(Electronic Supplementary Information)

Kitchen Grinder: A Tool for the Synthesis of Metal-Organic Framework towards Size Selective Dye Adsorption

Mahalaxmi Samal,[a,‡] *Jagannath Panda,*[a,‡] *Bishnu P. Biswal**[b,c] *and Rojalin Sahu**[a]

[a]*Department of Chemistry, School of Applied Sciences, Kalinga Institute of Industrial Technology (KIIT),*
Deemed to be University, Bhubaneswar-24, Odisha, India.
E-mail: rsahufch@kiit.ac.in; Tel: (+91)-9778127994; Fax: (+91)-674 2725113.
[b]*Physical/Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road,*
Pune-411008, India. E-mail: bp.biswal@ncl.res.in.
[c]*Present Address: Max-Planck-Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany.*

[‡]*These authors have contributed equally to this work.*

Contents

Section S1: Experimental

General Remarks: The 2-methylimidazole (2-mIm), 1,3,5-benzenetricarboxylic acid (BTC), ZnO, $Cu(OAc)_2.H_2O$, $Fe(NO_3)_2.9H_2O$, methylene blue (MB) was procured from Sigma Aldrich Chemicals. All starting materials and solvents were purchased from a commercial source and used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded on STOE STADI P diffractometer for Cu Kα radiation (α = 1.5406 Å), with a scan speed of 1° min^{-1} and a step size of 0.02° in 2θ. UV-Vis spectra were measured on an Agilent Cary 5000 UV-VIS-NIR spectrophotometer by using 10 mm optical-path quartz cell at room temperature. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600–4000 cm^{-1}. Thermogravimetric analyses (TGA) were carried out on a TG50 analyzer (Mettler-Toledo) under N_2 atmosphere with a heating rate of 10 ºC min^{-1}. Low-pressure volumetric gas adsorption measurements were performed at 77 K for N_2, maintained by a liquid nitrogen bath, with pressures ranging from 0 to 760 Torr on a Micromeritics, TriStar II Plus automated, three-station, surface area and porosity analyzer. The Brunauer-Emmett-Teller surface area was calculated within the relative pressure range 0.01 to 0.2. Total volume was calculated at P/Po = 0.99. Nonlocal density functional theory (NLDFT) pore size distributions obtained using N_2 as the adsorbate. Prior to surface area analysis the samples were activated at 120 °C for overnight. SEM images were obtained with a Zeiss DSM 950 scanning electron microscope and FEI, QUANTA 200 3D Scanning Electron Microscope with tungsten filament as electron source operated at 10 kV. The samples were sputtered with Au (nano-sized film) prior to imaging by a SCD 040 Balzers Union. TEM images were recorded using FEI Tecnai G2 F20 X-TWIN TEM at an accelerating voltage of 200 kV. For TEM, the samples were sonicated for 15 min in 2-propanol, followed by drop casting the sample on carbon coated copper TEM grids (TED PELLA, INC. 200 mesh). Similar methodology was followed for SEM sample preparation, in which the samples were coated on Silicon Oxide surface.

Synthesis of ZIF-8-KG:

ZIF-8-KG has been synthesized by placing a 2:1 mixture of 2-methylimidazole (2-mIm) (20 gm; 243.59 mmol) and ZnO (10 gm; 121.80 mmol) in a stainless steel kitchen grinder jar (manufactured by Bajaj India; 250 ml capacity) with 5 mL of ethanol. The mixture was grinded at 1st level speed (~500 r.p.m) and after 5, 15, 30 and 60 min. time intervals the samples were collected and washed with hot ethanol, hot water and acetone several times to minimize the content of residual ZnO . Finally dried the sample under vacuum at 90 °C for overnight to get 24 gm of ZIF-8-KG (Yield = 80%). The washed sample was further used for characterization and dye adsorption study.

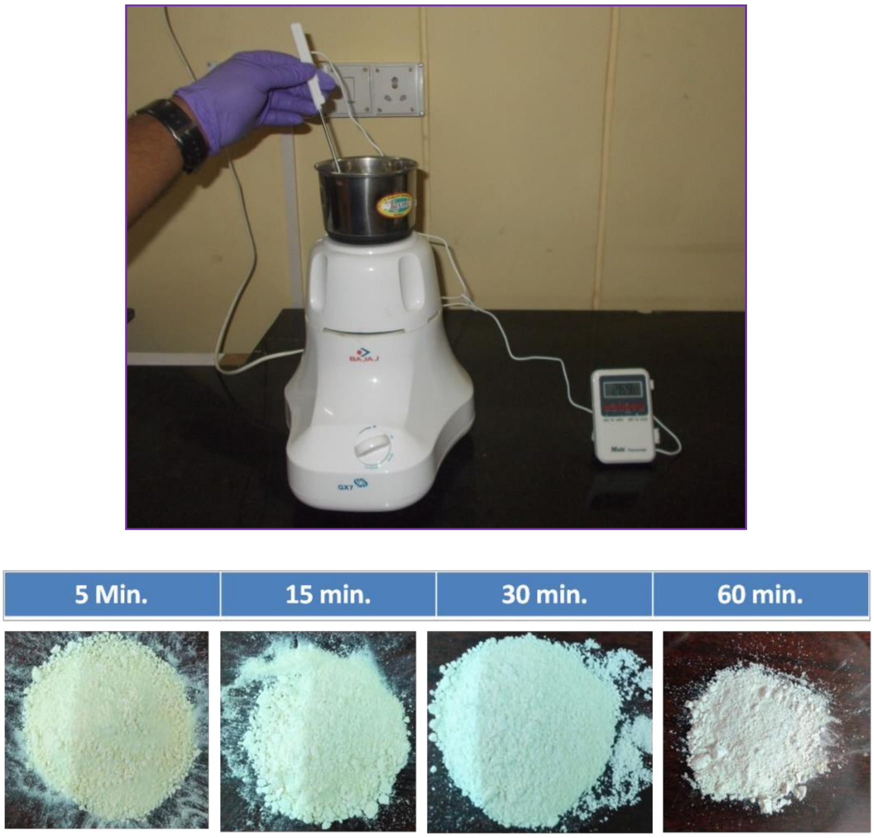
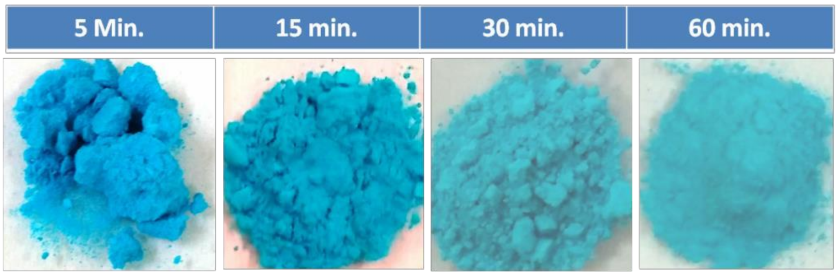


