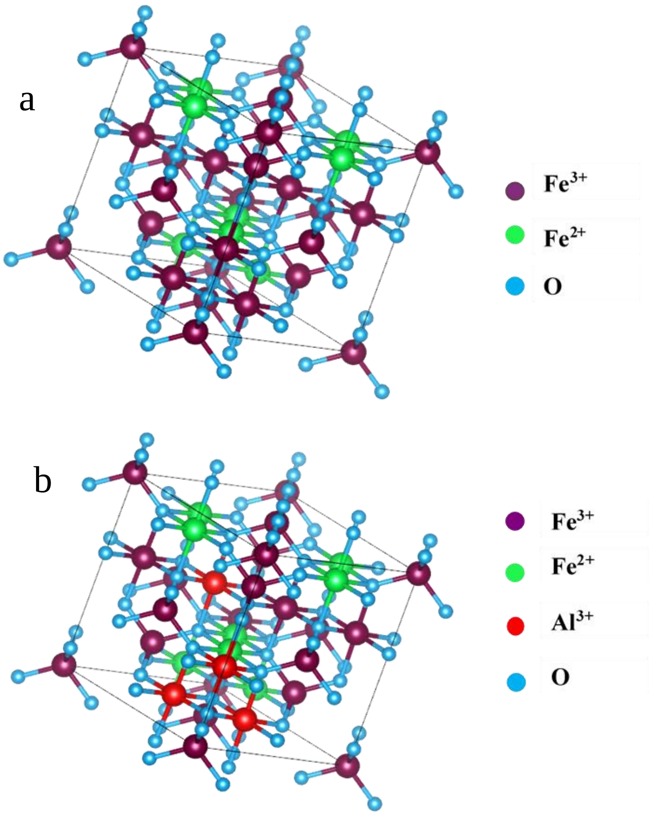


Fig. S1 The unit cells of Fe_3O_4 spinel (a) before and (b) after partial substitution of Fe^{3+} ions for Al^{3+}: (a) magnetite Fe_3O_4, (b) Al-substituted magnetite $Fe^{2+}(Fe^{3+}{}_xAl^{3+}{}_{(1-x)})_2O_4$

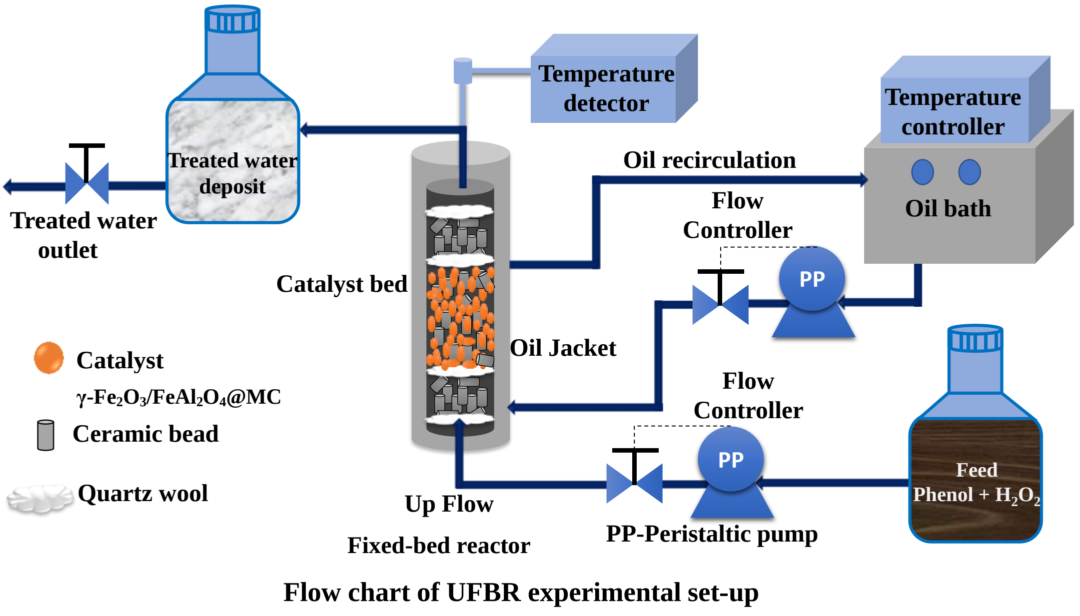


Fig. S2. Up-flow fixed bed reactor set-up for the CWPO of phenol aqueous solutions

