[Supporting Info]

Magnetic Nanocomposite Based on Polyacrylic Acid and Carboxylated Cellulose Nanocrystal for the Removal of Cationic Dye

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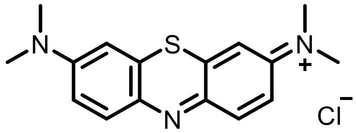
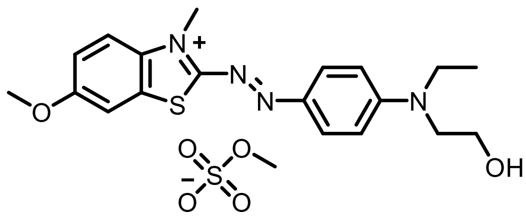
Chemical structures



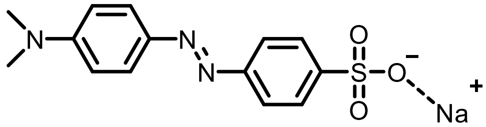
Methylene Blue (MB)

IUPAC Name*: [7-(dimethylamino)phenothiazin-3-ylidene]-dimethylazanium;chloride



Cationic Blue (CB)

IUPAC Name*: 2-[*N*-ethyl-4-[(6-methoxy-3-methyl-1,3-benzothiazol-3-ium-2-yl)diazenyl]anilino]ethanol;methyl sulfate

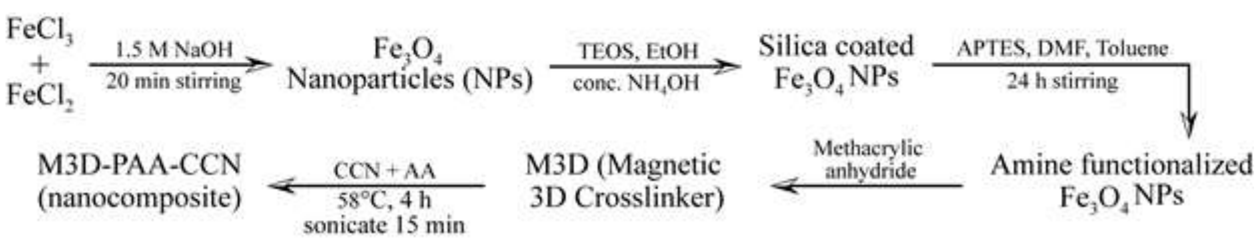


Methyl orange

IUPAC Name*: sodium;4-[[4-(dimethylamino)phenyl]diazenyl]benzenesulfonate

* Computed by LexiChem 2.6.6 (PubChem release 2019.06.18)

Synthesis of M3D-PAA-CCN nanocomposite



Scheme S1. A schematic illustration of the fabrication of M3D-PAA-CCN nanocomposite.

FTIR characterization

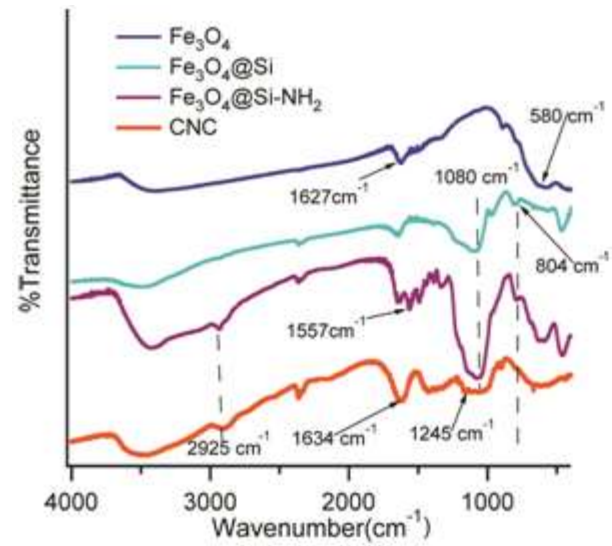
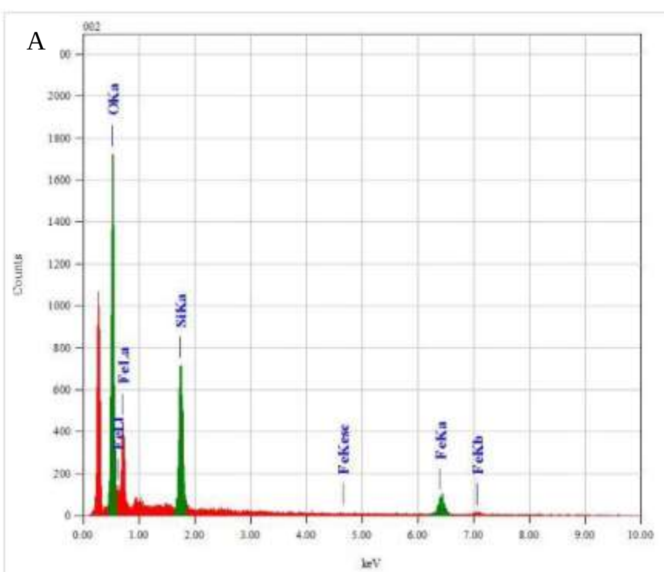