Figure S1. Real photograph taken during the ZIF-8-KG synthesis using kitchen grinder. It has been noted here that, while grinding the reaction temperature has been increased from 22 °C (0 min.) to 81 °C (60 min.) which was monitered by using an external thermometer installed in the wall of the jar as shown in the photograph.

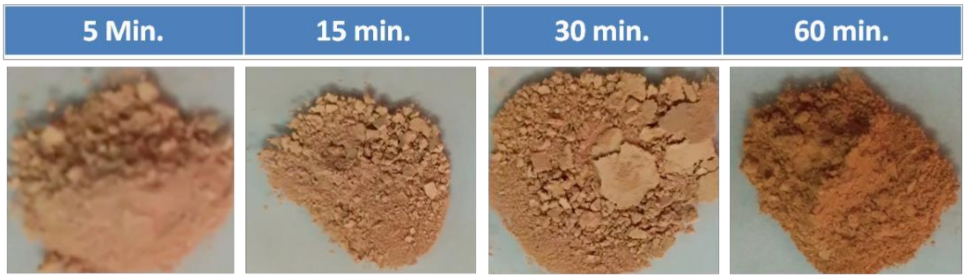
Synthesis of CuBTC-KG:

CuBTC-KG has been synthesized by placing a mixture of 1,3,5-benzenetricarboxylic acid (BTC) (10.8 gm; 51.39 mmol) and Cu(OAc)$_{2}$.H$_{2}$O (6.3 gm; 34.7 mmol) in a stainless steel kitchen grinder jar (manufactured by Bajaj India; 250 ml capacity) with 5 mL of N,N-dimethylformamide (DMF). The mixture was grinded at 1st level speed (~500 r.p.m) and after 5, 15, 30 and 60 min. time intervals, then the samples were collected and washed with DMF, followed by methanol and acetone several times to washout the unreacted starting materials. Finally, dried the sample under vacuum at 90 °C for overnight to get 15.39 gm of CuBTC-KG (Yield = 90%).



Synthesis of MIL-100(Fe)-KG:

MIL-100(Fe)-KG has been synthesized by placing a mixture of 1,3,5-benzenetricarboxylic acid (BTC) (2.63 gm; 12.52 mmol) and $Fe(NO_3)_2.9H_2O$ (5.08 gm; 14.85 mmol) in a stainless steel kitchen grinder jar with 5 mL aquous solution of NaOH (0.4M). The mixture was grinded at 1st level speed (~500 r.p.m) and after 5, 15, 30 and 60 min. time intervals, the samples were collected and washed with hot ethanol, hot water and acetone several times to minimize the content of residual $Fe(NO_3)_2$. Finally dried the sample under vacuum at 90 °C for overnight to get 5.67 gm of MIL-100(Fe)-KG (Yield =73%).



Solvothermal synthesis of ZIF-8:

The ZIF-8 has been synthesized according to the reported literature.[S1] 2-methylimidazole (2-mIm) [200 mg, 2.43 mmol] was added in 10 mL of methanol and the solution was poured into a 5 mL of methanolic solution of $Zn(NO_3)_2.6H_2O$ [95 mg, 0.5 mmol] drop wise. Immediately a white turbid solution resulted and left undisturbed for about 24 h. After the mentioned period, the resulting white precipitate were collected by centrifuge, washed with methanol and dried well under vacuum at 90 °C overnight to get ZIF-8 as white powder.

Solvothermal synthesis of CuBTC:

The CuBTC has been synthesized according to the reported literature.[S2] $Cu(OAc)_2.H_2O$ (1.75 gm, 8.76 mmol) and 1,3,5-benzenetricarboxylic acid (BTC) (0.84 gm, 3.99 mmol) was dissolved in 24 ml of distilled water and 24 ml of ethanol respectively. The resulting mixture was heated for 14h at 120 ºC to get a blue precipitate, collected via centrifuge. Further, the solid was washed with DMF and ethanol mixture several times and dried at 100 ºC for 12 h.