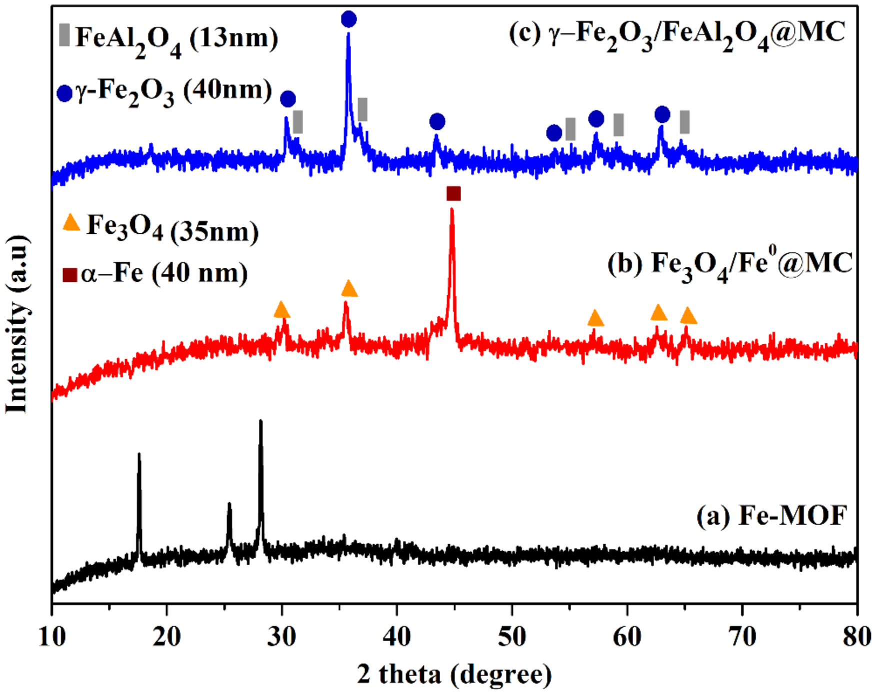
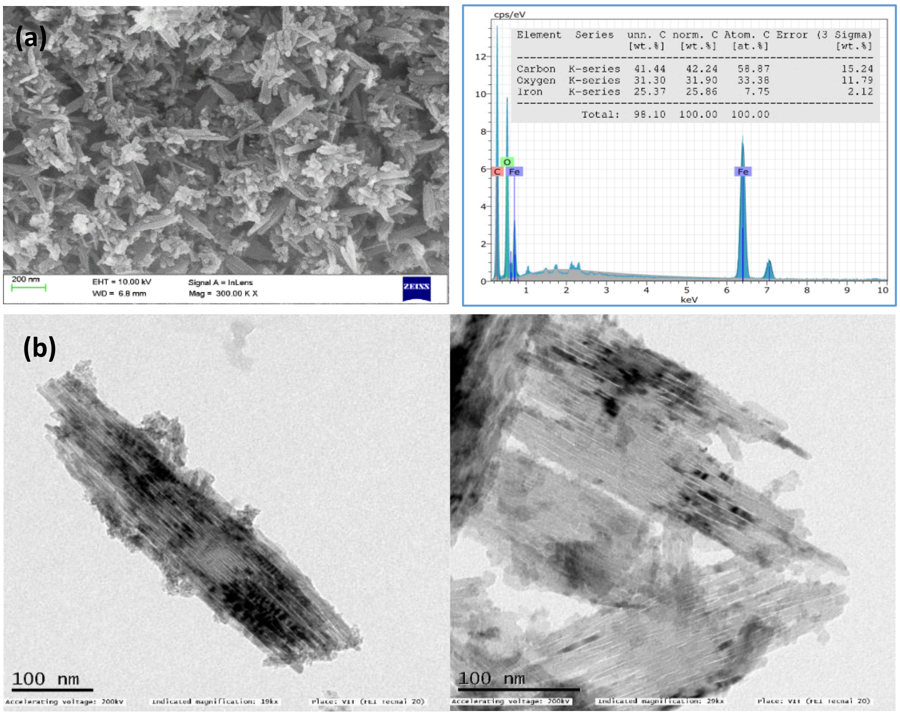


Fig. S3. XRD patterns of (a)Fe-MOF (b)Fe_3O_4/Fe^0@MC and (c) γ-$Fe_2O_3/FeAl_2O_4$@MC



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Element   Series   unn. C norm. C Atom. C Error (3 Sigma)
                   [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------------
Carbon   K-series   41.44   42.24   58.87           15.24
Oxygen   K-series   31.30   31.90   33.38           11.79
Iron     K-series   25.37   25.86    7.75            2.12
-----------------------------------------------------------
           Total:   98.10  100.00  100.00
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Fig. S4. (a) FE-SEM image with EDX and (b) HR-TEM images of Fe-MOF

