Supporting Information

Mesoporous poly-melamine-formaldehyde polymer as a solid sorbent for toxic metal removal

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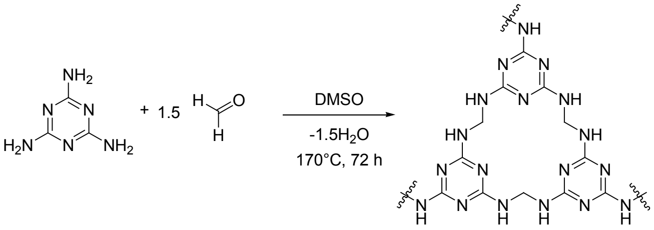
General Information

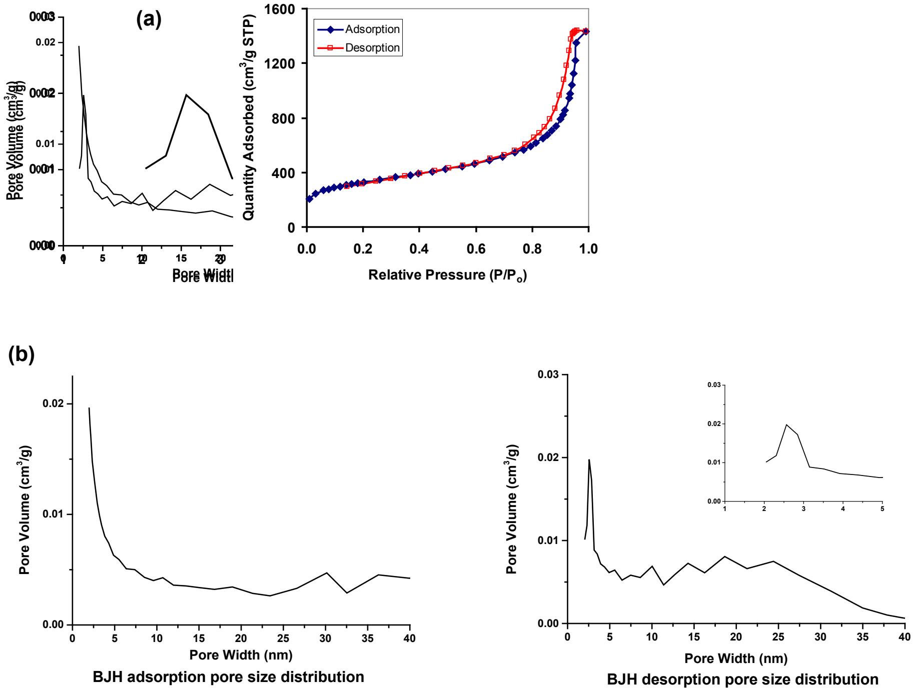
For metal ion removal experiments, all reagents were purchased and used as received unless otherwise stated. Metal ion solutions were prepared from their respective nitrate or chloride salts: lead nitrate (Sigma-Aldrich, 99%), anhydrous copper (II) chloride (Sigma-Aldrich, 99.995%), anhydrous cadmium chloride (Alfa Aesar, 99.99%), anhydrous nickel chloride (Merck, 99%) , anhydrous zinc chloride (Alfa Aesar, 98+%), palladium chloride (STREM, 99.999%), platinum (II) chloride (Sigma-Aldrich, 99.99%), sodium nitrate (Merck, 99.99%), potassium nitrate (Merck, 99.955%) and calcium nitrate tetrahydrate (Sigma-Aldrich, 99%). EDTA disodium salt dihydrate (Alfa Aesar, 99+%) was used. Deionized water treated by Milli-Q Synthesis A10 was used for all solutions. All solutions were prepared using plastic volumetric flask (PFA). Reagent-grade nitric acid (Merck, 65%), hydrochloric acid (Merck, 36.5%), anhydrous acetic acid (Merck, glacial, 100%) and anhydrous sodium hydroxide pellets (Sigma-Aldrich, reagent grade, ≥ 98%) were used. Calibration standards for 10 μg/ml of Pb, Bi, Cd, Cu, Ni, Zn in 2% HNO_3 and of Rh, Pd, Pt in 2% HCl for ICP-MS were purchased from High Purity Standards (SC, USA). Polypropylene (PP) conical tubes (BD Falcon) of 50 ml and 15 ml were used for equilibrium sorption experiments and sample preparation for ICP-MS analysis, respectively. Aliquots were taken using a 1-ml syringe and filtered through a 13 mm-diameter Cronus 0.2-µm syringe filter. Surface area and porosity of the polymer were analyzed via nitrogen sorption with a Micromeritics Tristar 3000 Surface Area and Pore Size Analyzer at 77 K. pH of the lead solutions was measured using SevenMulti pH meter calibrated with pH 4, 7 and 10 buffer solutions. pH adjustments were made using 0.1 M HNO_3 and 0.1 M NaOH solutions.

