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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

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

Zhongfei Lv, Changsheng Liang, Jiayang Cui, Yanan Zhang and Shiai Xu\*

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

A highly mesoporous melamine-formaldehyde resin (MMF) has been successfully synthesized through a facile route. It shows a relatively high surface area (317 m<sup>2</sup>/g), uniform pore sizes (8.0 nm), enhanced adsorption capacity (66.65 mg/g) and selectivity for hexavalent chromium.

Hexavalent chromium (Cr (VI)) is a highly toxic metallic element widely present in the industrial waste water from a variety of industrial process, such as metal finishing, dyes, inks, pigments, ceramics and leather tanning.<sup>1,2</sup> Cr (VI) can easily penetrate cell walls, damaging cell structure and resulting in various cancers.<sup>3-5</sup> Thus, removal of Cr (VI) from industrial waste water is of great public health importance. There are many methods available for this purpose, including sulfide precipitation, ion exchange, solvent extraction and adsorption. Among these methods, adsorption seems to be the most simple and effective one.<sup>6-10</sup> For example, activated carbon (AC) is often used as an adsorbent for the removal of Cr (VI) due to its high surface area and abundant micropores.<sup>11,12</sup> However, further treatment is often needed to enhance its adsorption capacity and selectivity, such as oxidation, acidation, alkalization and impregnation of foreign materials, thus increasing the cost and limiting its applications.<sup>13-21</sup> Therefore, many other adsorbents have also been synthesized, such as melamine-formaldehyde resins,<sup>22,23</sup> chitosans<sup>24</sup> and their chemical modifications.<sup>25-29</sup> These adsorbents have more functional groups and can increase the adsorption sites for Cr (VI).

In 1992, an ordered mesoporous material (OMM), MCM-41 was successfully synthesized from the liquid-crystal templates.<sup>30</sup> Over the past decades, some other OMMs have been reported and attracted great interest for their special pore structure, large surface area, uniform pore sizes and wide applications in the catalysis, adsorption, separation, and biomedicine.<sup>31-39</sup> However, for organic mesoporous materials, it seemed that such organic templates are not good for compatibility between the template and the polymer precursor, which should be carefully adjusted so that mesophase formation can occur. And so far, the organic-organic self-assemblies applied for the synthesis of mesoporous resins are mainly phenolic based polymers.<sup>35</sup> Besides, many other techniques such as templating method (hard-template and soft-template),<sup>40,41</sup> ionothermal method,<sup>42</sup> dynamic polymerization<sup>43</sup> or based on Schiff base chemistry method<sup>44</sup> were used to prepare the porous polymers and made some achievements in the application of energy<sup>45</sup> and catalysis.<sup>46</sup>

In this study, we report a facile route to synthesize mesoporous melamine-formaldehyde resins (MMF) from a mixture of copolymer (F127), melamine and paraformaldehyde in aqueous solution *via* a self-assembly method (Scheme S1 and Fig S1). Compared with the other synthetic methods for MMF, our approach is low cost (using melamine and paraformaldehyde rather than special monomer hexamethoxymethyl melamine),<sup>47</sup> easy to synthesis (hydrothermally synthesized in an autoclave without using any inorganic templates)<sup>48</sup> and less environment pollution (without using supervirulent organic solvent or carcinogenic formaldehyde).<sup>49-51</sup> The resulting MMF is proven to be an efficient adsorbent for Cr (VI), and has better adsorption capacity and selectivity than conventional AC. More importantly, temperature has little impact on the adsorption capacity of MMF for Cr (VI), indicating that this adsorbent is applicable in any season.