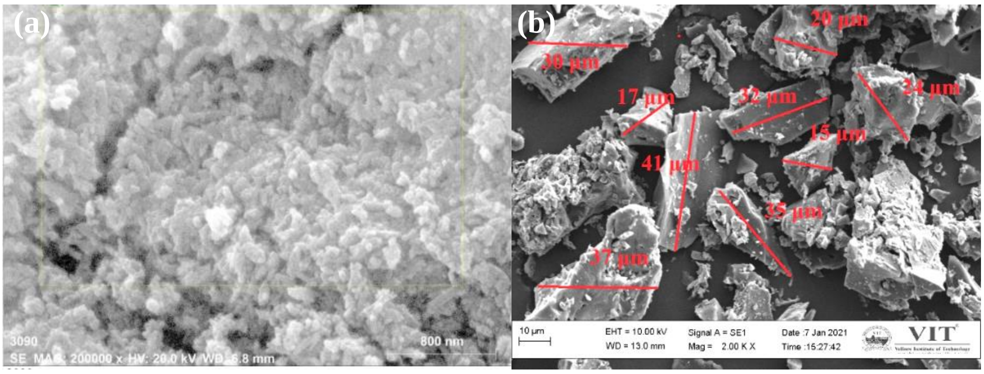


Fig. S5. FE-SEM and SEM image of (a) sucrose coated Fe-MOF and (b) γ-Fe_2O_3/$FeAl_2O_4$ @MC

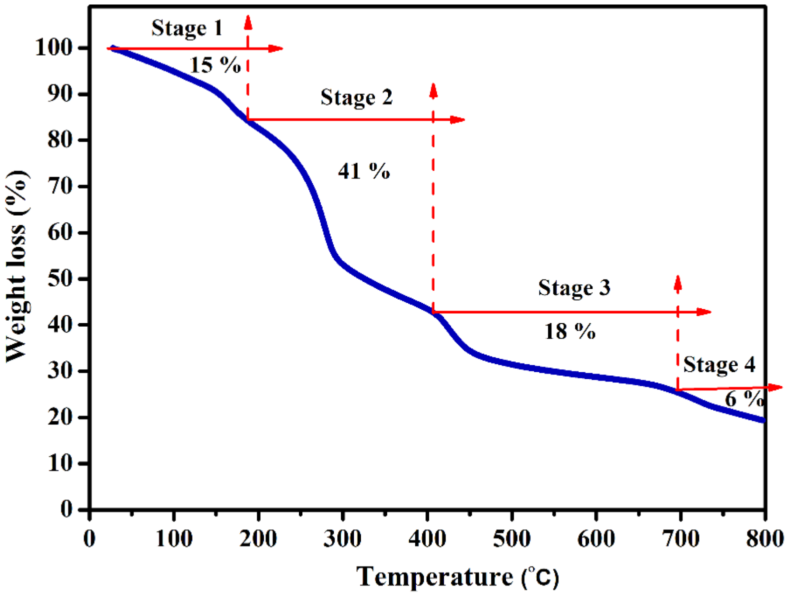


Fig. S6. TGA thermogram of Sucrose coated Fe-MOF

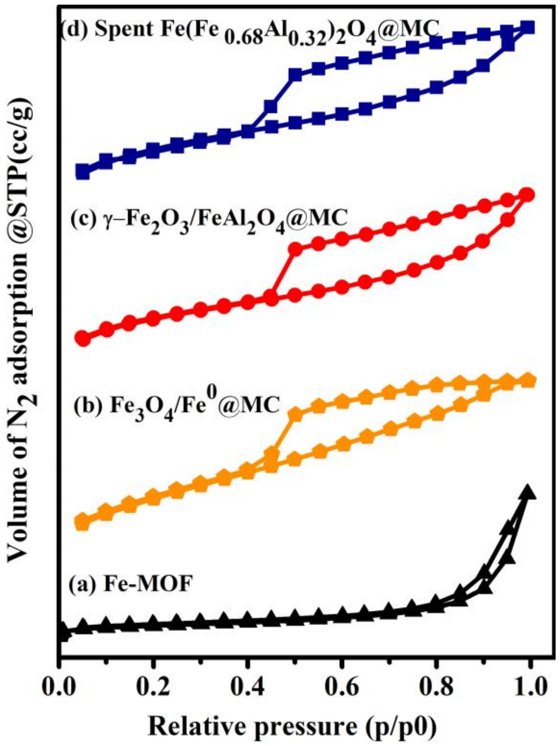


Fig. S7. N_2 adsorption-desorption isotherms of (a) Fe-MOF (b) Fe_3O_4/Fe^0@MC (c) γ-$Fe_2O_3/FeAl_2O_4$@MC and (d) Fe($_{Fe0.68}$$Al_{0.32}$)$_2$$O_4$@MC (500 h)

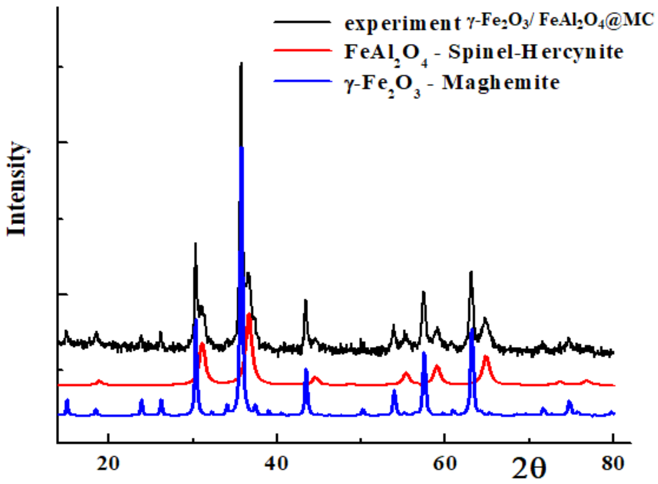


Fig. S8. XRD pattern of γ-$Fe_2O_3/FeAl_2O_4$@MC

Comparison of Fe/Al mole ratio of spent catalyst estimated theoretically with obtained from ICP-OES and XRD

