

Supporting Information

Carbon Hybridizing Montmorillonite Nanosheets: Preparation, Structural Evolution and Enhanced Adsorption Performance

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Experimental section

Materials. The montmorillonite (MMT) used was raw Na-montmorillonite obtained from Zhejiang, China. The chemical compositions of MMT were as follows: SiO₂ 61.5%, Al₂O₃ 19.3%, MgO 3.5%, Fe₂O₃ 1.4%, Na₂O 2.8%, CaO 2.5%, K₂O 0.6%, and the loss on ignition was approximately 8.4%. The cation exchange capacity (CEC) of MMT was 125.0 mmol/100g. Sucrose (C₁₂H₂₂O₁₁), hydrochloric acid (HCl), sodium hydroxide (NaOH), Rhodamine B (C₂₈H₃₁ClN₂O₃), methyl orange (C₁₄H₁₄N₃SO₃Na) and Congo red (C₃₂H₂₂N₆Na₂O₆S₂) were purchased from Sinopharm Chemical Reagent Co. Ltd.

Preparation. In a typical synthesis process, 1.000 g of sucrose was dissolved in 60 mL of distilled water under stirring at room temperature, and 1.000 g of MMT was added to above solution. The obtained mixture suspension was mechanically stirred for 30 min, and sonicated for 30 min at room temperature. Then, the final suspension was transferred into a Teflon-lined stainless steel autoclave (100 mL in capacity) and maintained at 200 °C for 24 h. The products were collected by a centrifuge, and subsequently washed several times with distilled water. HC/MMT was obtained after drying at 60 °C for 24 h. C/MMT was obtained after HC/MMT was calcined at 800 °C for 3 h with a heating rate of 10 °C/min in a nitrogen atmosphere. For comparison, hydrochar (HC) and pyrolytic carbon (C) were prepared by hydrothermal carbonization and calcination in the similar way without MMT, respectively. Other samples were similarly prepared with different ratio of sucrose and MMT. The samples prepared with 0.500 g of sucrose and 1.000 g of MMT were labeled as HC/MMT-0.5 and C/MMT-0.5, respectively. The samples with 2.000 g of sucrose and 1.000 g of MMT were labeled as HC/MMT-2 and C/MMT-2, respectively.

Characterization. Thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis of the sample were performed with a NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. The X-ray diffraction (XRD) data were collected on a RIGAKU D/max-2550 PC diffractometer at 40 kV and 40 mA, using Cu K α radiation ($\lambda=0.15406$ nm) with a scan step of

0.02 %s. Scanning electron microscope (SEM) was performed using a JEOL JSM-6360LV at an accelerating voltage of 5 kV, which equipped with an energy dispersive spectrometer (EDS). Transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM-2100F microscope operating at 200 kV. Raman spectra were measured using a Renishaw Micro-Raman System 2000 spectrometer at a spectral resolution of 2 cm^{-1} . Fourier transform infrared (FTIR) spectroscopy was recorded on a Nicolet Nexus 670 FTIR spectrophotometer with a resolution of 2 cm^{-1} using KBr pellets. X-ray photoelectron spectroscopy (XPS) measurements of samples were conducted on an ESCALAB 250 spectrometer. Nitrogen gas adsorption-desorption isotherms were obtained at 77 K using an ASAP 2020 surface area analyzer. Estimates of the pore size distributions were deduced by Barrett-Joyner-Halenda (BJH) methods.

Adsorption experiments. The adsorption performances of samples were evaluated with the adsorption experiments of Congo red. In a typical adsorption experiment, 2.5 mg of adsorbents were dispersed in 5 mL of Congo red solutions having concentration from 0.025 g/L to 1.0 g/L. In order to ensure the establishment of an adsorption-desorption equilibrium, the dispersions were vigorously shaken for 24 h at room temperature. The adsorbents were removed by centrifugation, and the supernatants were collected for UV-Vis analysis after appropriate dilutions. The absorbance of the peak located at 498 nm was measured to determine amount of Congo red adsorbed. The effects of temperature and pH of the solution on the adsorption performance of C/MMT were investigated at Congo red concentration of 1.0 g/L. The pH of the solution was adjusted by diluted hydrochloric acid and sodium hydroxide. The adsorption experiments of Rhodamine B and methyl orange were conducted under similar reaction conditions, the absorbance of the peak located at 554 nm and 461 nm was measured, respectively. The desorption experiment of Congo red from C/MMT were conducted in deionized water at ambient temperatures for 24 h. The used C/MMT was thermally regenerated through calcined at 800 °C for 3 h in a nitrogen atmosphere. The cycle adsorption experiments were conducted with the regenerated C/MMT at Congo red concentration of 1.0 g/L.

