Electronic Supplementary Material (ESI) for Green Chemistry.

Supplement Information

Construction of tunable pyrylium based porous ionic polymer network for efficient waterborne pollutant treatment

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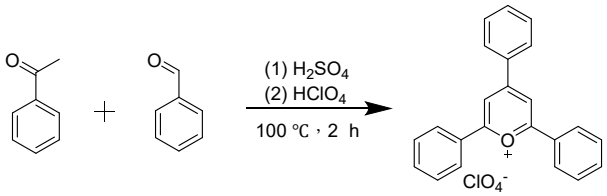
1 Experimental Procedures

1.1 Characterization

Liquid ^{1}H NMR spectra was recorded on Bruker DR X400 spectrometer at room temperature. The FTIR was recorded from in the range of 4000-400 cm^{-1} on a VERTEX 70+HYPERION 2000 spectrum instrument. Solid-state ^{13}C NMR was performed using a Solid State AVANCEIII/WB-400 101 MHz. X-ray photoelectron spectroscopy (XPS) measurements were performed with a EXCALAB 250 XI spectrometer. The specific surface area and porosity of the as prepared samples were measured by N_2 adsorption and desorption at 77 K using a volumetric sorption analyzer (BELsorp-Max). The thermostability of polymers was tested with a Perkin Elmer 4000 simultaneous thermogravimetric analysis (TGA) in the range of 30 to 750 °C at a heating rate of 10 °C min^{-1} under N_2 flow. XRD curves were recorded by a D8 VENTURE spectrometer. The morphologies were observed by scanning electron microscope (SEM, S-4700, Hitachi, Ltd.). The pH values were recorded by SARTORIUS- PB-10 pH METER.

1.2 Synthesis of Monomers

Synthesis of monomer 2,4,6-triphenylpyrylium perchlorate.



^{1}H NMR (300 MHz, DMSO-d6) δ 9.18 (s, 2H), 8.61 (d, *J* = 7.7 Hz, 6H), 7.87 (d, *J* = 7.1 Hz, 3H), 7.84 – 7.76 (m, 6H).

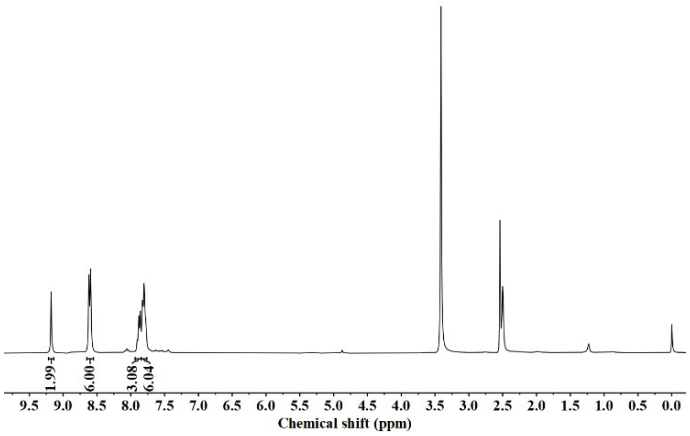
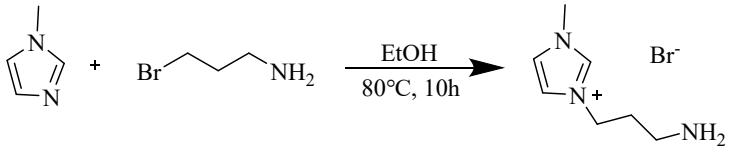


Figure S1. The ^{1}H NMR of monomer 2,4,6-triphenylpyrylium perchlorate.

Synthesis of 1-aminopropyl-3-methylimidazolium bromide and 1-(3-aminopropyl) pyridinium bromide.



^{1}H NMR (400 MHz, DMSO-d6) δ 9.20 (s, 1H), 7.81 (t, *J* = 1.8 Hz, 1H), 7.74 (t, *J* = 1.8 Hz, 1H), 4.30 (t, *J* = 6.9 Hz, 2H), 3.86 (s, 3H), 2.82 (q, J = 6.8 Hz, 2H), 2.10 (p, *J* = 7.1 Hz, 2H).

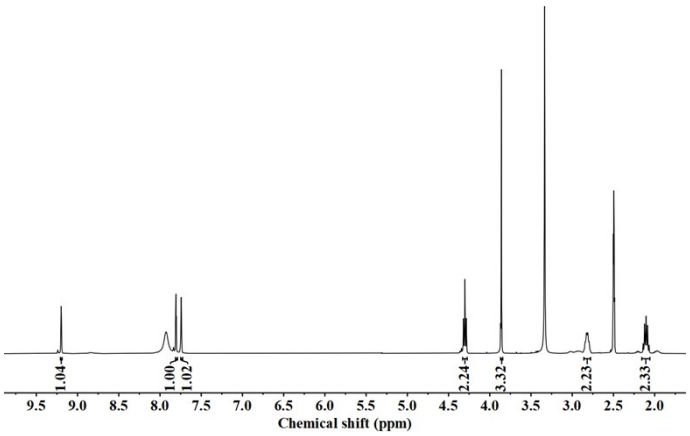
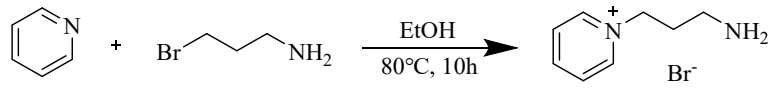


Figure S2. The ^{1}H NMR of 1-aminopropyl-3-methylimidazolium bromide.



^{1}H NMR (300 MHz, DMSO-d6) δ 9.15 (d, *J* = 5.9 Hz, 2H), 8.65 (t, *J* = 8.0 Hz, 1H), 8.21 (t, *J* = 6.9 Hz, 2H), 7.92 (s, 3H), 4.74 (t, *J* = 7.1 Hz, 2H), 2.86 (t, *J* = 6.7 Hz, 2H), 2.26 (q, *J* = 7.6 Hz, 2H).