As the resultant carbon composite material from Fe-MOF lost most of its carbon matrix during the carbonization process, sucrose has been used as additional carbon source. 1.9 g of sucrose was coated over 0.5 g of Fe-MOF. TGA analysis revealed that on thermal treatment sucrose coated Fe-MOF loses 78% of its weight (Fig.S6). Therefore 2.4g of sucrose coated Fe-MOF after thermal treatment reduced to 0.528 g to yield Fe^0/Fe_3O_4@MC (MC-Mesoporous carbon). BET analysis results confirmed the existence of mesopores in Fe^0/Fe_3O_4@MC with 0.40 cc/g pore volume (Table 1) and it can hold 688 mg of anhydride aluminium nitrate (Density of Aluminium nitrate = 1720 mg/cm^3). For aluminium loading, each batch 250 mg Fe^0/Fe_3O_4@MC has been employed and it can hold 172 mg $Al(NO_3)_3$ (688 mg/4=172 mg) having 21.8 mg of Al (Aluminium nitrate mol.wt. = 213g/mol). After aluminium precursor loading on 250mg of Fe^0/Fe_3O_4/MC and followed by thermal treatment at 550°C in inert atmosphere we received 250mg of γ-$Fe_2O_3/FeAl_2O_4$@MC.

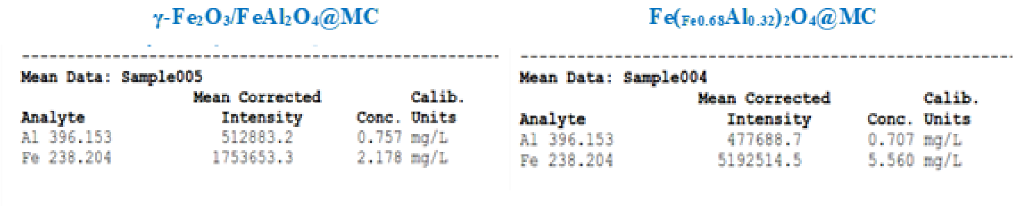
Al and $FeAl_2O_4$ weight in 100 mg of γ-$Fe_2O_3/FeAl_2O_4$@MC

Since the Al weight is not changed after the thermal treatment, 250mg of γ-$Fe_2O_3/FeAl_2O_4$@MC contain 21.8 mg of Al. Only 100 mg of γ-$Fe_2O_3/FeAl_2O_4$@MC was used for degradation study. Thus, 100 mg catalyst contains 8.72 mg of Al which can form 28 mg of $FeAl_2O_4$ (Molecular weight of $FeAl_2O_4$ = 174 g). Therefore 100 mg of γ-$Fe_2O_3/FeAl_2O_4$@MC catalyst contains **28 mg of $FeAl_2O_4$**.

Fe and γ-Fe_2O_3 weight in 100 mg of γ-$Fe_2O_3/FeAl_2O_4$@MC

The SEM-EDAX result of Fe-MOF confirmed the presence of 25 wt% of Fe (Fig. S4). 1.9 g of sucrose was coated over 0.5 g (125 mg Fe) of Fe-MOF. After thermal treatment of 2.4g of sucrose coated Fe-MOF yielded 0.528 g of Fe^0/Fe_3O_4@MC. Since Fe wt% did not change on thermal treatment, 528 mg of Fe^0/Fe_3O_4@MC contain 125 mg of Fe. Therefore 100 mg of Fe^0/Fe_3O_4@MC contains 23.6 mg of Fe. It should be noted that in 100 mg of Fe^0/Fe_3O_4@MC 14.6 mg of Fe has been consumed to form 28 mg of $FeAl_2O_4$ and remaining 9 mg of Fe has been utilized to form 21.2 mg γ-Fe_2O_3. Finally, 100 mg of γ-$Fe_2O_3/FeAl_2O_4$@MC catalyst theoretically has **21.2 mg γ-Fe_2O_3**, **28 mg of $FeAl_2O_4$**, 50.8 mg of Carbon matrix and **8.72 mg** of Al and **23.6 mg** of Fe.