The N<sub>2</sub> sorption isotherms, SEM and TEM images of MMF samples are showed in Fig. 1. The N<sub>2</sub> sorption isotherms of MMF (Fig. 1 A) exhibit a typical type-IV curve with a hysteresis loop at 0.44-0.90, confirming the presence of mesoporosity in MMF.<sup>52</sup> The pore size calculated using the Barrett-Joyner-Halenda (BJH) method centers at 8.0 nm (Fig. 1B), and the BET surface area is at 317 m<sup>2</sup>/g and pore volume is at 0.58 cm<sup>3</sup>/g (Table S1). The SEM image (Fig. 1C) shows that MMF is highly mesoporous with a few larger pores. In addition, the TEM image (Fig. 1D) clearly reveals the uniform pore size, which is well agreement with pore size distributions. Furthermore, MMF is rich in

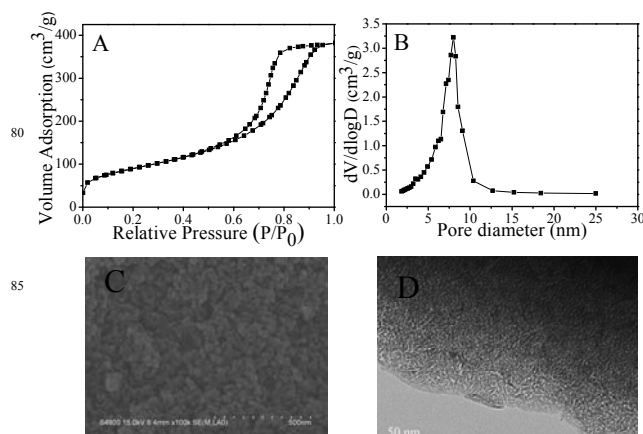
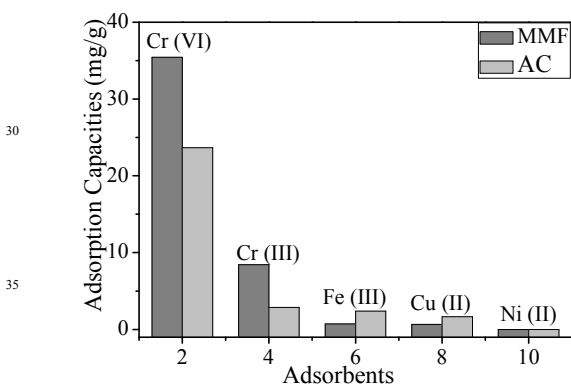


Fig. 1. (A) N<sub>2</sub> sorption isotherms, (B) pore size distributions, (C) SEM image and (D) TEM image of MMF samples.

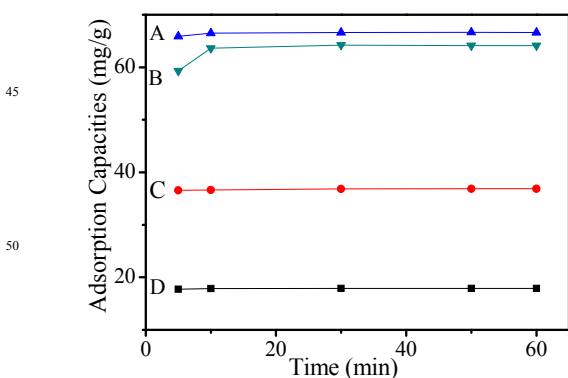
inherent amination (-NH-CH<sub>2</sub>-NH-) and triazine groups (Fig. S2 and S3), which could act as the activated sites for catching toxic Cr (VI) from water.<sup>51</sup> More interestingly, there is only methylene very important for the stability of the polymer networks.<sup>53,54</sup> Thus, the TGA profile shows that MMF is stable up to ~300 °C (Fig. S4). In addition, the elemental analysis of MMF shows that the molar ratio of C/H/N/O is 1.00/1.82/1.13/0.40 (Table S2).

Batch experiments were carried out to evaluate the adsorption capacity and selectivity of MMF and AC for Cr (VI). It is evident in Fig. 2 and Table S3 that MMF has higher adsorption capacity (35.45 mg/g) and better selectivity for Cr (VI), but lower adsorption capacity for some other ions, such as Fe (III), Cu (II) and Ni (II). In contrast, although the commercial adsorbent AC has higher surface area (1435 m<sup>2</sup>/g) and porosity, it has relatively lower adsorption capacity and selectivity for Cr (VI). Moreover, the other mesoporous melamine-formaldehyde resins such as MMF-1 and MMF-2 (N<sub>2</sub> sorption isotherms and pore size distributions of MMF-1 and MMF-2 are showed in Fig. S5) show relatively lower or similar adsorption property with the resulting MMF.

