Engineering Surface Hydrophobicity/Hydrophilicity of Magnetic Nanosorbents for Efficient Multipollutant Water Remediation

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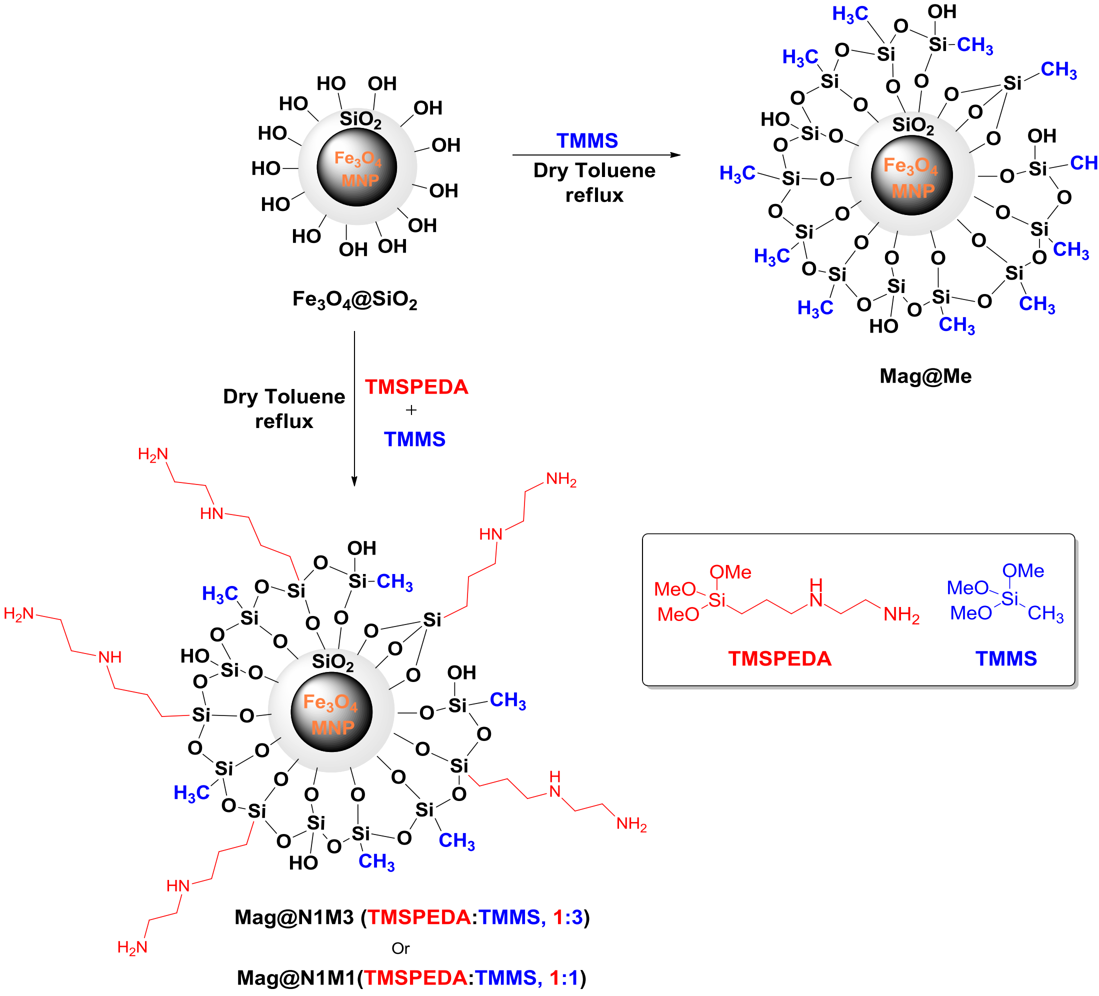
Experimental Procedure

Materials and methods

Ferrous chloride tetrahydrate, ferric chloride hexahydrate, ammonia, tetraethyl orthosilicate (TEOS), trimethoxymethylsilane (TMMS), *N*-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMSPEDA), ethanol, *n*-hexane, methanol, acetonitrile, ethyl acetate, and acetone, with synthesis and analytical grades were provided from Sigma-Aldrich and Merck Co.. Fourier transform infrared (FT-IR) spectra were acquired using a FT-IR spectrometer (Perkin-Elmer Spectrum RXI) at room temperature, with KBr discs. Transmission electron microscopy (TEM) images were captured by Philips EM 208S equipment. The X-ray diffraction (XRD) patterns were analyzed using a Philips PW1730 X-Ray Diffractometer equipped with Cu-Kα radiation. An Energy dispersive X-ray (EDX) analysis was carried out utilizing a TESCAN MIRA III analyzer, which is an environmental scanning electron microscope. The vibrating sample magnetometer (VSM) was utilized to calculate the magnetization curve of the magnetic samples by applying a 15 kOe magnetic field at room temperature. The thermal stability of the magnetic sorbents was examined by SDT Q600 V20.9 Build 20 Thermo-gravimetric Analyzer (TGA) in the temperature range of 0 to 800 °C. The MIRA III - TESCAN device was used to conduct Field Emission Scanning Electron Microscopy (FESEM). Elemental analyses for C, N, and H were performed using a Perkin-Elmer 2400 II analyzer. The N_2-sorptions were carried out in a Belsorp-mini-BEL Japan, Inc. at 298 K. An Avaspec-2048-TEC UV-Vis spectrophotometer was used to evaluate the chromium (VI) removal efficiency.

Preparation of the magnetic sorbents and their characterizations

The preparation of Fe_3O_4 MNPs was accomplished via methods reported in the literature [33]. In this experiment, 4.0 g (20.1 mmol) of Iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) and 11.0 g (40.7 mmol) of Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were dissolved in 250 mL of distilled water. The dissolution process took place under a nitrogen environment with a mechanical stirrer at a temperature of 85 °C. The solution's pH was modified to reach 9-11 using a 25% aqueous solution of NH_3. After undergoing continuous agitation for duration of 4 h, magnetite nanoparticles (Fe_3O_4) were generated as a result of precipitation. The black deposited solid was rinsed multiple times with distilled water and then gathered using an external magnet. The silica-coated magnetic nanoparticles were synthesized by ultrasonically pre-mixing a dispersion of 2.0 g of Fe_3O_4 black precipitate in 400 mL of ethanol for about 30 min at 25 °C. Afterward, 12 mL of aqueous solution of NH_3 (25%) and TEOS (4.0 mL) were sequentially and gradually introduced at the same temperature. The solution obtained was agitated mechanically for a continuous period of 24 h at a temperature of 25 °C. Following this, the Fe_3O_4@SiO_2 products were gathered using an ordinary magnet, rinsed multiple times with ethanol, and left to dry using vacuum at room temperature for the entire night. Ultimately, the process of modifying the surface of Fe_3O_4@SiO_2 core-shell MNPs with methyl group required a synthetic technique that utilized the grafting of trimethoxy(methyl)silane (TMMS) onto the Fe_3O_4@SiO_2 core-shell MNPs. To achieve this objective, 0.4 g of TMMS (2.94 mmol) was introduced into 35 mL of anhydrous toluene that already contained Fe_3O_4@SiO_2 core-shell MNPs (1.0 g). The mixture was then agitated for 24 h under reflux conditions. The magnetic sample obtained was rinsed multiple times with toluene and ethanol. The appropriate magnetic Fe_3O_4-SiO_2@Me sorbent was obtained by drying it overnight at ambient temperature under vacuum (denoted as Mag@Me). The same procedure was employed for the synthesis of Fe_3O_4@SiO_2@N1M3 (denoted as Mag@N1M3) in which Fe_3O_4@SiO_2 functionalized with both TMMS and *N*-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMSPEDA) with molar ratio of 3:1. Also the procedure was applied for the synthesis of $Fe_3O_4@SiO_2@N1M1$ (denoted as Mag@N1M1) in which $Fe_3O_4@SiO_2$ was anchored with equal molar ratio (1:1) of both TMMS and TMSPEDA.



