

## SUPPORTING INFORMATION

### Enhanced Visible Light-Driven Photocatalytic Degradation of Methylene Blue and Ciprofloxacin by Magnetic NiFe<sub>2</sub>O<sub>4</sub>@ZIF 67

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#### Catalyst characterization

PXRD patterns of the fabricated materials were examined via an X-ray diffraction instrument (Bruker D8 advanced) equipped with Cu- $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) within the  $2\theta$  range of  $5^\circ$  to  $80^\circ$  to analyse the samples to determine the crystal phase of the materials. FTIR spectra were measured to detect the functional group present in the synthesized materials by Thermo Scientific Nicolet iS5 Fourier-transform infrared spectrometer in the range of wave number  $500$  to  $4000 \text{ cm}^{-1}$  at room temperature. The light absorption properties were measured by Jasco V 770 Ultraviolet-Visible Diffuse Reflectance (UV-Vis DRS) spectrophotometer. The Field Emission Scanning Electron Microscopy (FESEM) images were captured using Gemini SEM 450 instrument and Tungsten and LaB<sub>6</sub> as the source filament to analyse the morphology of the prepared samples. A Zeiss JEM-2010 F microscope was also used for transmission electron microscopy (TEM) investigation. The different vibration modes were analyzed using Renishaw Invia Raman microscope with a green  $532 \text{ nm}$  laser with a  $10 \text{ s}$  exposure time. The Photoluminescence (PL) spectra of the samples were measured by a fluorescence spectrophotometer (Perkin Elmer, LS55). The magnetic measurement of the nanocomposites was recorded using a VSM device (LBKFB model Meghnatis Daghig Kavir Company). A Quanta chrome instrument was used to analyse the produced samples' surface area and pore volume using N<sub>2</sub> adsorption-desorption isotherm data at  $77 \text{ K}$  bath temperature (version 5.21). Thermo Scientific's Escalab 250Xi equipment has an X-ray source of Al K $\alpha$  radiation capable of attaining ultrahigh vacuum ( $\sim 10^{-7} \text{ mbar}$ ) utilized to measure the XPS. TGA-DSC data were collected from room temperature ( $25^\circ\text{C}$ ) to  $800^\circ\text{C}$  with a heating rate of  $2^\circ\text{C}$  per minute while under compressed air flow by using STA6000 Perkin Elmer.