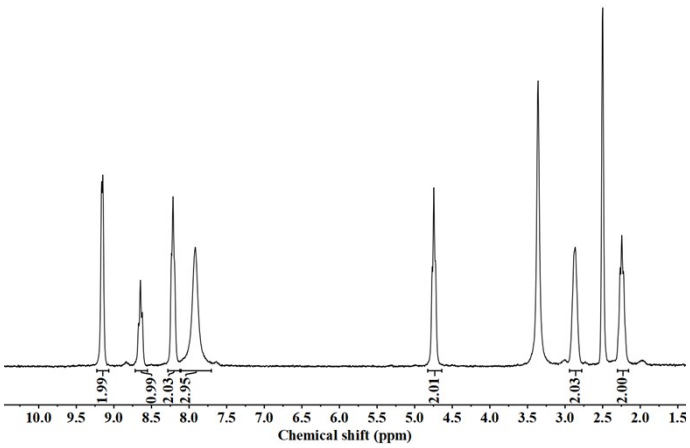
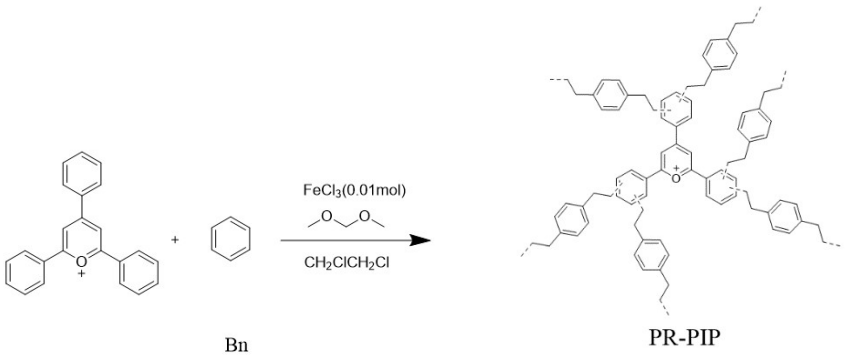


Figure S3. The ^{1}H NMR of 1-(3-aminopropyl) pyridinium bromide.

Table S1. Screening and optimization of synthesis conditions.



Item	Bn/mL	FDA/mL	Solvent /mL	Specific surface area（m^2/g）
1	0.14	0.2	2	934
2	0.14	0.4	2	995
3	0.14	0.6	2	993
4	0.14	0.9	2	1101
5	0.14	1.2	2	992
6	0.09	0.4	2	969
7	0.18	0.4	2	872
8	0.14	0.4	4	1024
9	0.14	0.4	8	870

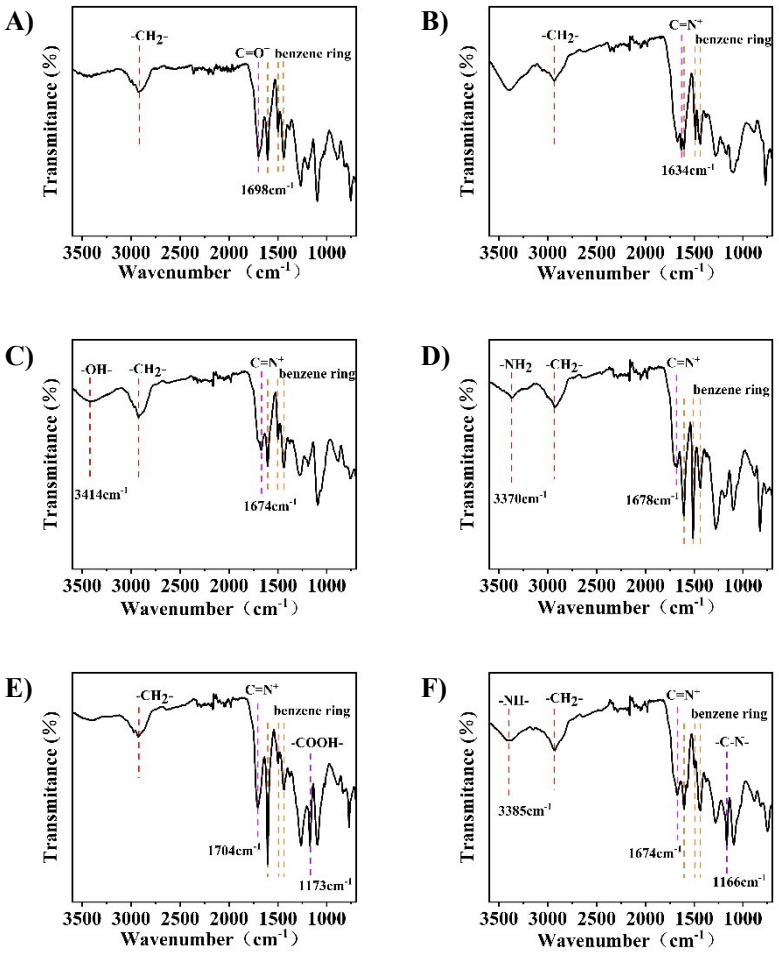


Figure S4. FT-IR of (A) PR-PIP (B) PY-PY-PIP (C) OH-PY-PIP (D) NH-PY-PIP (E) COOH-PY-PIP (F) IM-PY-PIP.

