Supporting Information

Magnetically recyclable core-shell MOF nanoparticles of Fe$_3$O$_4$@PDA@ UIO-66-NH$_2$ grafted by organic acids for the intensified cationic dyes adsorption

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Text S1. Chemicals

Anhydrous sodium acetate (NaAc), tris (hydroxymethyl) aminomethane (TRIS), ethylene glycol, methylene blue trihydrate, rhodamine B (RhB)ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), dopamine hydrochloride (DAH), 2-aminoterephthalic acid (H$_2$BDC-NH$_2$), EDC·HCl, DMF, zirconium tetrachloride (ZrCl$_4$), 4-morpholineethane-sulfonic acid (MES), N-hydroxysuccinimide (NHS), tartaric acid (tar), citric acid (citr), methanol and anhydrous ethanol were purchased from Titan company (Songjiang, China). DI water for the solution preparation and material wash was supplied from a PureUP device from Ulupure company (Baoshan, China).

Text S2. General characterization

Field emission SEM images of the prepared adsorbents were acquired from a Leo1550 microscope (Carl Zeiss, Jena, Germany). A FTIR spectrometer (Perkin-Elmer, Norwalk, CT) was utilized for the analysis of the functional groups of adsorbents. Powder X-ray diffractograms of in-house constructed adsorbents were harvested using an X'Pert diffractometer supplied by Panalytical (Almelo, The Netherlands). The curves of magnetization saturation for modified materials at 298 K were obtained using a 7404 magnetometer (Lakeshore, Westerville, CA). N2 adsorption-desorption experiments for pore volume (V$_p$) and specific surface area (S$_a$) were determined on an Autosorb iQ machine (Quantachrome Instruments, Boynton Beach, FL) at 77 K. The pH-dependent surface zeta potentials were evaluated by a ZS nanosizer (Malvern, UK). XPS spectra were measured by a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, MA, USA).

Text S3. Reusability test of the two adsorbents

In a typical desorption process, the MB-loaded mUIO-66-NH-tar and mUIO-66- NH-citr nanoparticles were immersed respectively into a mixture of ethanol and 0.01 M HCl solution (V/V=4:1) at 298K for 1 h. The adsorbents were then transferred into ethanol and 0.01 M NaOH solution (V/V=4:1) for 1 h under constant shaking. The adsorbents were harvested through magnets and washed with about 200-300 mL DI water several times for the next adsorption.

Table S1

Deprotonation of the adsorbents under basic solution conditions.

	mUIO-66-NH-tar		mUIO-66-NH-citr	
Initial pH of aqueous solutions	9.03	11.00	9.03	11.00
Volume of solution (mL)	400	20	400	20
Solution pH after PE[a]	8.43	10.73	8.10	10.66
Mass of adsorbents (mg)	5	5	5	5
Deprotonation capacity (10^{-2} meq/g)	64.19	185.19	75.65	217.16

[a] PE represents the phase equilibrium achieved after immersing adsorbents into aqueous solutions

Table S2

The element surface composition from XPS wide survey spectra.

	Surface composition (at.%)			
	C	N	O	S
mUIO-66-NH-tar	63.69	6.95	29.36	-
mUIO-66-NH-tar-MB	68.62	9.07	19.76	2.56
mUIO-66-NH-citr	63.39	6.68	29.93	-
mUIO-66-NH-citr-MB	64.22	9.05	24.08	2.65

Table S3

Deconvolution results of XPS spectra of the two adsorbents adsorbed before and after MB.

