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Functional group effect of Isoreticular metal-organic frameworks on heavy metal ion adsorption

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1. Experimental Section

1.1. Synthesis of the ligands

1.1.1. Synthesis of bpfb and bpfn

The simple route for the synthesis of amide-containing compounds is the coupling of an acid chloride with an amine group. Note here that the acid chloride-amine reaction is exothermic. Therefore, all organic reactions performed in this study were carried out at low temperature in the presence of triethylamine (TEA) to capture *in situ* the generated side product HCl (Fig. S1).

1,4-phenylenediamine (1.081 g; 10 mmol; for bpfb) and 1,5-diaminonaphthalene (1.580 g; 10 mmol; for bpfn) were dissolved in 50 ml of dry THF containing 2.84 ml of TEA (20.4 mmol). Then, isonicotinoyl chloride hydrochloride (3.560 g, 20 mmol) was added into these solutions and heated under reflux for 24 h. Both reactions were then treated as above indicated for the synthesis of bpta. The yellowish powders were filtered and dried, obtaining the pure ligands in ca. 82% (bpfb) and 87 % (bpfn) yields.

1.1.2. Synthesis of bpmb and bpmn

4-pyridinecarboxaldehyde (1.88 ml; 20 mmol) was initially dissolved in 100 ml of CH_2Cl_2. This solution was added dropwise into a solution of *p*-phenylenediamine (1.081 g; 10 mmol; for **bpmb**) and 1,5-diaminonaphthalene (1.580 g; 10 mmol; for **bpmn**) in 100 ml of EtOH. Two drops of formic acid were then added to each reaction, and the mixtures were stirred at room temperature for 4 h (Fig. S1). The resulting yellow solids were collected by filtration and washed several times with ethanol-ether (1:1). Yields: 79 % (**bpmb**) and 76 % (**bpmn**).

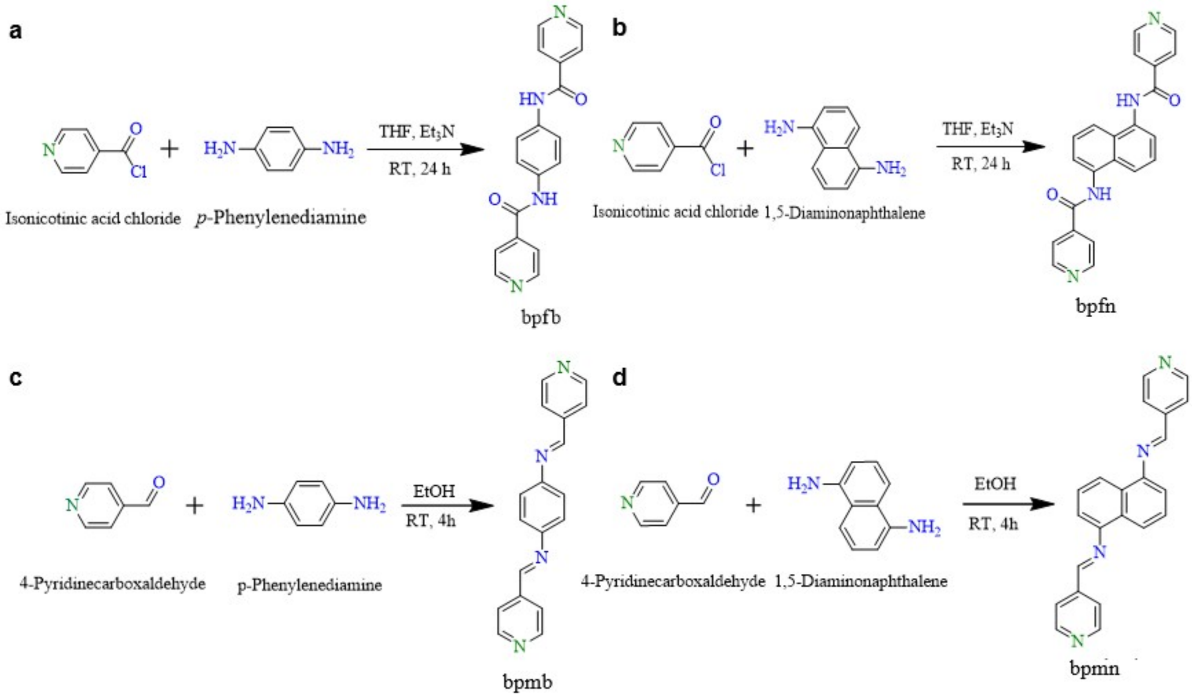


Figure S1. Synthesis procedure of amide containing ligands; (a-d) bpfb, bpfn, bpmb, and bpmn, respectively.

1.2. Synthesis of the MOFs

1.2.1. Solid state synthesis of TMU-6

$[Zn(oba)(4\text{-}bpmb)_{0.5}]\cdot(DMF)_{1.5}$ was synthesized by grinding $Zn(OAc)_2\cdot 2H_2O$ (1 mmol), H_2oba (1 mmol) and bpmb (0.5 mmol) by hand for 15 minutes. The resulting powder was washed with small amounts of DMF in order to remove any unreacted starting material. The product was heated at

100 °C for 8 h before and after washing with DMF (yield: 90%). IR data (KBr pellet, ν/cm^{-1}): 654(m), 773(m), 878(m), 1016(m), 1089(m), 1159(s), 1233(vs), 1404(vs), 1499(m), 1609(vs), 1675(s) and 3421(w-br).

1.2.2. Solid state synthesis of TMU-21

$[Zn(oba)(bpmn)_{0.5}]\cdot(DMF)_{1.5}$ was synthesized by grinding $Zn(OAc)_2\cdot2H_2O$ (1 mmol), H_2oba (1 mmol) and bpmn ligand (0.5 mmol) by hand for 30 minutes. The resulting powder was washed with small amounts of DMF in order to remove any unreacted starting materials. For activation, the product was heated at 120 °C for 12 h after washing with DMF (yield: 90%). IR data (KBr pellet, ν/cm^{-1}): 654(m), 763(m), 876(m), 1017(m), 1095(m), 1157(s), 1238(vs), 1404(vs), 1504(m), 1610(vs), 1671(s) and 3416(w).

1.2.3. Solid state synthesis of TMU-23

$[Zn_2(oba)_2(bpfb)]\cdot(DMF)_5$ was synthesized after grinding $Zn(OAc)_2\cdot2H_2O$ (0.64 mmol), H_2oba (1 mmol) and bpfb (1 mmol) by hand for 20 minutes. The resulting powder was washed with small amounts of DMF in order to remove any unreacted reactant, and then dried in air overnight (yield: 85%). IR data (KBr pellet, ν/cm^{-1}): 1673 (vs), 1597 (vs), 1540 (m), 1510 (m), 1399 (vs), 1309 (m), 1220 (vs), 1159 (s), 1088 (m), 1067 (m), 1014 (m), 801 (m), 658 (m), 524 (m). Elemental analysis (%) calculated on solvent free sample: C, 57.46; H, 3.15; N, 5.83; found: C, 57.00; H, 3.10; N, 5.65.

1.2.4. Solid state synthesis of TMU-24

$[Zn_2(oba)_2(bpfn)]\cdot(DMF)_2$ was also isolated by grinding $Zn(OAc)_2\cdot2H_2O$ (0.64 mmol), H_2oba (1 mmol) and bpfn (1 mmol) by hand for 20 minutes. The resulting powder was washed with small amounts of DMF in order to remove any unreacted reactant, and then dried in air overnight (yield: 80%). IR data (KBr pellet, ν/cm^{-1}): 1667 (vs), 1595 (vs), 1570 (m), 1505 (s), 1386 (vs), 1235(s), 1158 (vs), 1089 (m), 1065 (m), 1015 (m), 878 (m), 659 (m), 522 (m). Elemental analysis (%) calculated on solvent free sample: C, 59.37; H, 3.19; N, 5.54; found: C, 57.10; H, 3.12; N, 5.01.