Scheme S1. Synthetic route for Mag@Me, Mag@N1M3 and Mag@N1M1

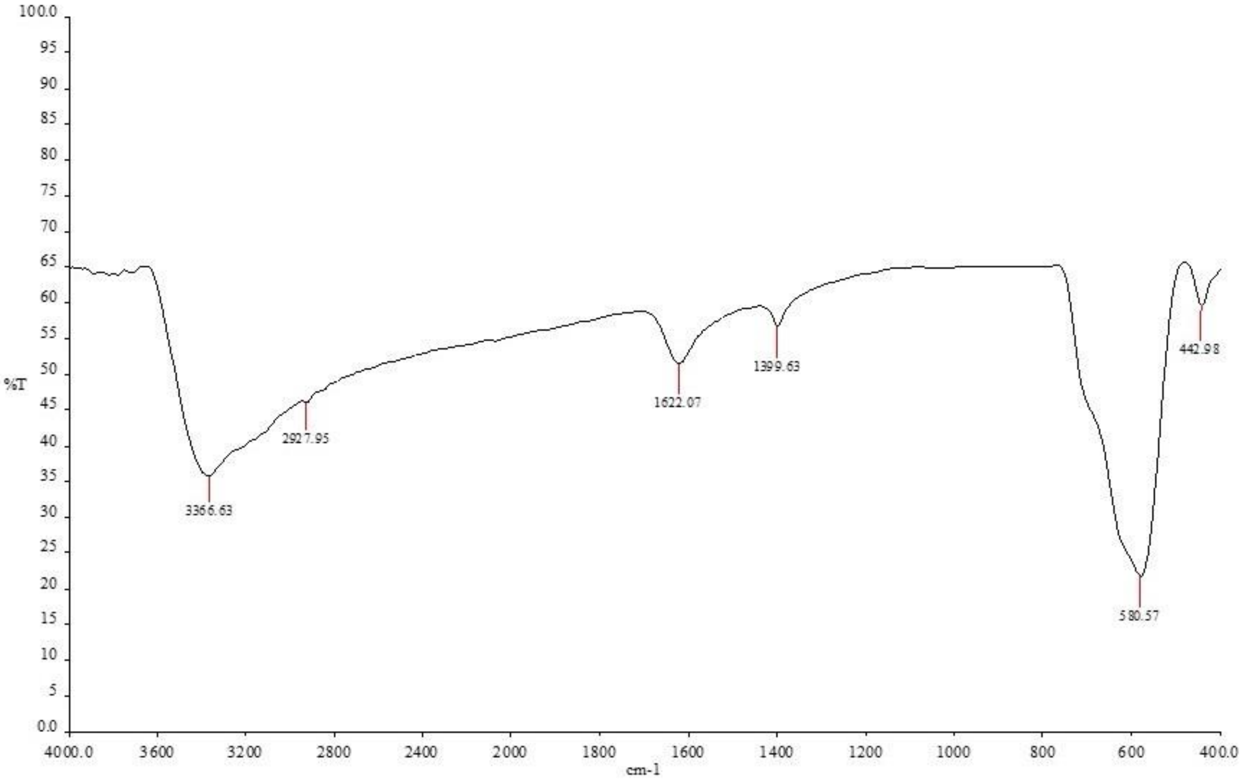


Figure S1. FT-IR spectrum of Fe_3O_4 MNPs

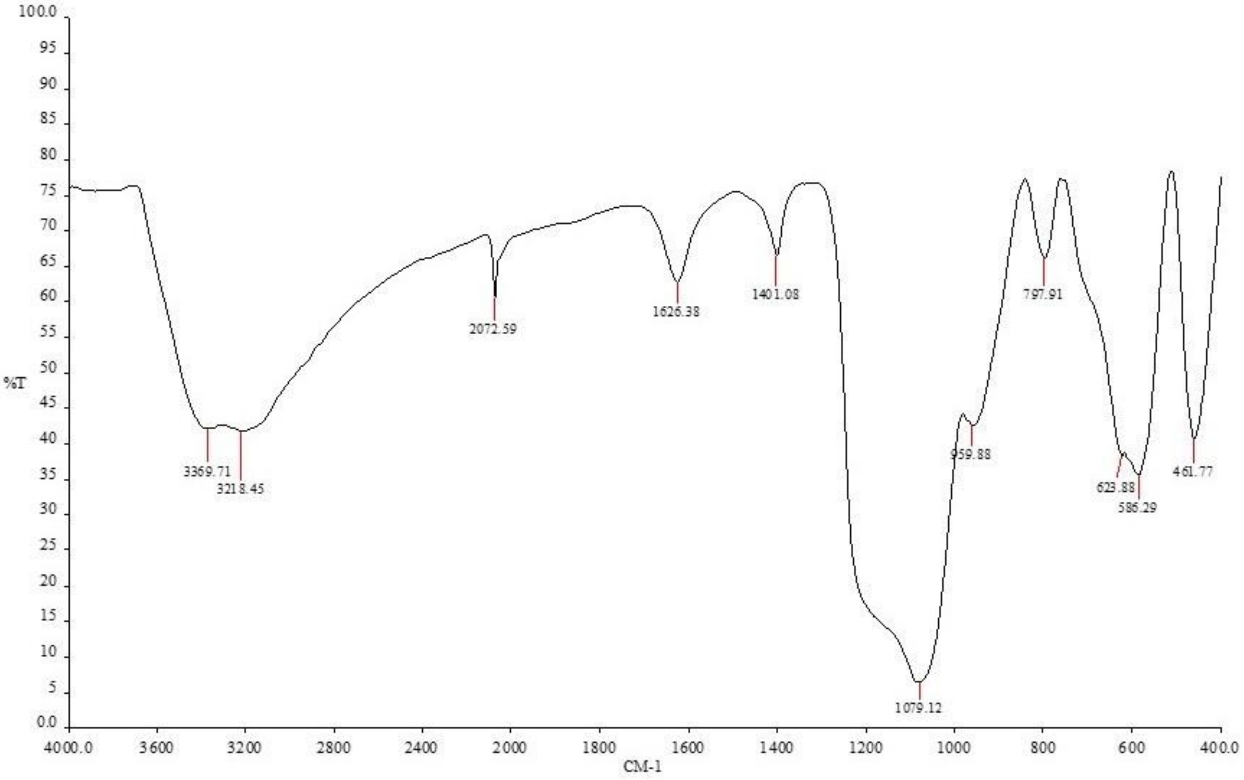


Figure S2. FT-IR spectrum of core-shell $Fe_3O_4@SiO_2$ MNPs

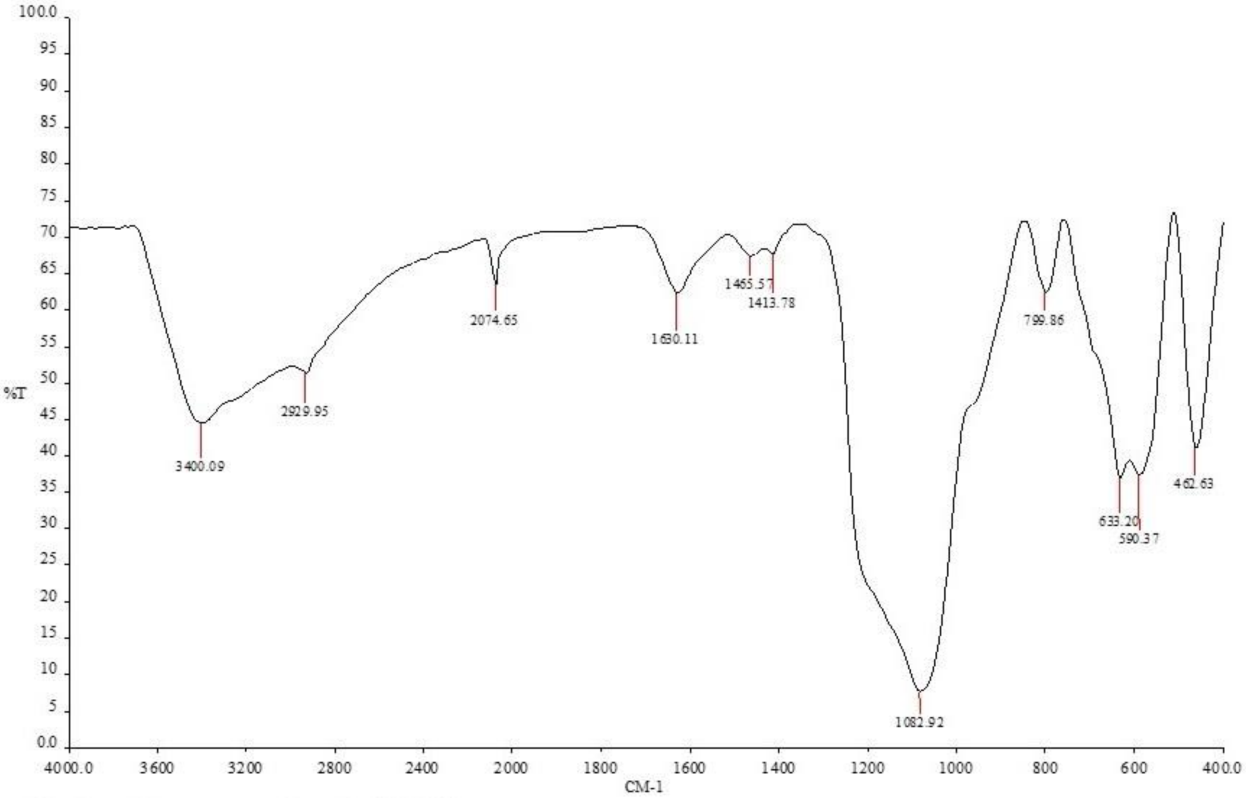


Figure S3. FT-IR spectrum of Mag@Me sorbent

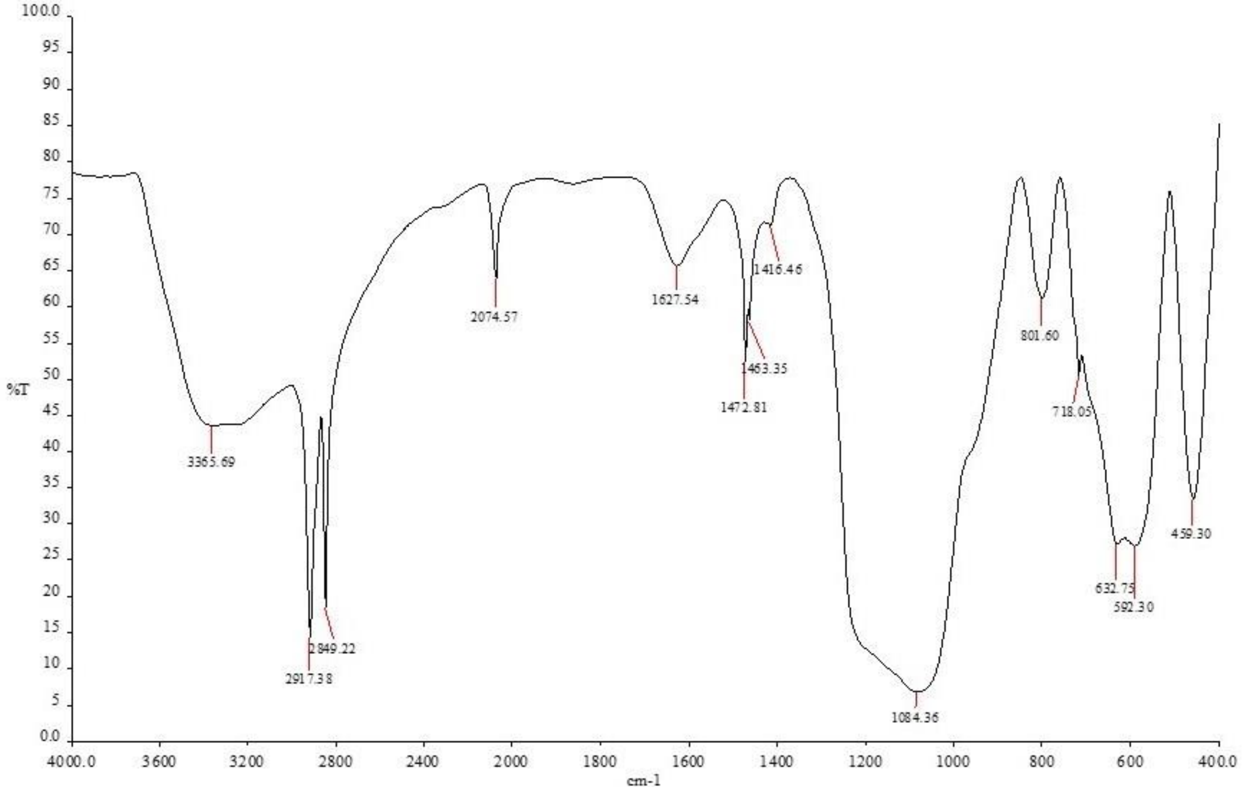


Figure S4. FT-IR spectrum of Mag@N1M1 sorbent

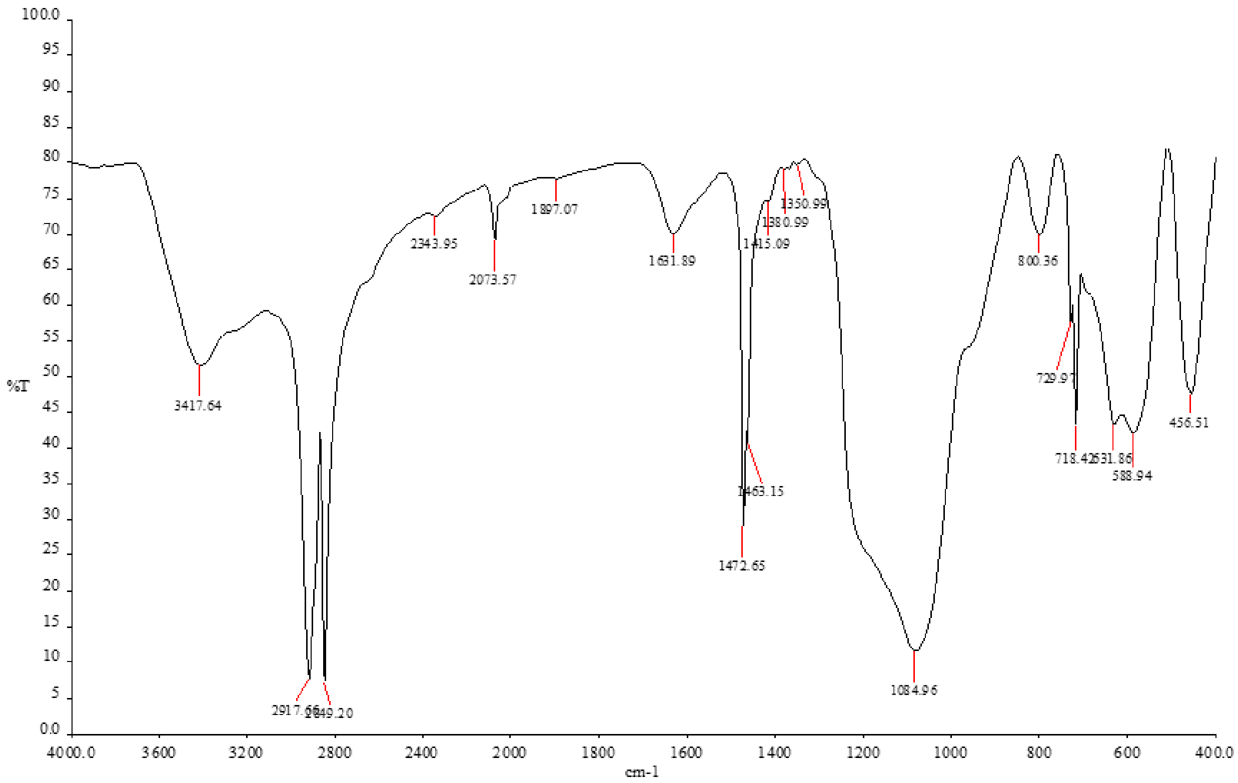


Figure S5. FT-IR spectrum of Mag@N1M3 sorbent