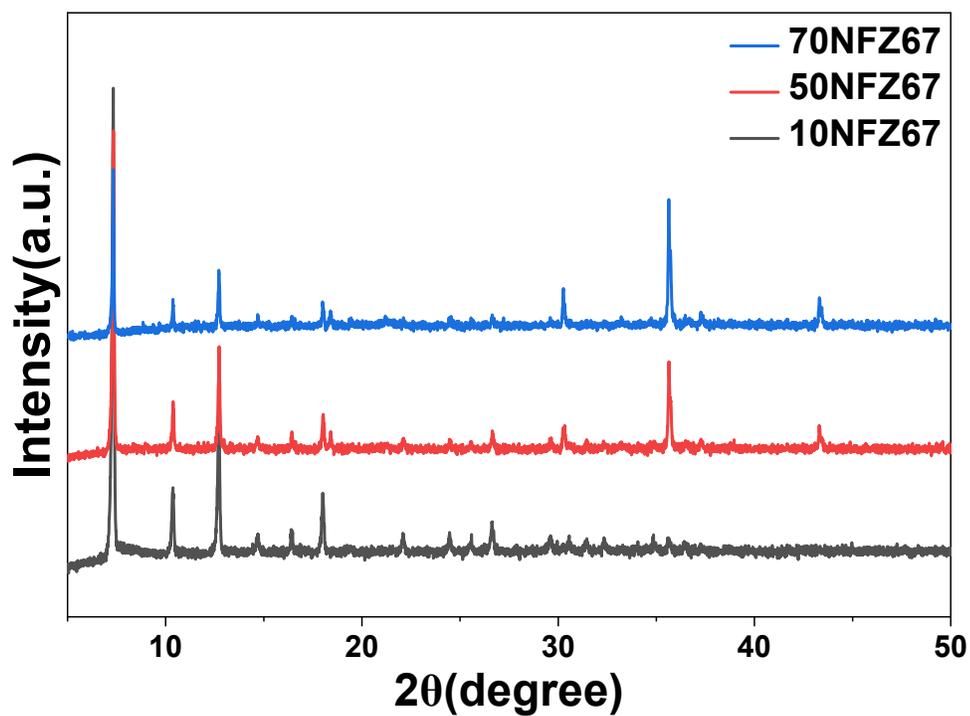


Figure S1: PXRD Pattern of 10NFZ67, 50NFZ67, 70NFZ67

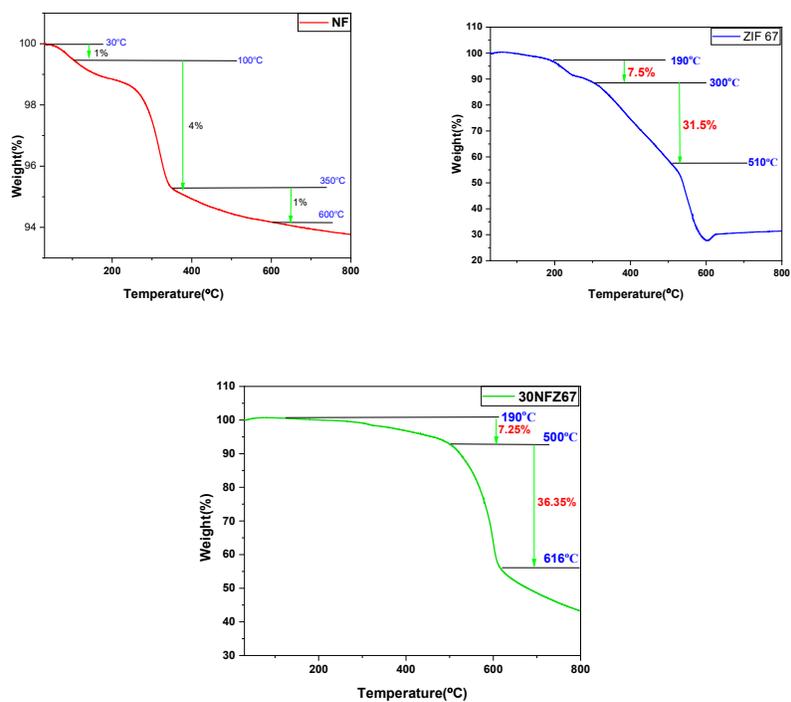