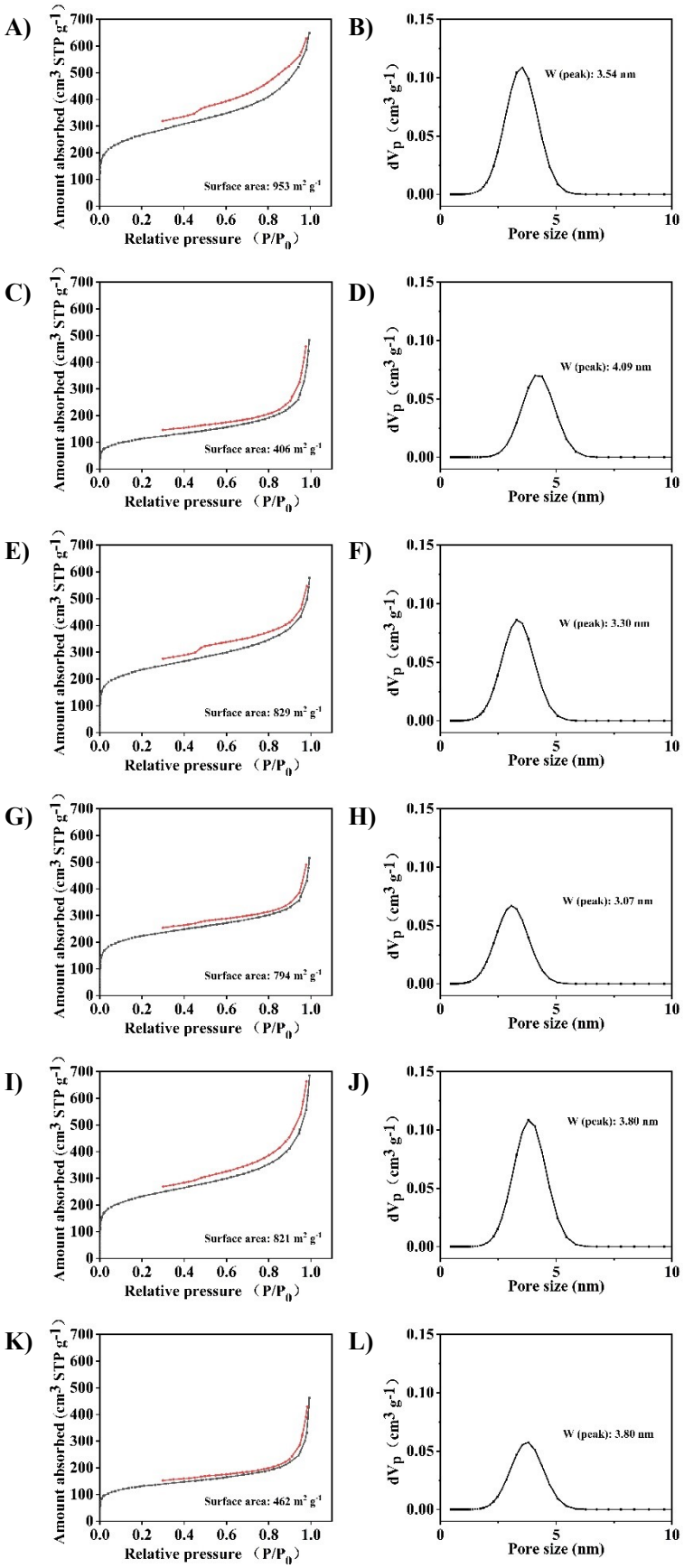


Figure S5. N_2 sorption/desorption isotherm analysis of (A) PR-PIP (C) PY-PY-PIP (E) OH-

PY-PIP (G) NH-PY-PIP (I) COOH-PY-PIP (K) IM-PY-PIP. Pore size distribution in (B) PR-PIP (D) PY-PY-PIP (F) OH-PY-PIP (H) NH-PY-PIP (J) COOH-PY-PIP (L) IM-PY-PIP.

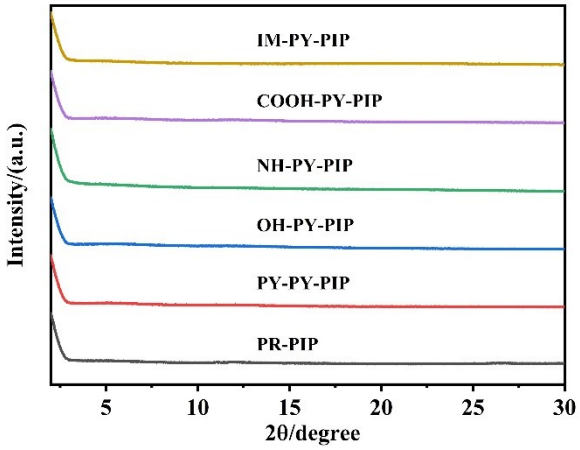


Figure S6. XRD patterns of PR-PIP, PY-PY-PIP, OH-PY-PIP, NH-PY-PIP, COOH-PY-PIP and IM-PY-PIP.

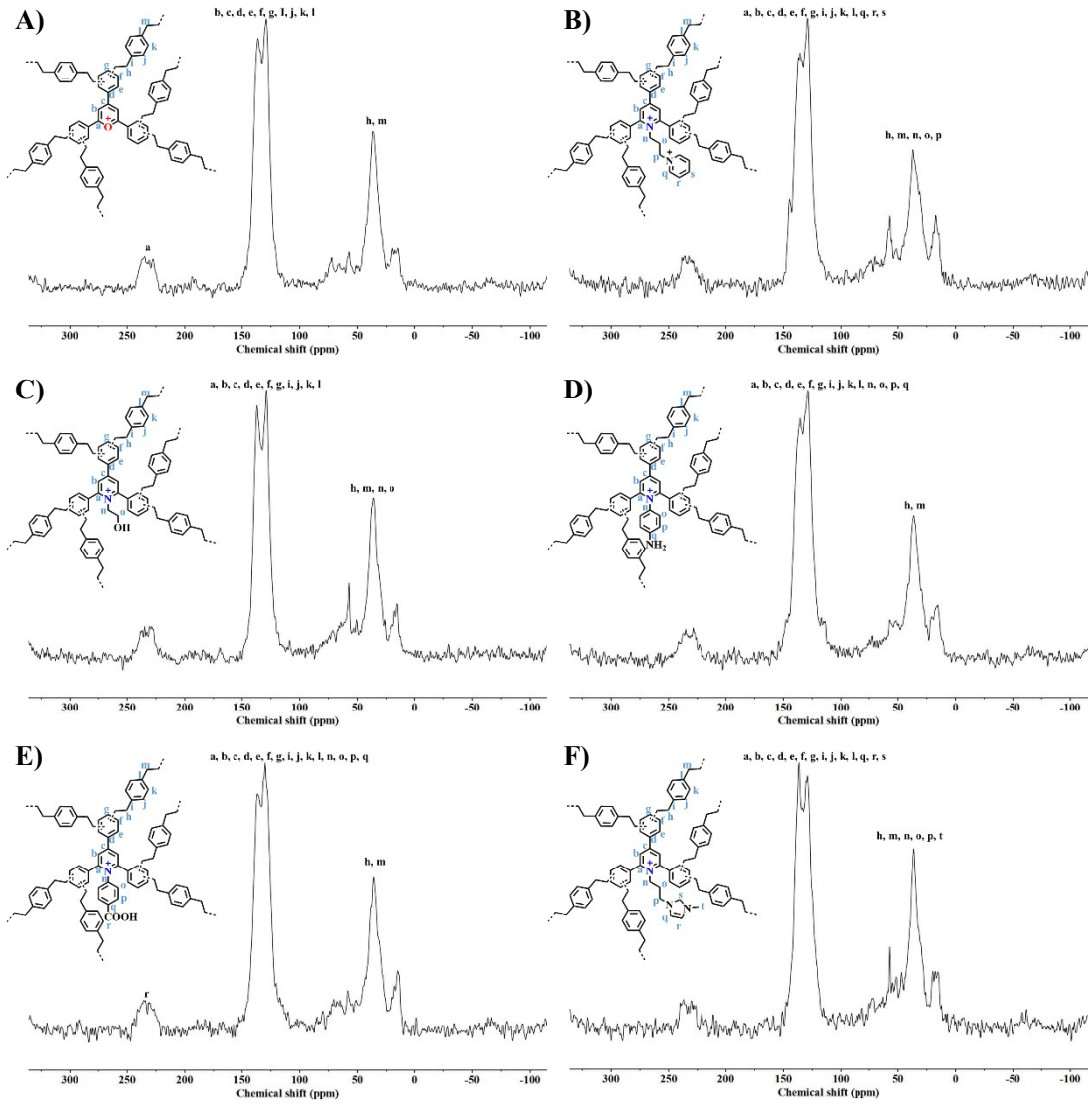


Figure S7. Solid-state ^{1}C NMR of (A) PR-PIP (B) PY-PY-PIP (C) OH-PY-PIP (D) NH-PY-PIP (E) COOH-PY-PIP (F) IM-PY-PIP.