Fe and Al wt% of fresh γ-$Fe_2O_3/FeAl_2O_4$@MC and spent $Fe(Fe_{0.66}Al_{0.33})_2O_4$@MC catalyst obtained from ICP-OES



γ-$Fe_2O_3/FeAl_2O_4$@MC

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--------------------------------------------------------
Mean Data: Sample005
                    Mean Corrected          Calib.
Analyte                  Intensity    Conc. Units
Al 396.153                512883.2    0.757 mg/L
Fe 238.204               1753653.3    2.178 mg/L
```

$Fe(_{Fe0.68}Al_{0.32})_2O_4$@MC

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---------------------------------------------------------
Mean Data: Sample004
                       Mean Corrected          Calib.
Analyte                     Intensity    Conc. Units
Al 396.153                   477688.7    0.707 mg/L
Fe 238.204                  5192514.5    5.560 mg/L
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ICPOES analysis of γ-$Fe_2O_3/FeAl_2O_4$@MC & $Fe(_{Fe0.68}Al_{0.32})_2O_4$@MC

100mg of fresh γ-Fe_2O_3/ $FeAl_2O_4$@MC catalyst was digested in microwave-assisted nitric acid method and it was diluted to 100 mL using Milli-Q water (stock solution). Further, it was diluted to 100 ml by taking 1 ml of stock before the analysis. Similarly, **70mg** of recovered spent catalyst $Fe(Fe_{0.68}Al_{0.32})_2O_4$ @MC digested in microwave-assisted nitric acid method and diluted to 25ml using Milli-Q water (stock solution). Along the line, 1ml of stock was diluted to 100ml before the analysis.