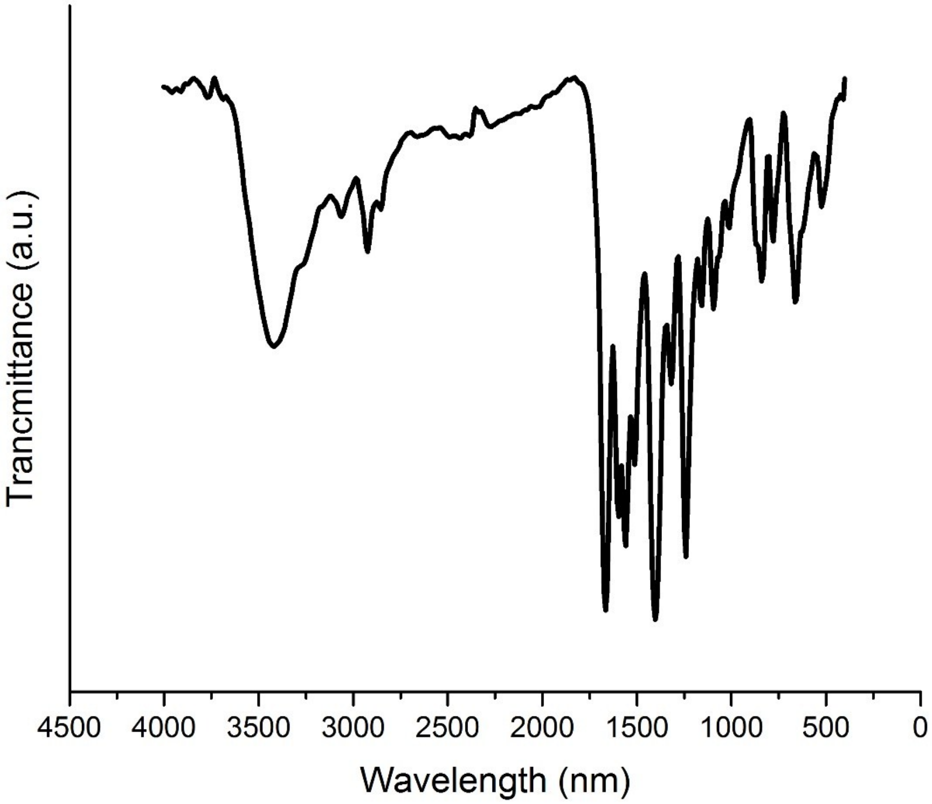


Figure S2. FT-IR spectra of TMU- 23

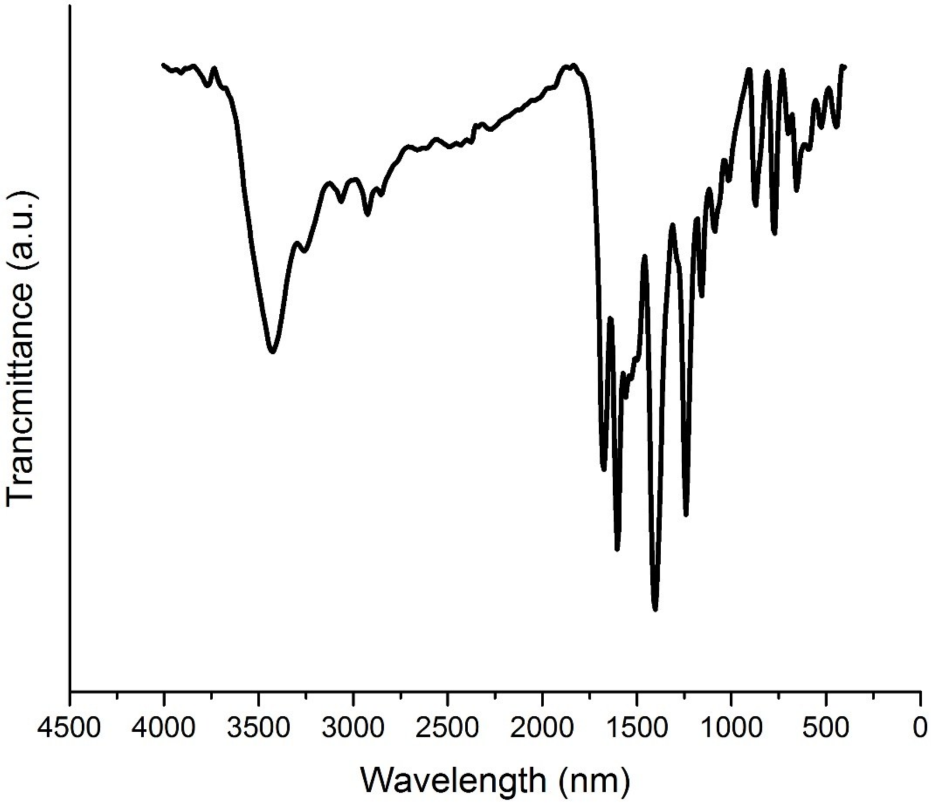


Figure S3. FT-IR spectra of as-synthesized (black) and activated (red) TMU-24

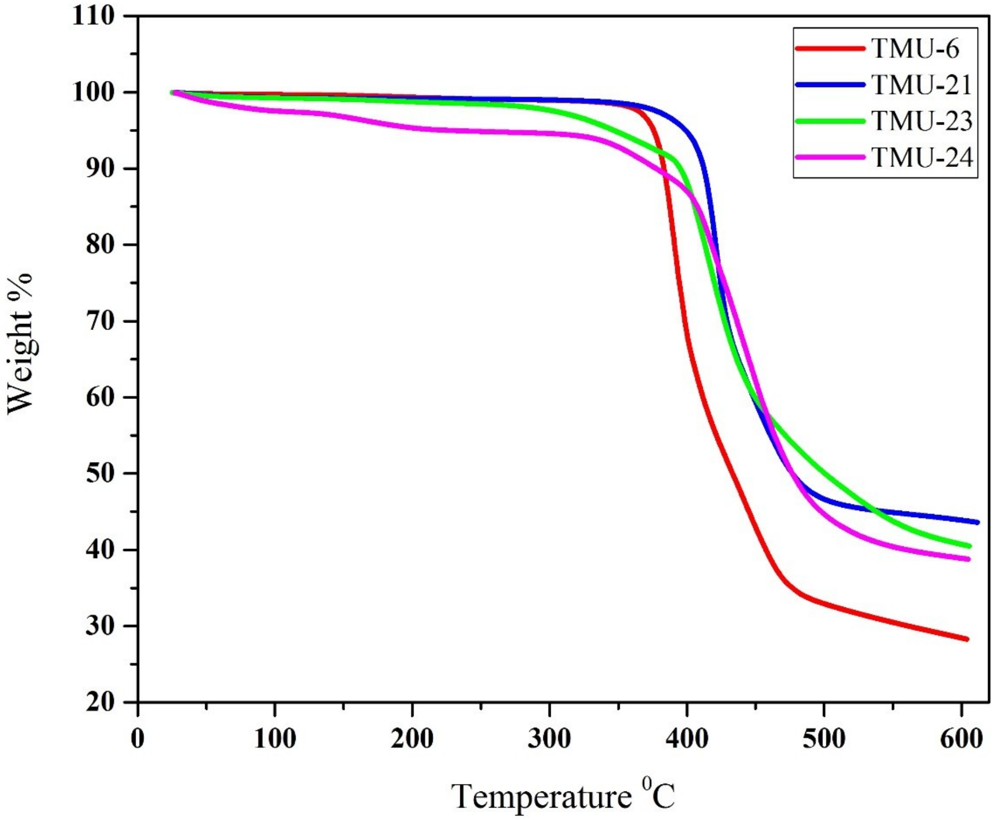


Figure S4. Thermogravimetric profiles of (a) TMU-6, (b) TMU-21, (c) TMU-23 and (d) TMU-24 isolated by mechanosynthesis. The atmosphere of the experiment is N_2 gas and heating rate is 10 C°/min.