Region	mUIO-66-NH-tar		mUIO-66-NH-tar-MB		mUIO-66-NH-citr		mUIO-66-NH-citr-MB		Assignment
	B.E.	%	B.E.	%	B.E.	%	B.E.	%	
N	398.86	24.49	-	-	398.89	42.19	-	-	$-NH_2$
	399.43	51.02	399.68	64.52	399.80	31.65	399.78	64.51	$-N-C=0$
	400.88	24.49	400.89	18.06	401.28	26.16	400.70	24.52	C-N
	-	-	401.97	17.42	-	-	402.09	10.97	N^+ of quaternary ammonium
O	529.91	13.61	529.68	25.31	529.91	16.52	529.28	15.46	Fe-O
	531.17	31.49	530.71	38.69	531.17	46.08	530.89	55.24	$-COO^-$
	532.47	54.91	531.81	35.99	532.27	37.40	531.84	29.30	O=C O-H

Table S4

Comparison with various adsorbents for ionic dyes.

Adsorbent	Dye type / Adsorbate	Equilibrium time (min)	Q_m (mg/g)	Refs
Fe_3O_4@UIO-66	Anionic / Acid blue 92	5	129.9	1
Fe_3O_4@UIO-66@PPI	Anionic / Direct red 31	5	173.3	1
Fe_3O_4@UIO-66	Cationic / MB	180	205.0	2
UIO-66	Cationic / MB	90	543.5	3
Amino-MIL-101	Cationic / MB	210	762.0	4
Fe_3O_4@$Cu_3(BTC)_2$	Cationic / MB	4	113.7	5
Fe_3O_4/MIL-101	Anionic / Methylene orange	15	80.0	6
$MgFe_2O_4$@MOF	Cationic / Rhodamine	3	219. 8	7
Fe_3O_4/MIL-88A	Anionic / Bromophenol blue	60	76.0	8
mUIO-66-NH-tar	Cationic / MB	50	381.7	This work
mUIO-66-NH-citr	Cationic / MB	50	432.9	This work
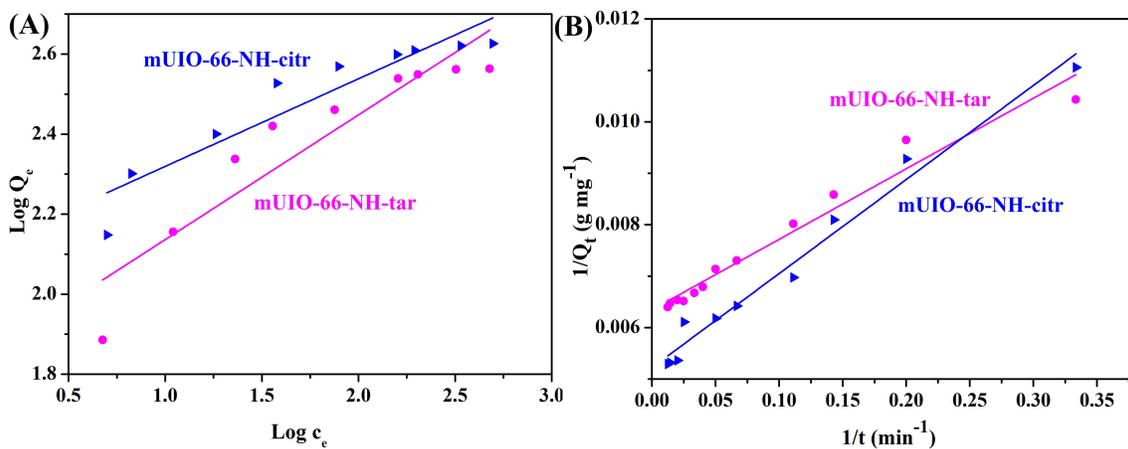
Fig. S1 Adsorption isotherms fitted by by Freundlich model (A) and kinetic curves fitted by PFO equation (B) for MB on two adsorbents.
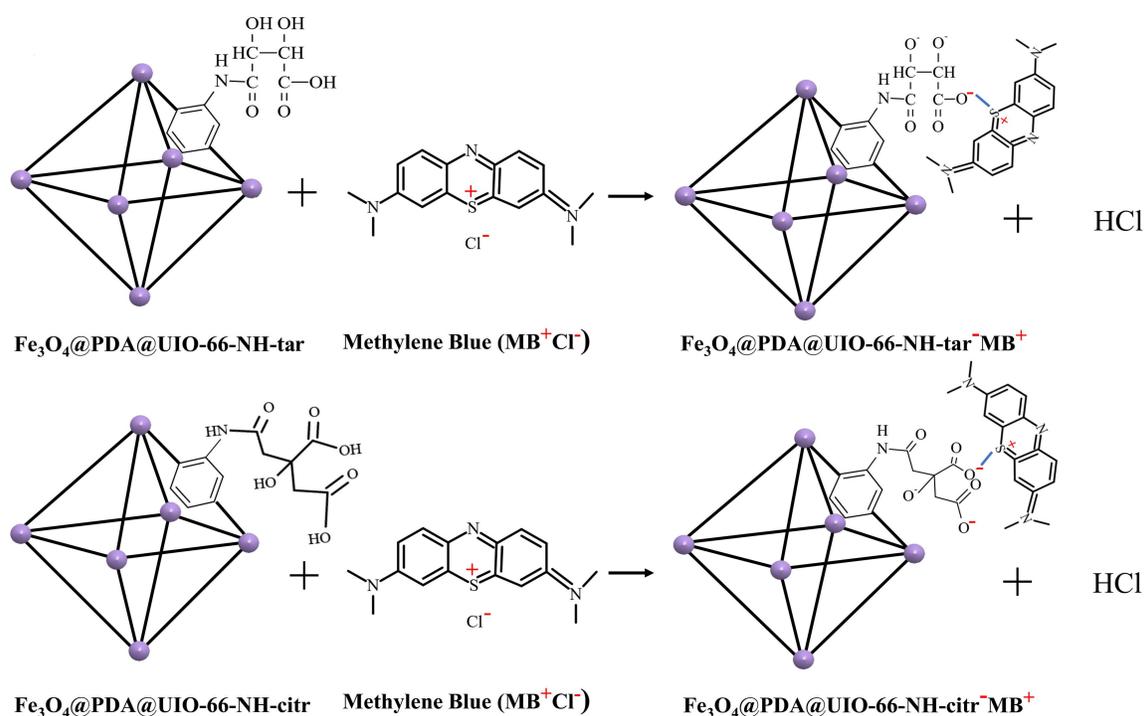
Fig. S2 cation exchange mechanism under pH < pH$_{PZC}$ of the adsorbents.