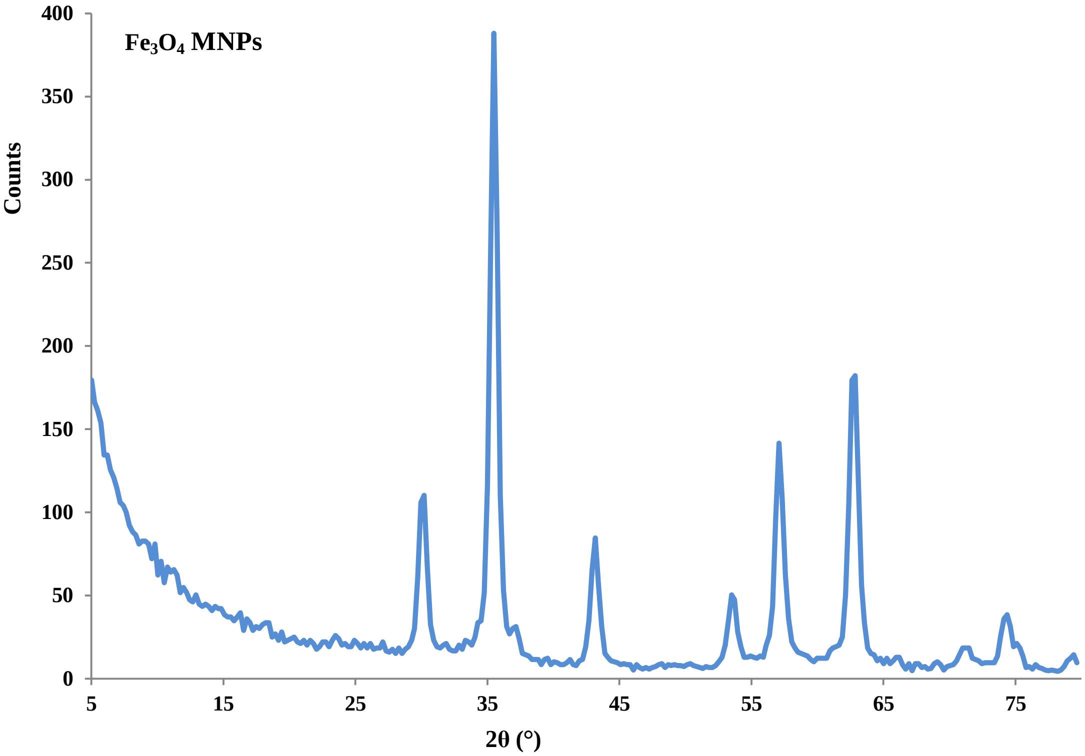


Figure S6. XRD pattern of Fe_3O_4 MNPs

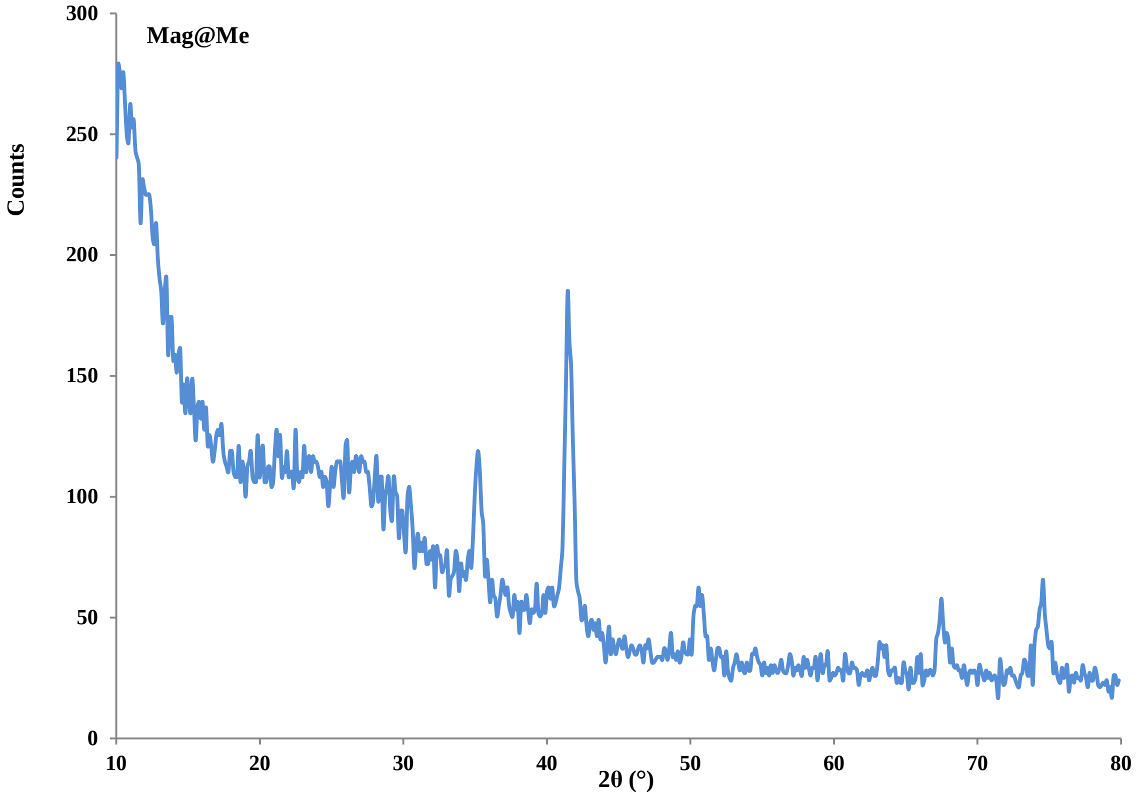


Figure S7. XRD pattern of Mag@Me sorbent

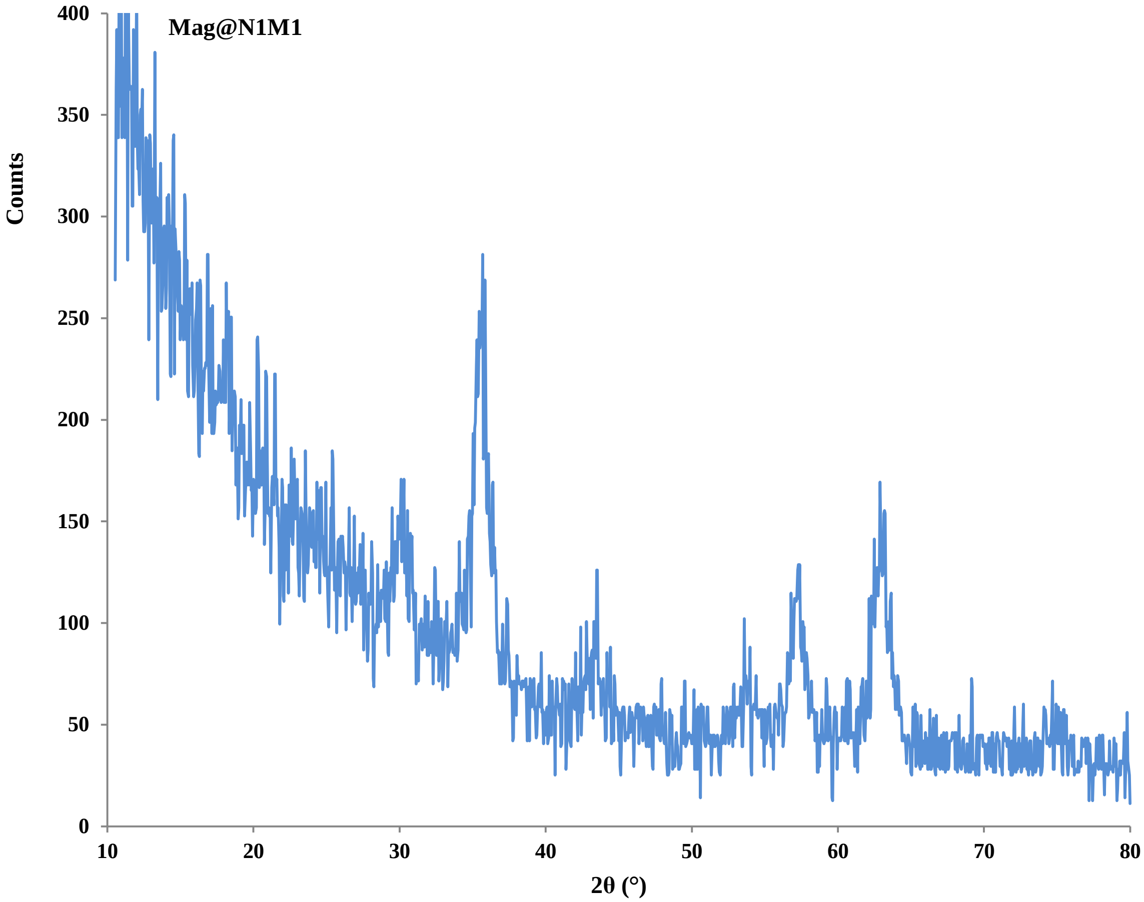


Figure S8. XRD pattern of Mag@N1M1 sorbent

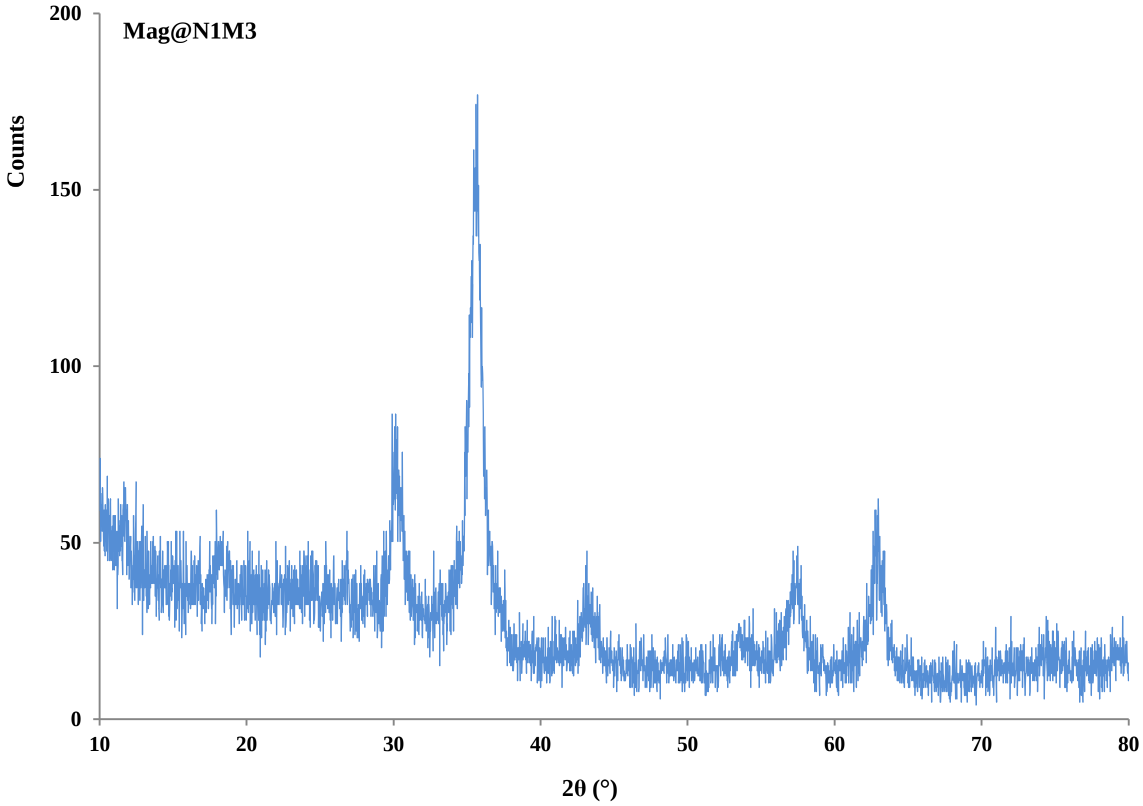


Figure S9. XRD pattern of Mag@N1M3 sorbent

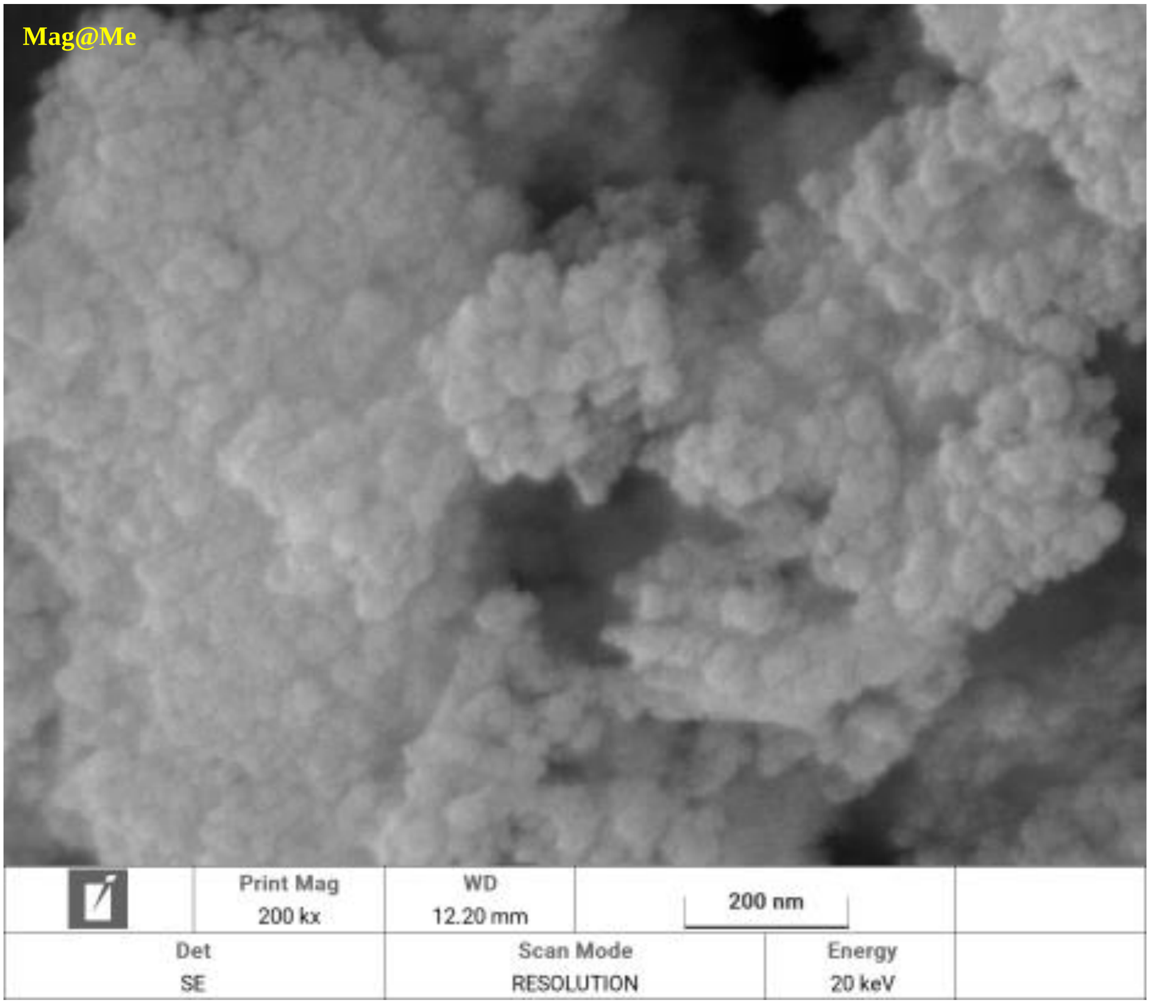


Figure S10. FESEM image of Mag@Me sorbent

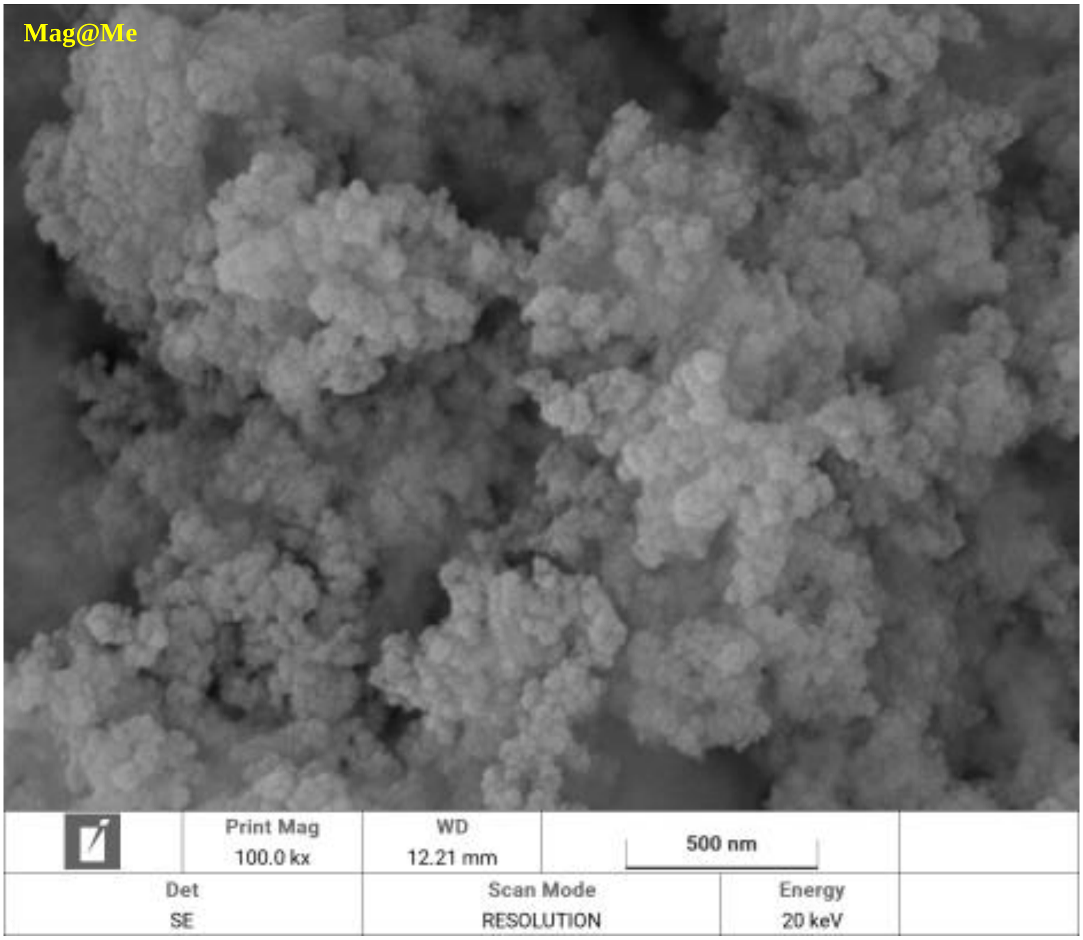


Figure S11. FESEM image of Mag@Me sorbent

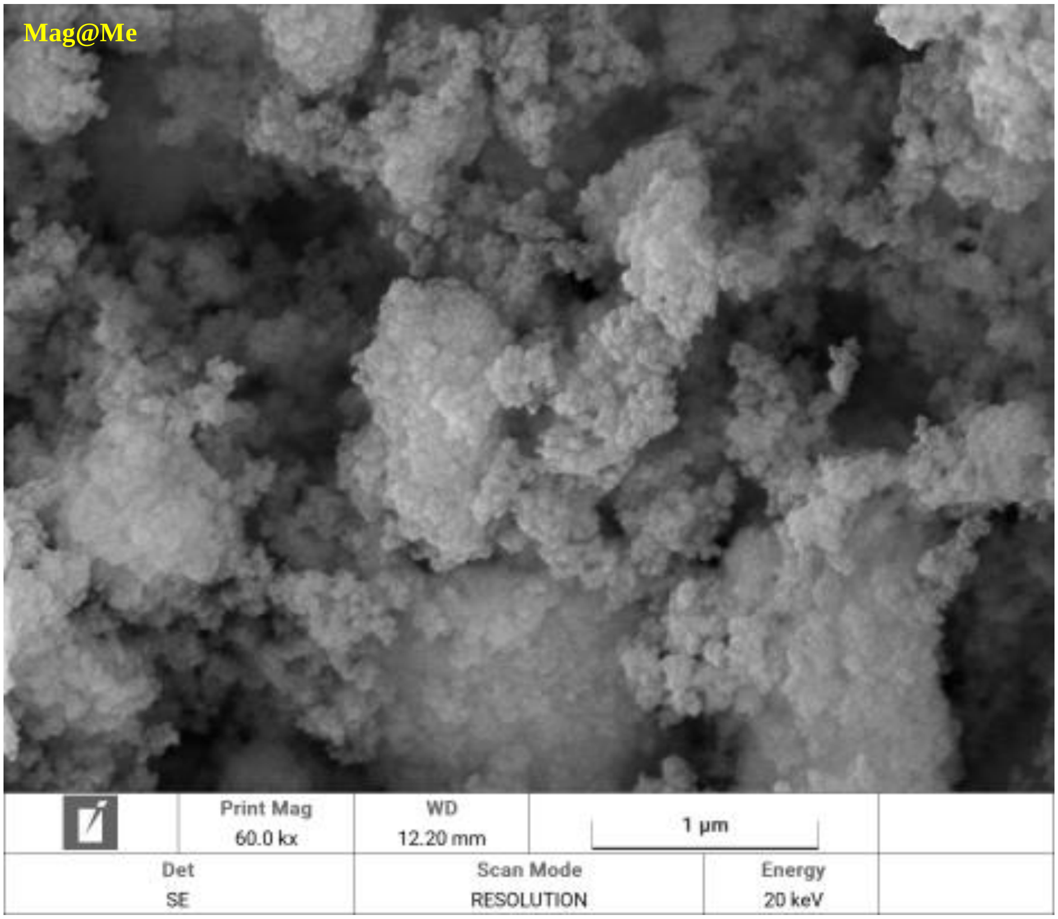