Solvothermal synthesis of MIL-100(Fe):

The MIL-100(Fe) has been synthesized according to the reported literature.[S3] $Fe(NO_3)_2.9H_2O$ (51.9 mg, 0.15 mmol) and 1,3,5-benzenetricarboxylic acid (BTC) (76.6 mg, 0.36 mmol) were dissolved in 8 ml glycol and 8 ml DMF respectively, and the resulting mixture was stirred for 5 min. at ambient temperature and then heated at 80 ºC in an oil bath for 2 h. The resulting precipitate was centrifuged, washed with DMF and ethanol mixture for several times and dried at 100 ºC for 12 h.

Section S2: FT-IR Analysis

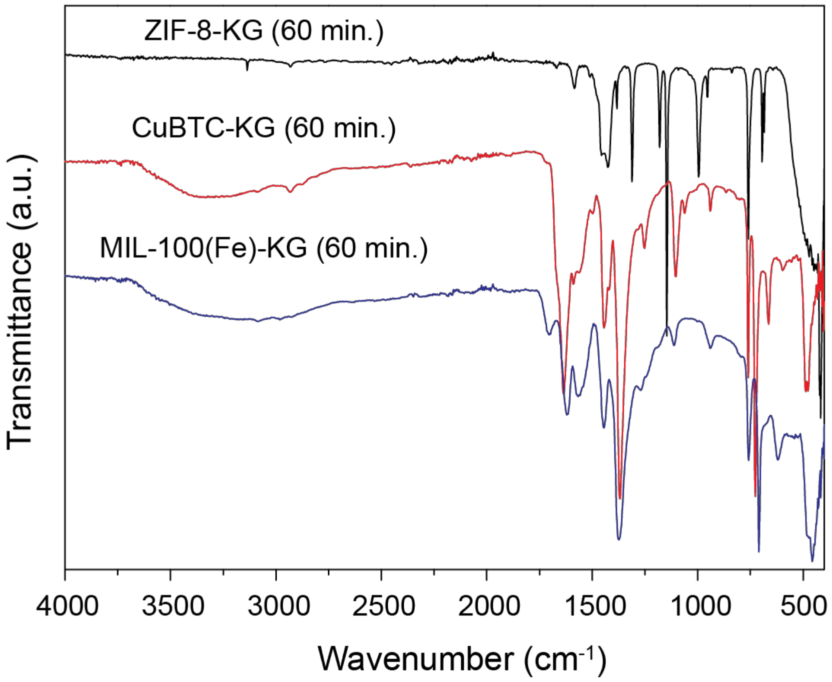


Figure S2. FT-IR spectra of ZIF-8-KG, CuBTC-KG and MIL-100(Fe)-KG synthesized using kitchen grinder.

Section S3: N_2 Adsorption and Pore Size Distribution

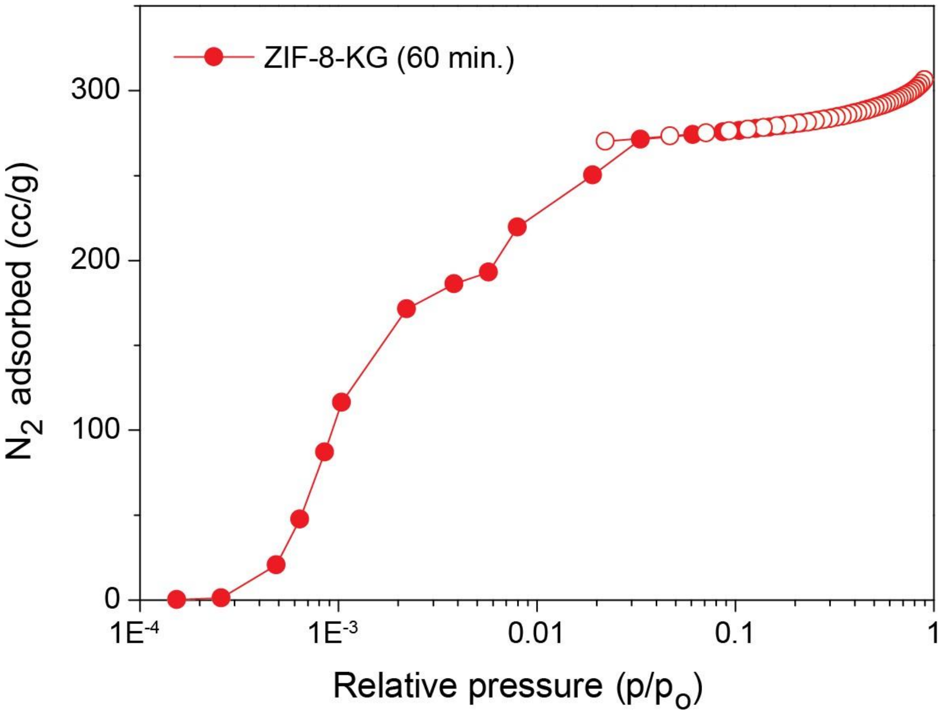


Figure S3. Log (10) plot of N_2 adsorption isotherms of ZIF-8-KG (60 min.) collected at 77K.