Figure S2: TGA of ZIF 67, NF, 30NFZ67

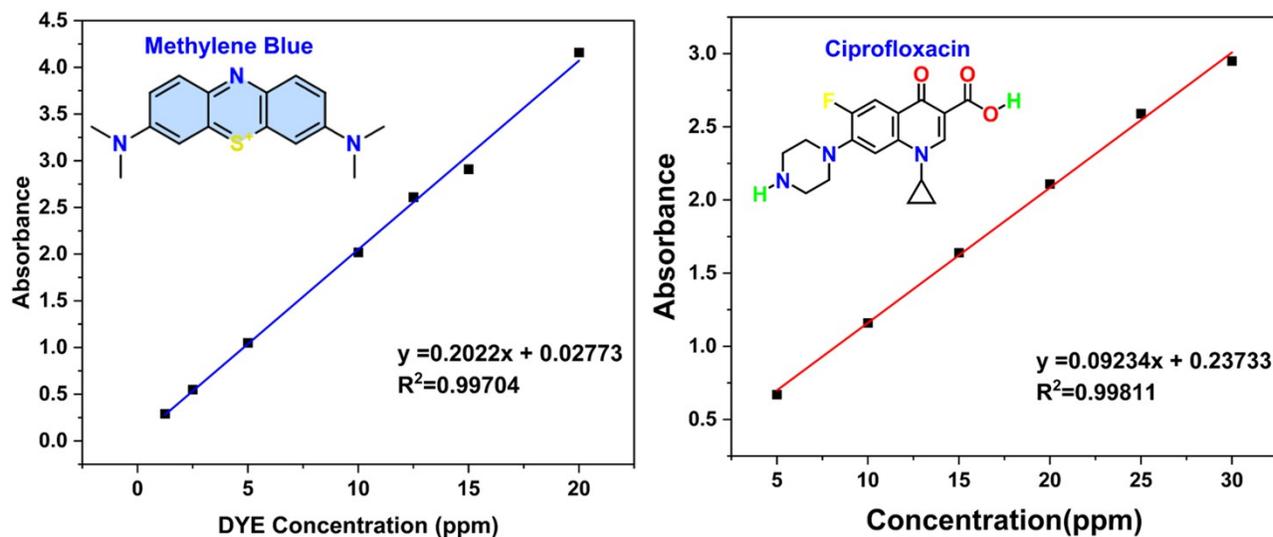


Figure S3: Calibration Curve for MB and CIP