Synthesis and Characterization of mPMF

Melamine (0.378 g, 3 mmol) and paraformaldehyde (1.8 eq, 0.162 g, 5.4 mmol) were added to a 15-ml Teflon container with a magnetic stir bar, and 3.36 ml (2.5 M) of anhydrous DMSO was added. The Teflon container was capped and secured within a steel bomb reactor, which was heated to 120 °C in an oven (Memmert Universal UNE 400) for 1 h. The reactor was then carefully removed from the oven for stirring on a magnetic plate to obtain a homogeneous solution. It was then heated in the oven to 170 °C for 72 h. The reaction was allowed to cool to room temperature, and the solid obtained was crushed, filtered, and washed with DMSO, acetone (3×), tetrahydrofuran (THF) (3×) and CH_2Cl_2. The resulting white solid was dried under vacuum at 80 °C for 24 h. Elemental analysis: C 33.90%, H 4.83%, N 39.61%, S 5.05%.



Scheme S1 Synthesis of mPMF.



BJH adsorption pore size distribution

BJH desorption pore size distribution

Figure S1 (a) N_2 adsorption-desorption isotherms (77 K), and (b) BJH adsorption (left) and desorption (right) pore size distributions of mPMF.

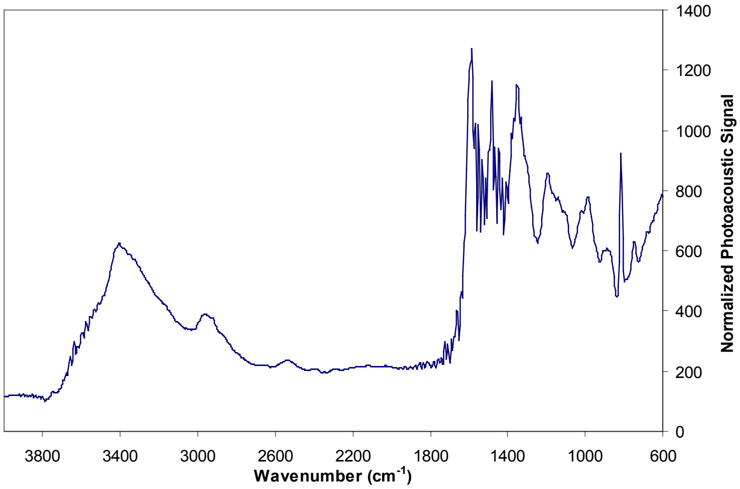


Figure S2 PA-FTIR spectrum of mPMF showing peaks associated with NH_2 or NH stretching at 3400 cm^{-1}, CH_2 stretching at 2950 cm^{-1}, imine stretching at 1600 cm^{-1}, and triazine stretching at 1550 cm^{-1} and 1480 cm^{-1}.