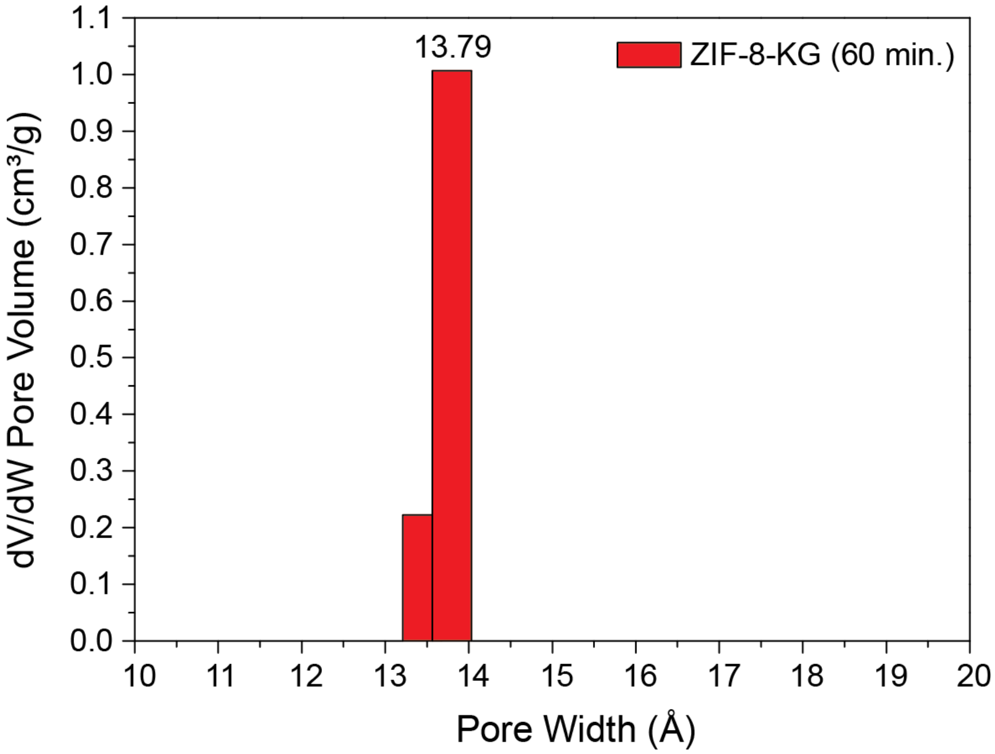


Figure S4. Pore size distributions of ZIF-8-KG (60 min.).

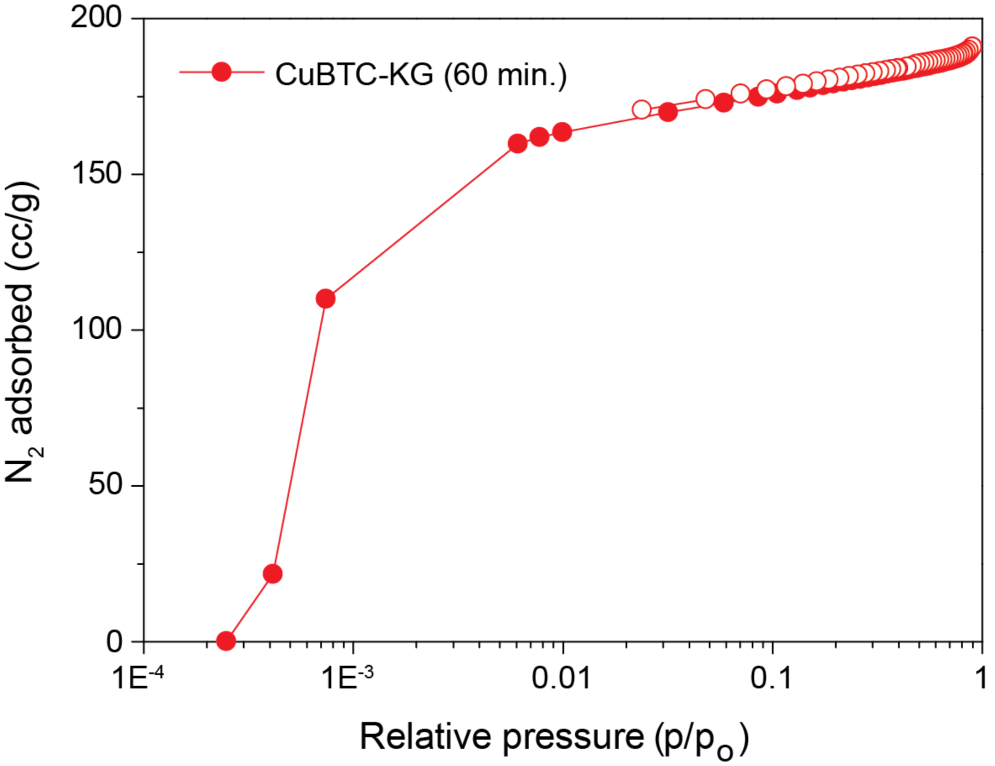


Figure S5. Log (10) plot of N_2 adsorption isotherms of CuBTC-KG (60 min.) collected at 77K.