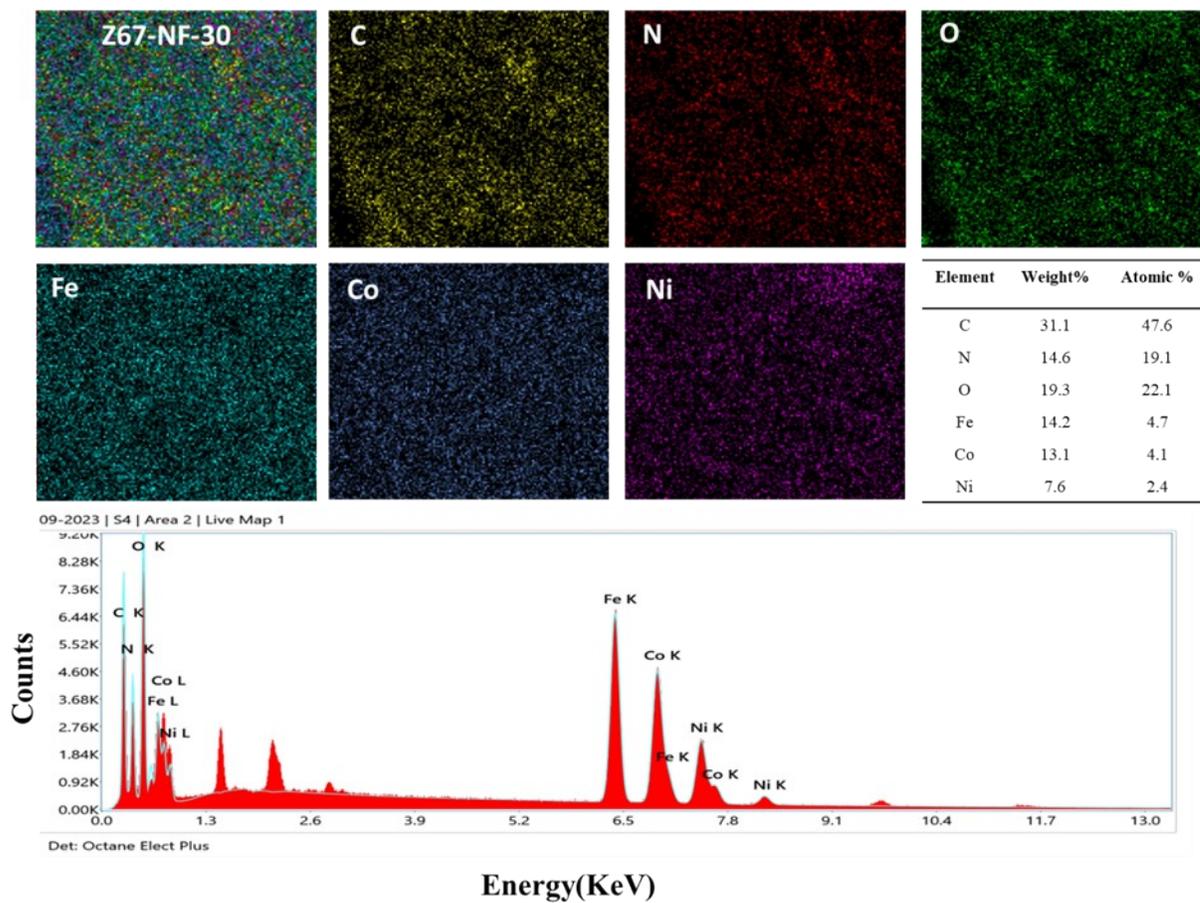
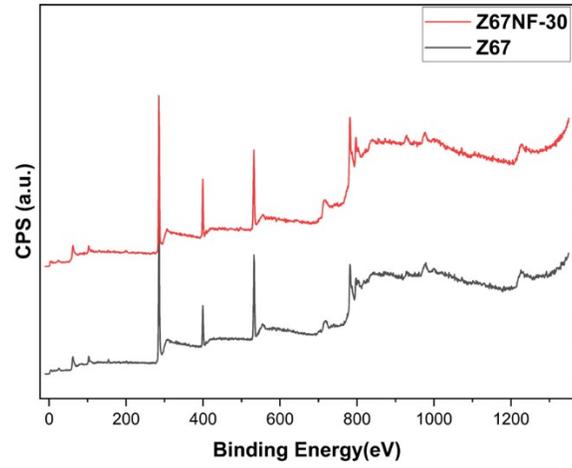
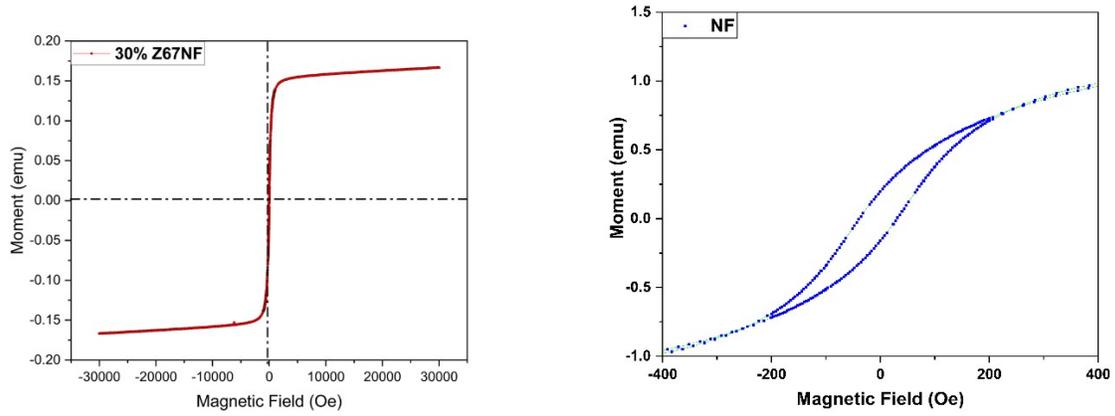