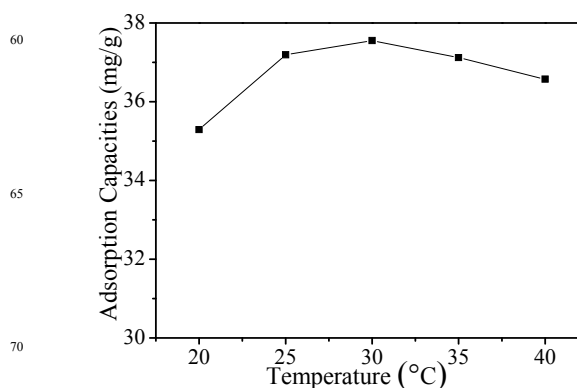
Fig. 3 and Table S4 show the adsorption capacity of MMF for Cr (VI) as a function of contact time with different initial concentrations. The adsorption rate of metal uptake is very rapid and the maximum uptake is reached within 5 min, after which there is no evident increase in adsorption. These results indicate



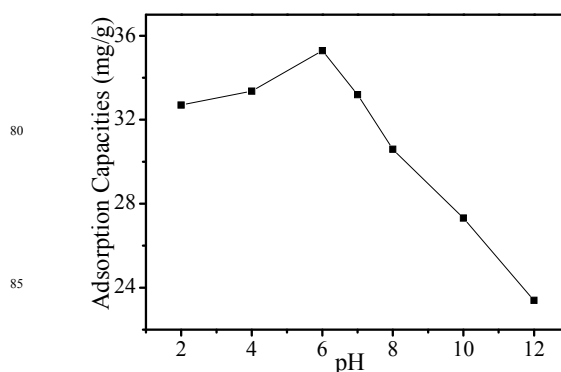
**Fig. 2.** Adsorption of Cr (VI), Cr (III), Fe (III), Cu (II) and Ni (II) by MMF and AC. (0.05 g of MMF or AC was added to 50 ml of 40.0 ppm metal ions solutions and stirred at 150 rpm at 20 °C for 20 min.)



**Fig. 3.** Effect of initial Cr (VI) concentration (A) 142.6 ppm, (B) 79.1 ppm, (C) 39.4 ppm and (D) 19.0 ppm on the adsorption of MMF. (0.05 g of MMF was added to 50 ml of Cr (VI) solutions and stirred at 150 rpm at 25 °C and pH 6.0 for different times.)



**Fig. 4.** Effect of temperature on the adsorption of Cr (VI) by MMF. (0.05 g of MMF was added to 50 ml of 40.7 ppm Cr (VI) solutions, and stirred at 150 rpm at pH 6.0 for 20 min.)



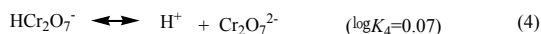
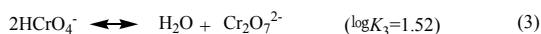
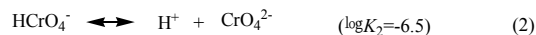
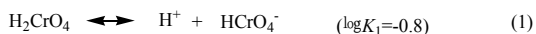
**Fig. 5.** Effect of pH on the Cr (VI) adsorption by MMF. (0.05 g of MMF was added to 50 ml of 40.7 ppm Cr (VI) solutions, and stirred at 150 rpm at 20 °C for 20 min, pH adjusted with 0.1 M HCl or 0.1 M NaOH.)

that the adsorption of Cr (VI) by MMF takes place rapidly, thus saving time and costs for waste water treatment. However, the adsorption rate of Cr (VI) by other adsorbents shows a wide range of adsorption times.<sup>55</sup> In addition, the adsorption isotherms are a function of the initial Cr (VI) concentration, but the concentration-dependent adsorption only works to a certain extent. As shown in Fig. 3, the adsorption capacity of MMF increases rapidly from 19.0 ppm to 79.1 ppm and obtains the maximum adsorption capacity (66.65 mg/g) at the initial Cr (VI) concentration of 142.6 ppm.