Figure S1. FTIR spectra of Fe_3O_4 (blue), Fe_3O_4@Si (paste), Fe_3O_4@Si-NH_2 (purple), and CNC (orange).

EDX Characterization



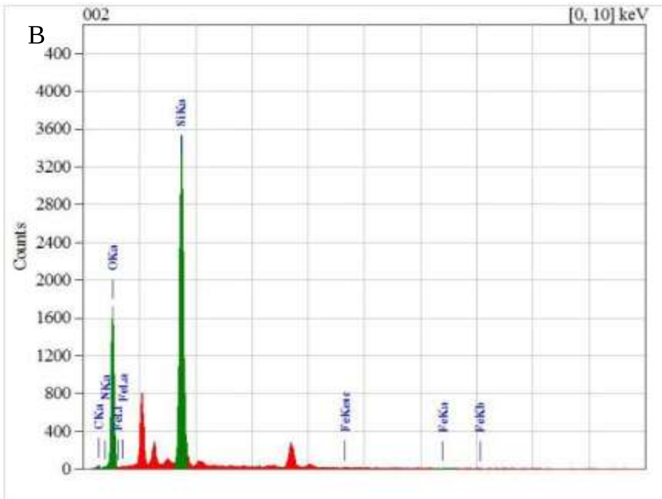


Figure S2. EDX spectra of M3D (A) and M3D-PAA-CCN (B).

Table S1. Atomic percentages of the elements obtained from EDX and XPS for M3D and M3D-PAA-CCN.

Atomic %						
Sample	Analysis	Fe	O	C	N	Si
M3D	EDX	15	42	26	5	12
	XPS	8	46	29	7	10
M3D-PAA-CCN	EDX	1	56	31	1	11
	XPS	-	60	35	1	4

Effect of different ratios of CCN, M3D, and acrylic acid on the properties of M3D-PAA-CCN