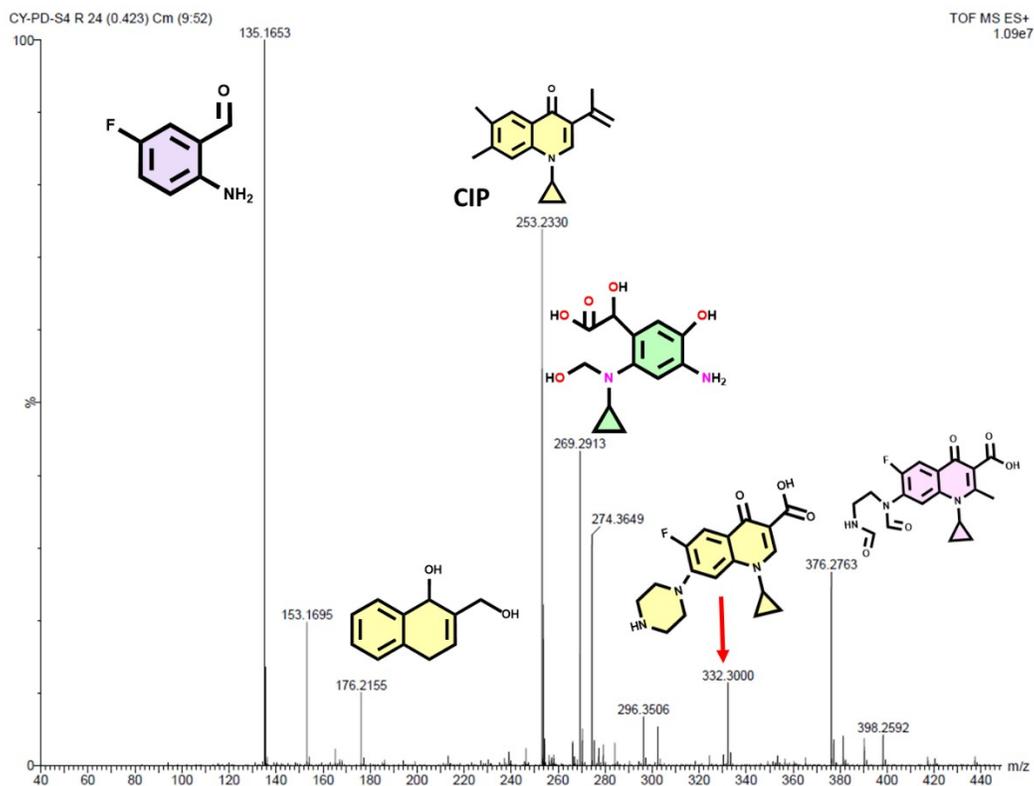
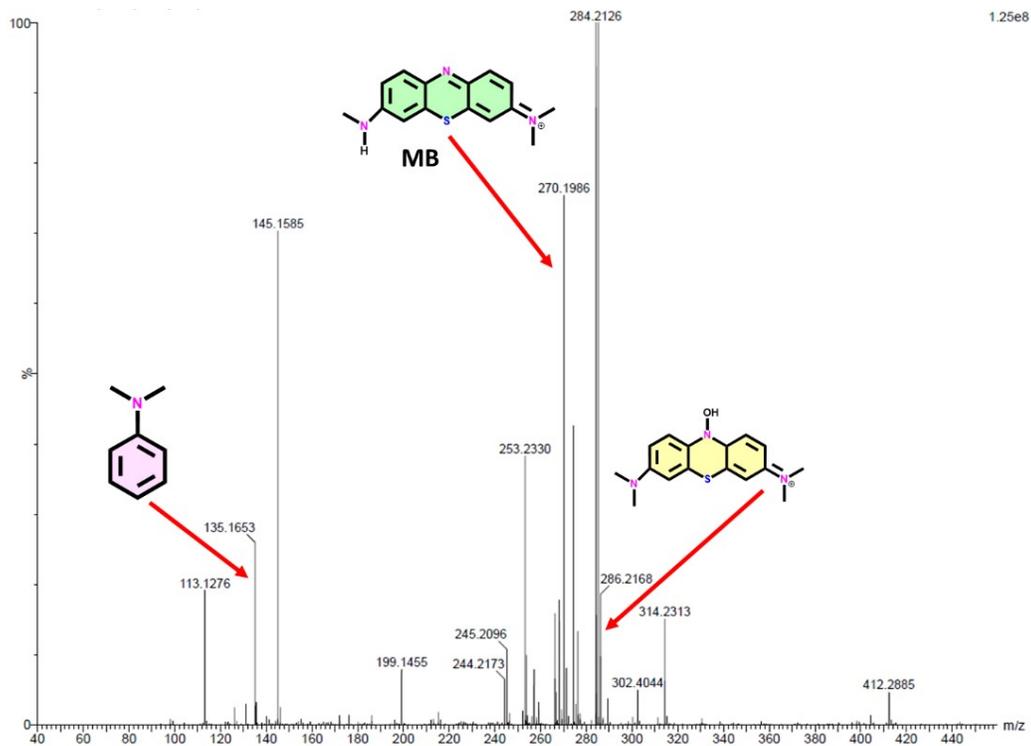
Figure S4: EDAX and elemental mapping of 30NFZ67