N₂ Adsorption/desorption Isotherm Data

To analysis the textural properties and pore structures of the samples, the specific surface area and pore size distribution of MMT, HC/MMT and C/MMT were measured by the N₂ adsorption/desorption isotherm. The N₂ adsorption/desorption isotherm curves of MMT, HC/MMT and C/MMT (Fig. S2a) exhibit a type IV adsorption branch with a H3 hysteresis loop, which is characteristic of the mesoporous structure. The Brunauer–Emmett–Teller (BET) specific surface areas of MMT, HC/MMT and C/MMT were calculated to be 38.02, 26.25 and 51.84 m²/g, respectively. HC/MMT has a relatively lower specific surface area than MMT, which might be because the interlayer space of montmorillonite was filled with hydrochar. The specific surface area of C/MMT is highest, which could be attributed to the microporous structure after the pyrolysis of hydrochar. The pore-size distributions MMT, HC/MMT and C/MMT are shown in Fig. S2b, which were calculated using the Barrett–Joyner–Halenda (BJH) method. The pore characteristic of MMT is mainly mesoporous structure. Both the microporous and mesoporous structures appear in the HC/MMT and C/MMT, which could be due to the hybrid of montmorillonite and carbon materials.

Different Ratio Experimental Data

HC/MMT-0.5, HC/MMT-2, C/MMT-0.5 and C/MMT-2 were synthesized to investigate the optimal ratio of carbon and montmorillonite, and the adsorption performances of samples were evaluated using the adsorption experiments of Congo red. The XRD patterns of the samples are shown in Fig. S3a. Compared with the HC/MMT-0.5, the d_{001} basal spacing of montmorillonite in HC/MMT-2 is larger, but the corresponding diffraction peaks is lower. It might be because more sucrose is intercalated into the interlayer space of montmorillonite, and part of montmorillonite is delaminated after hydrothermal carbonization. The XRD patterns of C/MMT-0.5 and C/MMT-2 are similar to that of C/MMT. As shown in Fig. S3b, the adsorption performances of HC/MMT-2 and C/MMT-2 are slightly higher than that of HC/MMT-0.5 and C/MMT-0.5, and all are lower than that of HC/MMT and C/MMT.

Scheme for the Synthesis

As illustrated in Fig. S4, C/MMT was prepared through mixing intercalation, hydrothermal carbonization and calcination pyrolysis. Firstly, the montmorillonite was mixed with sucrose, and the sucrose was intercalated in the interlayer space of montmorillonite with stir and ultrasound. Under hydrothermal conditions, the sucrose in the interlayer space of montmorillonite was carbonized into hydrochar, and HC/MMT was obtained with larger interlayer spacing than Na-montmorillonite. The hydrochar in the HC/MMT is amorphous carbon with abundant hydroxyl and carbonyl. Finally, the hydrochar in the interlayer of montmorillonite was calcined pyrolysis under the nitrogen atmosphere, and carbon materials with graphene-like structure were formed under the impact of montmorillonite layers. C/MMT with microporous and mesoporous structures was obtained via carbon hybridizing montmorillonite. The hybrid materials possess excellent adsorption performance for Congo red, which are promising candidates for organic wastewater treatment.

Dye Adsorption Experimental Data

C/MMT exhibits excellent adsorption performance at lower concentration of Congo red (Fig. S5). With the increase of temperature of the solution (Fig. S6), the amount adsorbed of C/MMT increases first and then decreases, which could be attributed to the higher desorption at the relatively high temperature. The amount adsorbed of C/MMT decreases slightly with the increase of pH value of the solution (Fig. S7), and C/MMT exhibits excellent adsorption performance for Rhodamine B and methyl orange (Fig. S8). The desorption ratio of Congo red from C/MMT is about 16.52% in deionized water, the amount adsorbed of C/MMT for Congo red maintains 96.77% after three cycles (Fig. S9).