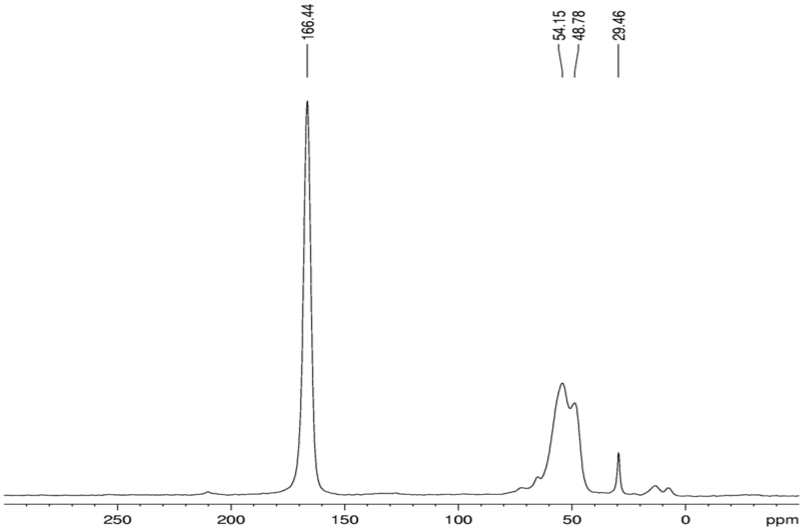


Figure S3 ^{13}C nuclear magnetic resonance (NMR) spectrum of mPMF showing peaks associated with triazine carbon at 166 ppm, and bridging CH_2 groups at 48−54 ppm. The signal at 29.46 is from DMSO.

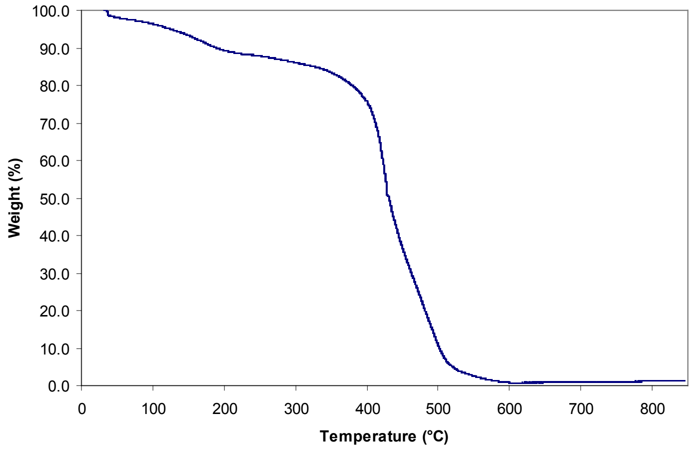


Figure S4 Thermogravimetric (TGA) profile of mPMF, showing thermal stability of up to ~ 400 °C.

ICP-MS Analysis

Samples were analyzed using Perkin Elmer SCIEX, ELAN DRC II ICP-MS with a quadrupole mass spectrometer. The solutions were fed through tubes via a peristaltic pump to the nebulizer and spray chamber. All samples were diluted using 2% HNO_3, and an internal standard was added. Bismuth was used as an internal standard for lead solutions, and rhodium was used an internal standard for other transition metals in the ICP-MS analysis. Calibration standards for ICP-MS were prepared by dilution of 10 μg/ml of standards purchased from High Purity Standards with 2% HNO_3. At least 5 calibration standard solutions with internal standard were prepared for the calibration curve in ICP-MS analysis. All sample concentration analyses were performed in duplicates under the same instrumental conditions. Reported values were the average of duplicates, with a standard deviation of < 5%.

Equilibrium Sorption Experiments

Stock solutions of 1000 ppm were prepared by dissolving metal salts in deionized water. Metal ion solutions were prepared by further dilution from the stock solution. Equilibrium sorption studies were conducted with 0.1 g of mPMF (fine powder, neutralized with diluted NaOH) in 25 ml of solution with stirring for 2 h. Aliquots were removed using a 1-ml syringe, and filtered through a 0.2-μm syringe filter. In the pH studies, 0.1 M HNO_3 or 0.1 M NaOH was added to the metal ion solutions prepared, and pH of the resulting solution was determined by a pH meter. In the kinetic studies, 0.4 g of mPMF was stirred in 100 ml of solution, and a maximum of 8 aliquots was removed at the specified time intervals. The filtered aliquots were diluted with 2% HNO_3, and the internal standard was added prior to the ICP-MS analysis.