**Figure S5: XPS Survey of ZIF 67 and 30NFZ67**



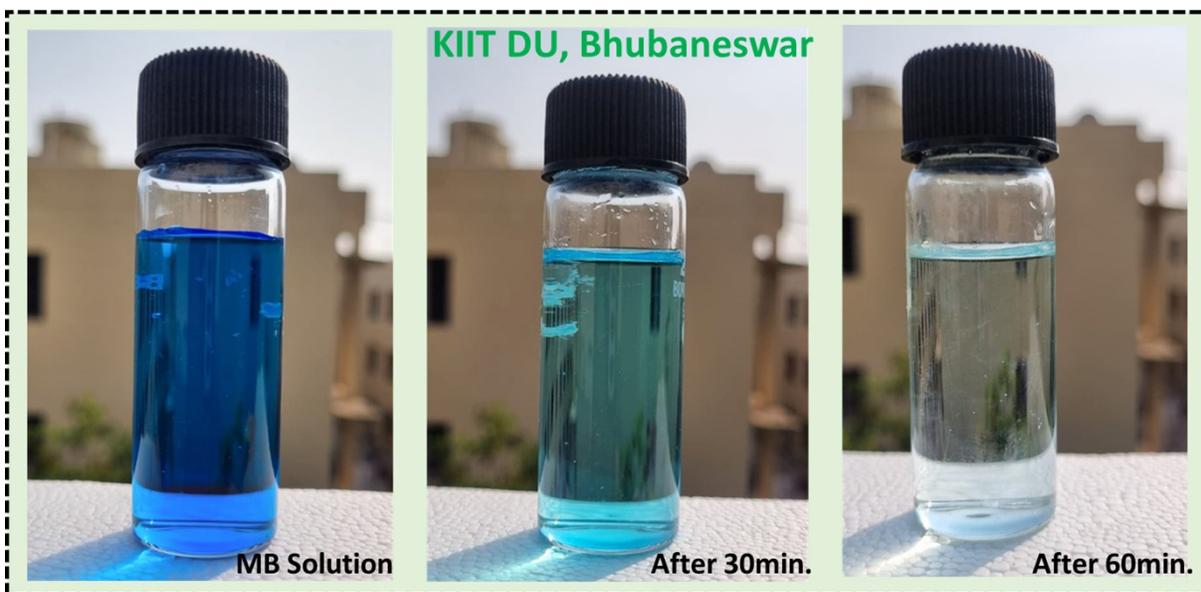
**Figure S6: VSM data of 30NFZ67(full scale) and NF**



**Figure S7: LC MS spectra and possible products of MB and CIP**

*Table S1: Detailed comparison of MOF/Ferrite hybrid synthesis method, solvent used.*

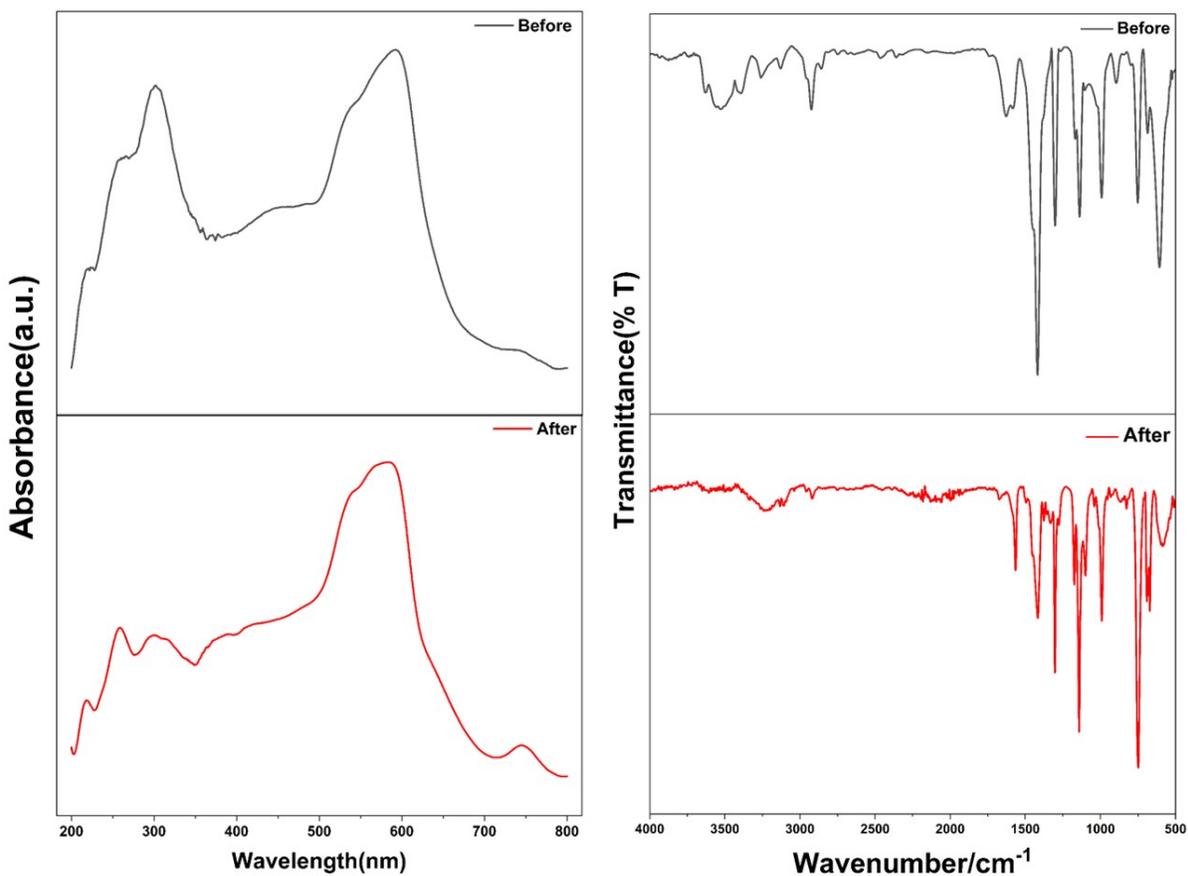
MOF/NiFe <sub>2</sub> O <sub>4</sub>	Synthesis method	Solvent	Condition	Ref.
Ni MOF/NiFe <sub>2</sub> O <sub>4</sub>	Solvothermal	DMF	170 °C for 12 h, NaOH	[1]
NiFe-MOF/NiFe <sub>2</sub> O <sub>4</sub>	Solvothermal	DMF	180 °C for 24 h	[2]
MgFe <sub>2</sub> O <sub>4</sub> @UiO-66(Zr)	Solvothermal	DMF	140°C for 24 h	[3]
{H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> }/MIL-88A(Fe)/MIL-88B(Fe)/NFO	Solvothermal	DMF	110 °C for 12 h.	[4]
ZIF 8/NiFe <sub>2</sub> O <sub>4</sub>	Room Temperature	Methanol	Stirred for 2hr.	[5]
NiFe <sub>2</sub> O <sub>4</sub> /ZIF 67 (30NFZ67)	Room temperature	Methanol	Stirred for 6hr.	<b>This work</b>