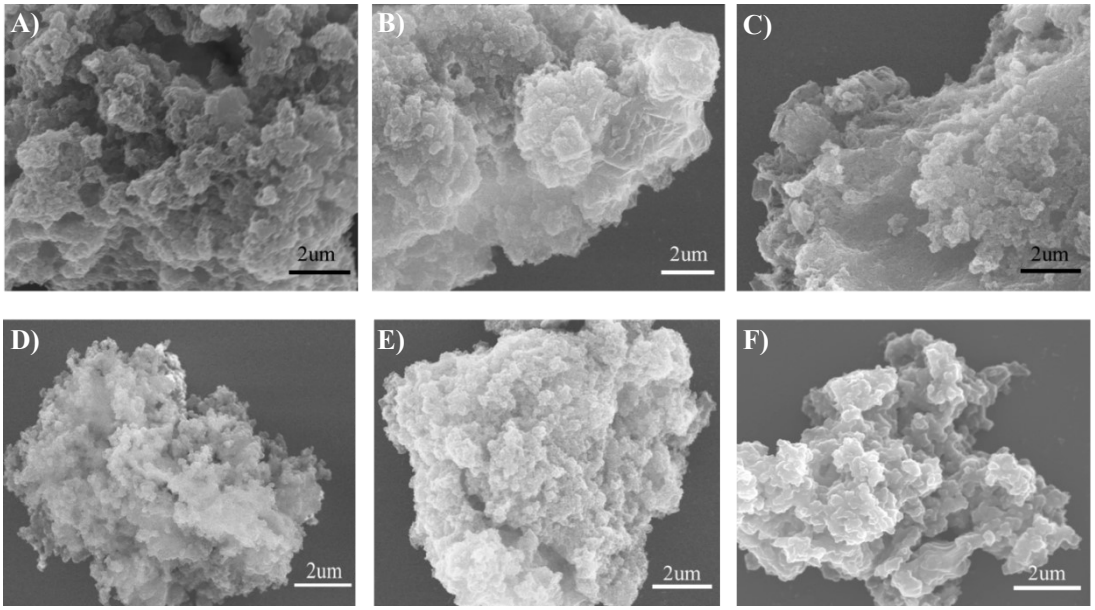


Figure S8. Scanning electron microscopy (SEM) images of (A) PR-PIP (B) PY-PY-PIP (C) OH-PY-PIP (D) NH-PY-PIP (E) COOH-PY-PIP (F) IM-PY-PIP.

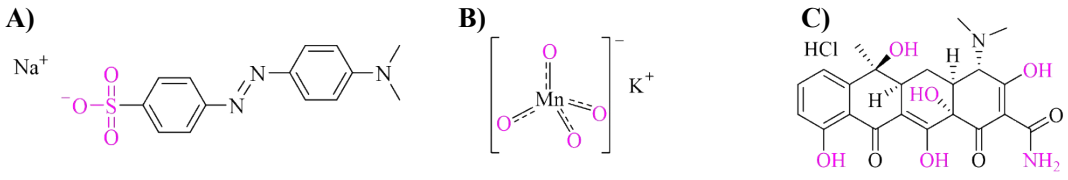


Figure S9. The structure of (A) Methyl Orange (B) Potassium Permanganate (C) Tetracycline Hydrochloride.

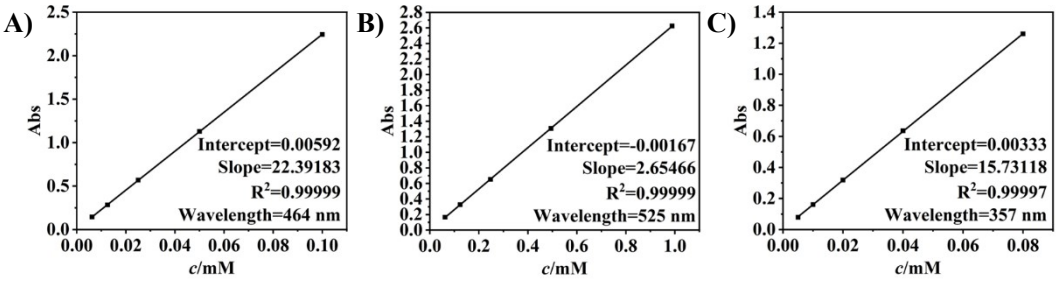


Figure S10. Absorbance-concentration standard curve of (A) Methyl Orange (B) Potassium Permanganate (C) Tetracycline Hydrochloride.

Table S2. Concentration of MO in adsorption experiments.

adsorbents		PR-PIP	PY-PY-PIP	OH-PY-PIP	NH-PY-PIP	COOH-PY-PIP	IM-PY-PIP
c (mM)	0 min	8.7940×10^{-2}	8.7940×10^{-2}	8.7940×10^{-2}	8.7940×10^{-2}	8.7940×10^{-2}	8.7940×10^{-2}
	20 min	6.6720×10^{-2}	4.5910×10^{-2}	5.6360×10^{-2}	5.9090×10^{-2}	6.4710×10^{-2}	3.9480×10^{-2}
	40 min	6.0610×10^{-2}	4.1400×10^{-2}	5.3100×10^{-2}	5.7700×10^{-2}	6.1990×10^{-2}	3.4930×10^{-2}
	60 min	5.7700×10^{-2}	3.9620×10^{-2}	5.1940×10^{-2}	5.5340×10^{-2}	6.1100×10^{-2}	3.1580×10^{-2}
	90 min	5.4980×10^{-2}	3.8140×10^{-2}	5.0870×10^{-2}	5.3820×10^{-2}	6.0520×10^{-2}	2.8410×10^{-2}
	120 min	5.3860×10^{-2}	3.7070×10^{-2}	4.9220×10^{-2}	5.2880×10^{-2}	6.0250×10^{-2}	2.8010×10^{-2}
	180 min	5.2660×10^{-2}	3.6710×10^{-2}	4.7250×10^{-2}	5.1760×10^{-2}	5.9850×10^{-2}	2.6620×10^{-2}
	300 min	5.0830×10^{-2}	3.6400×10^{-2}	4.6630×10^{-2}	5.0780×10^{-2}	5.9000×10^{-2}	2.5680×10^{-2}
	420 min	5.0920×10^{-2}	3.6220×10^{-2}	4.6090×10^{-2}	5.1500×10^{-2}	5.9710×10^{-2}	2.6040×10^{-2}
	600 min	5.0020×10^{-2}	3.6800×10^{-2}	4.5420×10^{-2}	5.1590×10^{-2}	5.9310×10^{-2}	2.6400×10^{-2}