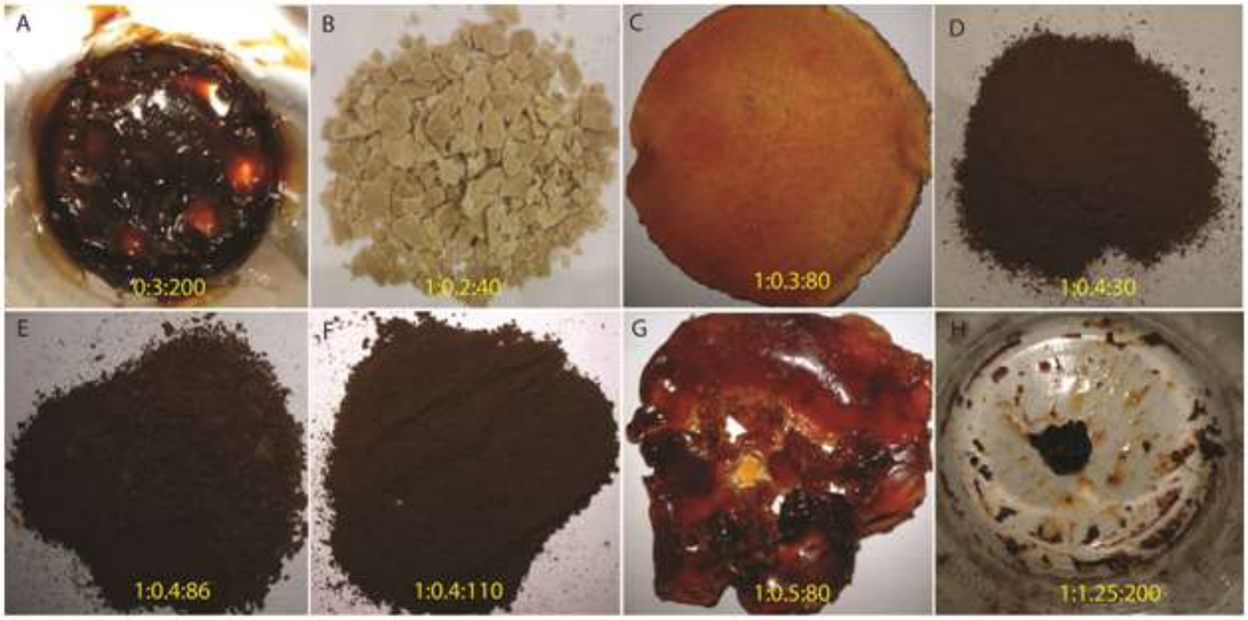


Figure S3. Photos of M3D-PAA-CCN nanocomposite prepared from different ratios (mentioned on images) of CCN, M3D, and acrylic acid.

The easy magnetic separation of M3D-PAA-CCN nanocomposites from the application sites and the ability to serve as a desired adsorbent depend on the proper use of M3D crosslinker and CCN. With an increase in the amount of M3D, the magnetic property was enhanced but the composite became very sticky and adhesive leading to low adsorbability. The amount of CCN was then increased to improve the dispersibility and adsorption capacity as well. As the amount of CCN was much higher compared to M3D, the nanocomposite was dispersible but not enough magnetic. For this reason, optimizing a condition for the synthesis of nanocomposite with high dispersibility and adequate magnetic properties was necessary. We chose different ratios of CCN, M3D, and acrylic acid for developing a fabrication strategy (Figure S3). In absence of CCN (Figure S3 A), M3D-PAA-CCN was highly adhesive. In the nanocomposites shown in Figure S3 B, C, G, and H the amount of CCN was fixed and with an increase in M3D the adhesiveness increased. According to Figure S2 D-F, when the ratio of CCN to M3D was 1:0.4 M3D-PAA-CCN was enough dispersive and magnetic and no noticeable effect was observed on increasing the amount of acrylic acid. We also studied the effect of temperature on the properties of M3D-PAA-CCN. When the temperature was higher than 60 °C the composite was very sticky which may be attributed to the increased rate of polymerization. The ideal temperature for the synthesis of M3D-PAA-CCN was found at 55-58 °C.

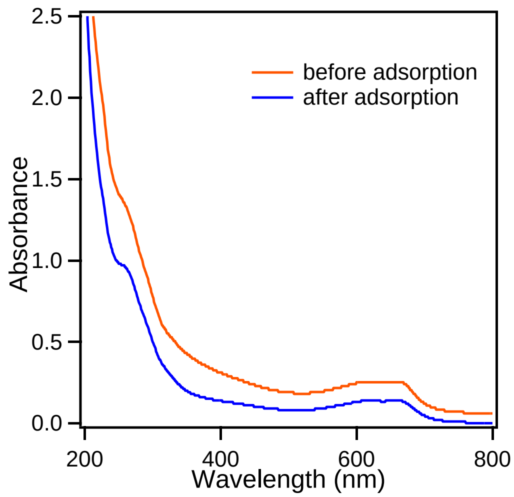


Figure S4. UV-visible spectra demonstrating the adsorption capacity of real wastewater from textile industry by the M3D-PAA-CCN composite.