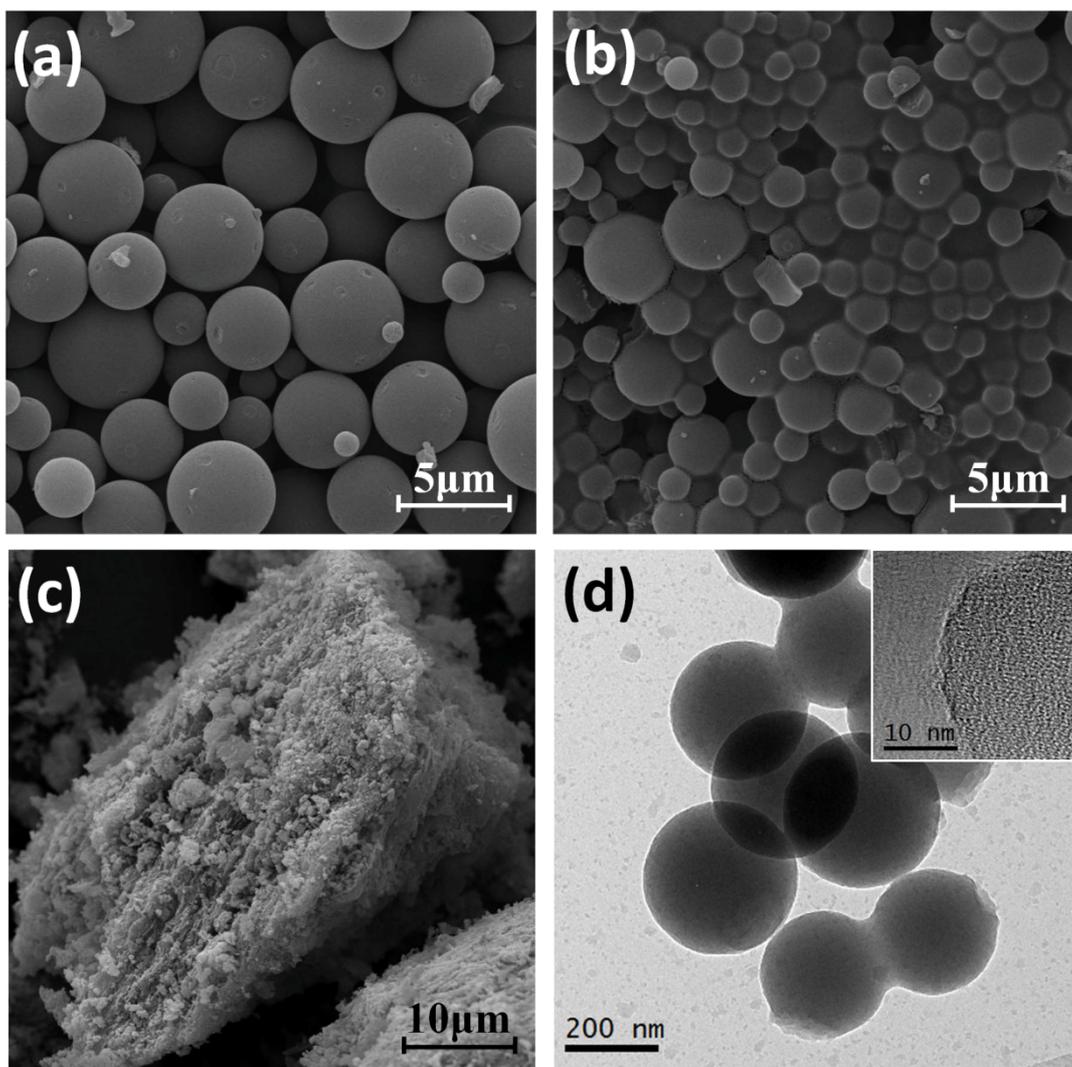


Fig. S1. SEM images of (a) HC, (b) C, (c) C/MMT, (d) HC, the inset shows the corresponding HRTEM images.

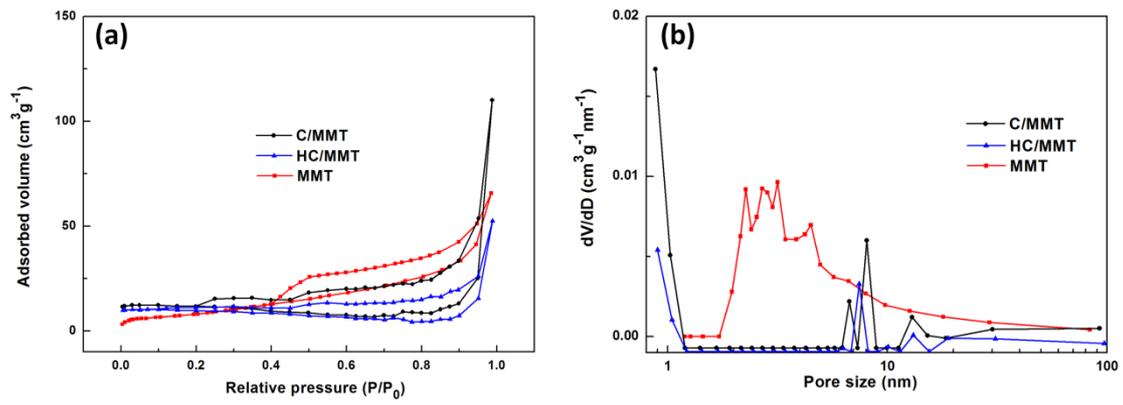


Fig. S2. (a) N₂ adsorption/desorption isotherm curves and (b) BJH pore-size distributions of MMT, HC/MMT and C/MMT.