Table S3. Concentration of PP in adsorption experiments.

adsorbents		PR-PIP	PY-PY-PIP	OH-PY-PIP	NH-PY-PIP	COOH-PY-PIP	IM-PY-PIP
c (mM)	0 min	6.7944×10^{-1}	6.7944×10^{-1}	6.7944×10^{-1}	6.7944×10^{-1}	6.7944×10^{-1}	6.7944×10^{-1}
	20 min	6.1653×10^{-1}	5.0163×10^{-1}	5.3930×10^{-1}	4.1236×10^{-1}	5.6567×10^{-1}	4.8242×10^{-1}
	40 min	5.8940×10^{-1}	4.7037×10^{-1}	5.1407×10^{-1}	3.5774×10^{-1}	5.4495×10^{-1}	4.6208×10^{-1}
	60 min	5.7170×10^{-1}	4.5040×10^{-1}	4.9787×10^{-1}	3.2421×10^{-1}	5.3290×10^{-1}	4.5040×10^{-1}
	90 min	5.4872×10^{-1}	4.3044×10^{-1}	4.8205×10^{-1}	2.9596×10^{-1}	5.2047×10^{-1}	4.3647×10^{-1}
	120 min	5.2876×10^{-1}	4.1311×10^{-1}	4.6622×10^{-1}	2.6356×10^{-1}	5.0653×10^{-1}	4.2064×10^{-1}
	180 min	5.0013×10^{-1}	3.8411×10^{-1}	4.3684×10^{-1}	2.2702×10^{-1}	4.8581×10^{-1}	4.0181×10^{-1}
	300 min	4.6208×10^{-1}	3.4455×10^{-1}	3.9428×10^{-1}	1.7240×10^{-1}	4.5266×10^{-1}	3.7092×10^{-1}

420 min	4.4551×10^{-1}	3.1366×10^{-1}	3.6113×10^{-1}	1.3285×10^{-1}	4.2893×10^{-1}	3.4041×10^{-1}
600 min	4.2140×10^{-1}	2.7938×10^{-1}	3.2459×10^{-1}	9.9320×10^{-1}	4.0558×10^{-1}	3.1253×10^{-1}

Table S4. Concentration of TH in adsorption experiments.

adsorbents		PR-PIP	PY-PY-PIP	OH-PY-PIP	NH-PY-PIP	COOH-PY-PIP	IM-PY-PIP
c (mM)	0 min	1.5240×10^{-2}	1.5240×10^{-2}	1.5240×10^{-2}	1.5240×10^{-2}	1.5240×10^{-2}	1.5240×10^{-2}
	20 min	4.5600×10^{-3}	7.8000×10^{-3}	3.0300×10^{-3}	5.0600×10^{-3}	2.9000×10^{-3}	4.4900×10^{-3}
	40 min	2.6500×10^{-3}	7.0300×10^{-3}	1.9500×10^{-3}	4.4300×10^{-3}	2.3900×10^{-3}	4.1100×10^{-3}
	60 min	1.9500×10^{-3}	7.1600×10^{-3}	1.6300×10^{-3}	4.1100×10^{-3}	2.0800×10^{-3}	3.5400×10^{-3}
	90 min	1.5700×10^{-3}	7.4200×10^{-3}	1.5000×10^{-3}	3.7900×10^{-3}	2.0100×10^{-3}	3.6000×10^{-3}
	120 min	9.3233×10^{-4}	8.7500×10^{-3}	1.1900×10^{-3}	3.2800×10^{-3}	1.6300×10^{-3}	4.4300×10^{-3}
	180 min	4.8736×10^{-4}	5.8300×10^{-3}	1.1200×10^{-3}	3.1600×10^{-3}	1.5700×10^{-3}	4.2400×10^{-3}
	300 min	3.6022×10^{-4}	5.3200×10^{-3}	8.6876×10^{-4}	2.5900×10^{-3}	1.4400×10^{-3}	1.8200×10^{-3}
	420 min	4.2379×10^{-4}	4.9400×10^{-3}	8.6876×10^{-4}	2.3300×10^{-3}	1.1900×10^{-3}	2.7800×10^{-3}
	600 min	6.1449×10^{-4}	6.4600×10^{-3}	8.0520×10^{-4}	2.1400×10^{-3}	1.0600×10^{-3}	3.9200×10^{-3}

adsorbents	q_t (mg/g)								
	20 min	40 min	60 min	90 min	120 min	180 min	300 min	420 min	600 min
PR-PIP	69.5	89.5	99.0	107.9	111.6	115.5	121.5	121.2	124.1
PY-PY-PIP	137.6	152.3	158.2	163.0	166.5	167.7	168.7	169.3	167.4
OH-PY-PIP	103.4	114.0	117.8	121.3	126.7	133.2	135.2	137.0	139.2
NH-PY-PIP	94.4	99.0	106.7	111.7	114.8	118.4	121.6	119.3	119.0
COOH-PY-PIP	76.0	84.9	87.9	89.8	90.6	91.9	94.7	92.4	93.7
IM-PY-PIP	158.6	173.5	184.5	194.9	196.2	200.7	203.8	202.6	201.4

Table S5. q_t of different absorbents for MO adsorption.