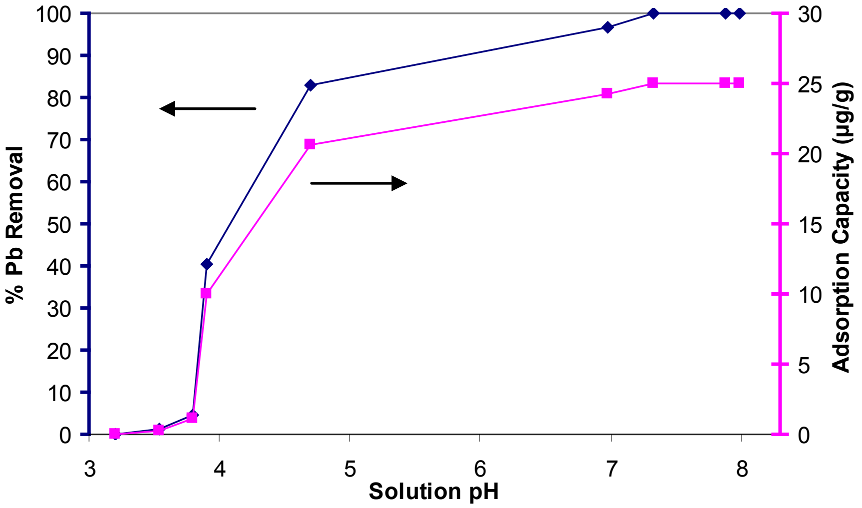


Figure S5 Effect of solution pH on lead removal by mPMF. 0.1 g of mPMF was stirred in 25 ml of aqueous solution containing 100 ppb of lead for 2 h. Solution pH was adjusted with 0.1 M HNO_3 or 0.1 M NaOH.

Metal Ion Recovery and mPMF Recycling

After the equilibrium sorption experiments, the mPMF materials with adsorbed metal ions were filtered, and rinsed with deionized water. For lead recovery, the mPMF materials with adsorbed metal ions were placed on a filter, and 5 ml of acid (3×) was flowed through them. They were then washed with deionized water, and the filtrate was analyzed for the recovery of metal ions. The recycled mPMF materials were further treated with 0.2 M NaOH, and washed with deionized water until the filtrate became neutral. They were dried in the vacuum oven at 80 °C before further equilibrium sorption studies.

Table S1 Adsorption of lead ions under over-loaded conditions, and recycling of mPMF for 2 runs.

Recovery Conditions	Run #	Actual Initial Conc. (ppb)	Equilibrium Conc. (ppb)	% Removal	Capacity (µg/g)
50 mM HCl	1[a]	97.10	46.33	52.29	63.47
	2[b]	97.16	58.76	39.52	48.00
	3[b]	97.10	60.81	37.38	45.37
5% Acetic acid	1[a]	95.15	45.61	52.07	61.93
	2[b]	96.79	62.27	35.66	43.14
	3[b]	97.19	67.93	30.11	36.58

Conditions: [a] 0.1 g of mPMF was stirred in 125 ml of lead solution of 100 ppb for 2 h. [b] 0.1 g of recycled mPMF was stirred in 125 ml of lead solution of 100 ppb for 2 h.

Adsorption Model Analysis

Adsorption behavior of mPMF was analyzed based on Freundlich and Langmuir equations. The Freundlich equation is expressed as $\log Q_e = 1/n \log C_e + \log K$, where 1/n and K are Freundlich constants corresponding to sorption intensity and sorption capacity, respectively. The Langmuir equation is expressed as $C_e/Q_e = 1/(bQ_{max}) + C_e/Q_{max}$, where b is the Langmuir adsorption equilibrium constant (L/µg), and Q_{max} is the maximum adsorption at monolayer coverage (µg/g). Q_e and C_e are the amount of lead ions adsorbed per unit weight of polymer (µg/g) and the concentration of solution (µg/L) at equilibrium, respectively. Log Q_e versus log C_e for the Freundlich equation and C_e/Q_e versus C_e for the Langmuir equation both gave linear plots (ESI Figure S6). Under good adsorption conditions, the value of 1/n for the Freundlich equation should be between 0.1 and 1. The 1/n value obtained for lead adsorption over mPMF was 0.264 (ESI Table S2). The adsorption is defined as favorable if the dimensionless Langmuir equilibrium parameter R_L is between 0 to 1, where $R_L^2 = 1/(1 + bC_e)$. The adsorption is defined as (i) irreversible if Langmuir parameter $R_L = 0$, (ii) linear if $R_L = 1$, and (iii) unfavorable if $R_L > 1$.[37] For the range of data obtained, the calculated R_L values varied from 0.104 to 0.999, indicating favorable adsorption.

Table S2 Freundlich and Langmuir parameters for lead adsorption on mPMF.