*Figure S8: Visual representation of MB dye solution over time*

**Table S2: A list of ferrite based MOF heterostructures for the degradation of organic pollutants and their stability**

Catalyst	Organic Pollutant(s)	Time	Degradation Efficiency	Energy Source / Activation	Recyclability	Ref.
ZIF-8/NiFe <sub>2</sub> O <sub>4</sub>	Methylene Blue	120 min	94%	Visible light (500 W halogen lamp)	4 cycles	[5]
ZIF-67/MnFe <sub>2</sub> O <sub>4</sub>	TCH (tetracycline hydrochloride)	15 min	82.6%	PMS-activated	4 cycles	[6]
ZrFe <sub>2</sub> O <sub>4</sub> @ZIF-8	Dopamine & sulfamethoxazole	120 min	100%	Visible light	10 cycles	[7]
VFe <sub>2</sub> O <sub>4</sub> @mono-ZIF-8	Ciprofloxacin, ampicillin, erythromycin	160 min	100%	Visible light (150 W Xe lamp)	10 cycles	[8]
ZIF-67/Bi <sub>25</sub> FeO <sub>40</sub>	Ofloxacin	60 min	95.5%	Visible light	5 cycles	[9]
CuFe <sub>2</sub> O <sub>4</sub> /ZIF-67	Methylene Blue	30 min	98.9%	PMS-activated	4 cycles	[10]
MIL-101(Cr)/CoFe <sub>2</sub> O <sub>4</sub>	RhB & Methyl Orange	140 min	96% (RhB); 88% (MO)	Ultrasound irradiation	4 cycles	[11]
MIL-101 (Fe)/CoFe <sub>2</sub> O <sub>4</sub>	Tetracycline	40 min	83%	Visible light PMS-Activated	5 cycles	[12]
30NFZ67 (NiFe <sub>2</sub> O <sub>4</sub> @ZIF-67)	Methylene Blue & Ciprofloxacin	60 min	~98% (MB), ~88% (CIP)	Sunlight	20 cycles	<b>This work</b>



*Figure S9: UV-DRS & FTIR graph of 30NFZ67 catalyst before and after the recyclability study (after 20<sup>th</sup> Cycle)*