Figure S12. FESEM image of Mag@Me sorbent

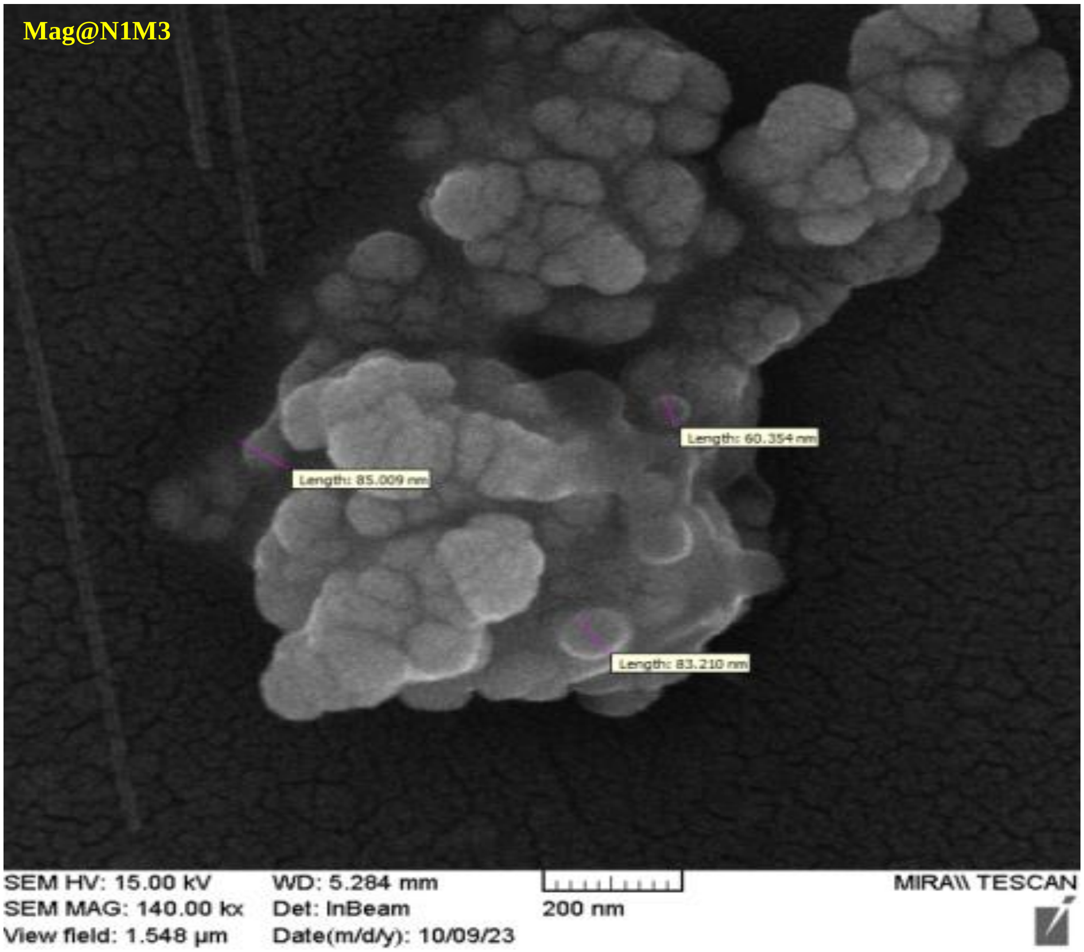


Figure S13. FESEM image of Mag@N1M3 sorbent

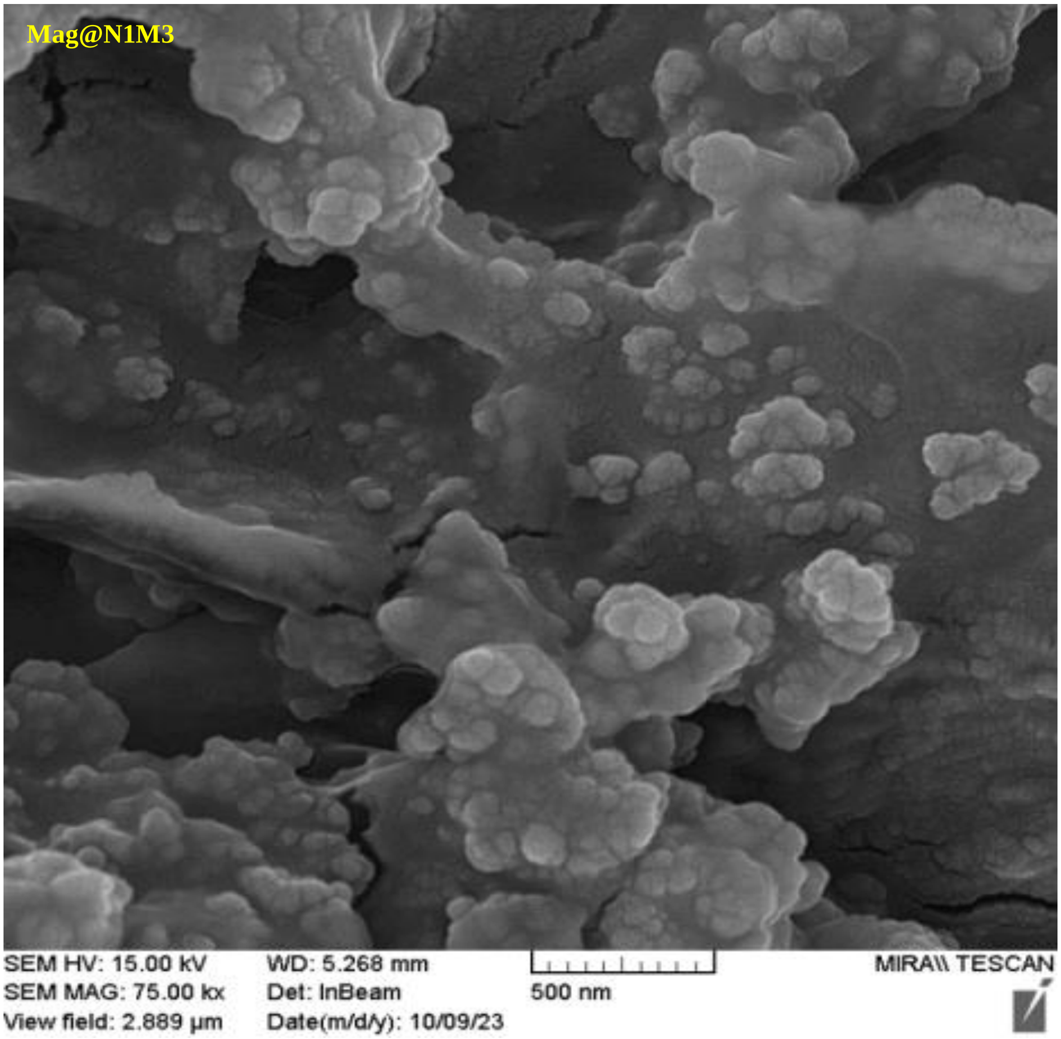


Figure S14. FESEM image of Mag@N1M3 sorbent

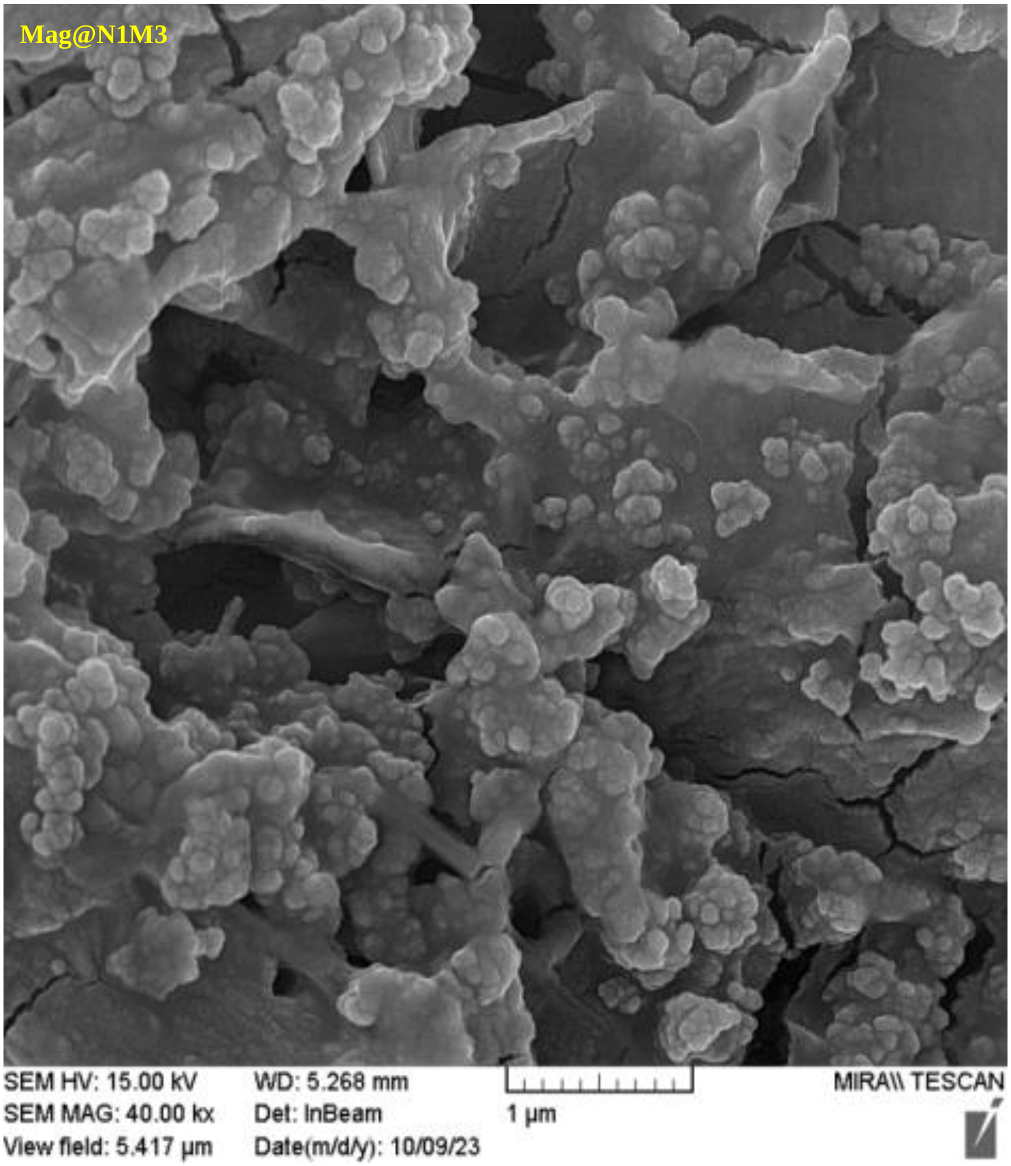


Figure S15. FESEM image of Mag@N1M3 sorbent

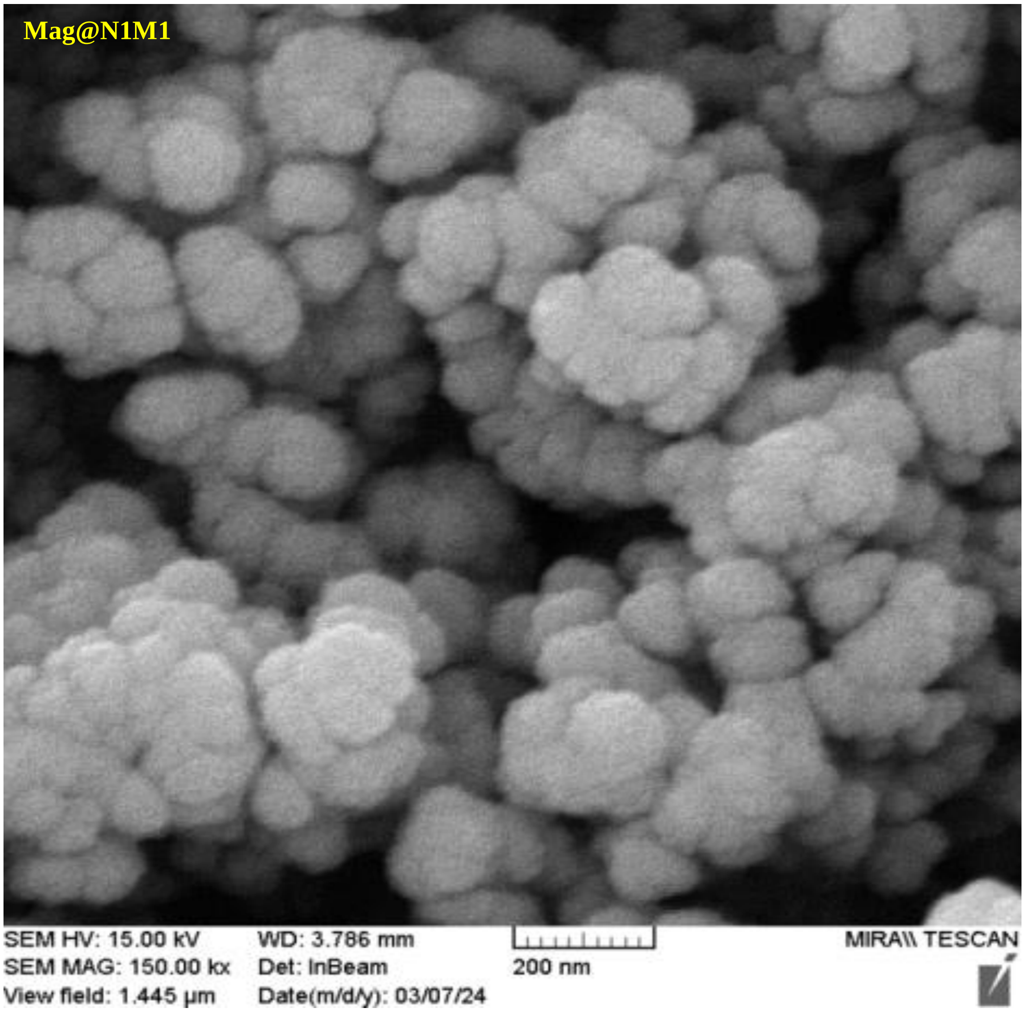


Figure S16. FESEM image of Mag@N1M1 sorbent

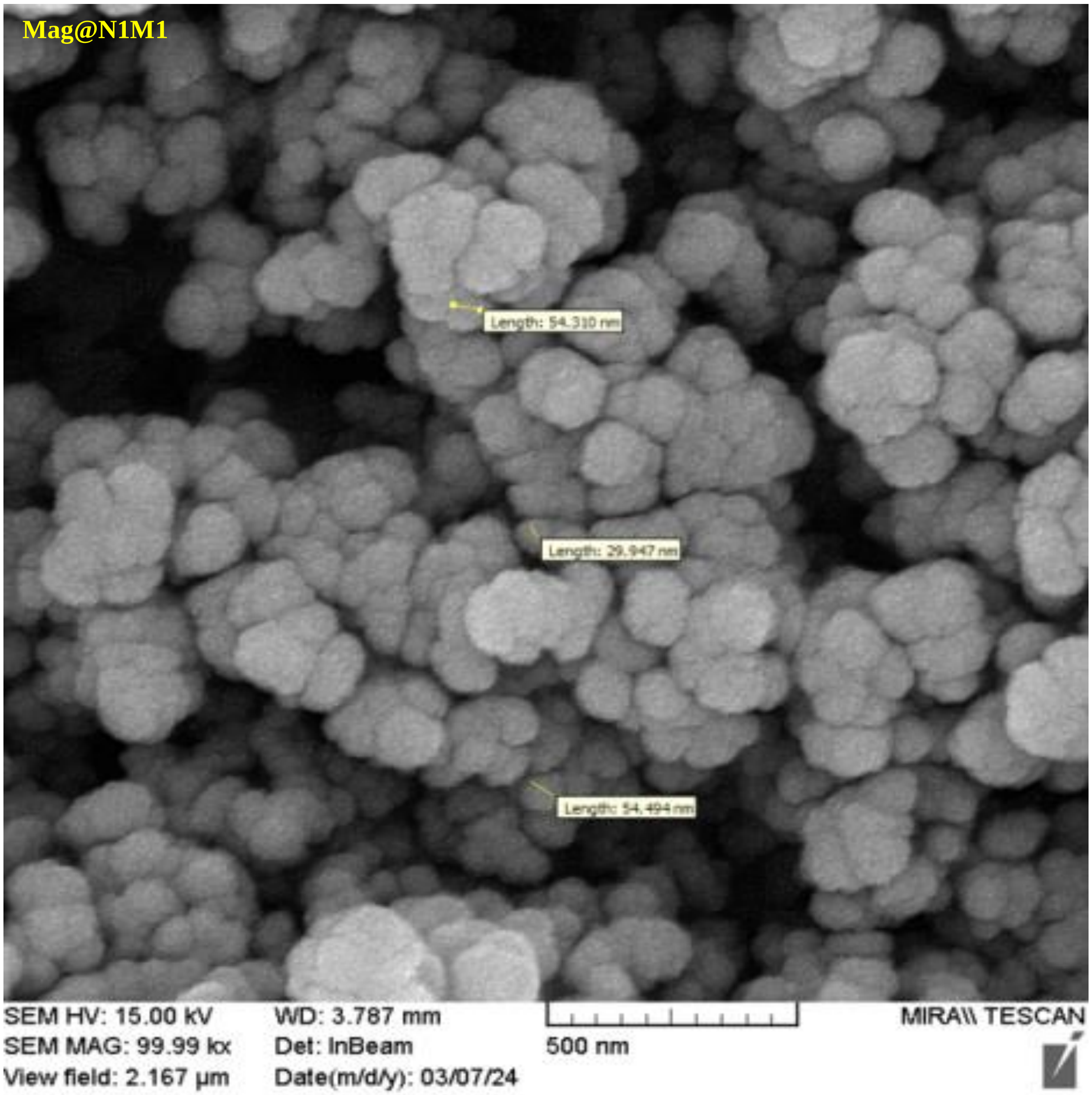


Figure S17. FESEM image of Mag@N1M1 sorbent

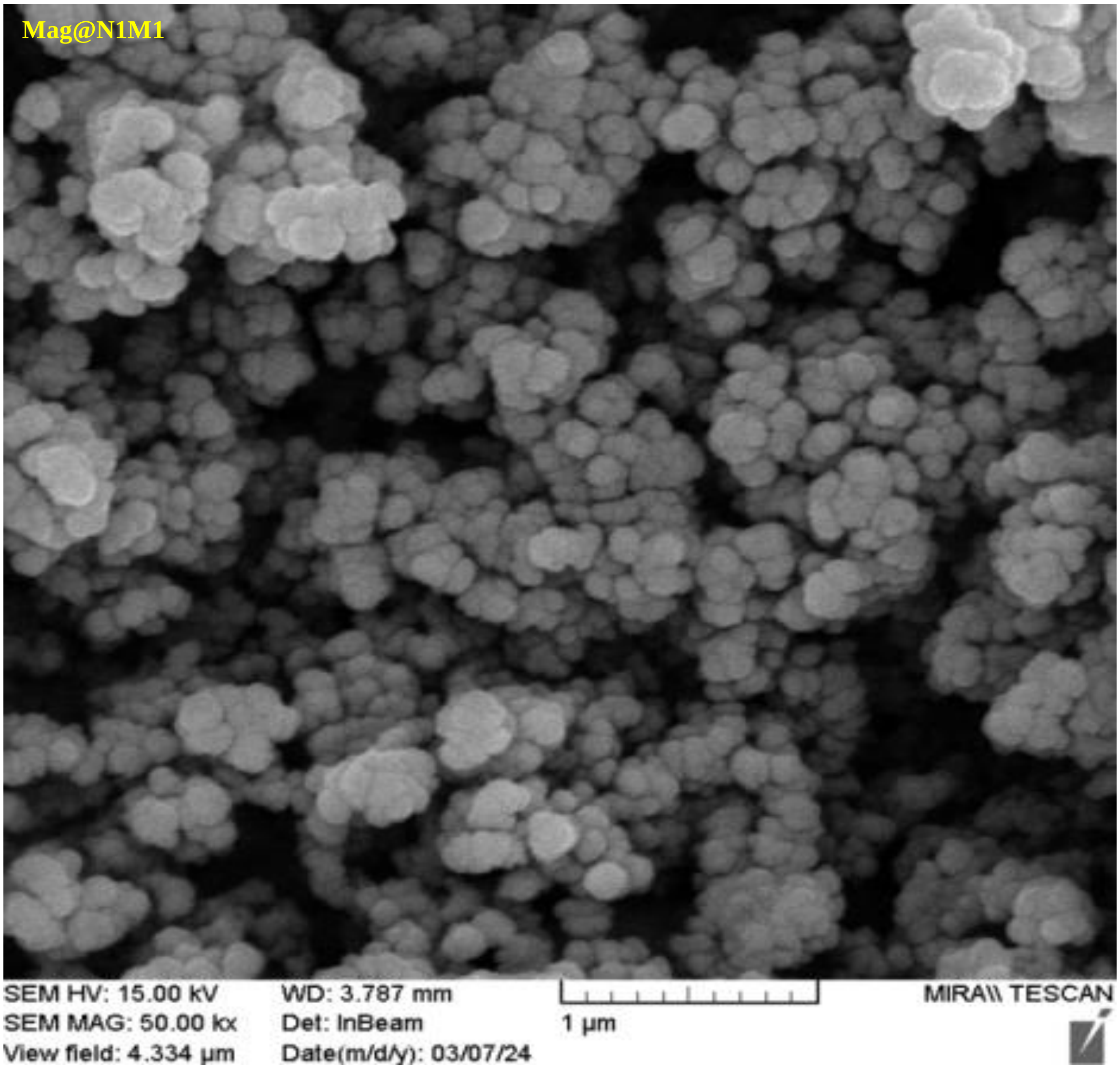


