# A facile route to the synthesis of mesoporous melamine-formaldehyde resins for hexavalent chromium removal

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## **Experimental Section**

## Chemicals

All chemicals were analytical grade and used without any purification. Triblock poly (ethylene oxide)-b-poly (propylene oxide)-b-poly (ethylene oxide) copolymer Pluronic F127 (PEO106-PPO70-PEO106,  $M_W$ =12600) was purchased from Sigma-Aldich Co. LLC. Melamine, paraformaldehyde, sodium hydroxide, hydrochloric acid and ethanol were purchased from Shanghai Lingfeng Chemical Reagent Co., LTD (Shanghai, China). Chromium oxide, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were purchased from Sinopharm Chemical Reagent Co. (China).

#### Synthesis of MMF

MMF sample was hydrothermally synthesized from a mixture of melamine,  $(HCHO)_n$ , F127, NaOH and H<sub>2</sub>O at a molar ratio of 1.0:3.0:0.002:0.042:18.0 at 150 °C for 24 h. As a typical run, 7.56 g of melamine, 5.40 g of paraformaldehyde and 0.10 g of NaOH were dissolved in 20 mL of deionized water and stirred at 80 °C for 15 min. Another 20 mL of deionized water containing 1.50 g of F127 and 3.5 ml of HCl aqueous solution (wt. 36%) was added, and the mixture was then stirred at room temperature for another 2 h, after which the mixture was transferred to an autoclave and heated at 150 °C for 24 h. After filtrating, washing and drying, a white solid was finally obtained (Fig. S1). F127 was removed by extraction with ethanol at 60 °C for 3 h. The synthesis route is proposed in Scheme S1.



Scheme S1. Synthesis of MMF.

#### **Adsorption experiments**

Batch adsorption experiments were conducted by adding 0.05 g of MMF to 50 mL of different Cr (VI) test solutions (19.0, 39.4, 40.7, 79.1 and 142.6 ppm) at different pH values (2-12) and temperatures (20, 25, 30, 35 and 40 °C) in a 100-ml Erlenmeyer flask. The initial solution pH was adjusted using 0.1 M HCl or 0.1 M NaOH. The mixtures were stirred at 150 rpm for different contact times (5-60 min). The selectivities of MMF for Cr (VI) were studied with Fe (III), Cu (II), Ni (II) and Cr (III) as competitive ions in the adsorption process. 0.05 g MMF was added into 50 ml of the metal salts solution at 20 °C and with a pH of 4.0. The adsorbent MMF was separated from the test solution by centrifugation, and the amount of Cr (VI), Fe (III), Cu (II), Ni (II) and Cr (III) adsorbed was calculated from the difference between its concentration in the test solution and the supernatant liquid, which was determined by Furnace Atomic Absorption Spectrometry (FAAS).

The adsorption capacity of MMF was calculated by means of equilibrium studies and then summarized using the equilibrium equation of Langmuir.

$$q_t = \frac{V(c_0 c_t)}{m} \tag{1}$$

Where  $q_t$  is the adsorption capacity of MMF (mg/g),  $c_t$  is the concentration of equilibrium (mg/L),  $c_0$  is the initial concentration (mg/L), m is the mass of adsorbent (g), V is the solution volume (L), and t is the contact time (min).

#### **Desorption experiments**

50 ml of 0.1 M NaOH was added as the elutent to a 100-ml Erlenmeyer flask containing 0.05 g Cr/MMF (MMF-adsorbed Cr). The mixture was stirred at 150 rpm for different contact times (5-120 min). Cr/MMF was separated from the test solution by centrifugation. The amount of Cr (VI) desorbed was calculated from the difference between the adsorption capacity of MMF and the final concentration of Cr (VI) ions in the desorption medium. The initial solution and the supernatant liquid of chromium (adsorbed medium and desorbed medium) were analyzed by FAAS.

The desorption percent of Cr (VI) ions from Cr/MMF was calculated from the amount of Cr (VI) ions adsorbed and the final concentration of Cr (VI) ions in the desorption medium by the following equation:

desorption (%) = 
$$\frac{c_t'}{c_0 - c_t}$$
 (2)

Where '*desorption* (%)' is the percent of desorption,  $c_t$ ' is the concentration of desorption (mg/L).