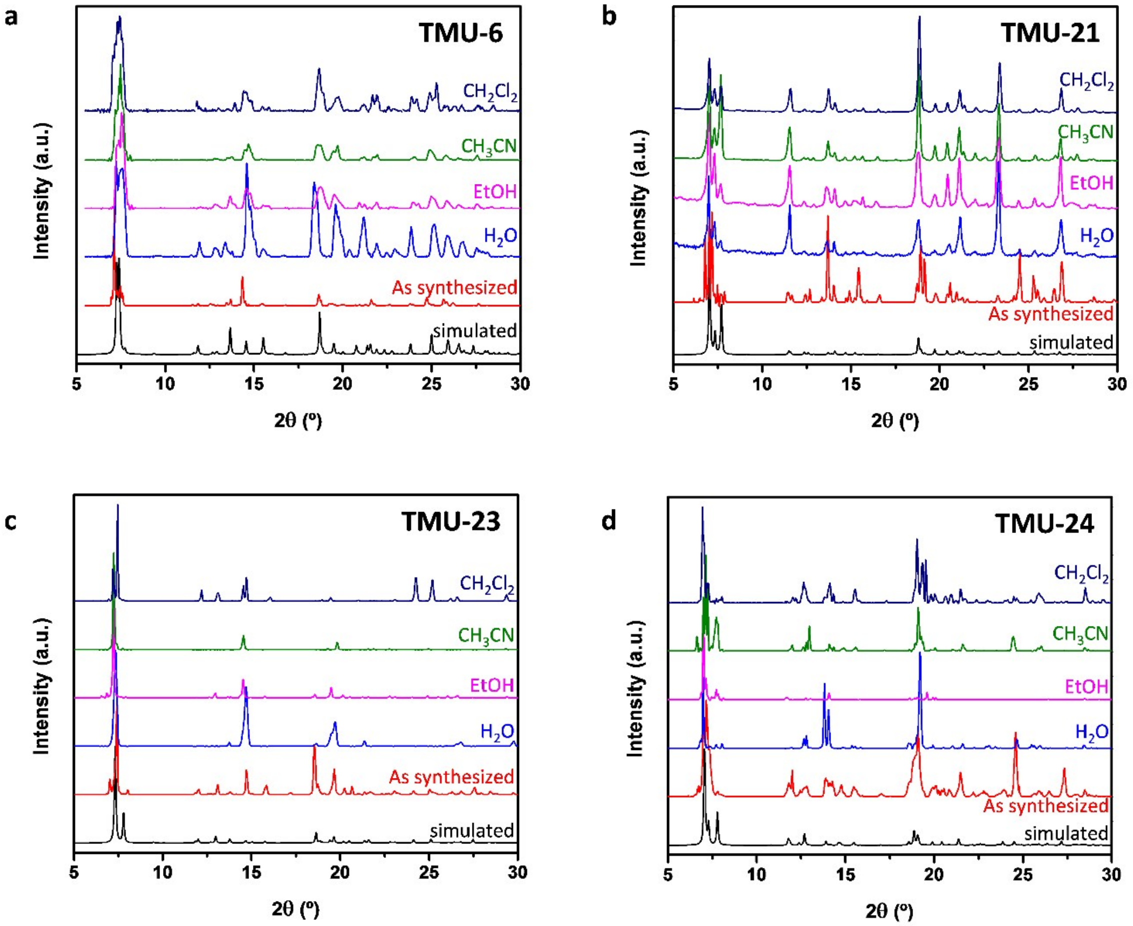


Figure S5. PXRD patterns of (a) TMU-6, (b) TMU-21, (c) TMU-23 and (d) TMU-24 in different solvents for 24 h. Simulated (black), as-synthesized (red), water (blue), ethanol (green), acetonitrile (brown) and dichloromethane (purple). Note that, due to their interdigitated nature, some of the materials seems to exhibit small structural changes; characteristic from swelling of "soft" materials when immersed in solvents.

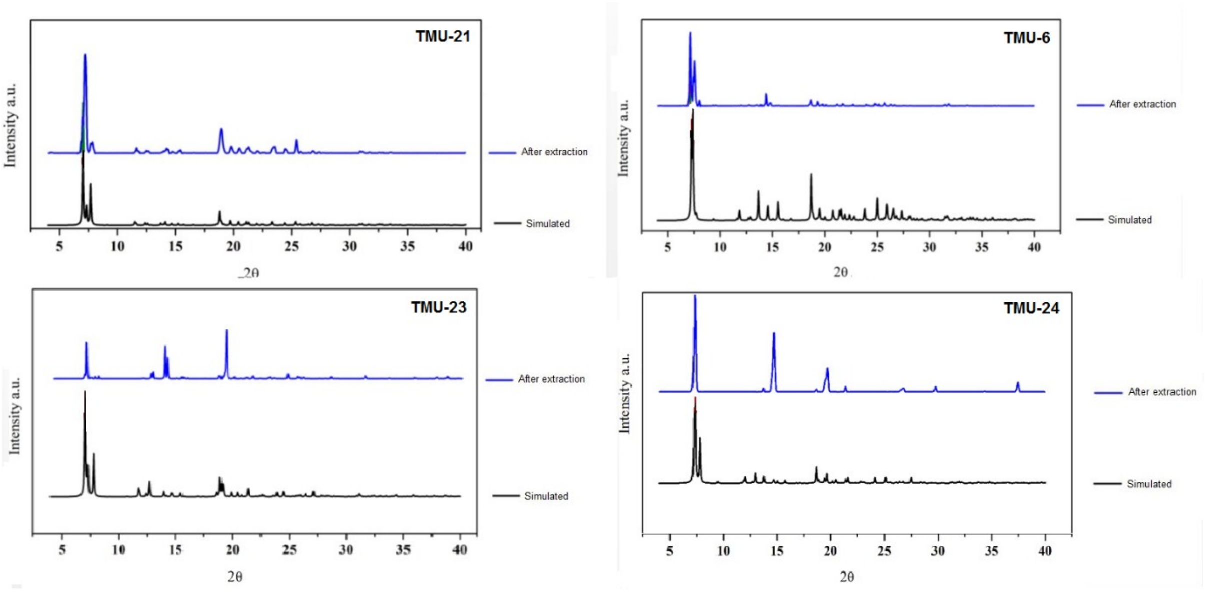


Figure S6. PXRD patterns of (a) TMU-21, (b) TMU-6, (c) TMU-23 and (d) TMU-24 after extraction. Simulated (black), after adsorption (blue).