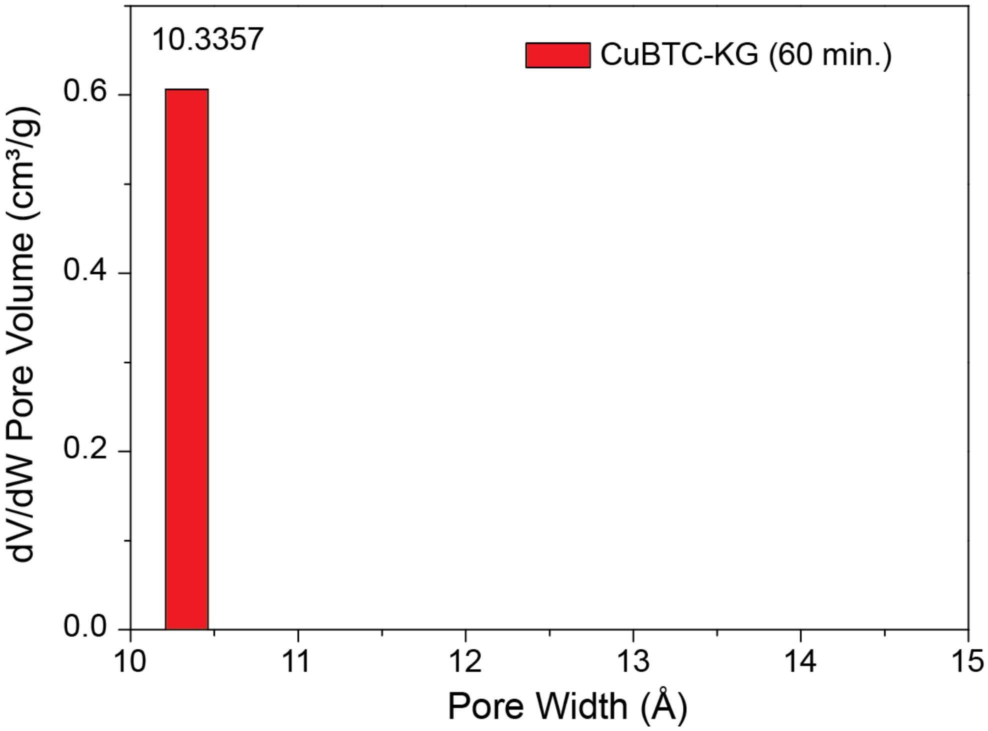


Figure S6. Pore size distributions of CuBTC-KG (60 min.).

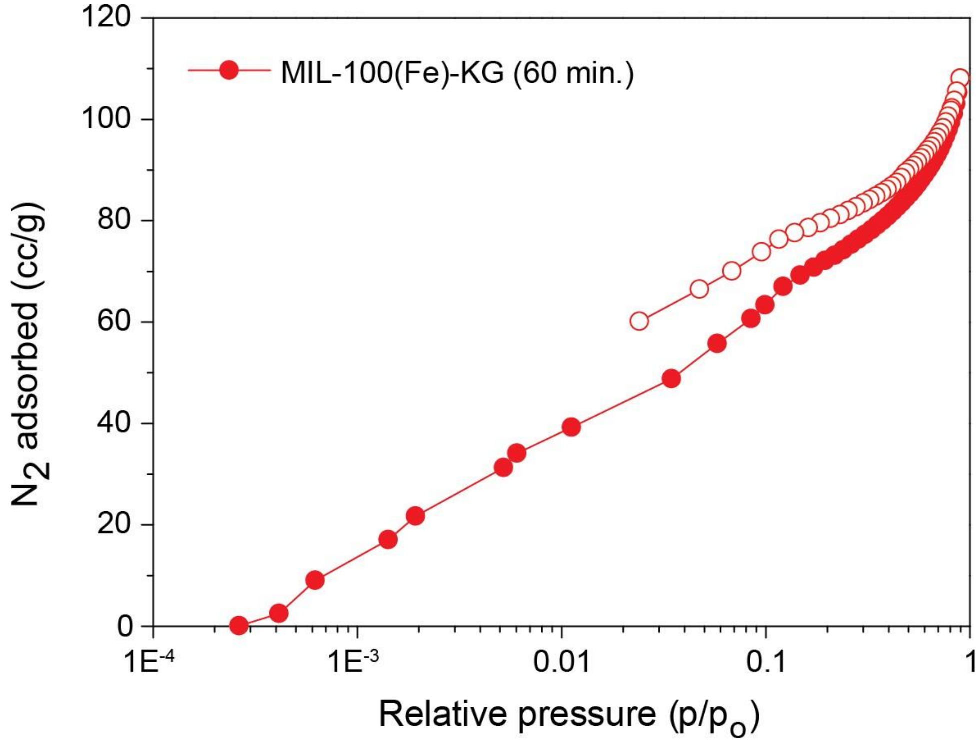


Figure S7. Log (10) plot of N_2 adsorption isotherms of MIL-100(Fe)-KG (60 min.) collected at 77K.