*Figure S10: 30NFZ67 catalyst before and after the recyclability study*

## References:

1. Guo, X.Y., Yang, Z.Q., Zhao, J. and Liu, R., 2024. One-pot modulated construction of Ni-MOF/NiFe<sub>2</sub>O<sub>4</sub> heterostructured catalyst for efficient oxygen evolution. *Rare Metals*, 43(12), pp.6751-6757.
2. Lan, T., Du, H., Li, Y., Qu, K., Zhao, J., Zhang, X., Dong, Y., Zhang, Y., Zhang, X. and Zhang, D., 2023. One-pot synthesis of NiFe-MOF/NiFe<sub>2</sub>O<sub>4</sub> hollow spheres and their application as bifunctional ORR/OER electrocatalysts in Zn-air batteries. *Journal of Alloys and Compounds*, 943, p.169144.
3. Vo, T.K. and Kim, J., 2021. Facile synthesis of magnetic framework composite MgFe<sub>2</sub>O<sub>4</sub>@UiO-66 (Zr) and its applications in the adsorption–photocatalytic degradation of tetracycline. *Environmental Science and Pollution Research*, 28(48), pp.68261-68275.
4. Fatahi, F., Farhadi, S., Zabardasti, A. and Mahmoudi, F., 2024. H3PW12O<sub>40</sub>/MIL-88A (Fe)/MIL-88B (Fe)/NiFe<sub>2</sub>O<sub>4</sub> nanocomposite: A new magnetic sorbent based on MOF/MOF hybrid coupled with PW12O<sub>40</sub><sup>3-</sup> polyanions for efficient removal of hazardous antibiotics and dyes from water. *Inorganic Chemistry Communications*, 162, p.112231.
5. Faraji, A., Mehrdadi, N., Mahmoodi, N.M., Baghdadi, M. and Pardakhti, A., 2021. Enhanced photocatalytic activity by synergic action of ZIF-8 and NiFe<sub>2</sub>O<sub>4</sub> under visible light irradiation. *Journal of Molecular Structure*, 1223, p.129028.
6. Lu, S., You, S., Hu, J., Li, X. and Li, L., 2024. Magnetic MnFe<sub>2</sub>O<sub>4</sub>/ZIF-67 nanocomposites with high activation of peroxymonosulfate for the degradation of tetracycline hydrochloride in wastewater. *RSC advances*, 14(11), pp.7528-7539.
7. Adewuyi, A., Ogunkunle, O.A. and Oderinde, R.A., 2023. Zirconium ferrite incorporated zeolitic imidazolate framework-8: a suitable photocatalyst for degradation of dopamine and sulfamethoxazole in aqueous solution. *RSC advances*, 13(14), pp.9563-9575.
8. Adewuyi, A., Akinbola, W.B., Otuechere, C.A., Adesina, A., Ogunkunle, O.A., Olalekan, O.A., Ajibade, S.O. and Adeyemi, O.G., 2025. Zeolitic imidazolate framework improved vanadium ferrite: toxicological profile and its utility in the photodegradation of some selected antibiotics in aqueous solution. *RSC Sustainability*, 3(1), pp.427-439.
9. Mahmoud, S.M., Ammar, S.H., Ali, N.D., Ali, F.D. and Jabbar, Z.H., 2024. Visible-light-prompted photocatalytic degradation of emerging contaminants over facile constructed ZIF-67/Bi<sub>25</sub>FeO<sub>40</sub> hybrids. *Journal of Water Process Engineering*, 59, p.104990.
10. Wu, X., Sun, D., Ma, H., Ma, C., Zhang, X. and Hao, J., 2022. Activation of peroxymonosulfate by magnetic CuFe<sub>2</sub>O<sub>4</sub>@ ZIF-67 composite catalyst for the study on the degradation of methylene blue. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 637, p.128278.

11. Andani, A.M., Tabatabaie, T., Farhadi, S. and Ramavandi, B., 2020. MIL-101 (Cr)–cobalt ferrite magnetic nanocomposite: synthesis, characterization and applications for the sonocatalytic degradation of organic dye pollutants. *RSC advances*, 10(54), pp.32845-32855.
12. Rui, G., Hu, Z., Wu, H. and Ma, J., 2025. Degradation of tetracycline by MIL-101 (Fe)/CoFe<sub>2</sub>O<sub>4</sub> activated persulfate under visible light. *Journal of Porous Materials*, pp.1-17.