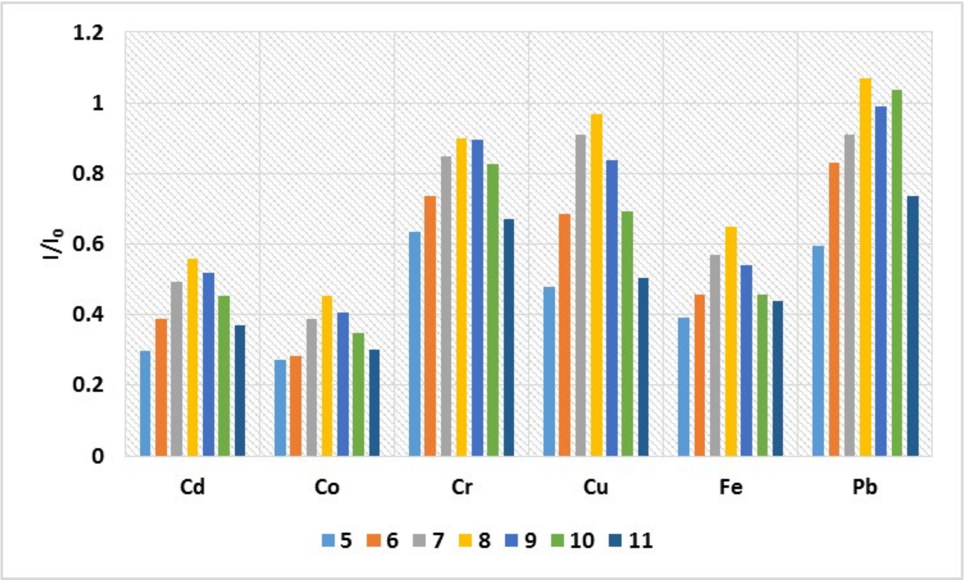


Figure S7. Effect of sample pH on extraction efficiency. Extraction conditions: sample solution, 100 mL of 100 µg L^{-1} of target metal ions; MOF, 5 mg; eluent, 300 µL of 0.4 M EDTA; extraction time, 10 min; desorption time, 1 min. (I: signal intensity of ICP, I/I_0 is the ratio of the signal of determination of target metal ion in eluate to the signal of determination of its standard solution at concentration 5mg.L^{-1})

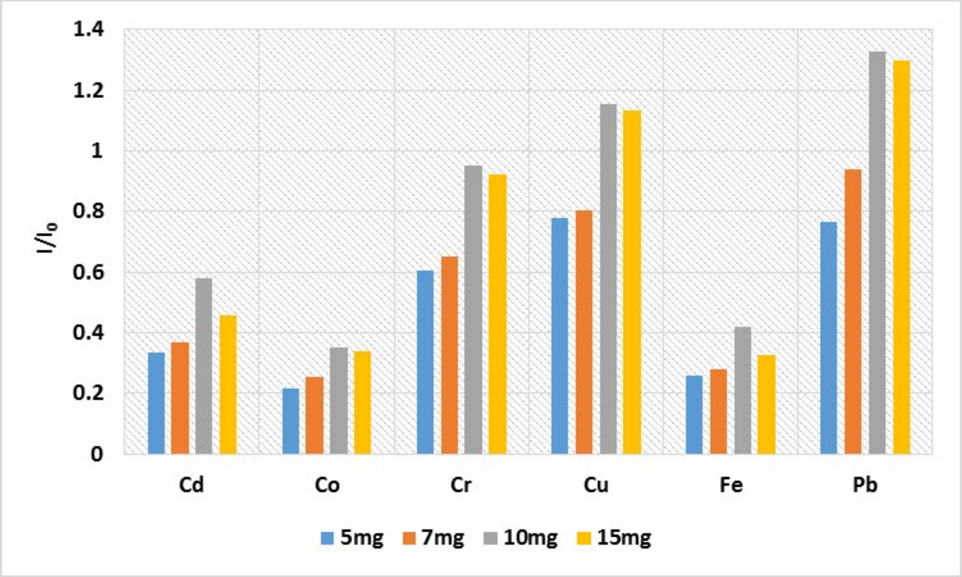


Figure S8. Effect of MOF amount on extraction efficiency. Extraction conditions: sample solution, 100 mL of 100 µg L^{-1} target metal ions at pH 8; eluent, 300 µL of 0.4 M EDTA; extraction time, 10 min; desorption time, 1 min. (I: signal intensity of ICP, I/I_0 is the ratio of the signal of determination of target metal ion in eluate to the signal of determination of its standard solution at concentration 5mg.L^{-1})

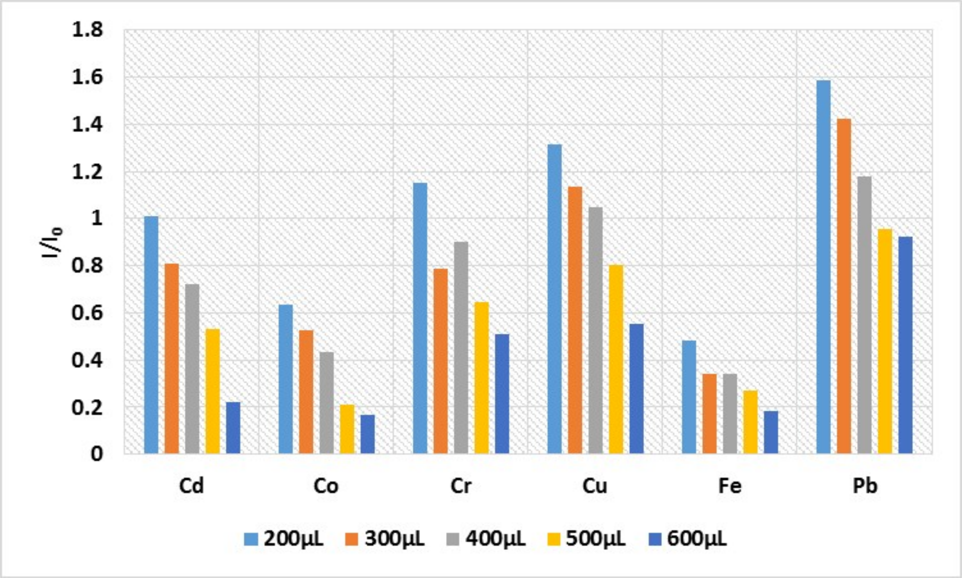


Figure S9. Effect of eluent volume on extraction efficiency. Extraction conditions: sample solution, 100 mL of 100 µg L^{-1} target metal ions at pH 8; MOF 10 mg; eluent 0.4 M EDTA; extraction time, 10 min; desorption time, 1 min. (I: signal intensity of ICP, I/I_0 is the ratio of the signal of determination of target metal ion in eluate to the signal of determination of its standard solution at concentration 5mg.L^{-1})