### Characterization

N<sub>2</sub> sorption isotherms were measured on a Micromeritics Tristar 3020 system at liquid nitrogen temperature. Samples were outgassed for 10 h at 150 °C before the measurements. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas, the pore volume and pore size distributions were derived from the adsorption branches for isotherms using Barrett-Joyner-Halenda (BJH) model. Scanning electron microscopic (SEM) images were obtained using a S4800 field emission scanning electron microscope (FE-SEM) and a thin film of gold was sprayed on the samples before the characterization. Transmission electron microscope (TEM) images were obtained using a JEM-2100 microscope operated at 200 kV. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 6700 FTIR spectrometer in the range of 400-4000 cm<sup>-1</sup>. <sup>13</sup>C MAS spectra were obtained using a Bruker Avance-400 spectrometer at 11 kHz using densely packed powders of the MMF. CHNS elemental analyses were performed on a VARIO EL III elemental analyzer from Thermo Scientific. Thermo gravimetric (TGA) analysis was performed on a STA449C thermal analyzer from room temperature to 800 °C at a heating rate of 5 °/min under nitrogen atmosphere. XPS spectra were recorded on a Thermo ESCALAB 250 with Al K $\alpha$  irradiation at  $\theta$ =90 ° for X-ray sources and the binding energies were calibrated using the C1s peak at 284.6 eV. The concentrations of various metal ions (Cr (VI), Cr (III), Fe (III), Cu (II) and Ni (II)) were measured by FAAS on a novAA.

# Supplementary tables.

Sample	BET $(m^2/g)$	BJH pore size	Pore volume	Micropore
		(nm)	$(cm^3/g)$	BET area
				$(m^2/g)$
MMF	317	8.0	0.58	
AC	1435		0.83	476
MMF-1	262	7.2	0.54	35
MMF-2	385		11.45	12.9

**Table S1** Textural parameters of MMF, AC,  $MMF-1^{a}$  and  $MMF-2^{b}$ .

<sup>*a*</sup> MMF-1 sample was synthesized using formaldehyde instead of paraformaldehyde through the route of MMF.

<sup>b</sup> MMF-2 sample was synthesized by the method provided by the ref. 49-51.

Table S2 Molar ratio of C/H/N/O of MMF, MMF-1 and MMF-2 by element analysis.

Element	С	Н	Ν	0
Molar ratio of MMF	1.00	1.82	1.13	0.40
Molar ratio of MMF-1	1.00	1.74	0.99	0.43
Molar ratio of MMF-2	1.00	1.80	1.11	0.34
Molar ratio of MMF-2	1.00	1.80	1.11	0.34

Adsorbent	Metal ions	qt /mg/g
MMF	Cr (VI)	35.45
MMF	Cr (III)	8.45
MMF	Fe (III)	0.73
MMF	Cu (II)	0.65
MMF	Ni (II)	0
AC	Cr (VI)	23.68
AC	Cr (III)	2.86
AC	Fe (III)	2.38
AC	Cu (II)	1.67
AC	Ni (II)	0
MMF-1	Cr (VI)	32.99
MMF-1	Cr (III)	4.51
MMF-1	Fe (III)	0.47
MMF-1	Cu (II)	0.62
MMF-1	Ni (II)	0.16
MMF-2	Cr (VI)	35.25
MMF-2	Cr (III)	5.53
MMF-2	Fe (III)	0.34
MMF-2	Cu (II)	0.25
MMF-2	Ni (II)	0.09

**Table S3** Adsorption capacity of MMF, AC, MMF-1 and MMF-2 for different metal ions.<sup>a</sup>

<sup>*a*</sup> Reaction conditions: 0.05 g of MMF, AC, MMF-1 or MMF-2 was added to 50 ml of metal solutions (Cr (VI), Cr (III), Fe (III), Cu (II) and Ni (II)) and stirred at 150 rpm at 20 °C for 20 min. The pH of the initial Cr (VI) solution is 6.0 and the metal salts solution of Cr (III), Fe (III), Cu (II) and Ni (II) is 4.0.