Figure S18. FESEM image of Mag@N1M1 sorbent

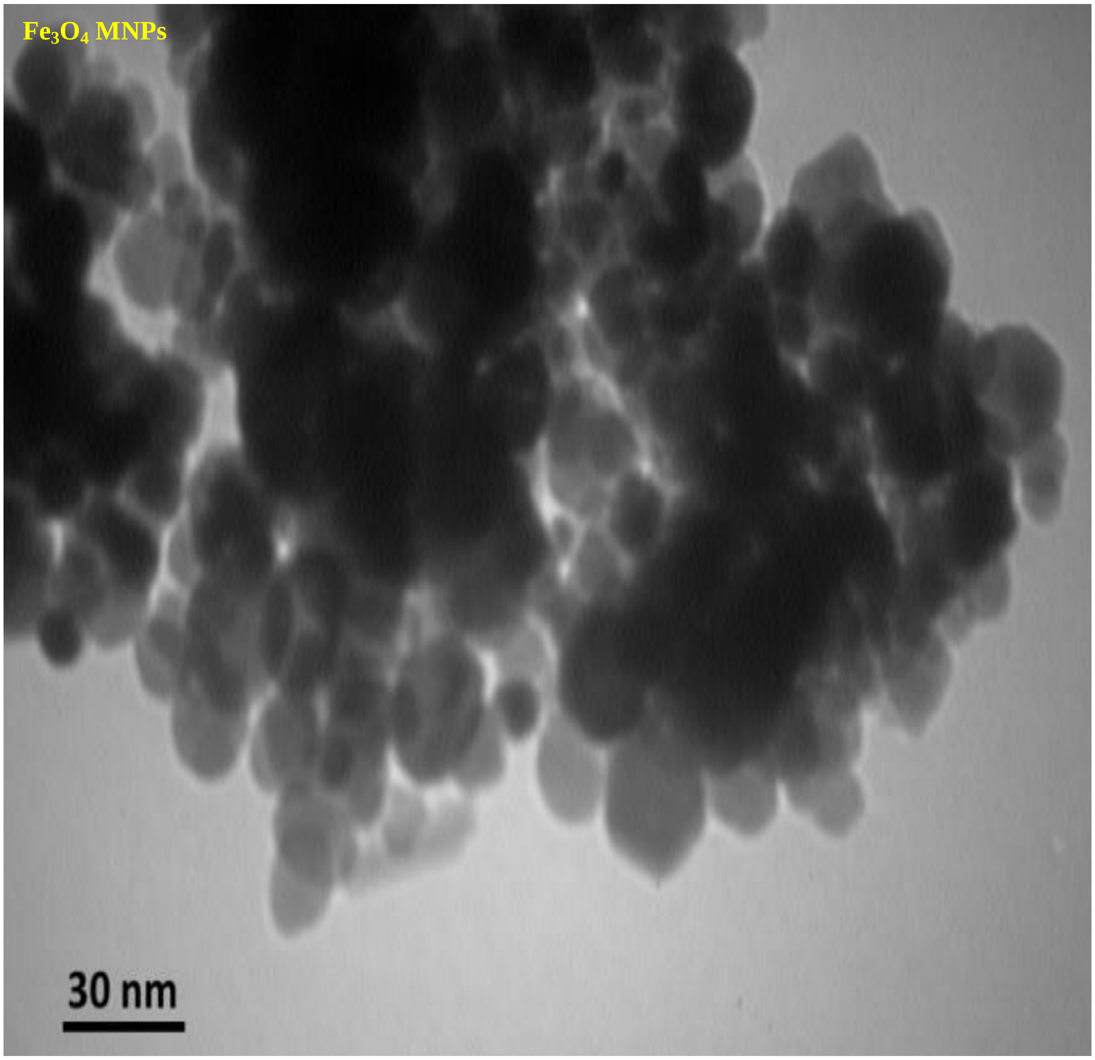


Figure S19. TEM image of Fe_3O_4 MNPs

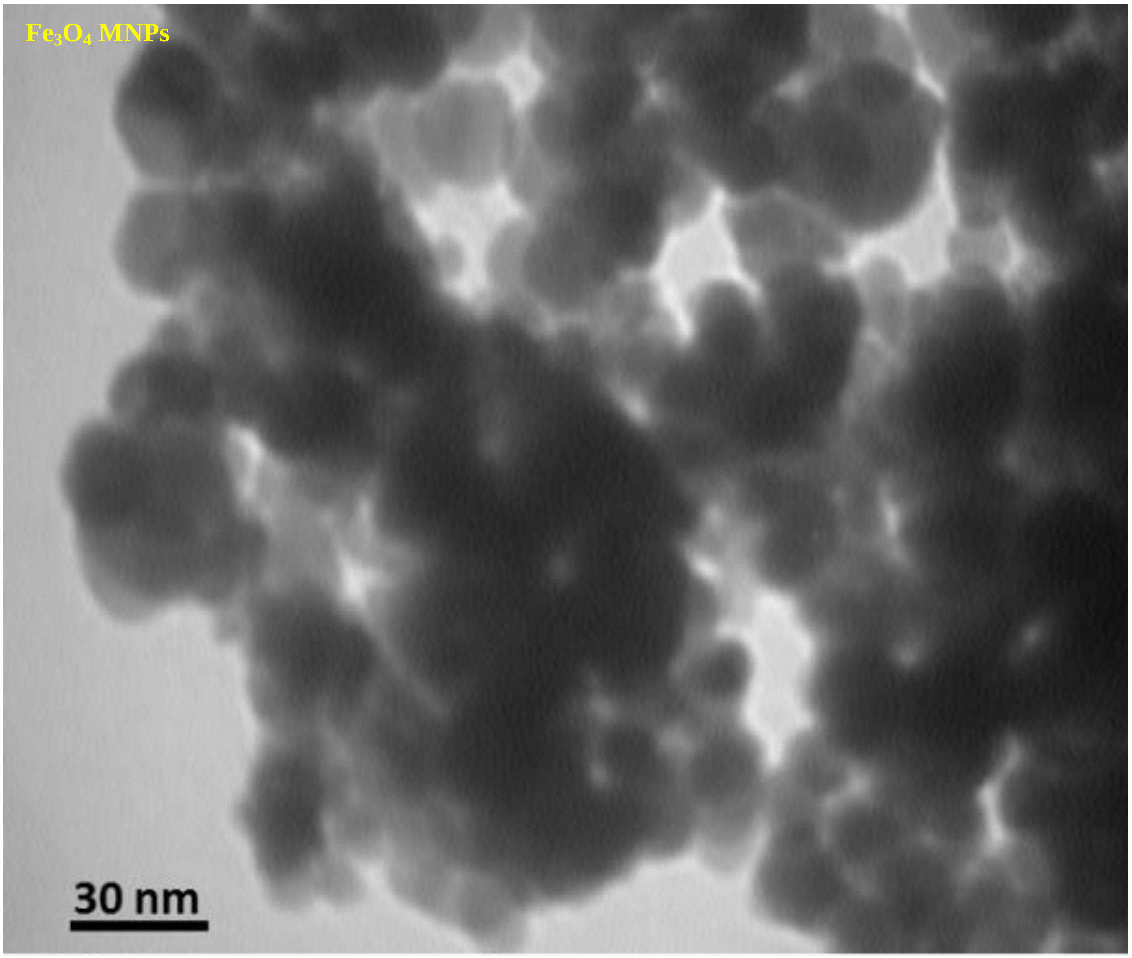


Figure S20. TEM image of Fe_3O_4 MNPs

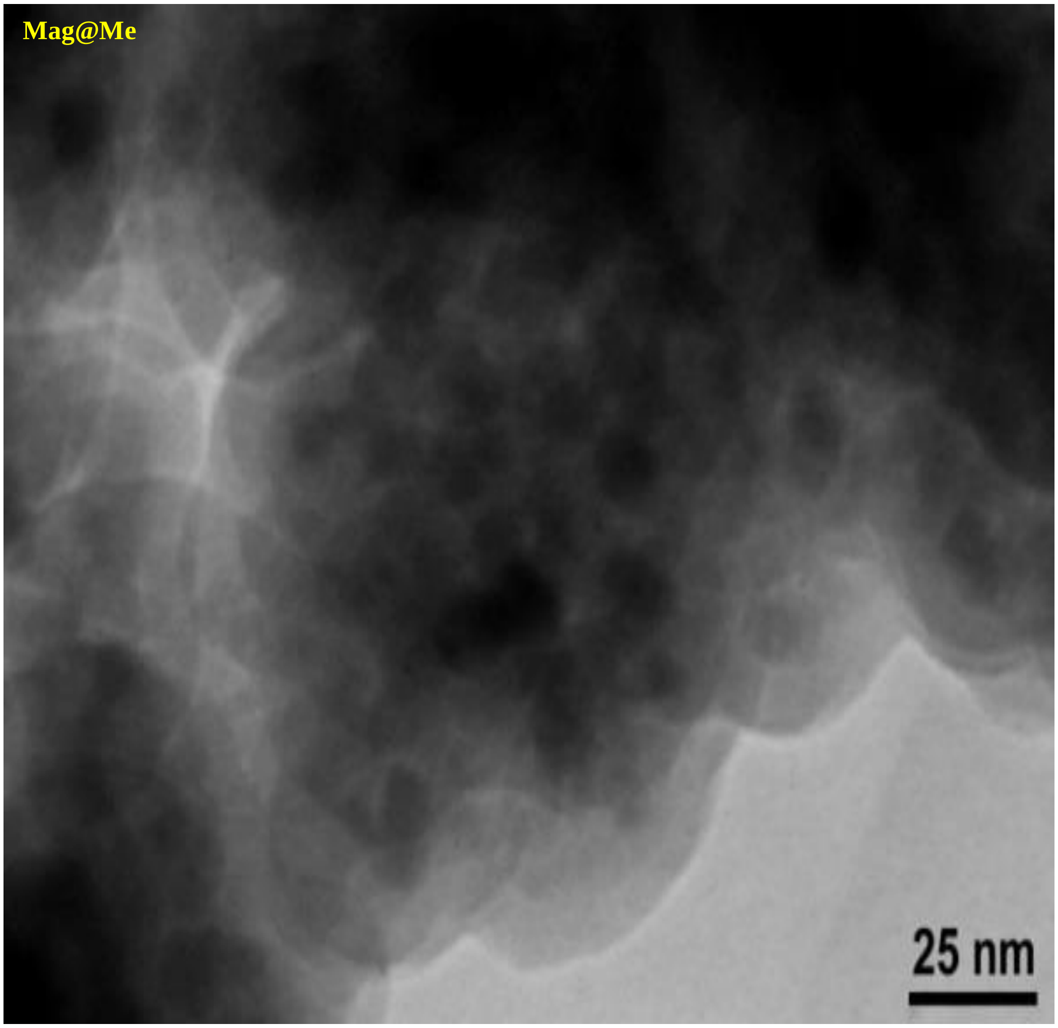


Figure S21. TEM image of Mag@Me sorbent

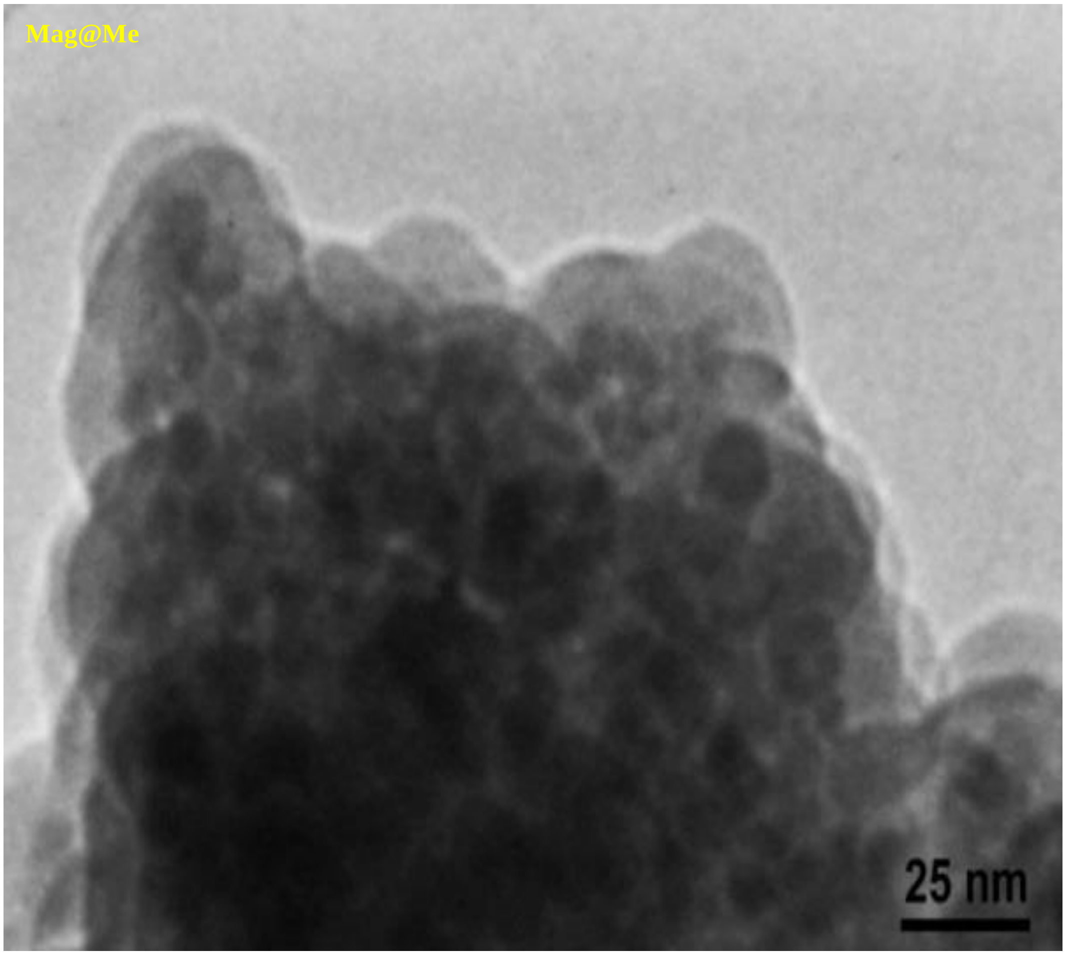


Figure S22. TEM image of Mag@Me sorbent

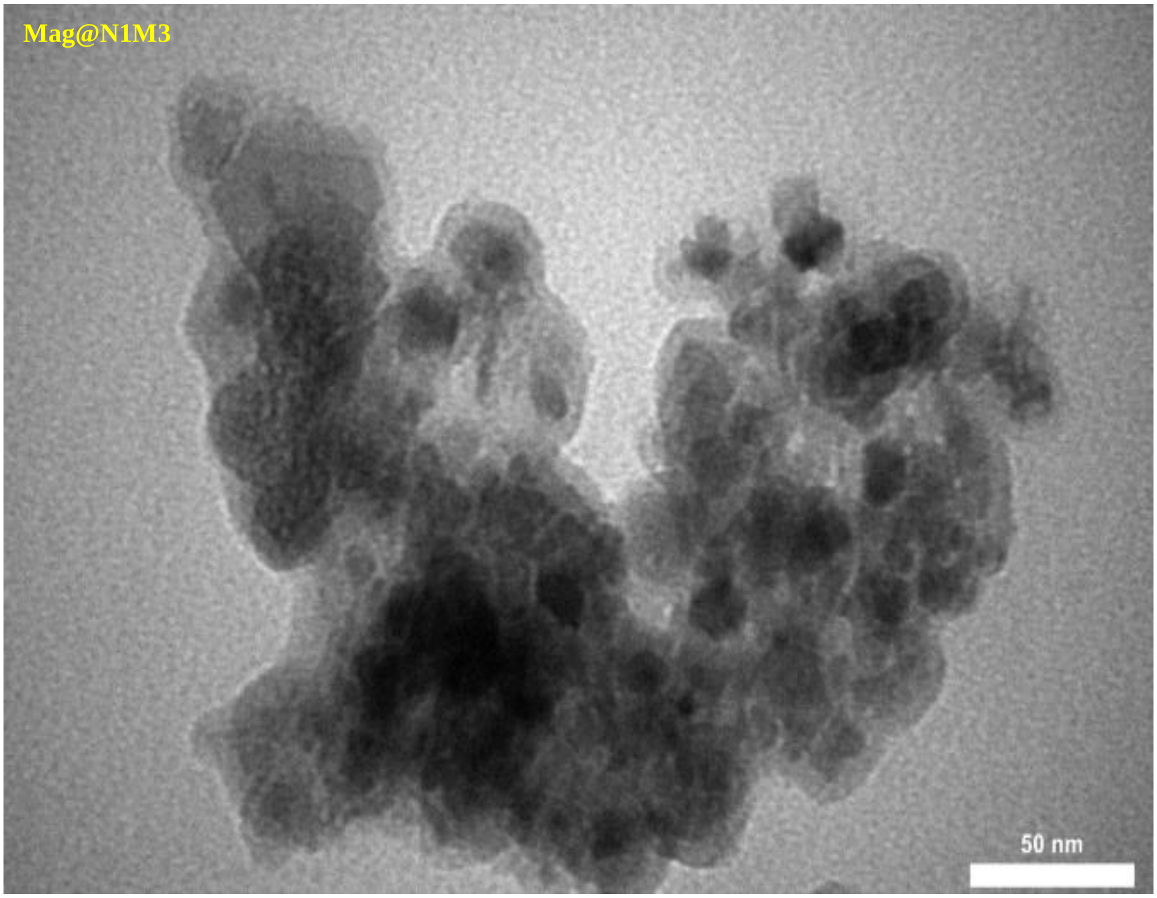


Figure S23. TEM image of Mag@N1M3 sorbent

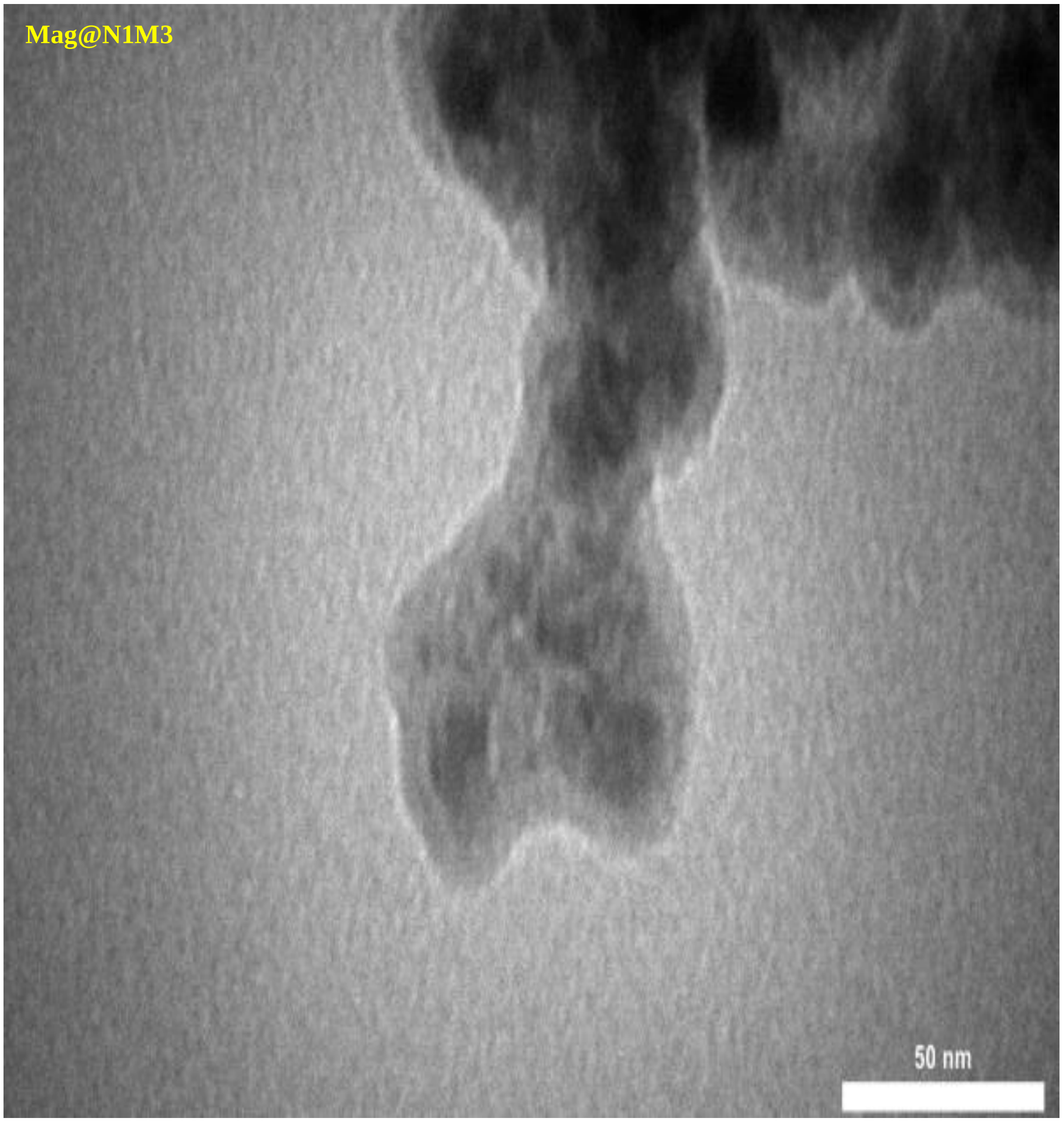