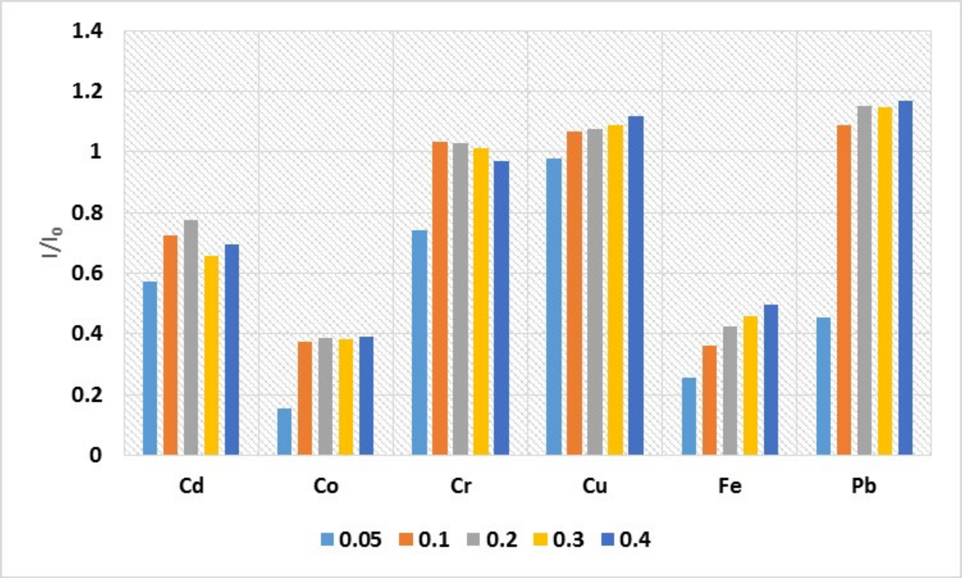


Figure S10. Effect of eluent concentration on extraction efficiency. Extraction conditions: sample solution, 100 mL of 100μg L^{-1} target metal ions at pH 8; MOF, 10mg; eluent, 300 μL; extraction time, 10 min; desorption time, 1 min (I: signal intensity of ICP, I/I$_0$ is the ratio of the signal of determination of target metal ion in eluate to the signal of determination of its standard solution at concentration 5mg.L^{-1})

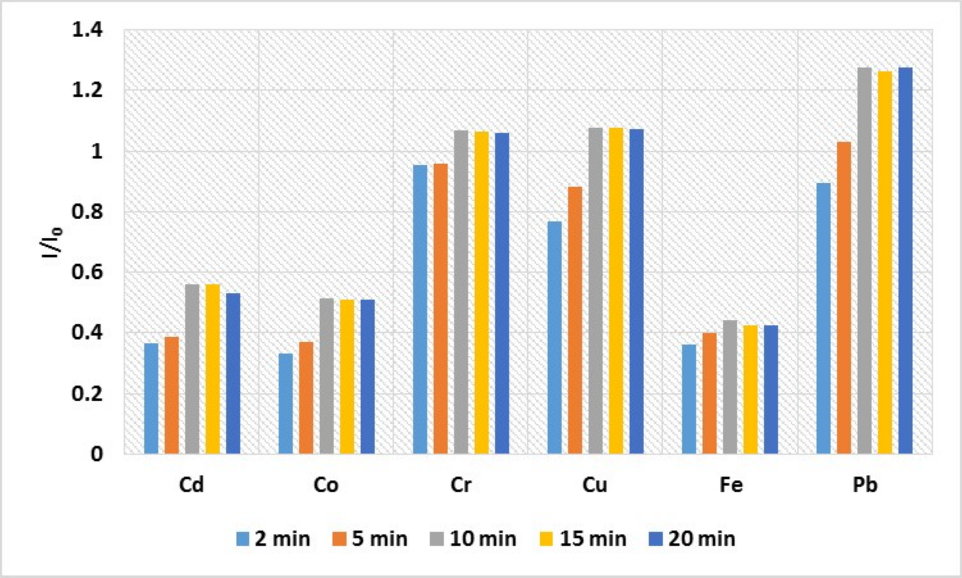


Figure S11. Effect of extraction time on extraction efficiency. Extraction conditions: sample solution, 100 mL of 100 µg L^{-1} target metal ions at pH 8; 200 eluent µL of 0.4 M EDTA; MOF, 10 mg; desorption time, 1 min (I: signal intensity of ICP, I/I_0 is the ratio of the signal of determination of target metal ion in eluate to the signal of determination of its standard solution at concentration 5mg.L^{-1})

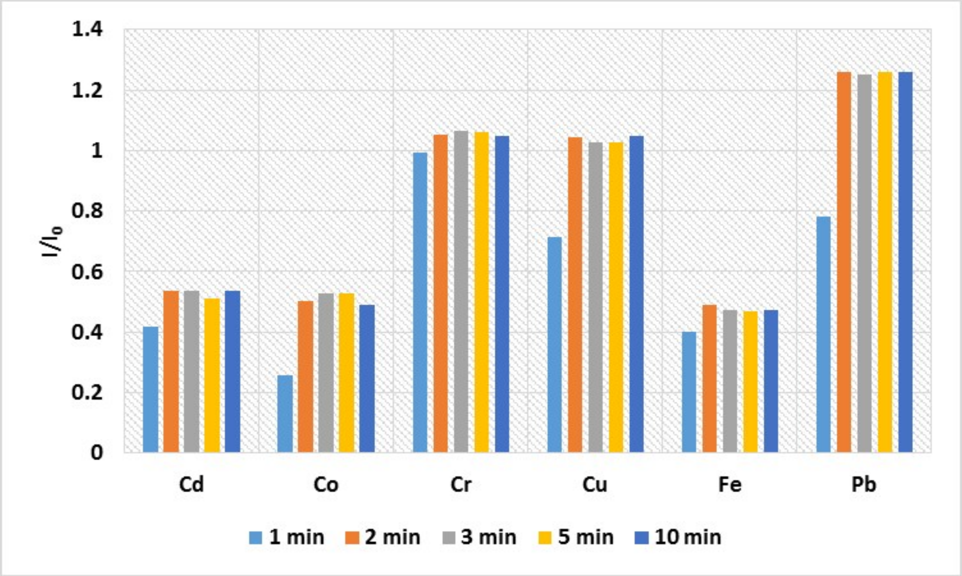


Figure S12. Effect of desorption time on extraction efficiency. Extraction conditions: sample solution, 100 mL of 100 µg L^{-1} target metal ions at pH 8; eluent, 200 µL of 0.4 M EDTA; MOF, 10 mg; extraction time, 10 min (I: signal intensity of ICP, I/I_0 is the ratio of the signal of determination of target metal ion in eluate to the signal of determination of its standard solution at concentration 5mg.L^{-1})