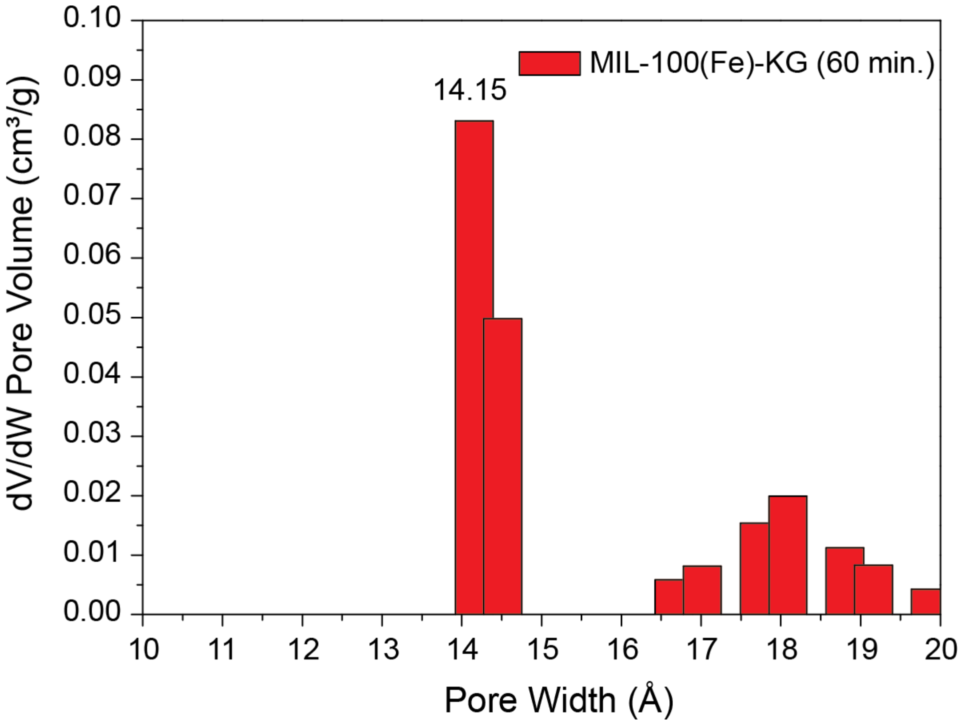


Figure S8. Pore size distributions of MIL-100(Fe)-KG (60 min.).

Section S4: Dye (methylene blue) adsorption study

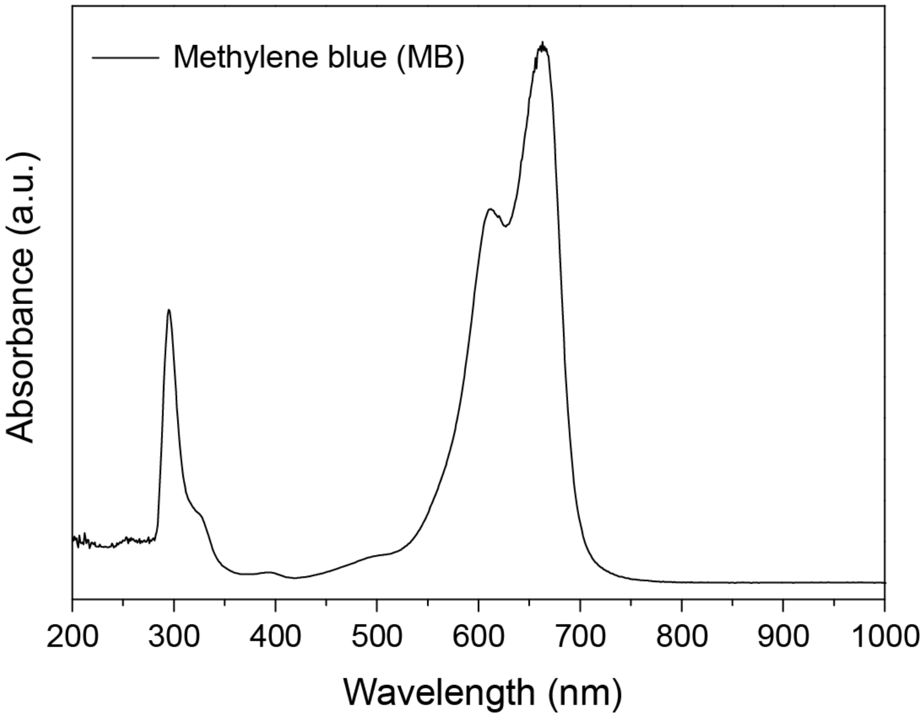


Figure S9. UV-Vis absorption spectra of aquoues solution of methylene blue (20 ppm).