Freundlich Model	**K**	119.06
	1/n	0.264
	R^2	0.906
Langmuir Model	**Q_{max} (μg/g)**	677.36
	b (L/μg)	0.041
	R^2	0.995

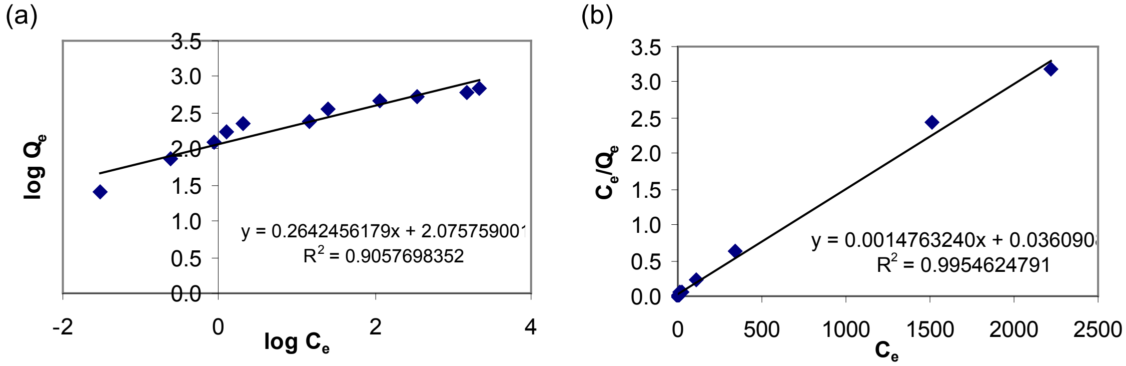


Figure S6 Data of lead adsorption on mPMF plotted with (a) Freundlich equation and (b) Langmuir equation.

Kinetic Model Analysis

The adsorption data were analyzed using Lagergren pseudo-first-order and pseudo-second-order kinetic models. Lagergren first-order equation is expressed as log $(Q_e - Q_t) = \log Q_e - k_1t/2.303$, and Lagergren second-order equation is expressed as $t/Q_t = 1/(k_2Q_e)^2 + t/Q_e$, where Q_e and Q_t are the amount of lead ions adsorbed per unit weight of polymer (μg/g) at equilibrium and time t (s), respectively, k_1 is the rate constant (s^{-1}) of pseudo-first-order adsorption, and k_2 is the rate constant (g/(μg s)) of pseudo-second-order adsorption. $\log(Q_e - Q_t)$ versus t for the pseudo-first-order equation and t/Q_t versus t for the pseudo-second-order equation were plotted for lead solutions of 100 ppb and 500 ppb.

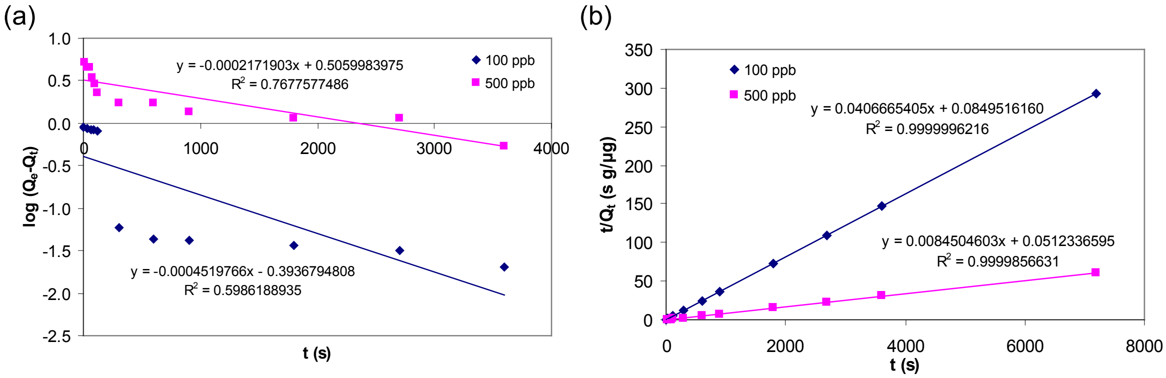


Figure S7 Lead adsorption kinetics of mPMF for solutions with (♦) 100 ppb and (■) 500 ppb of lead, plotted with (a) Lagergren pseudo-first-order equation and (b) Lagergren pseudo-second-order equation.