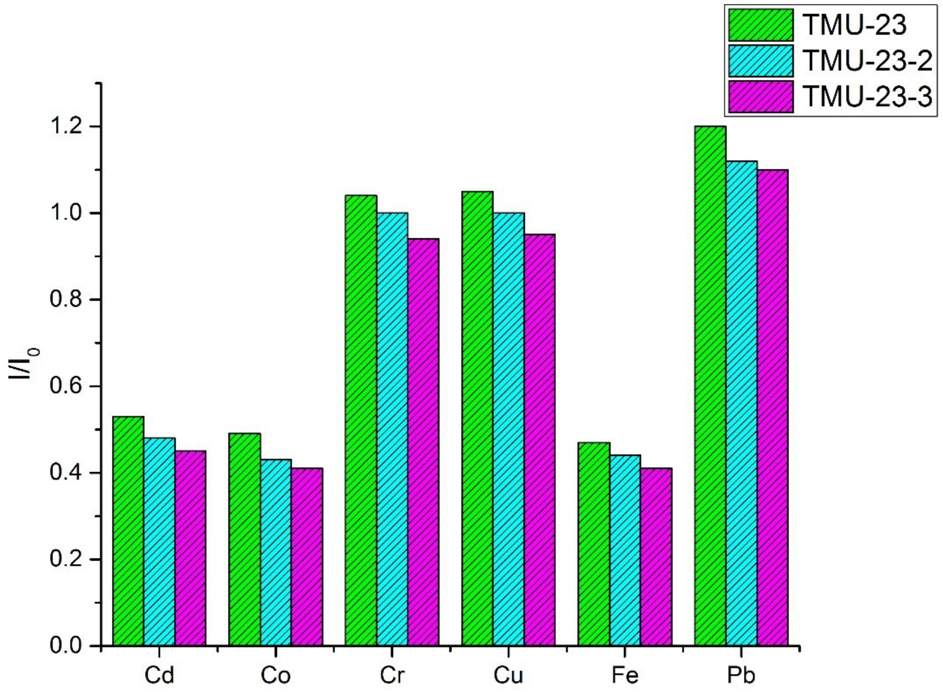
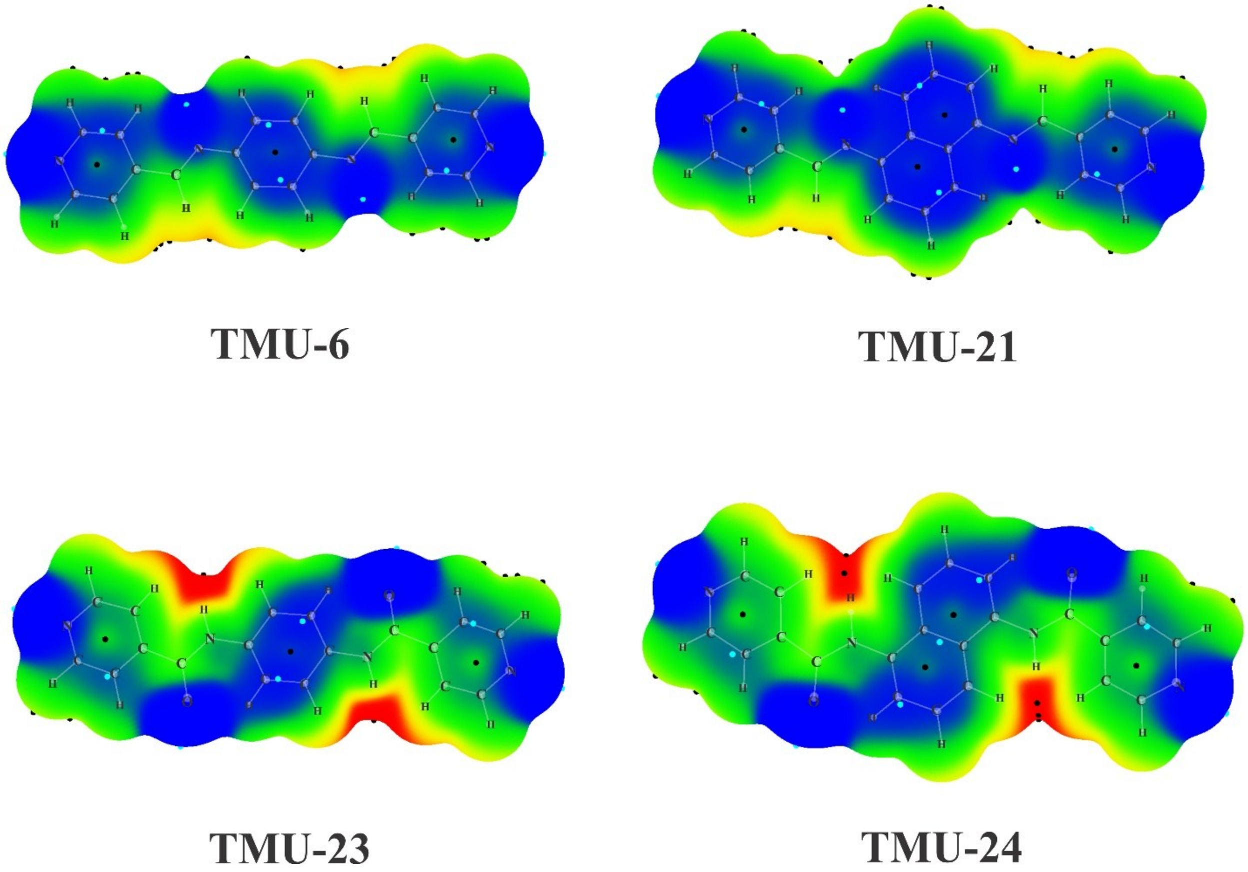


Figure S13: Regeneration and reusing of TMU-23. Extraction conditions: sample solution, 100 mL of 100 μg L^{-1} target metal ions at pH 8; eluent, 200 μL of 0.4 M EDTA; MOF, 10 mg; extraction time, 10 min; desorption time:2 min (I: signal intensity of ICP, I/I_0 is the ratio of the signal of determination of target metal ion in eluate to the signal of determination of its standard solution at concentration 5mg.L^{-1})



TMU-6

TMU-21

TMU-23

TMU-24

Figure S14. The MEP plot (isovalue=0.001 atomic unit) of the isolated ligands. The color code, in kcal/mol, is: red > 30; 30 > yellow > 15; 15 > green > 0 and blue < 0. The black and blue circles indicate the surface maxima and minima, respectively.

Table S1: ICP-OES operating conditions and metal ions emission lines.

Plasma gas	Argon
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.5 L min^{-1}
Frequency of RF generator	40 MHz
RF generator power	1.2 kW
Observation height	8 mm
Nebulizer pressure	180 kPa
Eluent	Deionized water
Elution rate	2 mL min^{-1}
Analytical lines	Cd (228.802), Co (230.786), Cr (267.716), Cu (324.754), Pb (220.353)

1.3. Kinetics study

Ten samples were prepared by adding a fixed concentration of target ions (30 mg L^{-1}) to Falcon 50 mL conical tubes containing 3 mg of TMU-24 at 298 K. The adsorption process was stopped at different times from 1 to 60 min. Then, the mixture was centrifuged at 6000 rpm for 5 min and sampled for ICP analysis. The amount of adsorbed target ions was calculated using:

$$q_t = \frac{C_0 - C_t}{m} \times v$$

Where q_t and Ct are the amount of metal ions adsorbed per unit mass of adsorbent (mg g^{-1}) and the ions concentration (mg L^{-1}) at time t (min), respectively; m is the adsorbent mass (g), and V is the volume (L) of the sample.

It is of great importance to determine kinetic parameters because they can be used to define the adsorption process and efficiency. Fast kinetics is very crucial, acceptable, and beneficial in aqueous phase adsorption. The metal ions all rapidly reached the equilibrium at 10 min. In fact, 95% of the metal ions were adsorbed at about 30 min. Compared to other reported adsorbents in the literature, the TMUs prepared in our laboratory exhibit fast adsorption. For defining the adsorption rate, a pseudo-second-order model with the highest value of correlation coefficient (R2 = 0.99) was employed to fit the kinetic results.