Conc (ppm)	19.0	39.4	79.1	142.6
Time (min)				
5	17.71 mg/g	36.56 mg/g	59.32 mg/g	65.90 mg/g
10	17.85 mg/g	36.62 mg/g	63.64 mg/g	66.51 mg/g
30	17.90 mg/g	36.82 mg/g	64.23 mg/g	66.62 mg/g
50	17.90 mg/g	36.87 mg/g	64.15 mg/g	66.65 mg/g
60	17.90 mg/g	36.86 mg/g	64.13 mg/g	66.63 mg/g

Table S4 Adsorption capacity of MMF at different Cr (VI) solutions.<sup>a</sup>

<sup>*a*</sup> Reaction conditions: 0.05 g of MMF was added to 50 ml of x ppm Cr (VI) solutions (x=19.0, 39.4, 79.1, 142.6) and stirred at 150 rpm at 20 °C and pH 6.0 for y min (y=5, 10, 30, 50, 60).

**Table S5** Adsorption capacity of MMF at different temperature.<sup>*a*</sup>

Temperature (°C)	20	25	30	35	40
$q_t / mg/g$	35.29	37.19	37.55	37.12	36.57

<sup>*a*</sup> Reaction conditions: 0.05 g of MMF was added to 50 ml of 40.7 ppm Cr (VI) solutions and stirred at 150 rpm at x  $^{\circ}$ C (x = 20, 25, 30, 40) and pH 6.0 for 20 min.

pН	2.0	4.0	6.0	7.0	8.0	10.0	12.0
q <sub>t</sub> / mg/g	32.69	33.36	35.29	33.19	30.59	27.31	23.39

Table S6 Adsorption capacity of MMF for Cr (VI) at different pH.<sup>a</sup>

<sup>a</sup> Reaction conditions: 0.05 g of MMF was added to 50 ml of 40.7 ppm Cr (VI) solutions and stirred at 150 rpm at 20 °C and pH X (X was adjusted to 2.0, 4.0, 6.0, 7.0, 8.0, 10.0, and 12.0 using 0.1 M HCl or 0.1 M NaOH. ) for 20 min.

Table S7 Desorption percent of Cr/MMF in 0.1 M NaOH solution at different times.<sup>a</sup>

Time (min)	5	10	20	30	40	50	60	120
desorption	100.00	98.16	100.00	100.00	98.54	97.44	100.00	98.63
rate/ %								

<sup>*a*</sup> Reaction conditions: 0.05 g of Cr/MMF was added to 50 ml of 0.1 M NaOH solutions and stirred at 150 rpm at 20 °C for x min (X = 5, 10, 20, 30, 40, 50, 60, 120).

Entry	Concentration/ ppm	$q_t / mg/g$
1	4.00	35.29
2	21.87	17.53
3	29.87	9.53

Table S8 Adsorption capacity of MMF for Cr (VI) under various recycles.<sup>a</sup>

<sup>*a*</sup> Reaction conditions: 0.05 g of MMF was added to 50 ml of 40.7 ppm Cr (VI) solution and stirred at 150 rpm at 20 °C and pH 6.0 for 20 min. Unfortunately, the mass of the sample MMF inevitably decreases for the recycle by centrifugation, results in the decrease of the qt.

# **Figure captions**

Fig. S1. Photographs of the synthesized MMF.

**Fig. S2.** <sup>13</sup>C MAS NMR of MMF sample.

Fig. S3. IR spectra of MMF sample.

Fig. S4. Thermo gravimetric (TGA) curve of MMF sample.

Fig. S5. N<sub>2</sub> sorption isotherms of MMF-1 (A) and MMF-2 (B); pore size distributions

of MMF-1 (a) and MMF-2 (b).

Fig. S6. (A) Survey spectra of MMF (a) and Cr/MMF (b). (B) Cr 2p XPS spectrum of

Cr/MMF.

Fig. S7. (A) C 1s spectrum of MMF, (B) C 1s spectrum of Cr/MMF, (C) O 1s spectra

of MMF (a) and Cr/MMF (b), (D) N 1s spectra of MMF (a) and Cr/MMF (b).



Fig. S1



Fig. S2



Fig. S3



Fig. S4



Fig. S5



Fig. S6



Fig. S7