Table S6. q_t of different absorbents for PP adsorption.

adsorbents	q_t (mg/g)								
	20 min	40 min	60 min	90 min	120 min	180 min	300 min	420 min	600 min
PR-PIP	99.4	142.3	170.3	206.6	238.1	283.4	343.5	369.7	407.8
PY-PY-PIP	281.0	330.4	362.0	393.5	420.9	466.7	529.2	578.1	632.2
OH-PY-PIP	221.5	261.3	286.9	311.9	337.0	383.4	450.6	503.0	560.8
NH-PY-PIP	422.1	508.4	561.4	606.0	657.2	715.0	801.3	863.8	916.8
COOH-PY-PIP	179.8	212.5	231.6	251.2	273.3	306.0	358.4	395.9	432.8
IM-PY-PIP	311.4	343.5	362.0	384.0	409.0	438.7	487.6	535.8	579.8

Table S7. q_t of different absorbents for TH adsorption.

adsorbents	q_t (mg/g)								
	20 min	40 min	60 min	90 min	120 min	180 min	300 min	420 min	600 min
PR-PIP	25.7	30.3	32.0	32.9	34.4	35.5	35.8	35.6	35.2
PY-PY-PIP	17.9	19.7	19.4	18.8	15.6	22.6	23.9	24.8	21.1
OH-PY-PIP	29.4	32.0	32.7	33.0	33.8	34.0	34.6	34.6	34.7
NH-PY-PIP	24.5	26.0	26.8	27.5	28.8	29.0	30.4	31.0	31.5
COOH-PY-PIP	29.7	30.9	31.6	31.8	32.7	32.9	33.2	33.8	34.1
IM-PY-PIP	25.8	26.8	28.1	28.0	26.0	26.4	32.3	30.0	27.2

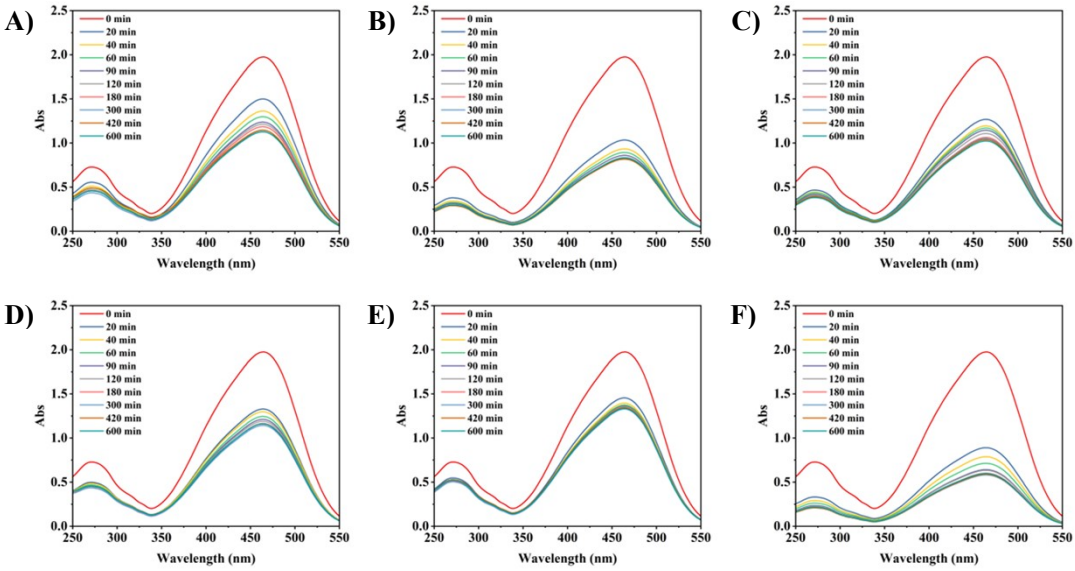


Figure S11. UV-Vis spectroscopy in the presence of (A) PR-PIP (B) PY-PY-PIP (C) OH-PY-PIP (D) NH-PY-PIP (E) COOH-PY-PIP (F) IM-PY-PIP for the water solution of Methyl Orange.

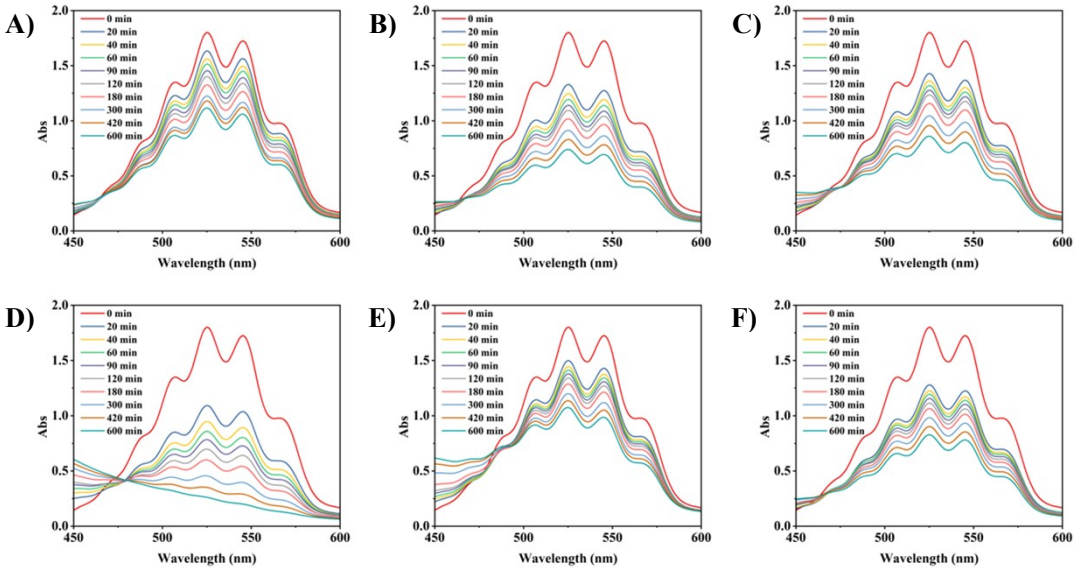


Figure S12. UV-Vis spectroscopy in the presence of (A) PR-PIP (B) PY-PY-PIP (C) OH-PY-PIP (D) NH-PY-PIP (E) COOH-PY-PIP (F) IM-PY-PIP for the water solution of Potassium Permanganate.