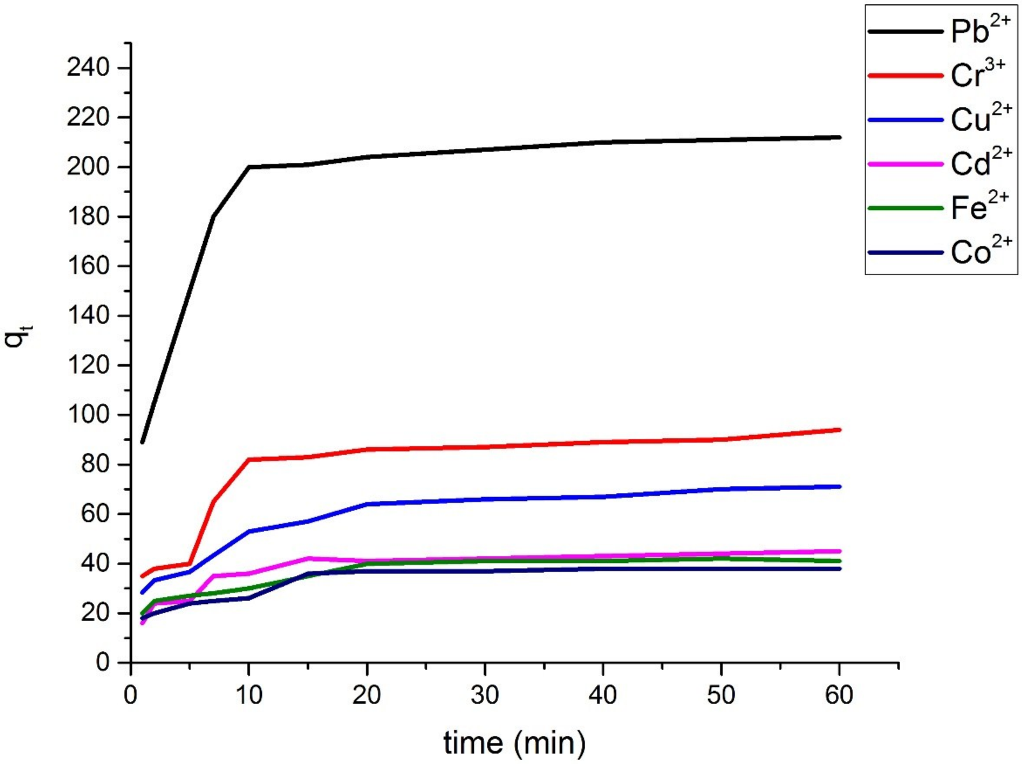


Figure S15: Effect of time on the heavy metal ions adsorption by 3 mg of TMU-24 with initial concentration of 30 ppm

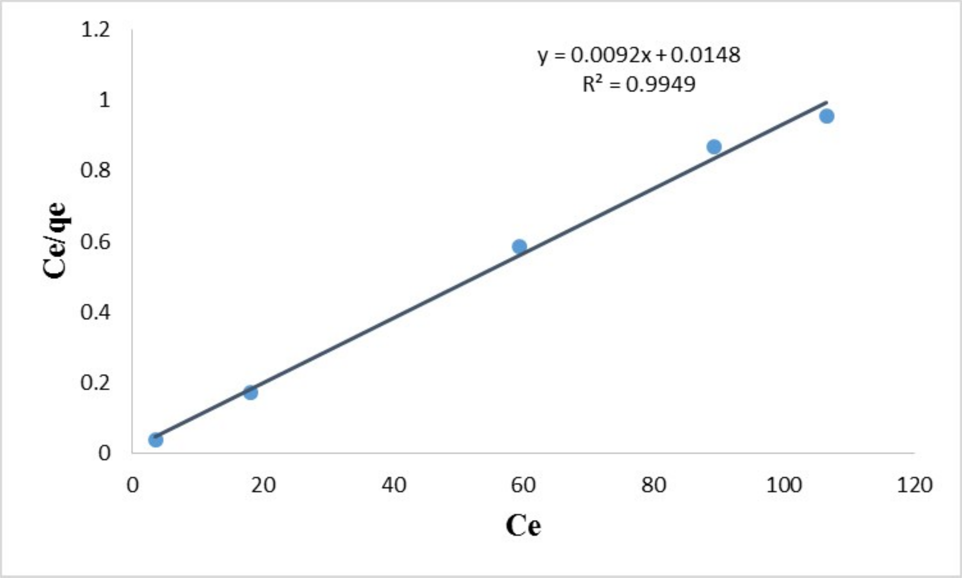


Figure S16: Effect of initial Cr^{3+} concentration on adsorption by 3 mg of TMU-24

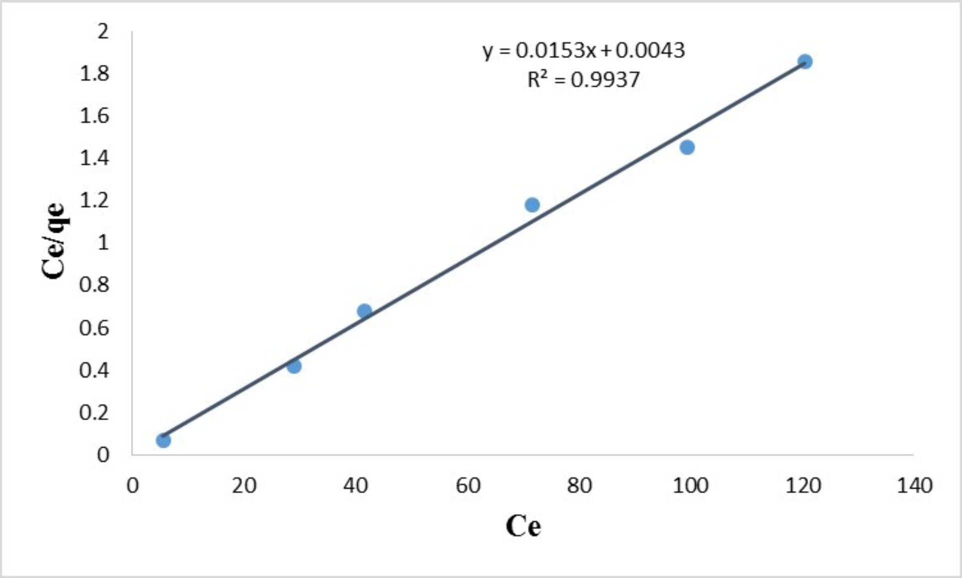


Figure S17: Effect of initial Cu^{2+} concentration on adsorption by 3 mg of TMU-24

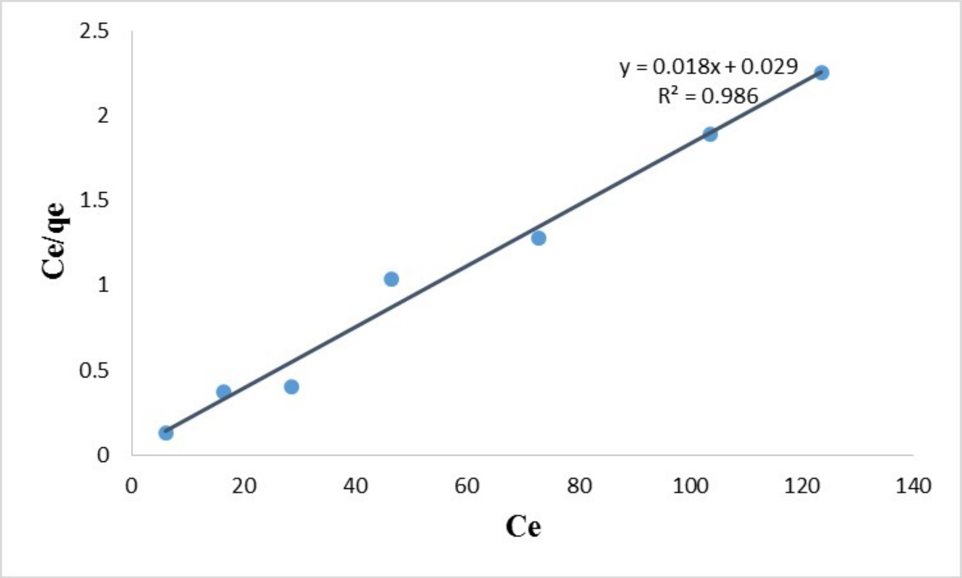


Figure S18: Effect of initial Cd^{2+} concentration on adsorption by 3 mg of TMU-24