The as-synthesized was also tested against an industrial dye sample collected from a local textile dye company in Dhaka EPZ, Bangladesh. The industrial wastewater may contain many unknown dyes and other pollutants such as heavy metals that would make any conclusion difficult from this experiment as we claimed in our manuscript that the as-synthesized M3D-PAA-CCN can selectively adsorb the cationic dyes. However, we observed in our adsorption experiment the overall absorbance of the dye in the range of 200 to 800 nm decreased significantly.

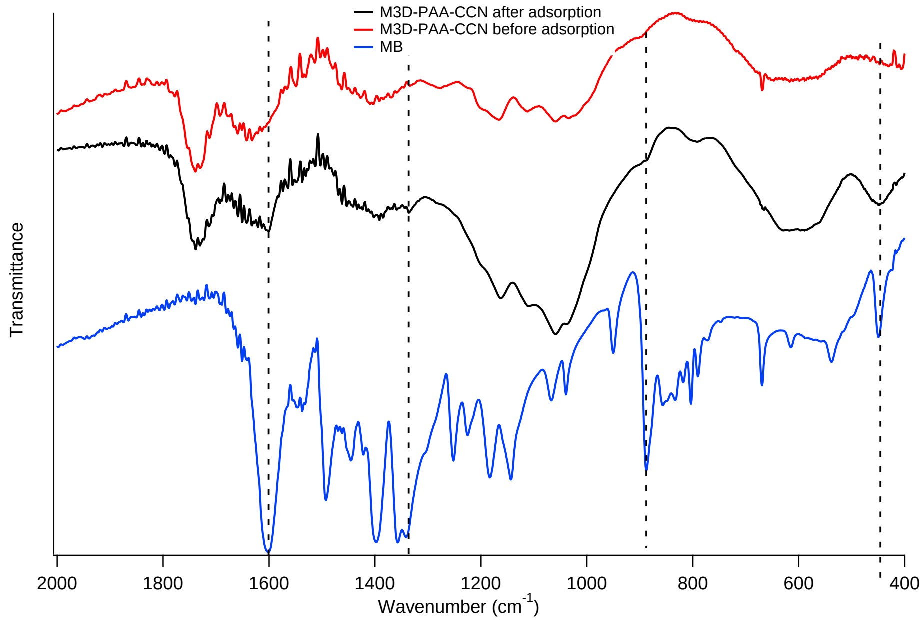


Figure S5. FTIR spectra of MB (blue), and M3D-PAA-CCN before (red) and after (black) adsorption.

The FTIR spectra of MB, and M3D-PAA-CCN before and after adsorption are shown in Figure S6. Although it was challenging to see the MB adsorption clearly by FTIR owing to the inadequate sensitivity to very trace amount of MB adsorbed, we observed a few changes in the spectra. A new peak appeared at 448 cm^{-1} indicating the characteristic fingerprint peak of MB demonstrated the adsorption of MB onto the composite. We also observed some small peaks or shoulders appearing after the MB adsorption onto the M3D-PAA-CCN at 890, 1340, 1600 cm^{-1} attributing the adsorption of MB.

Adsorption of MB and CB by M3D-PAA-CCN

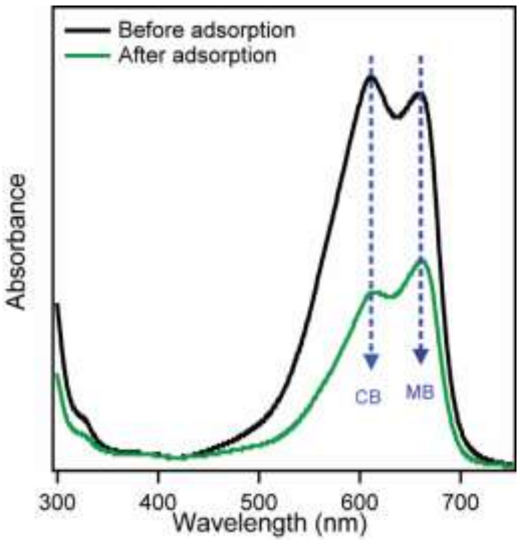


Figure S6. UV-visible spectra demonstrating the adsorption of MB and CB by the M3D-PAA-CCN composite.