Fe and Al concentration of γ-Fe_2O_3/$FeAl_2O_4$@MC catalyst obtained from ICP analysis are 2.178 and 0.757 ppm, respectively. Therefore, 0.2178 mg of Fe and 0.0757 mg of Al present in 100 ml of analysed solution. As 1 ml of stock is diluted to 100 ml, the same weight is present in 1 ml of the stock solution. Thus, 100 ml of stock solution contains **21.78 mg** of Fe and **7.57 mg** of Al which in turn the weight % of Fe and Al in the 100 mg of γ-Fe_2O_3/$FeAl_2O_4$@MC. The Fe and Al wt% of the fresh catalyst obtained from ICP-OES analysis is close with the theoretical value **23.60 mg Fe** and **8.72 mg Al**.

Similarly, Fe and Al concentration of $Fe(Fe_{0.68}Al_{0.32})_2O_4$ @MC catalyst obtained from ICP analysis are 5.560 and 0.707 ppm, respectively. Therefore, 0.556 mg of Fe and 0.0707 mg of Al present in 100 ml of analysed solution. As 1 ml of stock is diluted to 100 ml, the same weight is present in 1 ml of the stock solution. Thus, 25 ml of the stock solution contains 13.9 mg of Fe and 1.765 mg of Al which in turn which in turn the weight % of Fe and Al in the 70 mg of $Fe(Fe_{0.68}Al_{0.32})_2O_4$ @MC. Hence, for 100 mg of the catalyst **19.85 mg** of Fe and **2.52 mg** of Al. Theoretically 100 mg of Fresh catalyst γ-Fe_2O_3/$FeAl_2O_4$@MC should have **23.60 mg** of Fe and **8.72 mg** of Al and based on the 3 ppm iron and 6 ppm Al leaching in 500 h run the spent catalyst $Fe(Fe_{0.68}Al_{0.32})_2O_4$ @MC should have **20.60 mg** of Fe and **2.72 mg Al.** The Fe and Al wt% of the spent catalyst obtained from ICP-OES analysis is in good agreement with the theoretical value.

Outcome of ICP-OES results

Fe and Al present in the fresh γ-Fe_2O_3/$FeAl_2O_4$@MC catalyst= **21.78 mg** Fe **and 7.57 mg** Al.

Fe and Al leached during the 500 h run = **3 mg** Fe and **6 mg** Al