Adsorption experiments were performed at 20, 25, 30, 35 and 40 °C to investigate the effect of temperature on the adsorption of Cr (VI) by MMF (Fig. 4 and Table S5) show that the adsorption of Cr (VI) ions increases slightly with increment of temperature from 20 to 30 °C, and then decreases with further increase of temperature from 30 to 40 °C. The adsorption capacity of MMF reaches the maximum of 37.55 mg/g at 30 °C. However, it needs to be pointed out that the overall change in the adsorption of Cr (VI) with the temperature is fairly subtle, indicating that MMF could be widely used for the removal of Cr (VI) without seasonal restrictions.

The effect of pH on the adsorption of Cr (VI) by MMF is shown in Fig. 5 and Table S6. The maximum adsorption of Cr (VI) is observed at pH 6.0. The pH dependence of metal

adsorption has been shown to be largely related to the type and ionic state of the functional groups present in the adsorbent and the metal chemistry in the solution. The distributions of various forms of Cr (VI) ions in the aqueous solution were determined using appropriate chemical reaction equilibrium analyses. Cr anions are known to exist in the following forms depending on the pH of the aqueous solution.<sup>56</sup>



$\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  are the predominant species in total chromium concentration.  $\text{HCrO}_4^-$  is the predominant at pH 2-6.5, whereas  $\text{CrO}_4^{2-}$  is predominant at pH > 6.5.<sup>57</sup> Under a lower pH, the surface of MMF becomes highly protonated and would not bind with metal ions. As pH increases, the amine groups of MMF become non-protonated and could act as coordinating ligands for metal ions. However, if pH continues to increase, the surface will be negatively charged, greatly weakening the electrostatic attraction between the sorbent and negatively charged Cr (VI) anions, thus reducing the removal efficiency. Moreover, there is a competition between  $\text{OH}^-$  and Cr ions, especially at a high pH. More interestingly, the effect of pH on the adsorption of Cr (VI) indicates that the Cr (VI) adsorbed by MMF could be recovered, and the sorbent could be reused. In this study, Cr/MMF (MMF-adsorbed Cr) was subjected to basic treatment to recover the adsorbed Cr (VI) ions. Table S7 shows the desorption rate of Cr/MMF at different times. It shows that the use of 0.1 M NaOH solution allows a ~ 100% recovery of the adsorbed Cr (VI). After basic treatment, MMF shows relatively higher adsorption capacity for Cr (VI) again (Table S8).

The XPS spectra (Fig. S6 and Fig. S7) of MMF before and after the adsorption of Cr (Cr/MMF) show that the binding energy of N1s and O1s decrease in the Cr/MMF (Fig. S7). More importantly, the C=N groups of MMF at binding energy of 287.6 eV become stronger, which is possibly attributed to the enhancement of the chelating ligands between the groups of Cr (VI), C, N and O. Thus, there may be some interactions between C, N and O with Cr (VI), which could explain the excellent adsorption capacity and selectivity of MMF.<sup>58-62</sup> These results indicate that the presence of the surface functional groups rather than surface area or pore volumes, contributes to increasing the adsorption and selectivity of MMF for Cr (VI).

## Conclusions

In this study, we reported a facile route to synthesize MMF, which could quickly and efficiently remove toxic Cr (VI) from water within 5 minutes. Such fast adsorption rate and high adsorption capacity of MMF is mainly attributed to its abundant functional groups, such as high densities of amine and triazine groups. More importantly, the adsorbed Cr (VI) could be recovered and the MMF is easily recycled by basic treatment. The MMF is easy to synthesis, low cost and environment-friendly, especially, it can remove the toxic Cr (VI) efficiently and quickly, these advantages make it to be an attractive adsorbent for the

purification of waste and contaminated water.

## Acknowledgements

This work is supported by the National Natural Science Foundation of China (NO. 51463020) and the Fundamental Research Funds for the Central Universities (WD1315012).

## Notes and references

- <sup>a</sup> Shanghai Key Laboratory of Advanced Polymeric Material, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China. Fax: (+86) 021 6425 3775; Tel: (+86) 021 6425 3353; E-mail: saxu@ecust.edu.cn
- † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
- ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
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