References

[1] H.S. Far, M. Hasanzadeh, M.S. Nashtaei, M. Rabbani, A. Haji, B.H. Moghadam, *ACS Appl. Mater. Interfaces*, 2020, **12** 25294-25303.

[2] S. Ahmadipouya, M.H. Haris, F. Ahmadijokani, A. Jarahiyan, H. Molavi, F.M. Moghaddam, M. Rezakazemi, M. Arjmand, *J. Mol. Liq.*, 2021, **322**, 114910.

[3] X. Song, P. Yang, D. Wu, P. Zhao, X. Zhao, L. Yang, Y. Zhou, *Chem. Phys.* 2020, **531**, 110655.

[4] E. Haque, V.Lo, A.I. Minett, A.T. Harris, T.L. Church, *J. Mater. Chem. A*, 2014, **2**, 193-203.

[5] H. Sun, H. Zhang, H. Mao, B. Yu, J. Han, G. Bhat, *Environ. Chem. Lett.*, 2018, **17**, 1091-1096.

[6] Z. Jiang, Y. Li, *J. Taiwan Inst. Chem. Eng.*, 2016, **59** 373-379.

[7] H. Tian, J. Peng, T. Lv, C. Sun, H. He, *J. Solid State Chem.* 2018, **257**, 40-48.

[8] Y. Liu, Y. Huang, A. Xiao, H. Qiu, L. Liu, *Nanomaterials*, 2019, **9**, 51.