To further investigate the ionic interaction of the adsorbent and the cationic dyes, we performed the adsorption experiments using a mixture of two cationic dyes such as MB and cationic blue (CB) at ambient pH. We observed that the adsorption of both cationic dyes, MB and CB, by the as-synthesized M3D-PAA-CCN were somewhat similar as shown in Figure S7. Although it was challenging to quantitatively investigate the speciation of this adsorbent to these two dyes because of their same color and close appearance of the maximum absorbance on the UV-visible spectra, we were still able to qualitatively say that the extent of adsorption was more or less similar to MB and CB. This behavior was expected because the major mode of interaction of the adsorbent and dye is the ionic interaction as explained in the previous sections of this article.

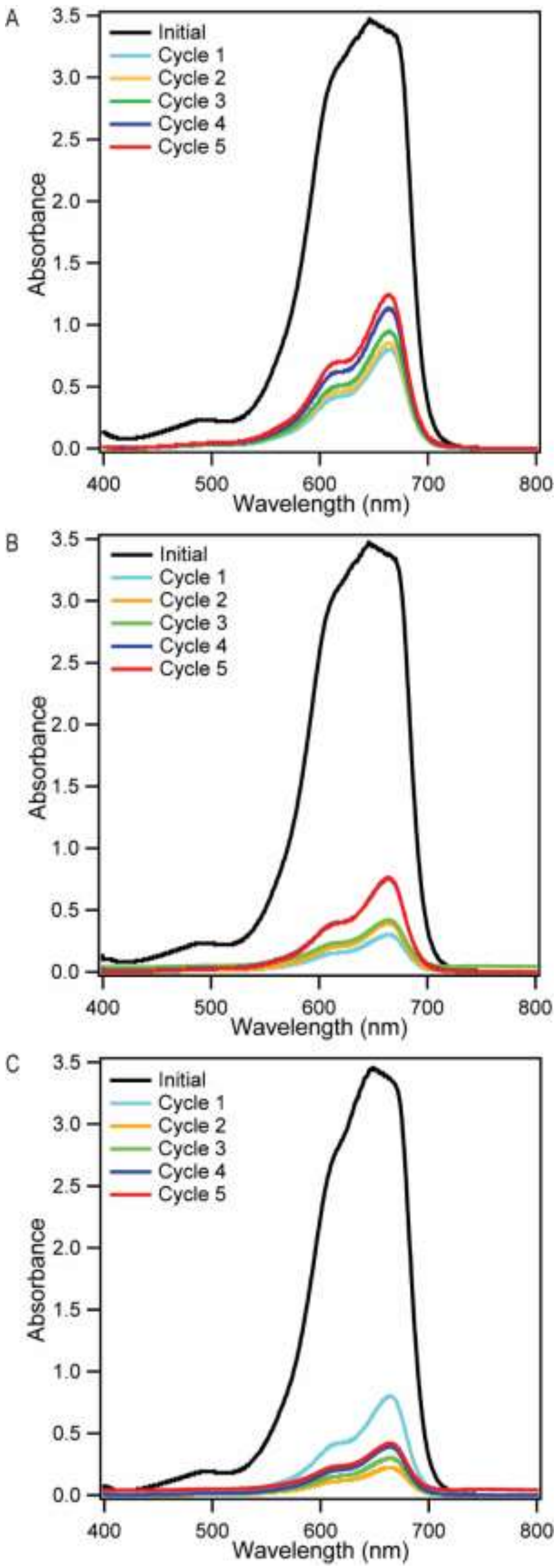

A
Initial
Cycle 1
Cycle 2
Cycle 3
Cycle 4
Cycle 5
Absorbance
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5
400 500 600 700 800
Wavelength (nm)
B
Initial
Cycle 1
Cycle 2
Cycle 3
Cycle 4
Cycle 5
Absorbance
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5
400 500 600 700 800
Wavelength (nm)
C
Initial
Cycle 1
Cycle 2
Cycle 3
Cycle 4
Cycle 5
Absorbance
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5
400 500 600 700 800
Wavelength (nm)

Figure S7. UV-visible spectra demonstrating the recyclability capacity in pH 7 (A), pH 9 (B), and pH 11 (C) by the M3D-PAA-CCN composite.