Fe and Al present in the 500 h spent $Fe(Fe_{0.68}Al_{0.32})_2O_4$ @MC = **19.85 mg** Fe and **2.52 mg** Al.Based on the ICP-OES result the 500 h spent catalyst has Fe/Al mole ratio of **3.8**. Spent catalyst XRD result endorses the formation of $Fe(Fe_{0.68}Al_{0.32})_2O_4$ structure with the molar composition of $FeAl_{\mathbf{0.27}}O_{1.7}$ and Fe/Al mole ratio of **3.7**.

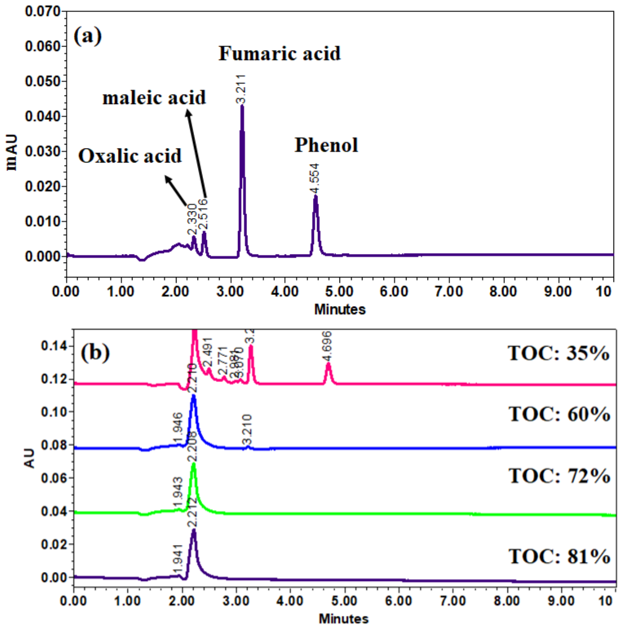
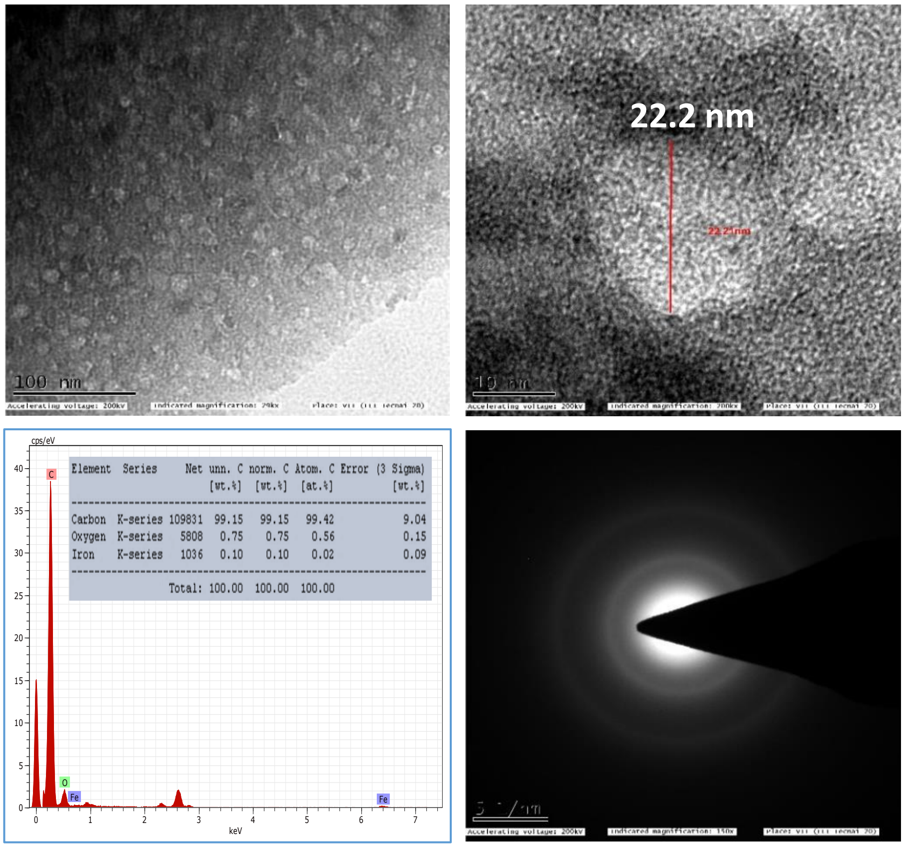


Fig. S9. UPLC chromatogram of (a) phenol and intermediates, (b) effluent water with various TOC removal percentage.



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Element  Series     Net unn. C norm. C Atom. C Error (3 Sigma)
                        [wt.%]  [wt.%]  [at.%]          [wt.%]
--------------------------------------------------------------
Carbon  K-series 109831  99.15   99.15   99.42            9.04
Oxygen  K-series   5808   0.75    0.75    0.56            0.15
Iron    K-series   1036   0.10    0.10    0.02            0.09
--------------------------------------------------------------
                Total: 100.00  100.00  100.00
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Fig. S10. HR-TEM images, EDAX and SAED pattern of iron washed graphitic MC

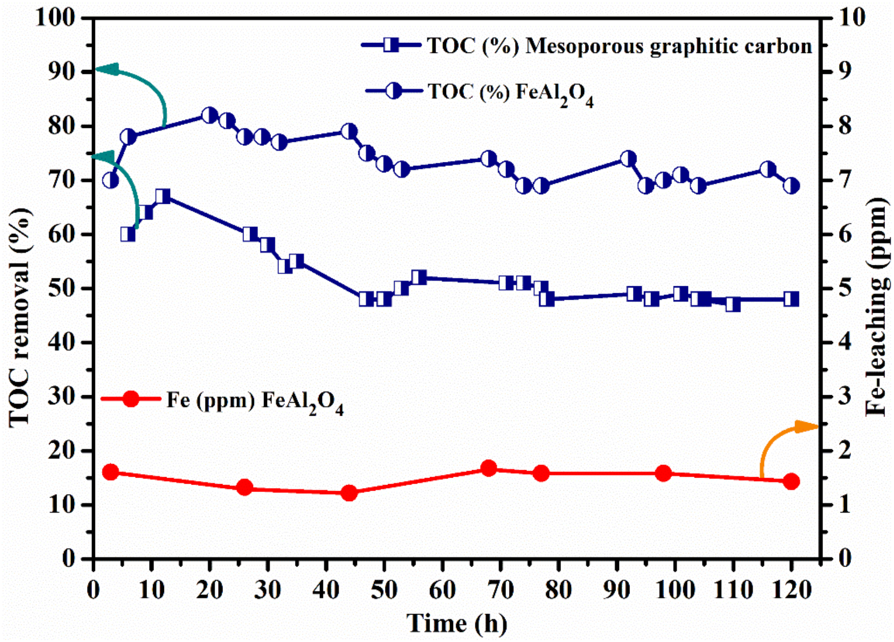

Fig. S11 Catalytic activity of Graphitic MC and $FeAl_2O_4$ nanoparticles towards phenol degradation in fixed bed reactor (Reaction condition: 200 ppm phenol, pH:5, 40 °C, H_2O_2: 1.2S, Flow rate: 0.1 mL/min., Catalyst weight: 28 mg $FeAl_2O_4$, 50 mg mesoporous graphitic carbon,).

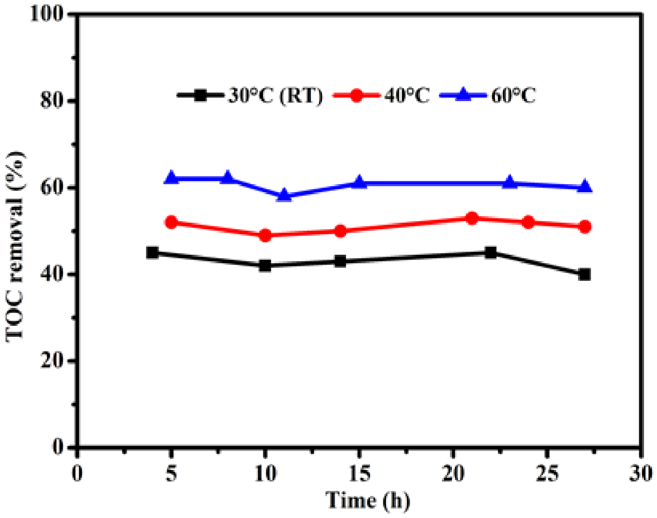