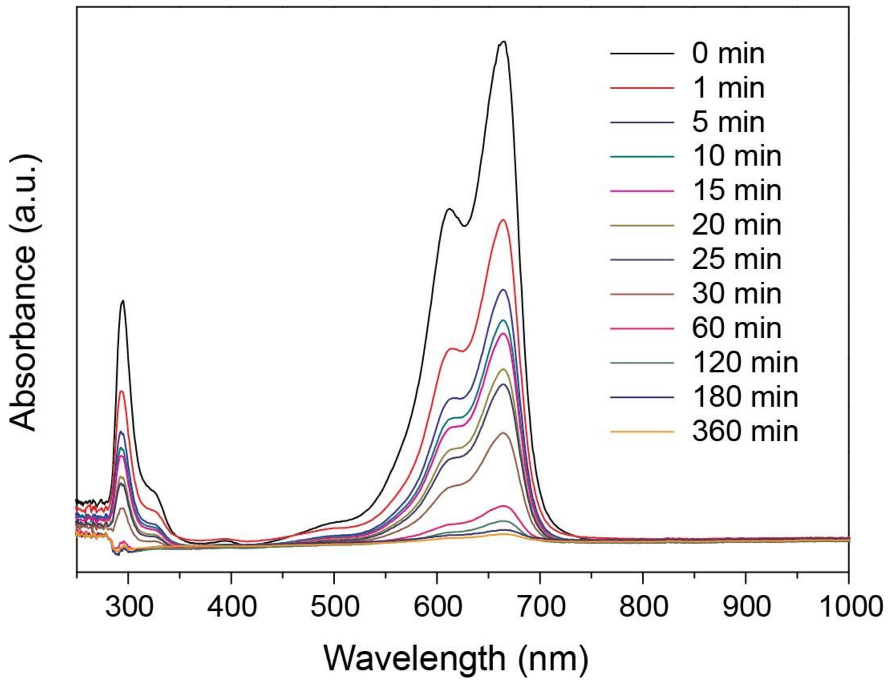


Figure S10. Comparison of UV-Vis absorption spectra of aqueous solutions of MB (20 ppm), after treatment with MIL-100(Fe)-KG at different time intervals.

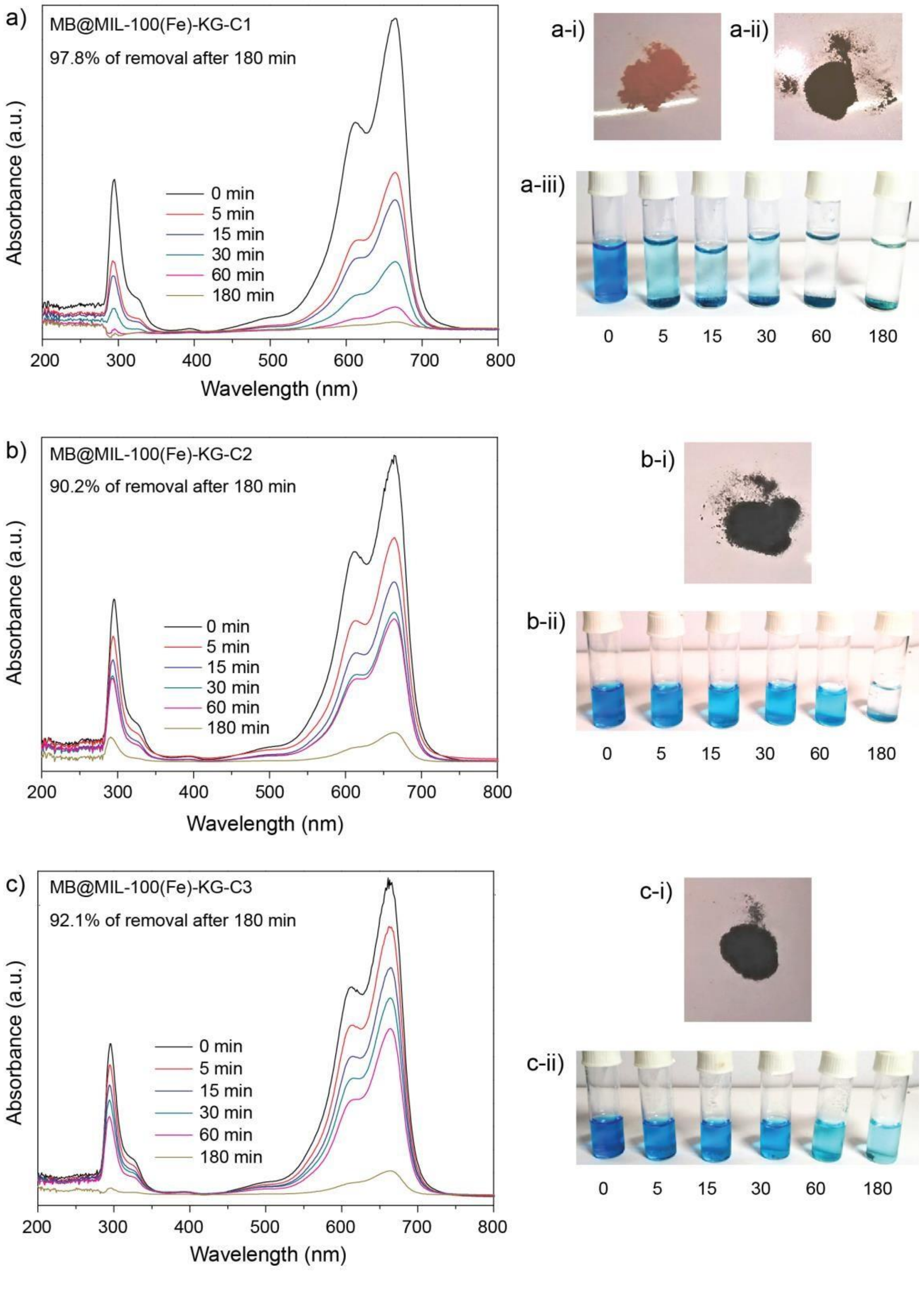


Figure S11. Recyclability test: comparison of UV-Vis absorption spectra of aqueous solutions of MB (20 ppm), after treatment with MIL-100(Fe)-KG at different time intervals, a) 1st cycle; b) 2nd cycle and c) 3rd cycle. a-i), a-ii), b-i) and c-i) real digital photograph of pristine MIL-100(Fe)-KG; MIL-100(Fe)-KG-C1, MIL-100(Fe)-KG-C2 and MIL-100(Fe)-KG-C3 sample recovered and after washing of 1st, 2nd and 3rd cycles respectively; a-iii), b-ii) and c-ii) real photographs of aqueous solution of MB after treatment with MIL-100(Fe)-KG, MIL-100(Fe)-KG-C1 and MIL-100(Fe)-KG-C2 samples at different intervals presented in minutes.