Figure S24. TEM image of Mag@N1M3 sorbent

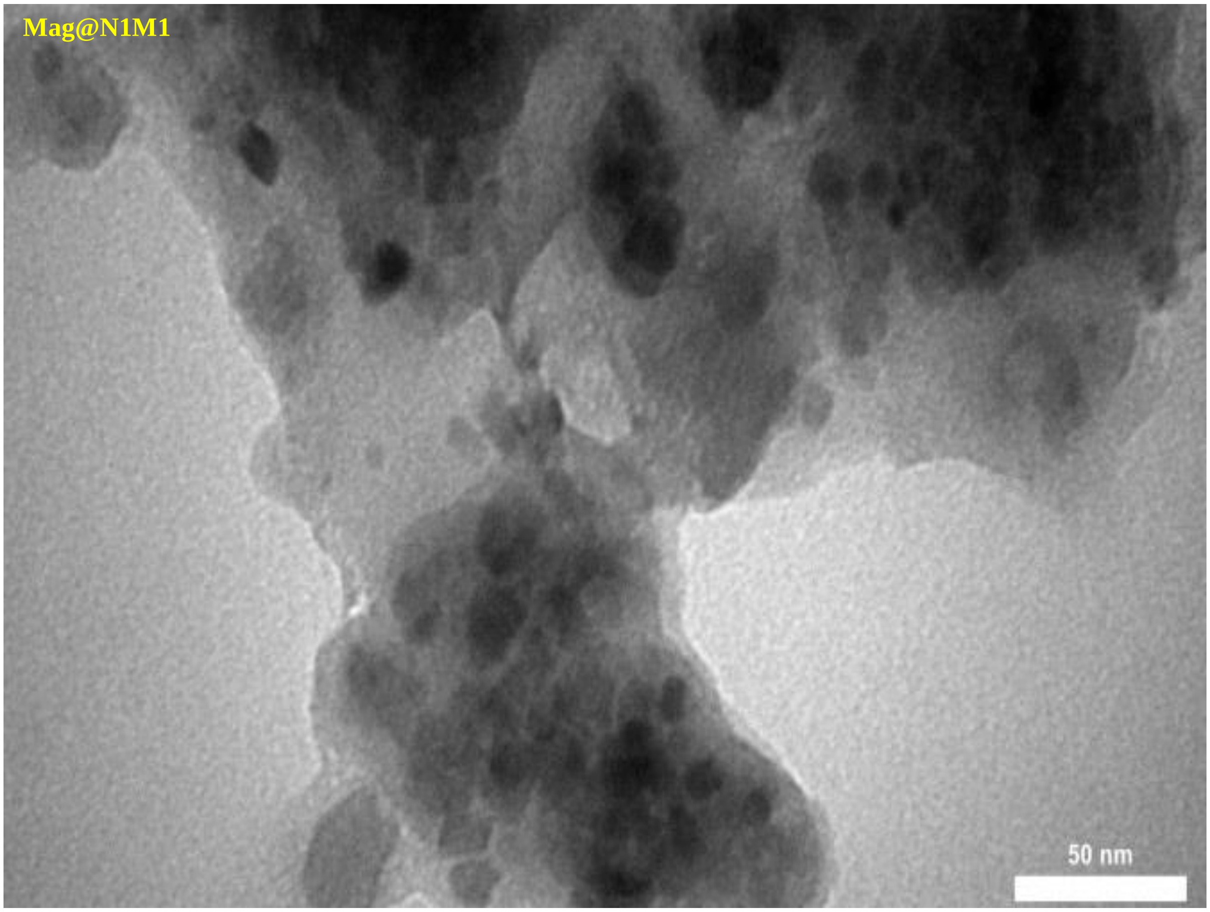


Figure S25. TEM image of Mag@N1M1 sorbent

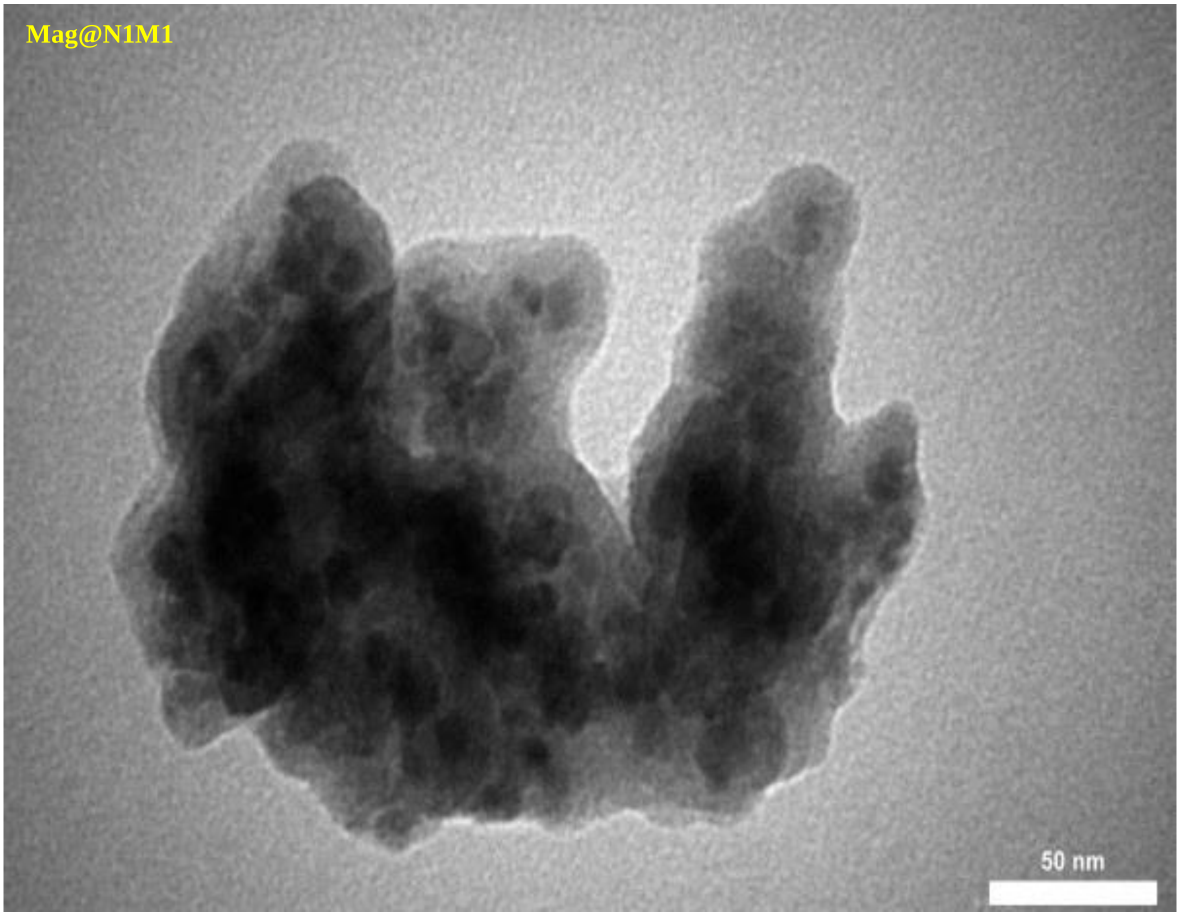


Figure S26. TEM image of Mag@N1M1 sorbent

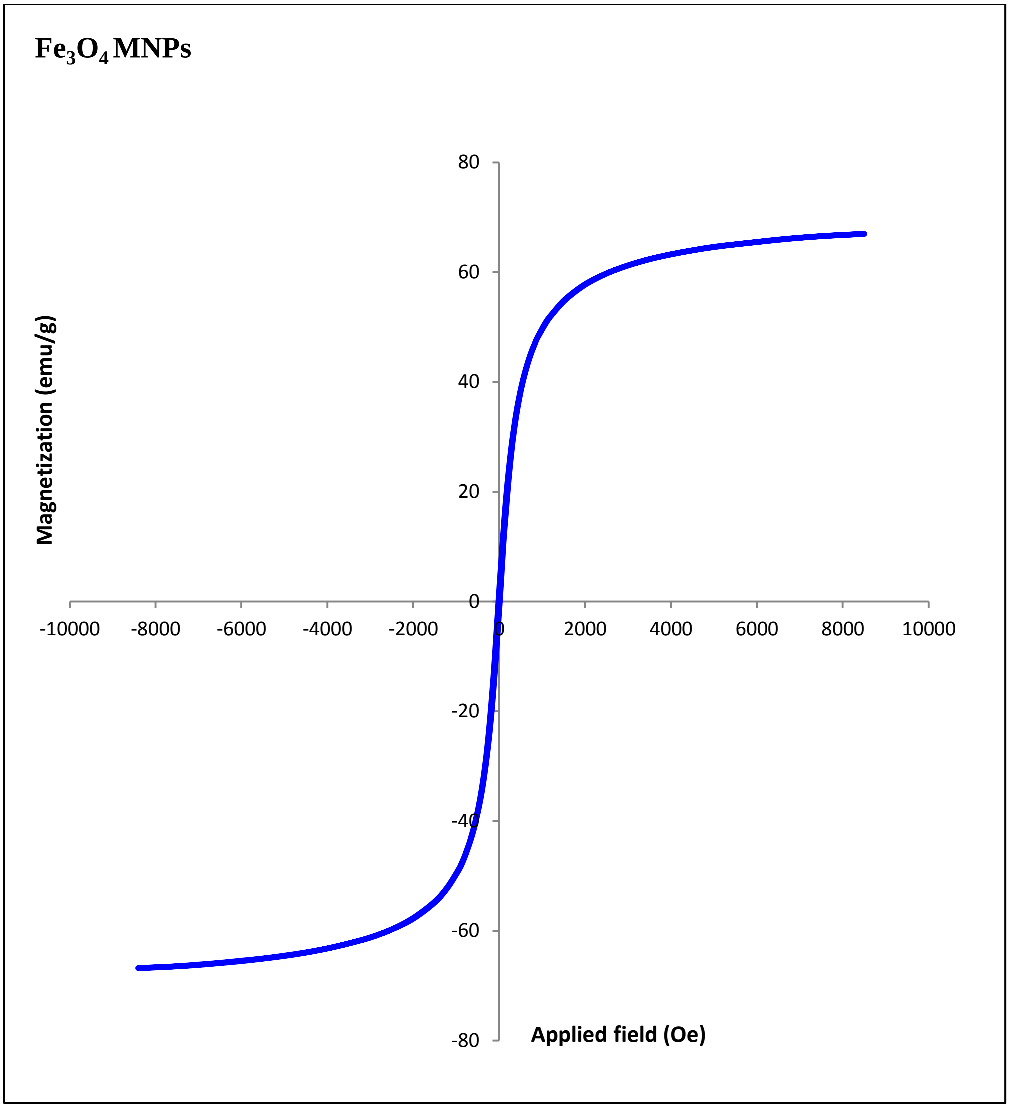


Figure S27. VSM curve of Fe_3O_4 MNPs

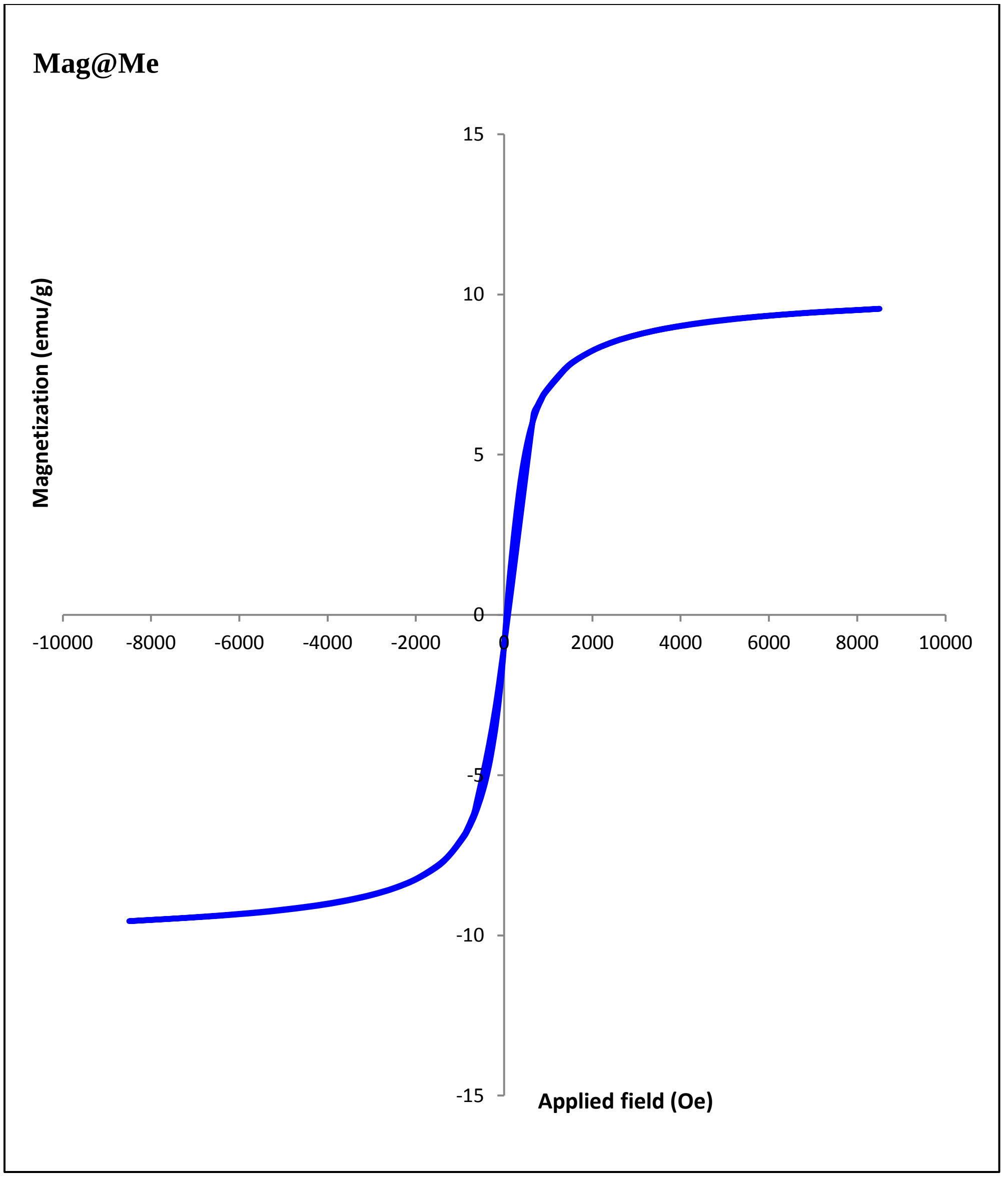


Figure S28. VSM curve of Mag@Me sorbent

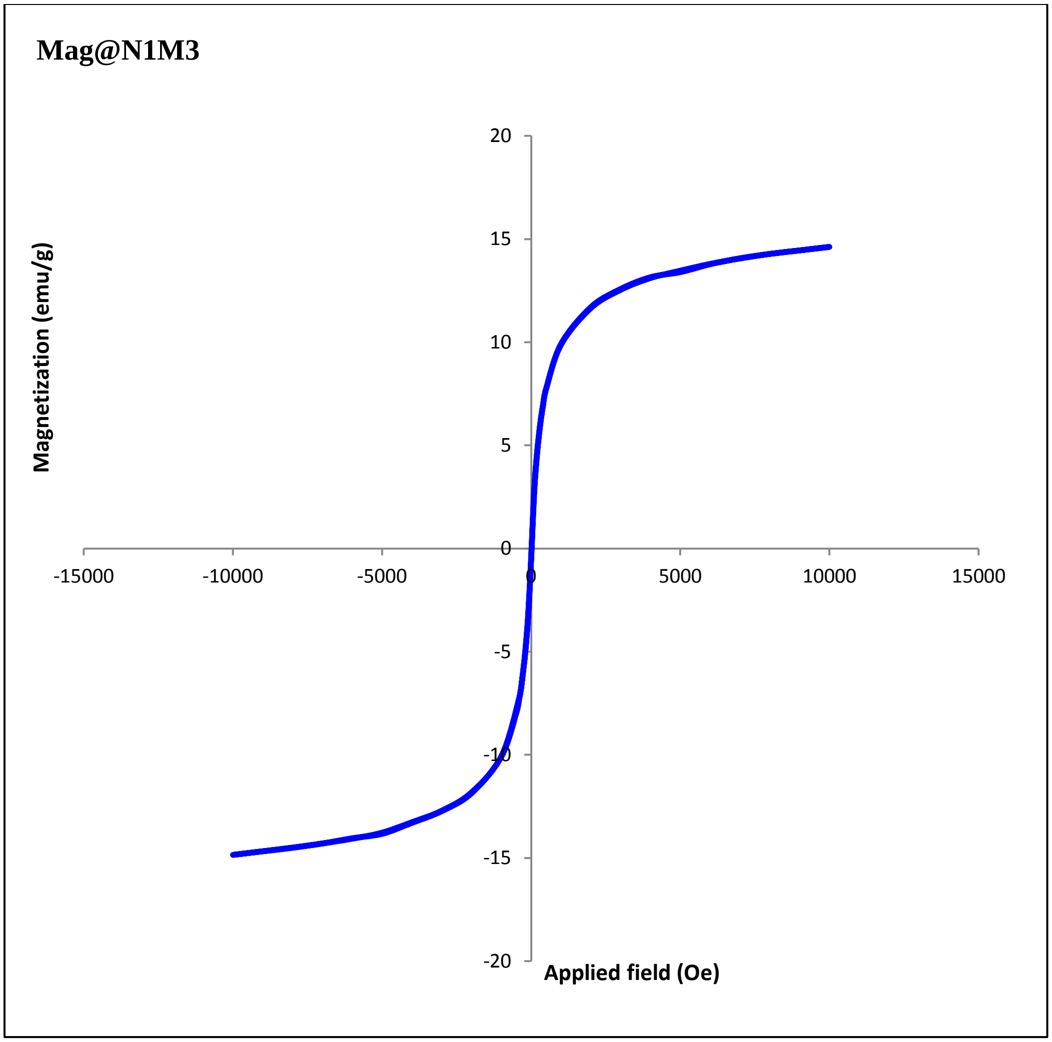


Figure S29. VSM curve of Mag@N1M3 sorbent

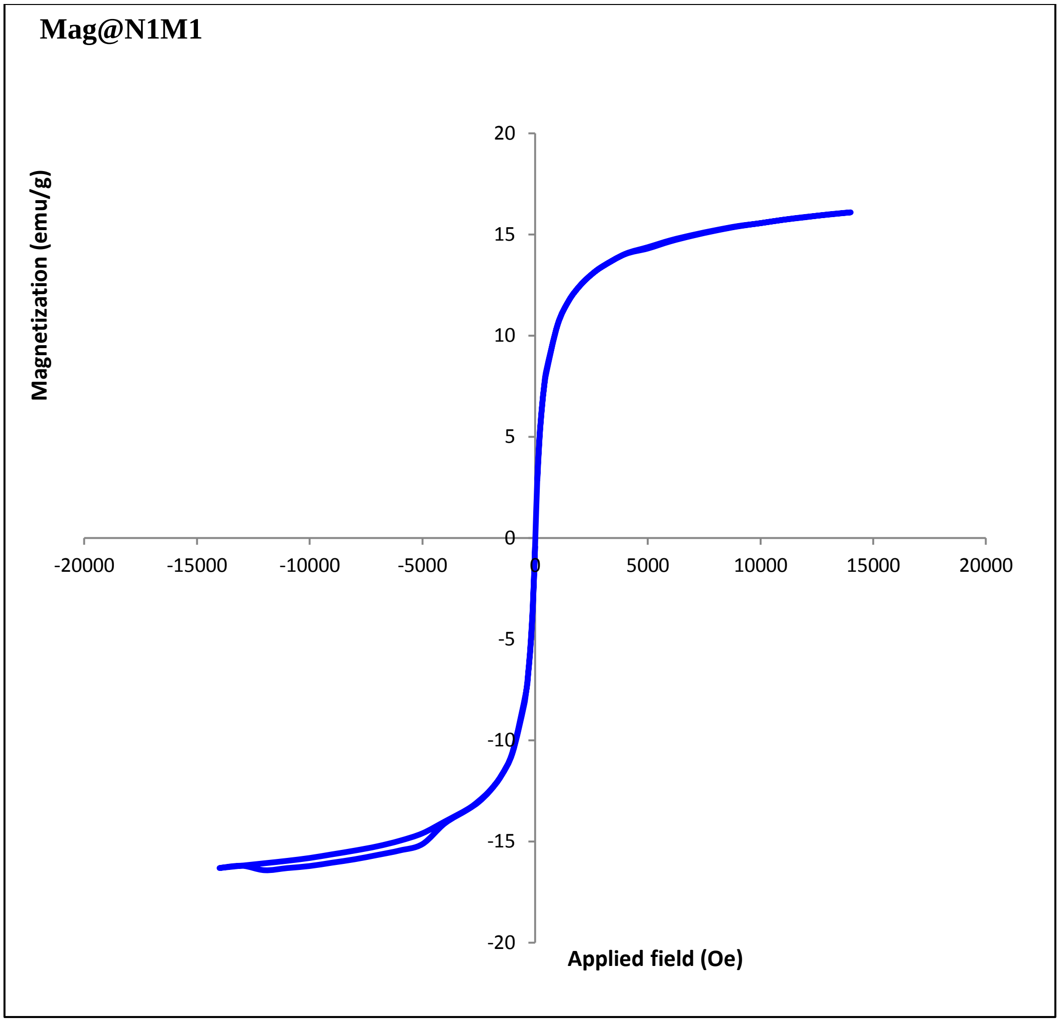
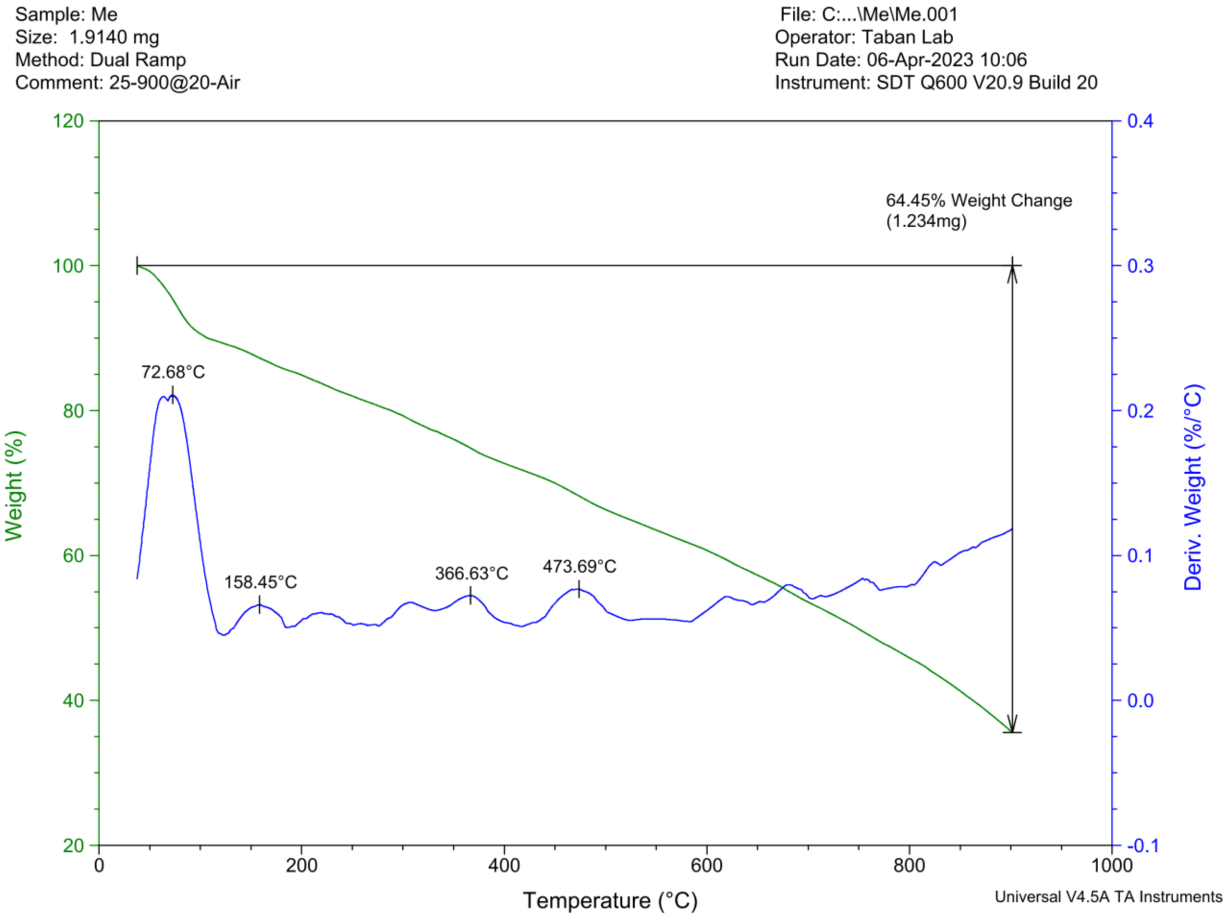