Fig. S12. The catalytic activity of homogeneous iron ($FeSO_4.7H_2O$) at various temperature towards phenol degradation in continues reactor (pH: 5, Fe:2ppm, 1.2 Stoichiometric, Phenol: 200ppm, flow rate 0.1mL/min**)**

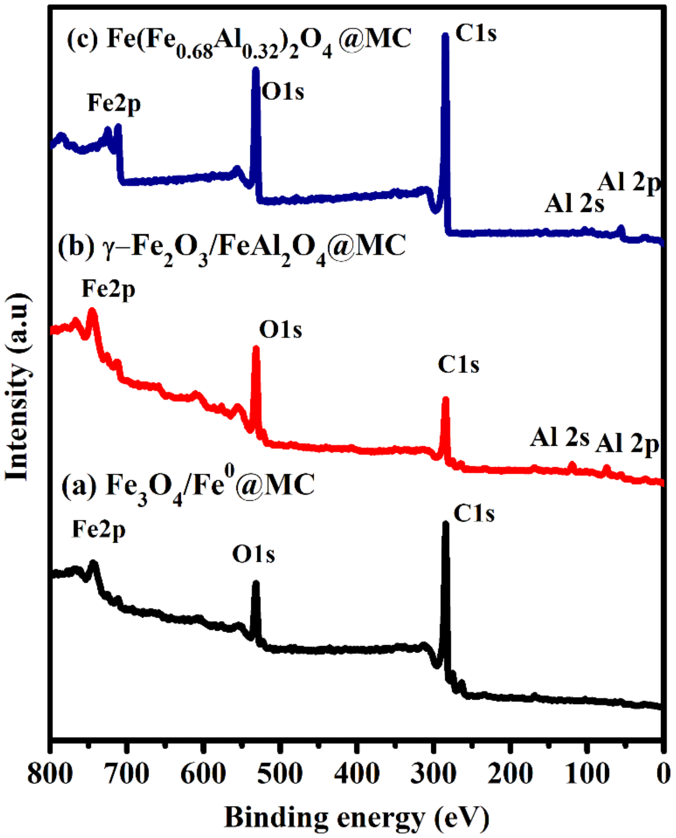

Fig. S13. XPS Survey spectra of prepared catalysts (a) Fe_3O_4/Fe^0@MC, (b) $Fe_2O_3/FeAl_2O_4$@MC and (c) Spent Fe($Fe_{0.68}$ $Al_{0.32}$)$_2O_4$@MC -500h

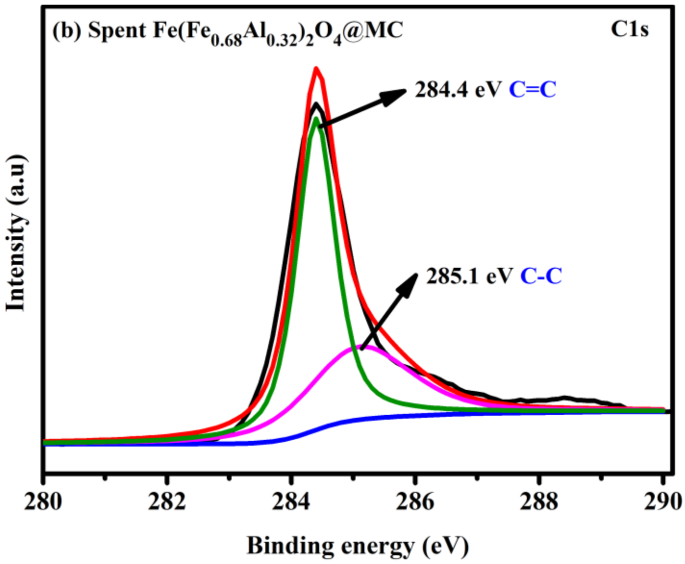

Fig. S14. C1s XPS spectra of 500 h spent Fe($Fe_{0.68}Al_{0.32}$)$_2O_4$@MC

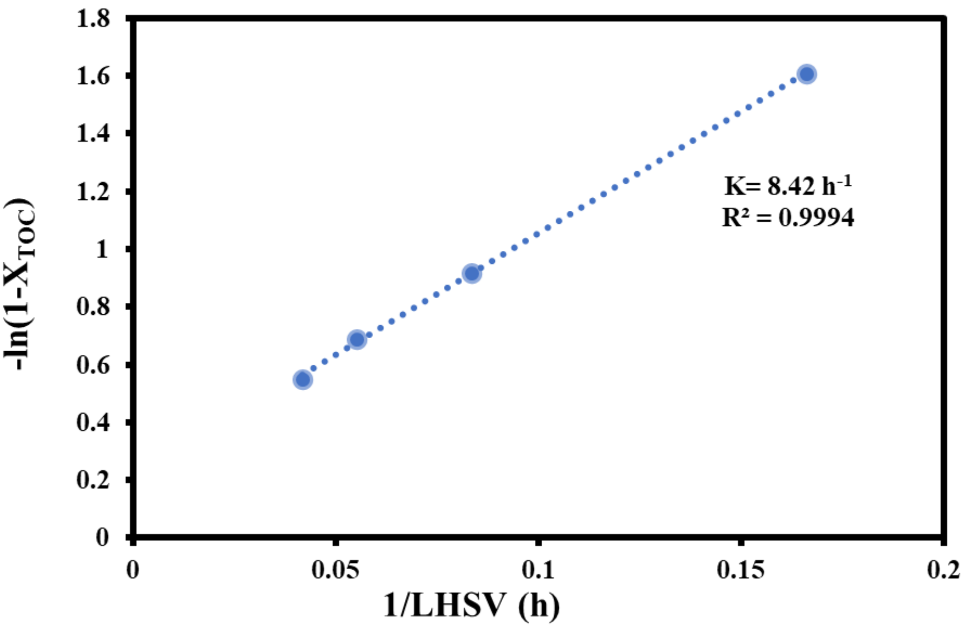

Fig. S15. First order kinetics of $Fe(Fe_{0.68}Al_{0.32})_2O_4$@MC towards CWPO of phenol. Testing condition: T=40°C, pH=5, 0.036mol H_2O_2 (1224 ppm), 200ppm phenol, LHSV = 6.25-25 h^{-1}

Table S1. Comparison of catalytic activity of Fe $(Fe_{0.68}\ Al_{0.32})_2O_4$ @MC with reported heterogeneous Fenton catalysts towards phenol degradation in fixed-bed reactor.

Catalyst	**Catalyst Weight (g)**	**Water flow (mL/min)**	**Specific flow rate, ml/g*min**	**Initial Phenol content (ppm)**	**Temp. (°C)**	**pH**	**H_2O_2 Conc. (mol)**	**X_{Phenol} (%)**	**X_{TOC} (%)**	**TOC removed from water, ppm/min**	**TOC removed from water by 1gram of catalyst, ppm/g*min**	**Fe leached (ppm)**	**Ref.**
Fe_2O_3/ SiO_2	2.9	1	0.34	1000	80	4.2	0.15(S)	100	64	640	221	20	2
Fe-ZSM-5	9.7	2	0.21	1000	80	4	0.15(S)	99	77	770	79.4	< 2	3
Fe^{3+}-Al_2O_3	20	1.2	0.06	1000	90	6	0.15(S)	100	90	900	45	< 3	4
Fe_2O_3/ SBA-15	2.9	1	0.31	1000	80	6.5	0.15(S)	100	66	660	227.6	20	5
$Fe(Fe_{0.68}Al_{0.32})_2O_4$@MC	0.5	1	2.0	1000	80	5	0.036 (1.2S)	100	75	750	1500	< 2	This work

Note: (S)-Stoichiometric (14 mol of H_2O_2 per 1 mol of phenol)

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