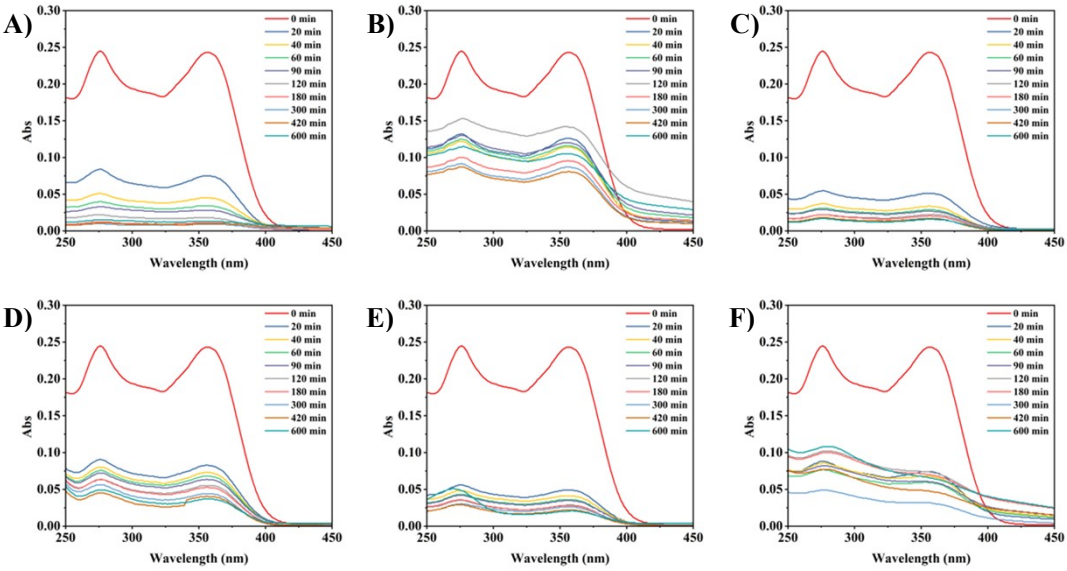


Figure S13. UV-Vis spectroscopy in the presence of (A) PR-PIP (B) PY-PY-PIP (C) OH-PY-PIP (D) NH-PY-PIP (E) COOH-PY-PIP (F) IM-PY-PIP for the water solution of Tetracycline Hydrochloride.

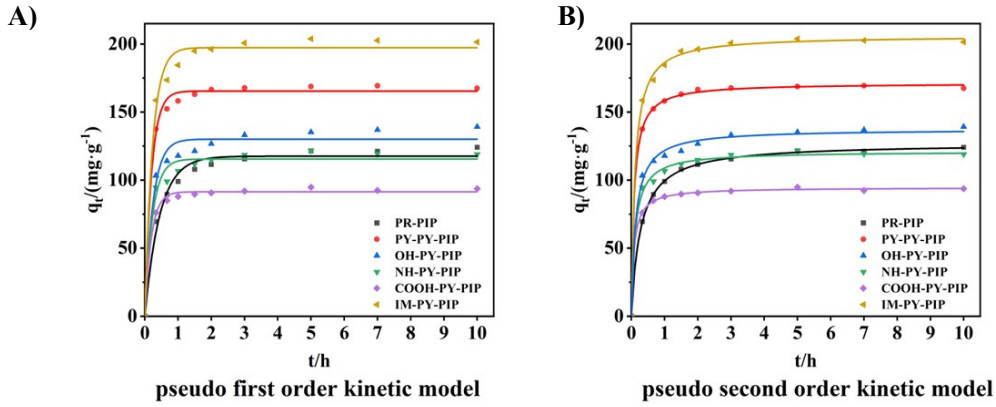


Figure S14. Pseudo (A) first (B) second order kinetic model of six samples for MO adsorption.

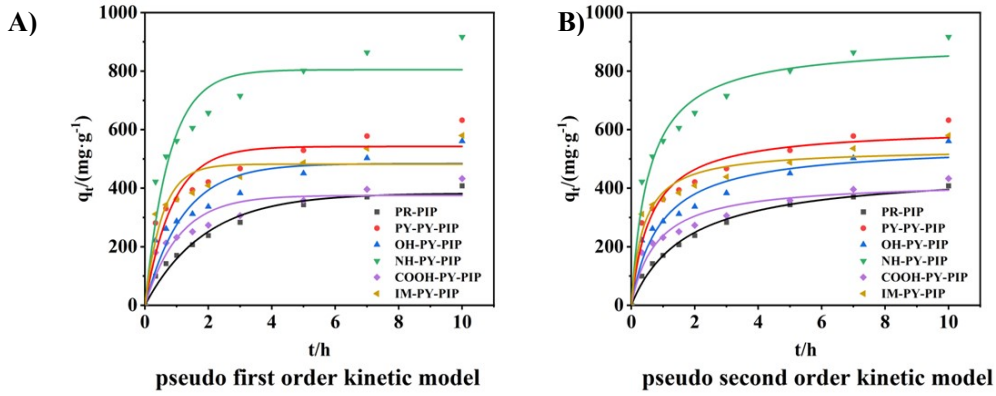


Figure S15. Pseudo (A) first (B) second order kinetic model of six samples for PP adsorption.

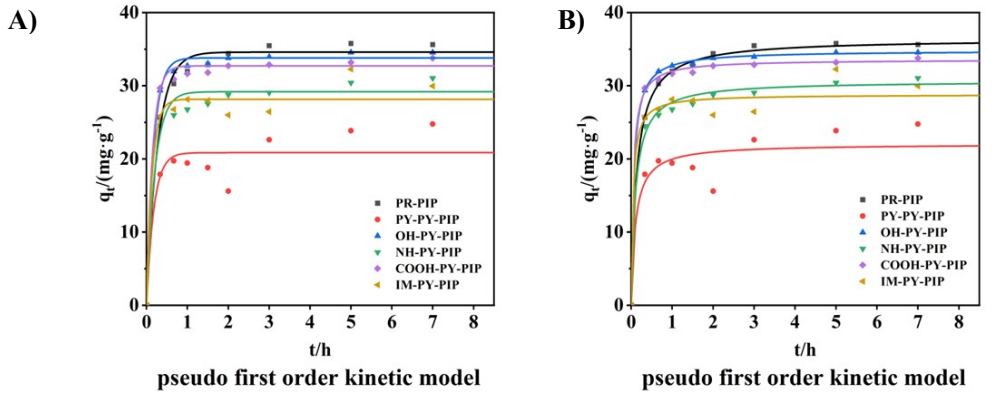


Figure S16. Pseudo (A) first (B) second order kinetic model of six samples for TH adsorption.