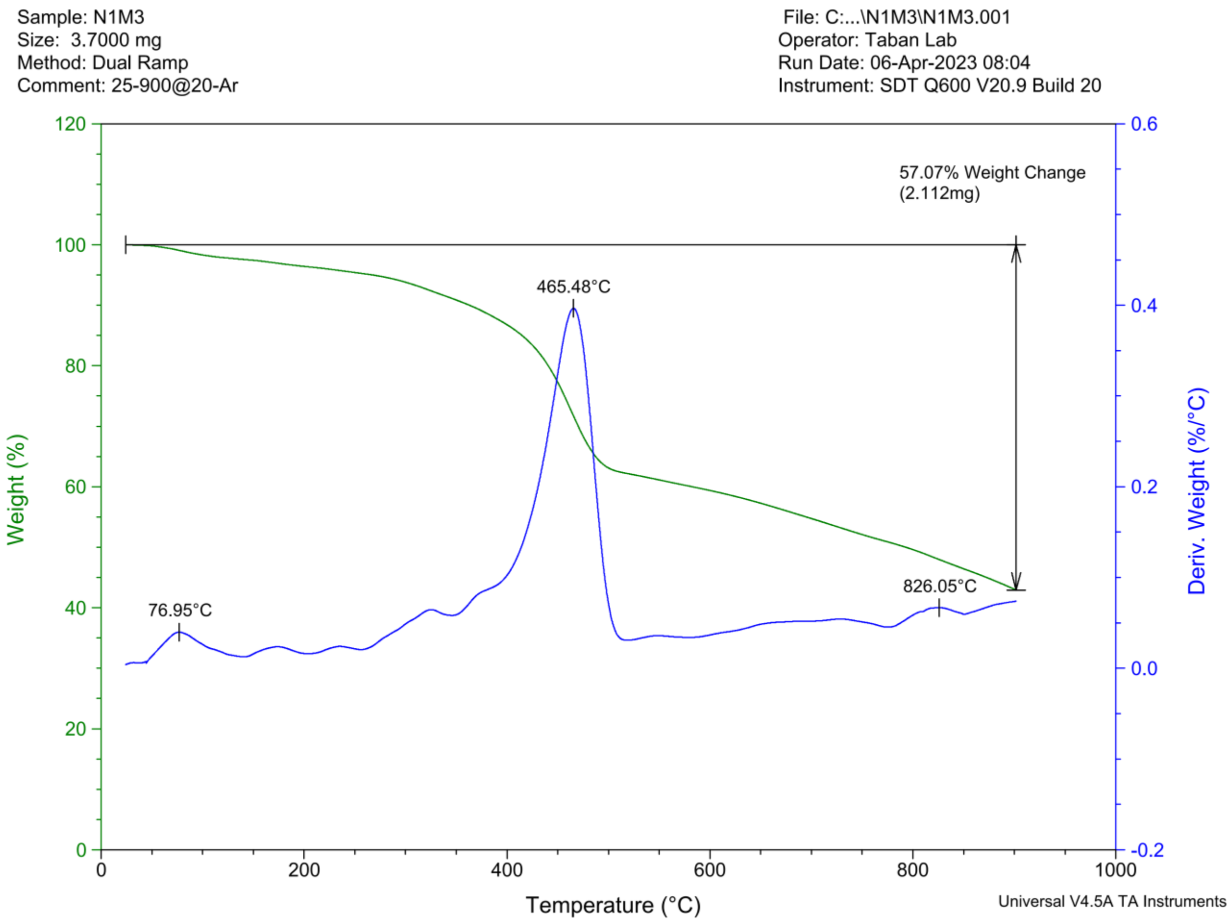
Figure S30. VSM curve of Mag@N1M1 sorbent



Sample: Me
Size: 1.9140 mg
Method: Dual Ramp
Comment: 25-900@20-Air

File: C:...\Me\Me.001
Operator: Taban Lab
Run Date: 06-Apr-2023 10:06
Instrument: SDT Q600 V20.9 Build 20

Figure S31. TGA termogram of Mag@Me sorbent



Sample: N1M3
Size: 3.7000 mg
Method: Dual Ramp
Comment: 25-900@20-Ar

File: C:...\N1M3\N1M3.001
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Run Date: 06-Apr-2023 08:04
Instrument: SDT Q600 V20.9 Build 20