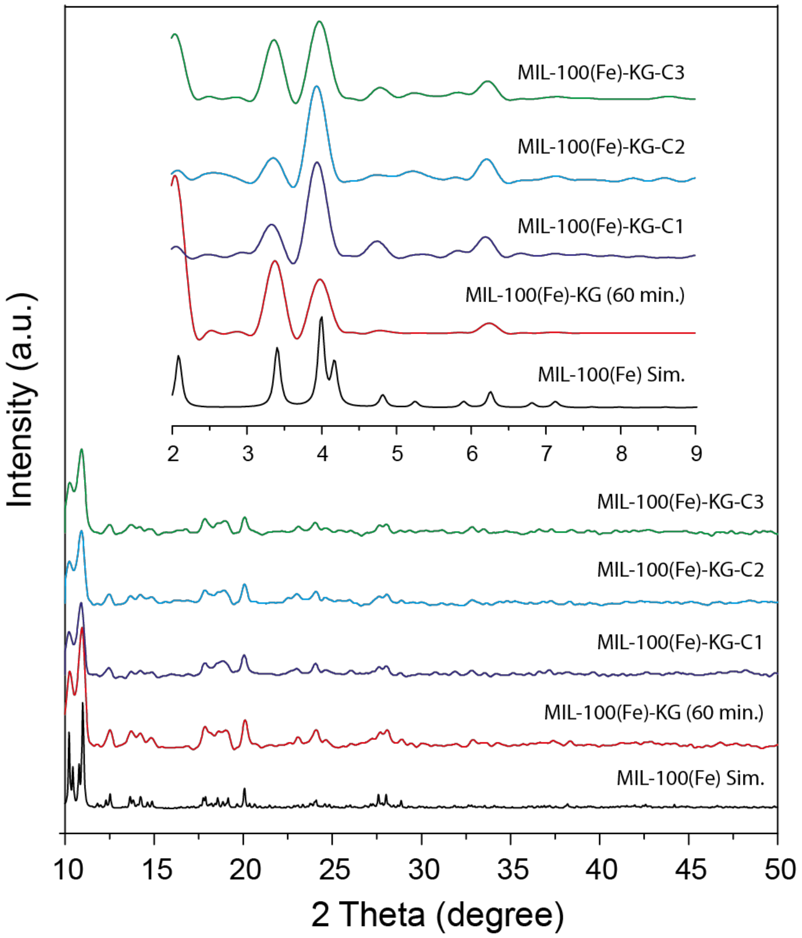


Figure S12. Comparision of PXRD (small-angle and wide-angle) patterns of MIL-100(Fe)-KG (simulated), MIL-100(Fe)-KG (60 min.) (as synthesized), MIL-100(Fe)-KG-C1 (after 1st cycle washed sample), MIL-100(Fe)-KG-C2 (after 2nd cycle washed sample) and MIL-100(Fe)-KG-C3 (after 3rd cycle washed sample) respectively.

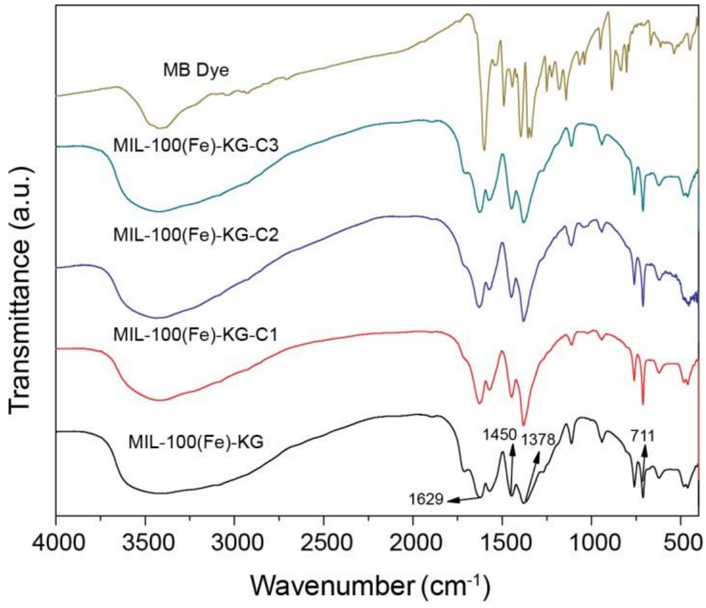


Figure S13. Comparision of FT-IR spectra of MIL-100(Fe)-KG (pristine), methylene blue (MB), MIL-100(Fe)-KG-C1 (after 1st cycle washed sample), MIL-100(Fe)-KG-C2 (after 2nd cycle washed sample) and MIL-100(Fe)-KG-C3 (after 3rd cycle washed sample) respectively.

Section S5: References

[S1] B. P. Biswal, D. B. Shinde, V. K. Pillai, R. Banerjee, *Nanoscale*, 2013, **5**, 10556.

[S2] J. Hu, H. Yu, W. Dai, X. Yan, X. Hu, H. Huang, *RSC Advances*, 2014, **4**, 35124.

[S3] B. Xu, X. Li, Z. Chen, T. Zhang, T. C. Li, *Microporous and Mesoporous Mater.*, 2018, **255**, 1.