Table S8. Kinetic parameters for the adsorption of two models for MO adsorption.

adsorbents	pseudo first order kinetic model			pseudo second order kinetic model			q_{exp} (mg/g)
	k_1 (1/h)	q_e (mg/g)	R^2	k_2 (g/mg•h)	q_e (mg/g)	R^2	
PR-PIP	2.2	118	0.982	0.028	127	1.000	124.3
PY-PY-PIP	5.0	165	0.994	0.072	171	1.000	166.3
OH-PY-PIP	4.1	130	0.971	0.056	137	0.994	140.1
NH-PY-PIP	4.3	115	0.977	0.074	121	0.995	119.7
COOH-PY-PIP	5.1	91	0.994	0.132	95	0.999	92.5
IM-PY-PIP	4.3	197	0.987	0.046	206	0.999	200.1

Table S9. Kinetic parameters for the adsorption of two models for PP adsorption.

adsorbents	pseudo first order kinetic model			pseudo second order kinetic model			q_{exp} (mg/g)
	k_1 (1/h)	q_e (mg/g)	R^2	k_2 (g/mg•h)	q_e (mg/g)	R^2	
PR-PIP	0.5	383	0.974	0.0012	464	0.992	520.9
PY-PY-PIP	1.2	542	0.883	0.0028	608	0.952	736.4
OH-PY-PIP	0.8	484	0.908	0.0020	550	0.938	676.3
NH-PY-PIP	1.3	805	0.908	0.0020	898	0.969	948.9
COOH-PY-PIP	0.9	376	0.877	0.0030	424	0.944	495.9
IM-PY-PIP	1.8	482	0.859	0.0048	535	0.938	645.3

Table S10. Kinetic parameters for the adsorption of two models for TH adsorption.

adsorbents	pseudo first order kinetic model			pseudo second order kinetic model			q_{exp} (mg/g)
	k_1 (1/h)	q_e (mg/g)	R^2	k_2 (g/mg•h)	q_e (mg/g)	R^2	
PR-PIP	3.6	35	0.988	0.199	36	0.999	36.2
PY-PY-PIP	5.6	21	0.862	0.310	31	0.992	24.6
OH-PY-PIP	5.8	34	0.995	0.592	34	0.998	36.1
NH-PY-PIP	4.8	29	0.970	0.803	29	0.963	34.6
COOH-PY-PIP	6.8	33	0.992	0.434	22	0.887	35.8
IM-PY-PIP	7.2	28	0.959	0.461	35	1.000	20.9

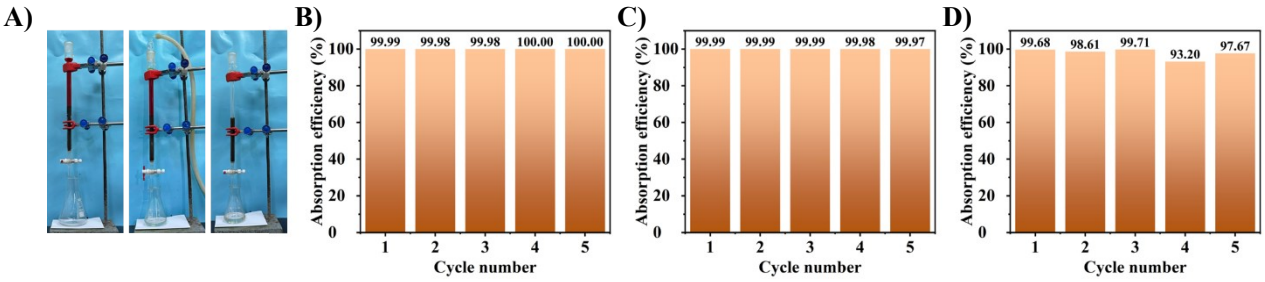


Figure S17. (A) Presentation of waste water treatment and the reusability of (B) 200 mg PY-PY-PIP for the adsorption of Methyl Orange (initial concentrations: 0.56 mM, volume: 100 mL), (C) 500 mg NH-PY-PIP for the adsorption of Potassium Permanganate (initial concentrations: 90.62 mM, volume: 40 mL), (D) 500 mg PR-PIP for the adsorption of Tetracycline Hydrochloride (initial concentrations: 0.37 mM, volume: 100 mL).

Table S11. Maximum adsorption capacity (q_e) of various adsorbents for MO.

Entry	Adsorbent	q_e (mg/g)	pH	reusability	Refs
1	MIL-100(Fe)[a]	1045.2	5	-	[1]
2	MIL-101(Cr)[b]	211.8	5	-	[1]
3	MOF-235[c]	501	-	-	[2]
4	FeOCl-MoS_2	1615.11	-	82.1% (5 times)	[3]
5	Pal/UiO-66	340	5	91% (5 times)	[4]
6	MIL-53(Fe，Cu)	294.43	7	70% (5 times)	[5]
7	PIL-GO/TiO2/Fe3O4 composites	67.88	3	66% (4 times)	[6]
8	**IM-PY-PIP**	**200.1**	**8.25[d]**	**99% (5 times)**	**This work**

[a] After 24 h, [b] after 22days, [c] 45 ℃, [d] unregulated pH.

Table S12. Maximum adsorption capacity (q_e) of various adsorbents for PP.

Entry	Adsorbent	q_e (mg/g)	pH	reusability	Refs
1	FVESP[a]	1428.57	1.5	-	[7]
2	NH2/MCM-41/NTAA	156	5	90% (5 times)	[8]
3	CuS[b]	1250.00	1.5	-	[9]
4	SiO2@NBDBIA	330	-	-	[10]
5	**NH-PY-PIP**	**948.9**	**6.27[c]**	**99%**	**This work**

[a] 45 ℃, [b] 45 ℃, [c] unregulated pH.

Table S13. Maximum adsorption capacity (q_e) of various adsorbents for TH.

Entry	Adsorbent	q_e (mg/g)	pH	reusability	Refs
1	nanocrystalline cellulose	7.73	5	89.6% (3 time)	[11]
2	WS300	17.19	6	-	[12]
3	WS450	21.19	6	-	[12]
4	WS600	21.29	6	-	[12]
5	BMWS300	51.04	6	-	[12]
6	BMWS450	96.69	6	-	[12]
7	BMWS600	75.95	6	-	[12]
8	biochar	57.66	6	-	[13]
9	FeB-11	190.84	6	29% (5 times)	[13]
10	101(Fe)	420.6	8	83% (3 times)	[14]
11	88A(Fe)	379.7	8	84% (3 times)	[14]
12	53(Fe)	254.9	8	78% (3 times)	[14]
13	MOF-525(Co)	461.2	-	-	[13]
14	Zr/Fe-MOFs/GO	760	7	51% (5 times)	[15]
15	Zr/Fe-MOFs	681	7	33% (5times)	[15]
16	**PR-PIP**	**36.2**	**5.86[a]**	**97%**	**This work**

[a] unregulated pH.

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