Figure S32. TGA termogram of Mag@N1M3 sorbent

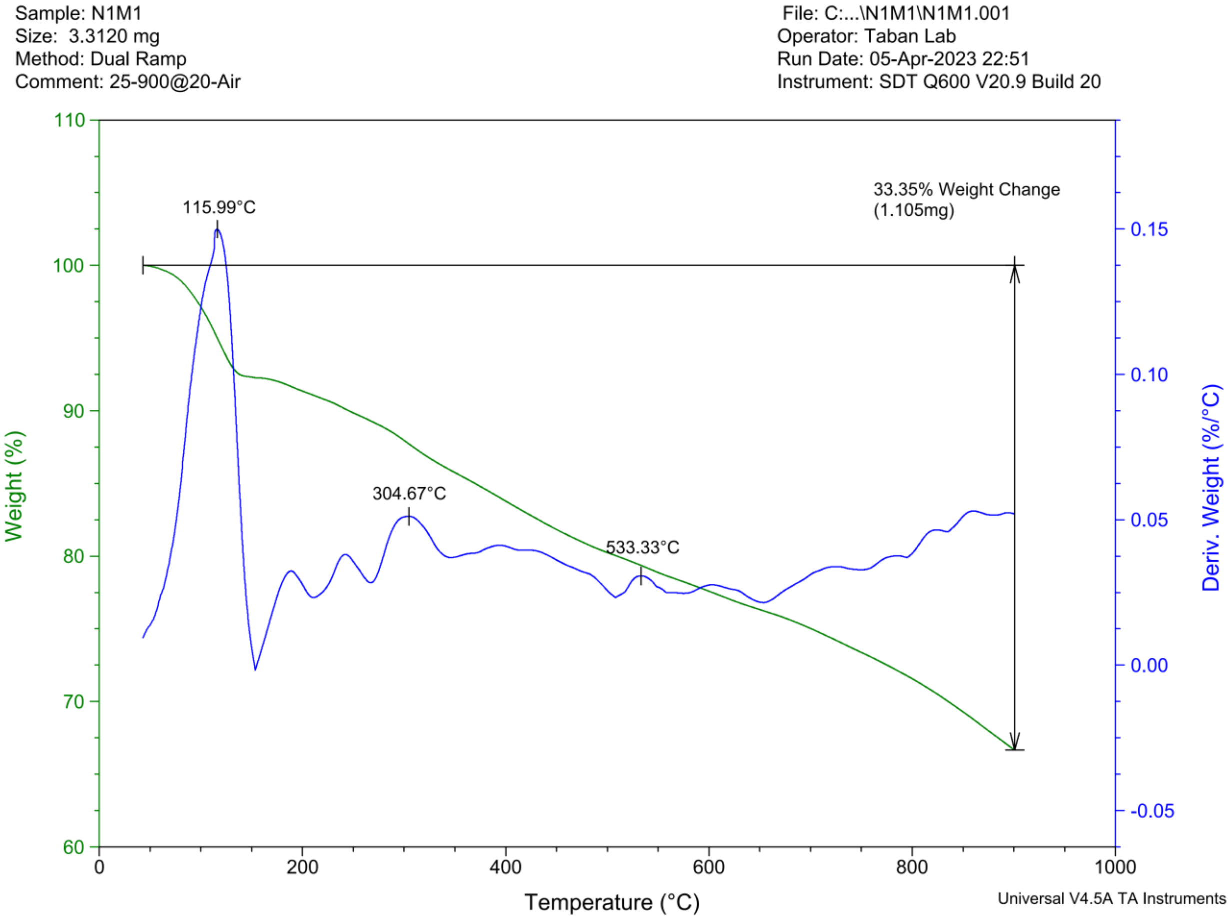


Figure S33. TGA termogram of Mag@N1M1 sorbent

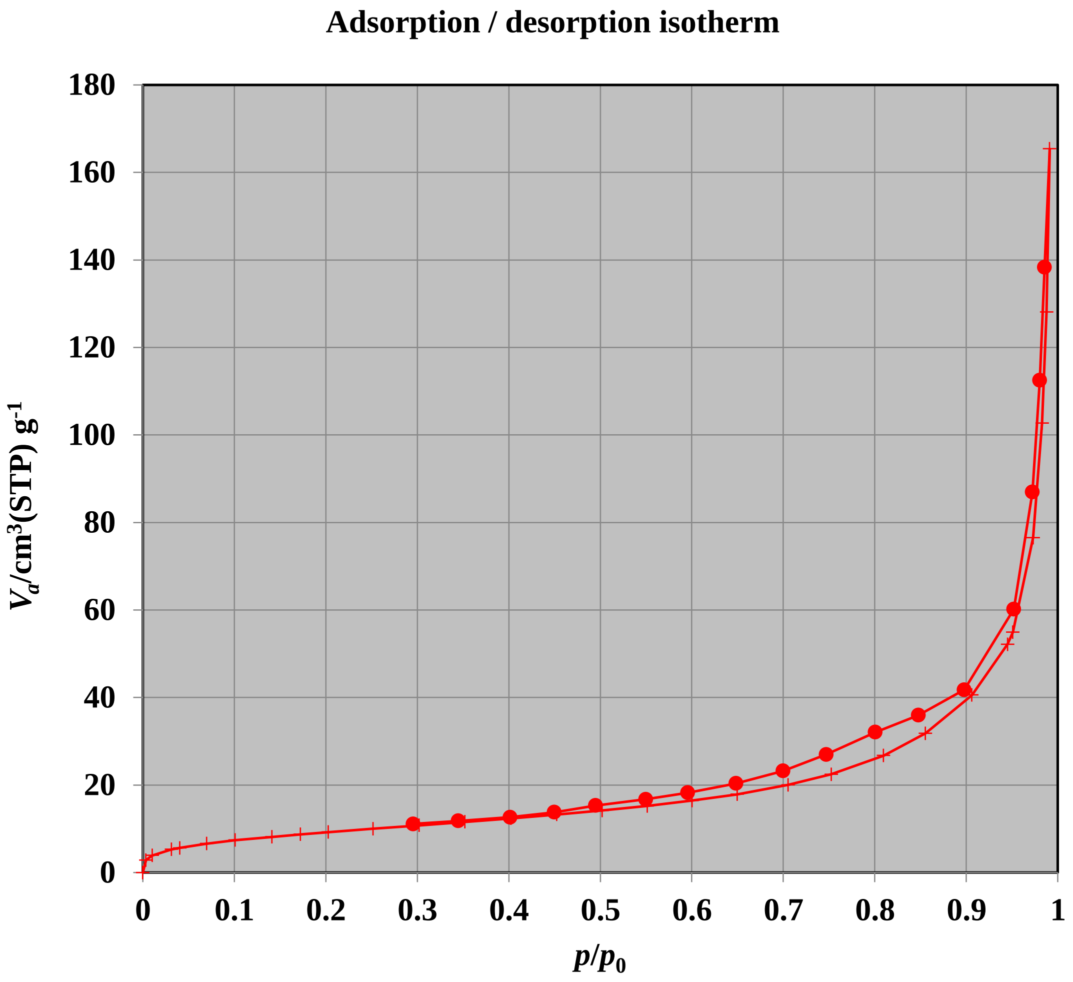


Figure S34. N_2 adsorption-desorption isotherm of Mag@N1M3 sorbent

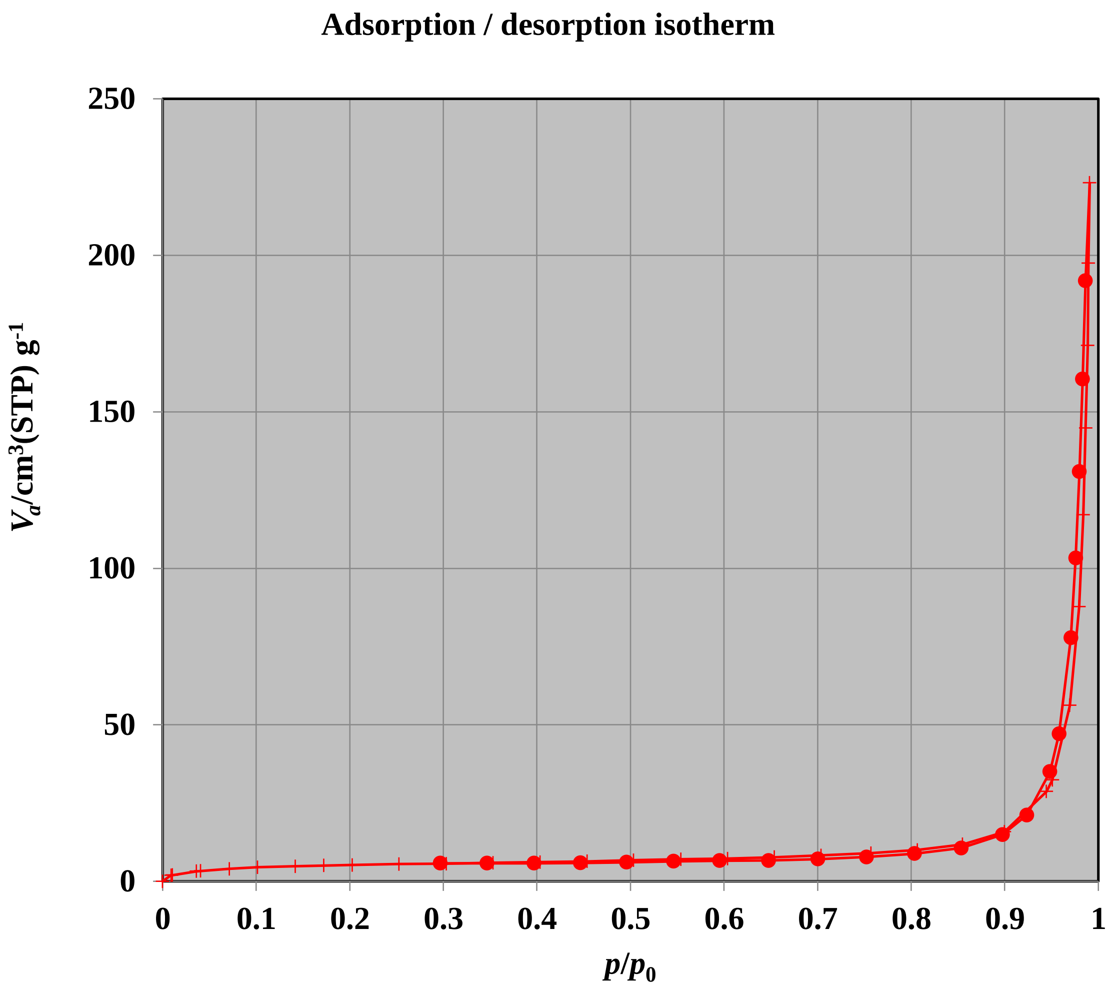


Figure S35. N_2 adsorption-desorption isotherm of Mag@N1M1 sorbent

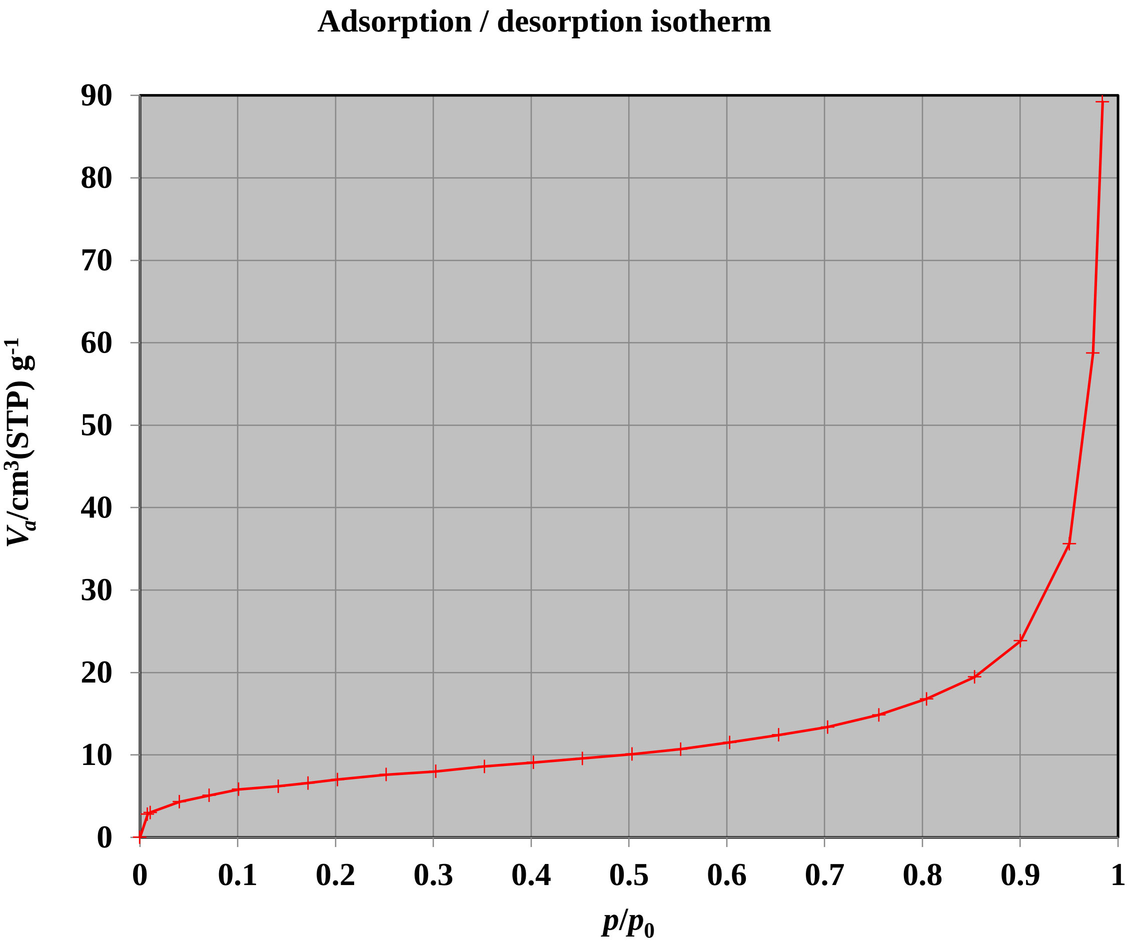
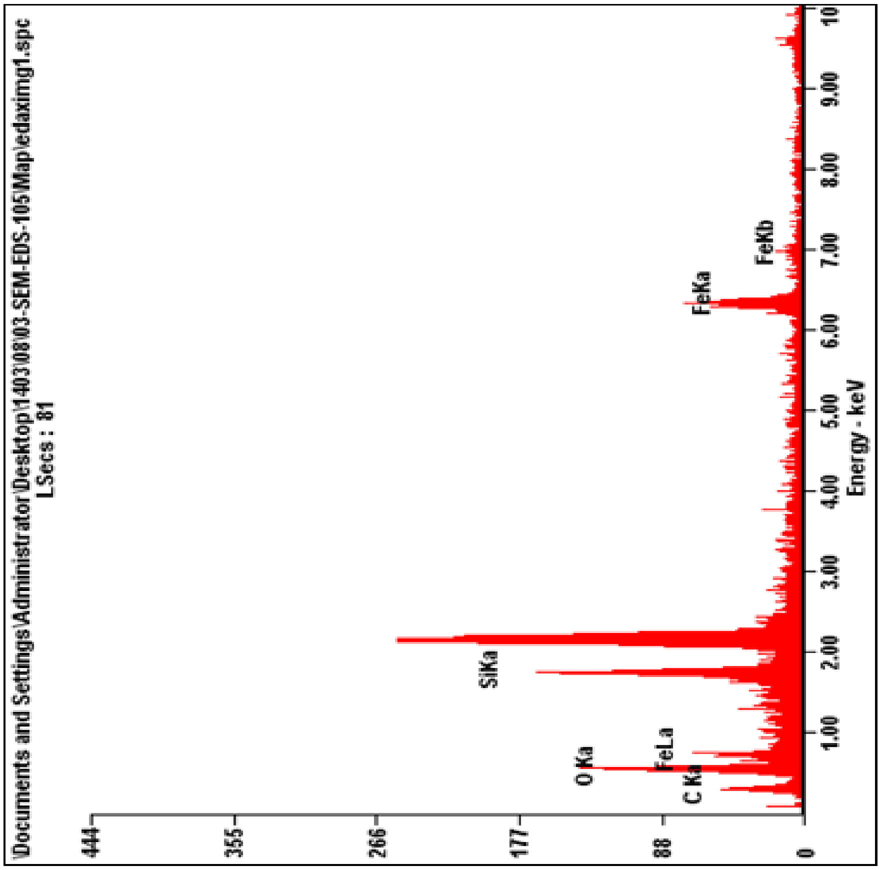
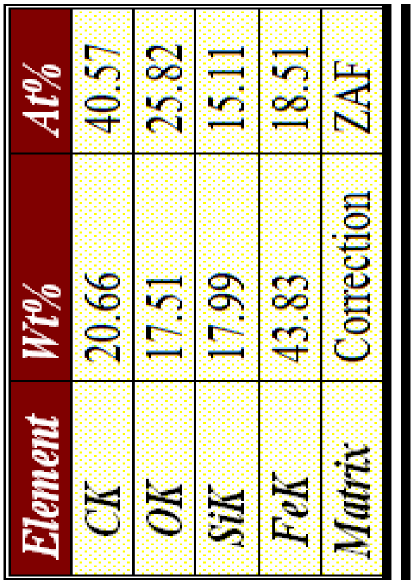


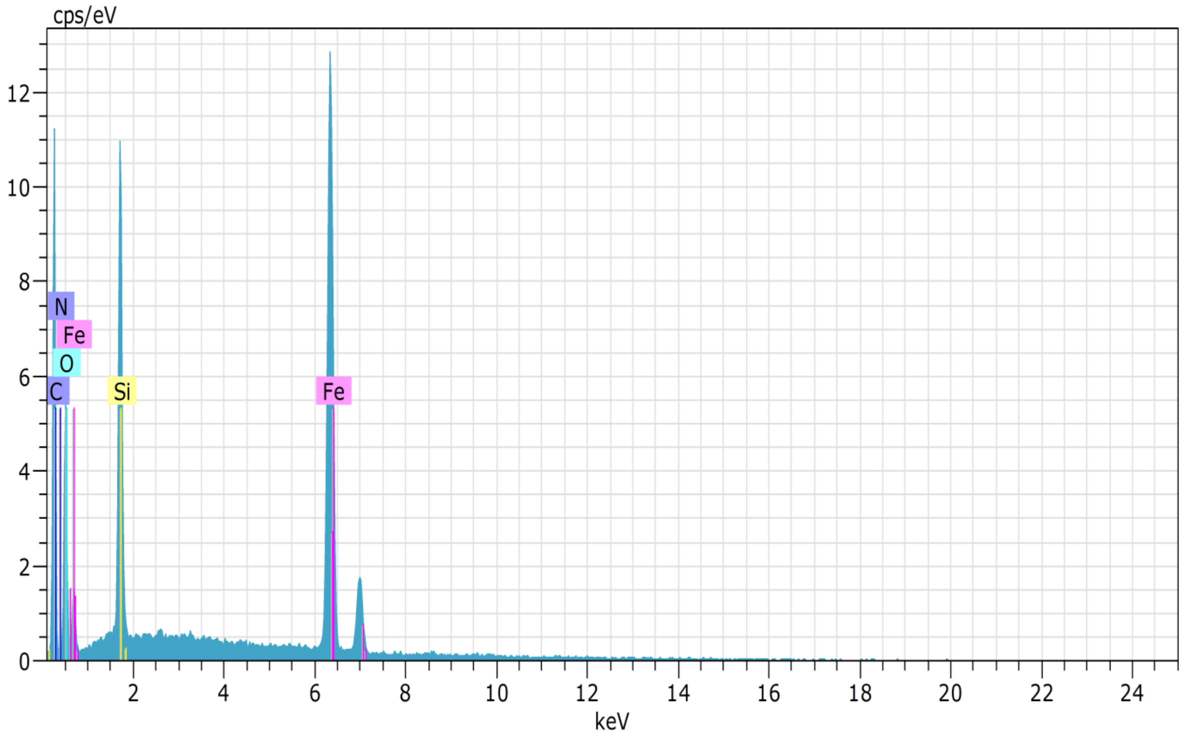
Figure S36. N_2 adsorption-desorption isotherm of Mag@Me sorbent





Element	Wt%	At%
CK	20.66	40.57
OK	17.51	25.82
SiK	17.99	15.11
FeK	43.83	18.51
Matrix	Correction	ZAF

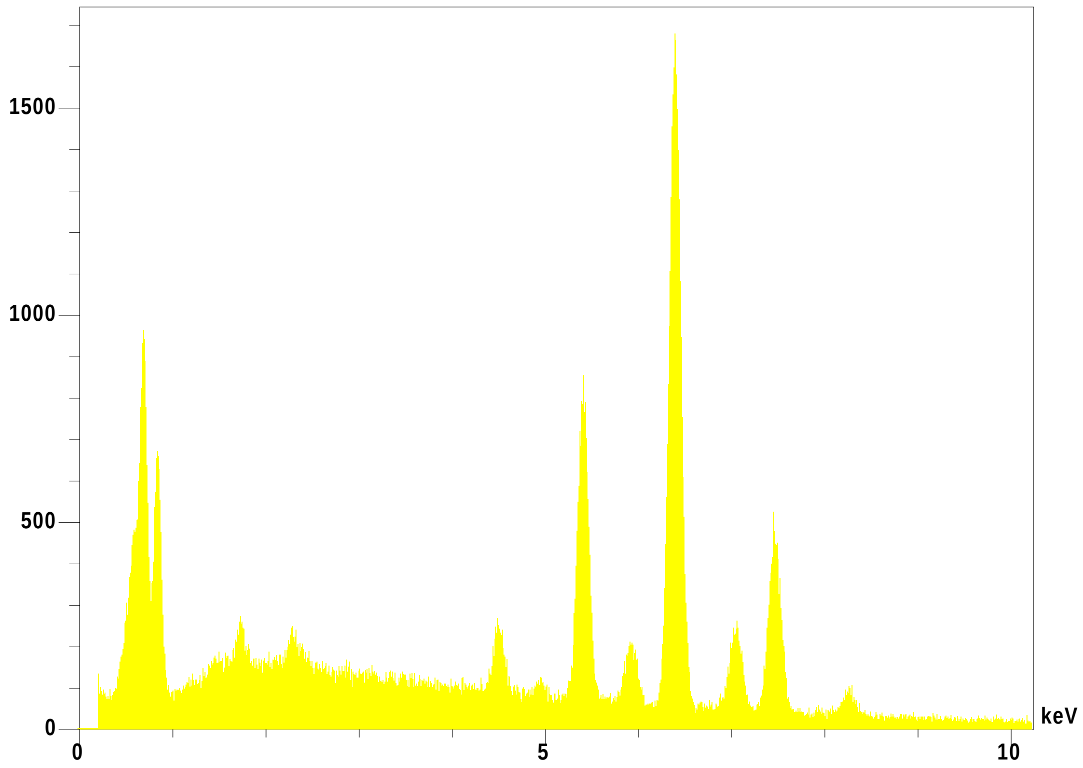
Figure S37. EDX spectrum, At% and Wt% of Mag@Me sorbent



```
HV:25.0kV       Puls th.:9.08kcps

El AN  Series  unn. C norm. C Atom. C Error (1 Sigma)
               [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------
C  6  K-series  46.10   47.88   64.00            6.84
O  8  K-series  22.83   23.71   23.79            3.83
Fe 26 K-series  19.35   20.10    5.78            0.54
Si 14 K-series   5.18    5.38    3.08            0.26
N  7  K-series   2.82    2.93    3.36            1.19
-----------------------------------------------------
        Total:  96.28  100.00  100.00
```

Figure S38. EDX spectrum, At% and Wt% of Mag@N1M3 sorbent



Quantitative Results

Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Pk/Bg	LConf	HConf	Cat#
C	Ka	25.2	7.4446	0.0797	0.0518	17.14	28.89	0.3023	112.64	15.89	18.38	0.00
N	Ka	3.6	7.4446	0.0114	0.0074	2.01	2.90	0.3707	7.76	1.62	2.39	0.00
O	Ka	89.0	7.4446	0.2866	0.1862	32.66	41.33	0.5702	142.87	31.40	33.92	0.00
Si	Ka	101.8	6.4498	0.3535	0.2297	26.21	18.90	0.8762	44.92	25.27	27.16	0.00
Fe	Ka	60.4	0.8086	0.2687	0.1746	21.98	7.97	0.7940	17.00	20.95	23.01	0.00
				1.0000	0.6497	100.00	100.00					0.00

Figure S39. EDX spectrum, At% and Wt% of Mag@N1M1 sorbent

General procedure for oil separation using magnetic sorbents

The procedure for evaluating the oil adsorption capacity of magnetic sorbents was accomplished based on weight measurement. The appropriate amount of magnetic sorbent nanoparticles (0.07-0.1 g) was weighed as m_1. 0.5 g of oil, denoted as m_2 was mixed with 40 mL distilled water, and then magnetic sorbent was added to it. The oil was adsorbed by the magnetic sorbent during a few minutes (7 min, unless stated). Afterwards, the magnetic sorbent together with the adsorbed oil were collected by nearing an external magnetic bar to the reaction vessel. The collected particles was left for 24 h to evaporate any possible adsorbed water and then weighed as m_3 (Refer to the SI for photos depicting the experimental section of oil separation). Finally, the sorption capacity (Q) of nanoparticles was calculated by the following formula:

$$Q = \frac{m3 - m1}{m2} \times 100$$

For the recovery test, magnetic sorbent nanoparticles were washed by acetone under ultrasonic irradiation (during 15 min) for three times to completely remove the adsorbed oil then collected with a magnetic bar and dried in oven at 50 °C for 2 h to remove residual acetone. Then it was reused to separate oil from water for the next runs. All experiments were repeated for 3 times and the average data was reported.

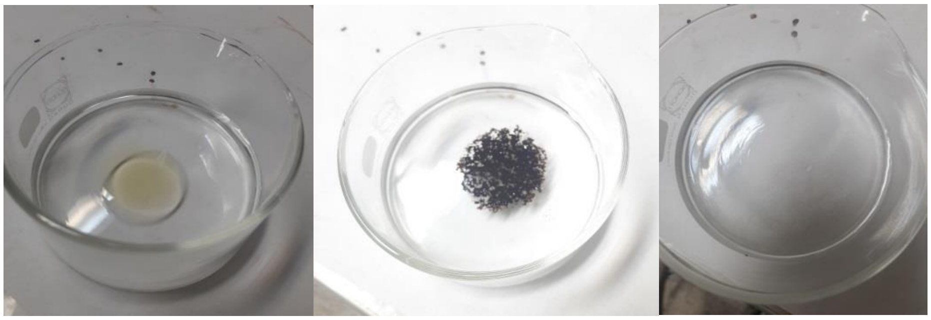


Figure S40. Photos of oil separation steps from water using Mag@N1M3 sorbent

General procedure for separation of chromium (VI) from aqueous medium using magnetic sorbents

Initially, 2 and 5 mg/L aqueous solutions of chromium (VI) were prepared via dissolving of appropriate amounts of $K_2Cr_2O_7$ in water. Then, 10 mL of light orange chromium (VI) solution was mixed with 0.05 g of each sorbent and stirred at room temperature using a shaker at 230 rpm during appropriate time. After the process, magnetic sorbent was separated with an external magnet and the remained solution was subjected to the analysis with spectrophotometer. Spectrophotometric measurement at 540 nm, in the presence of 1,5-diphenylcarbazide as indicator, was employed for the determination of chromium ion concentration before and after treatment with sorbents. To do this, 1,5-diphenylcarbazide solution was prepared via dissolving 0.5 g 1,5-diphenylcarbazide in 100 mL acetone followed by addition of 0.5 mL H_2SO_4 (0.5 N) to it. For the sample preparation, a 50 mL aqueous solution was prepared by mixing 5 mL of the chromium (VI) solutions (before or after treatment with sorbent) and 1 mL of 1,5-diphenylcarbazide solution. When these two are mixed in an acidic medium, a highly sensitive colorimetric reaction occurs. Chromium (VI) oxidizes 1,5-diphenylcarbazide to 1,5-diphenylcarbazone. Simultaneously, the chromium (VI) is reduced to chromium (III). The Cr (III) ions then immediately form a stable, soluble complex with the 1,5-diphenylcarbazone. This complex has an intense and characteristic violet color. Supernatants and standard solution of chromium ion were analyzed at 540 nm with the spectrophotometer. Finally, the removal efficiency was obtained using the following formula:

$$\text{Removal efficiency (\%)} = \frac{C0-Cf}{C0} \times 100$$

In which, C_0 and C_f are initial and final concentration of chromium (VI) based on mg/L, respectively.

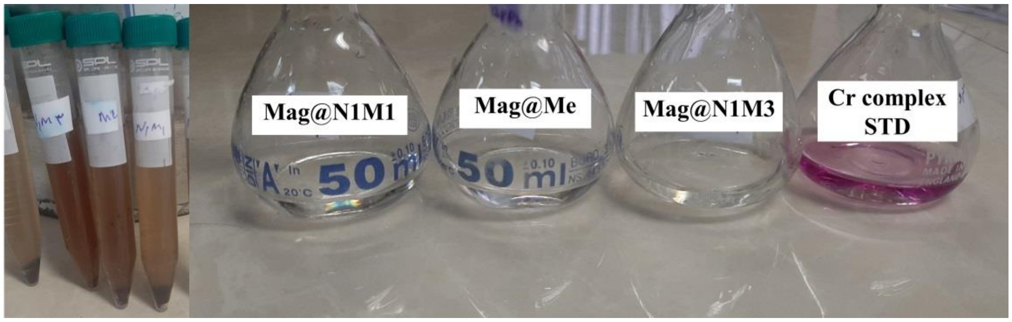


Figure S41. Photos of Cr (VI) separation from water using magnetic sorbents