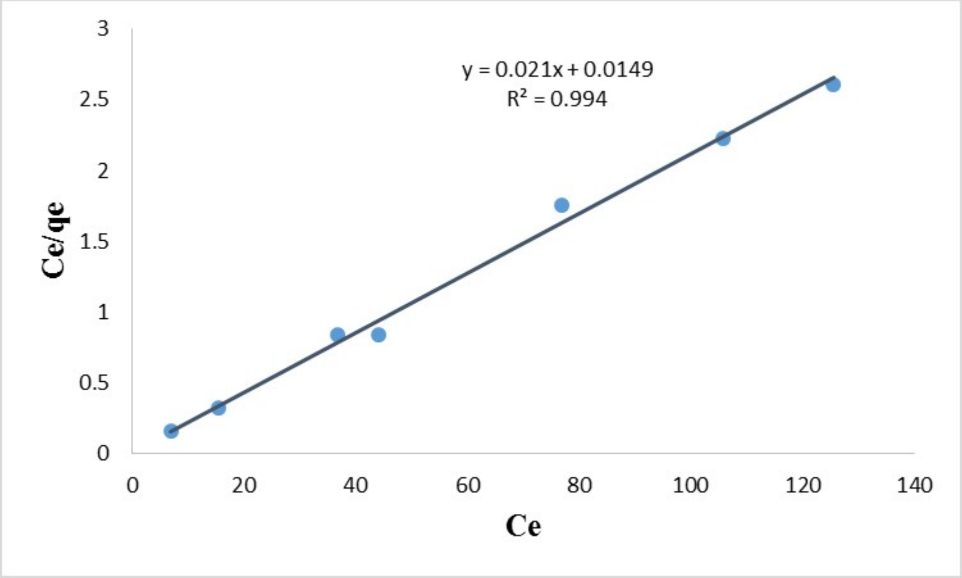


Figure S19: Effect of initial Co^{2+} concentration on adsorption by 3 mg of TMU-24

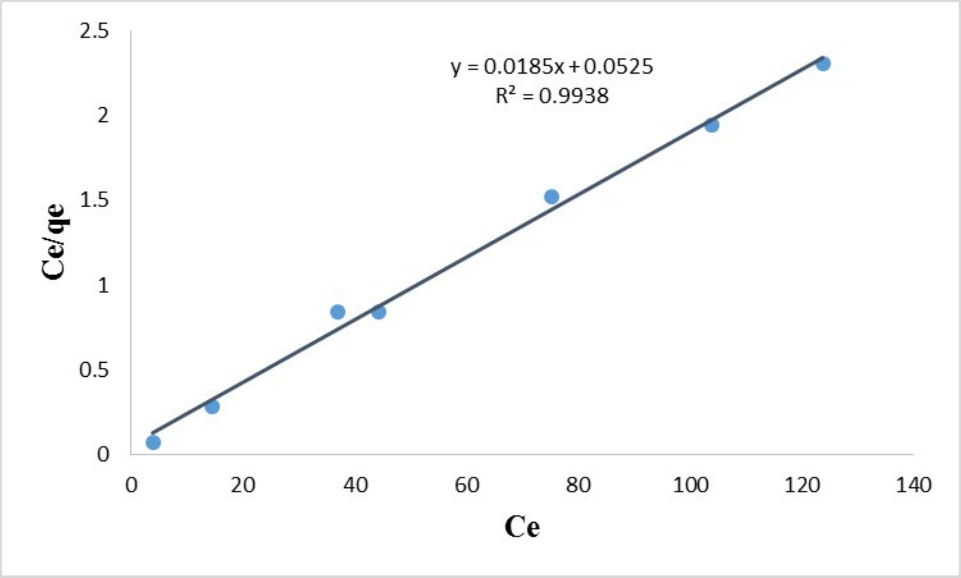


Figure S20: Effect of initial Fe^{2+} concentration on adsorption by 3 mg of TMU-24

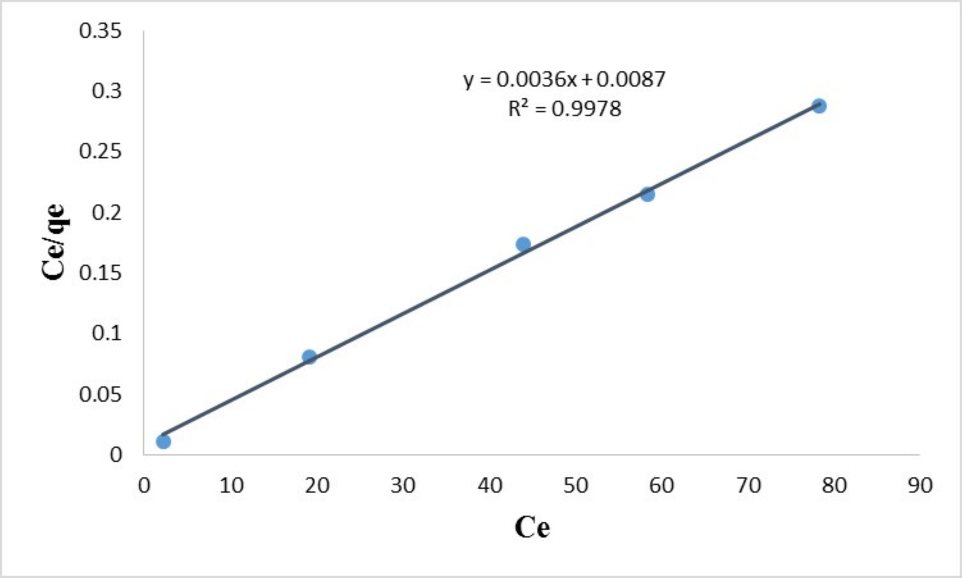


Figure S21: Effect of initial Pb^{2+} concentration on adsorption by 3 mg of TMU-24

Table S2: extraction and the direct calibration equations

	Extraction calibration equations	R^2	direct calibration equations
Cd^{2+}	376.24x + 253.37	0.9979	4486.6x - 268.56
Co^{2+}	90.563x + 322.1	0.9958	2178.7x + 361.07
Cu^{2+}	2536.9x + 2498.4	0.999	9373.2x - 1524.9
Cr^{3+}	2966.9x + 3339.6	0.9992	12845x - 3887.7

Fe^{2+}	320.34x + 535.46	0.9979	3678.3x - 2420.5
Pb^{2+}	50.21x + 71.244	0.9967	132.9x - 18.186

Table 3. Comparison of Maximum Adsorption Capacities (Q_m) and Preconcentration Factors (PF) of Some Sorbents Reported in the Literature for the Removal and Preconcentration of Target Metal Ions.

MOF		Cd^{+2}	Co^{+2}	Cr^{+3}	Cu^{+2}	Fe^{+2}	Pb^{+2}
silica-supported dithiocarbamate[1]	Q_m	40.3	-	-	-	-	70.4
magnetite nanorods (MNR)[2]	Q_m	88	-	-	76	127	112
Nanosized sponge like Mn3O4[3]	PF	-	-	-	20	-	40
	Q_m	-	-	-	3.25	-	21.9
Nano-TiO2 modified with 2-mercaptobenzothiazole[4]	PF	106	-	-	243	-	83
	Q_m	2.5	-	-	3.95	-	3.17
iminodiacetic acid functionalized multiwalled carbon nanotube[5]	PF	79	92	66	101	-	91
	Q_m	6.61	6.7	8.96	6.64	-	8.98

References

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