Table S3 Lagergren pseudo-first-order and pseudo-second-order kinetics parameters for lead adsorption kinetics of mPMF.

		100 ppb	**500 ppb**
First Order	**k_1 (s^{-1})**	1.041×10^{-3}	0.500×10^{-3}
	R^2	0.599	0.768
Second Order	**k_2 (g/(s μg))**	0.1395	0.0373
	Q_e (μg/g)	24.59	118.34
	R^2	0.999	0.999

Dynamic Sorption Experiments

About 0.3 g of mPMF (particle size = 0.5–1.0 mm) was packed in an Omnifit column of 6.6 mm in inner diameter and 70 mm in bed height. Lead solutions were prepared in deionized water. They were pumped through the column using a peristaltic pump at a constant flow rate. The mPMF-treated solution was collected in 2-ml portions and analyzed. The column was recycled by washing with 50 mM HCl (5 ml × 3) to remove the adsorbed lead ions, reactivated using 0.2 M NaOH (2.5 ml × 3), and washed with water (2.5 ml × 5) before the next run.

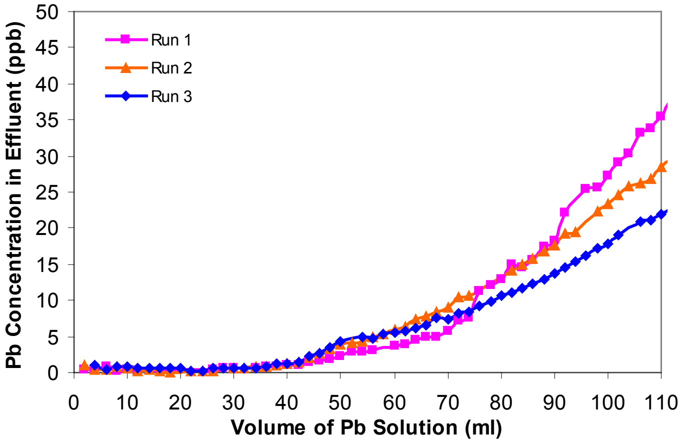


Figure S8 Lead adsorption over a dynamic column of 0.3 g of mPMF, which was recycled twice. A lead solution of 50 ppb was introduced in each run to the column at a flow rate of 1.0 ml/min.

Table S4 Effect of the presence of EDTA ligands in lead ion removal from water using PMF.

EDTA (mol%)	Actual Initial Conc. (ppb)	Equilibrium Conc. (ppb)	% Removal	Capacity (μg/g)
10	95.85	1.21	98.74	23.66
20	95.85	0.99	98.97	23.72
50	95.85	0.47	99.51	23.85
100	95.85	0.50	99.48	23.84
200	95.85	0.33	99.66	23.88
500	96.56	0.17	99.82	23.92
1000	96.56	0.32	99.67	23.88

Conditions: 10 ml of lead solution of 100 ppb was stirred with 40 mg of PMF for 2 h, with the addition of 0.1 mM $Na_2EDTA\cdot 2H_2O$ (at the mol% specified versus Pb^{2+} present).

Table S5 Removal efficiency of PMF for a multi-ion solution containing toxic metal ions of lead, cadmium, copper, nickel and zinc.

Metal Ion	Actual Initial Conc. (ppb)	Equilibrium Conc. (ppb)	% Removal
Pb	97.93	0.16	99.84
Cd	97.12	3.62	96.28
Cu	94.91	2.87	96.98
Ni	96.41	89.56	7.11
Zn	94.94	49.30	48.07

Conditions: 0.1 g of PMF was stirred in 25 ml of the multi-ion solution for 2 h.

Table S6 Lead removal efficiency of mPMF, nano-Al_2O_3 and chelating polymer.[a]

Sorbent	**Initial Conc. (ppb)**	**Equilibrium Conc. (ppb)**	**% Removal**
mPMF	93.73	0.15	99.85
Chelating polymer [b]	113	7	94
Nano-Al_2O_3[c]	94.60	0.045	99.95

[a] Conditions: 0.1 g of sorbent was stirred in 25 ml of metal ion solution for 2 h. [b] Reference [21b]. [c]Purchased from Merck (Product #1.01077.1000).