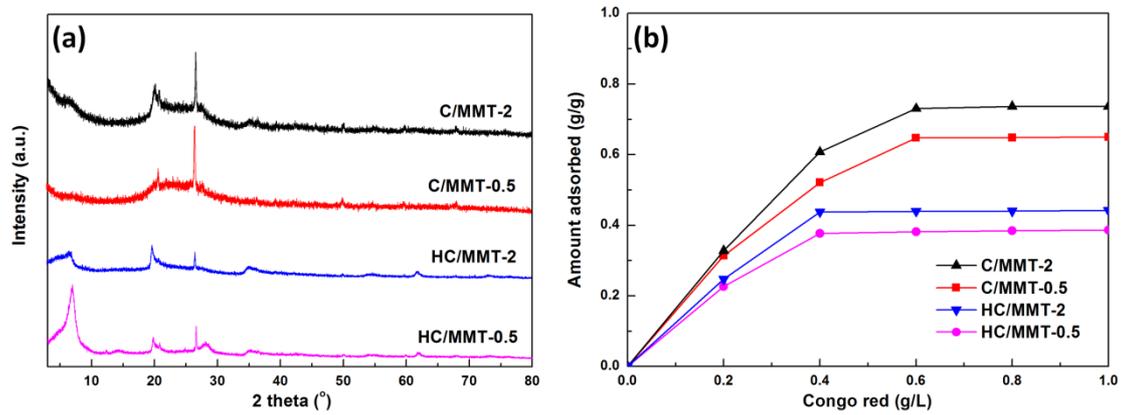


Fig. S3. (a) XRD patterns and (b) the adsorption performances of HC/MMT-0.5, HC/MMT-2, C/MMT-0.5 and C/MMT-2.

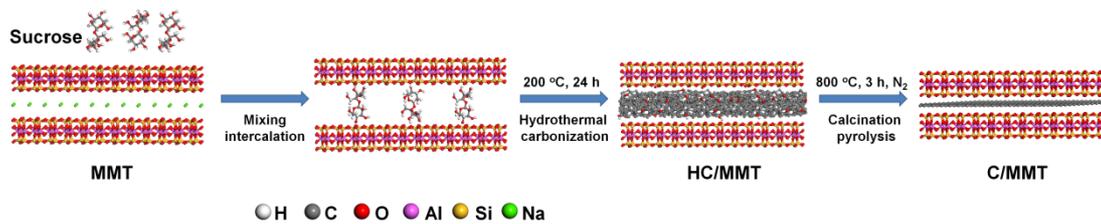


Fig. S4. Scheme for the synthesis of C/MMT and structural evolution process

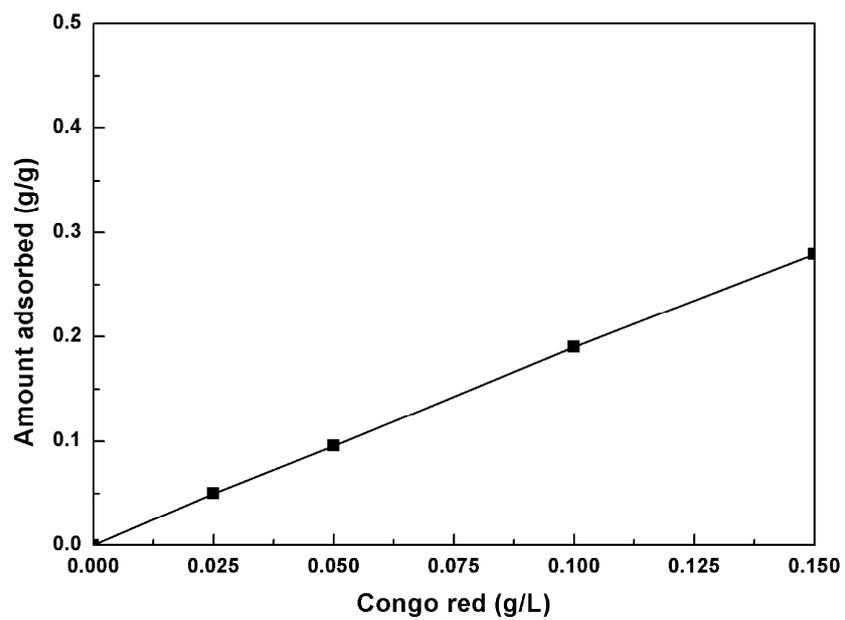


Fig. S5. The adsorption performance of C/MMT at lower concentration of Congo red.

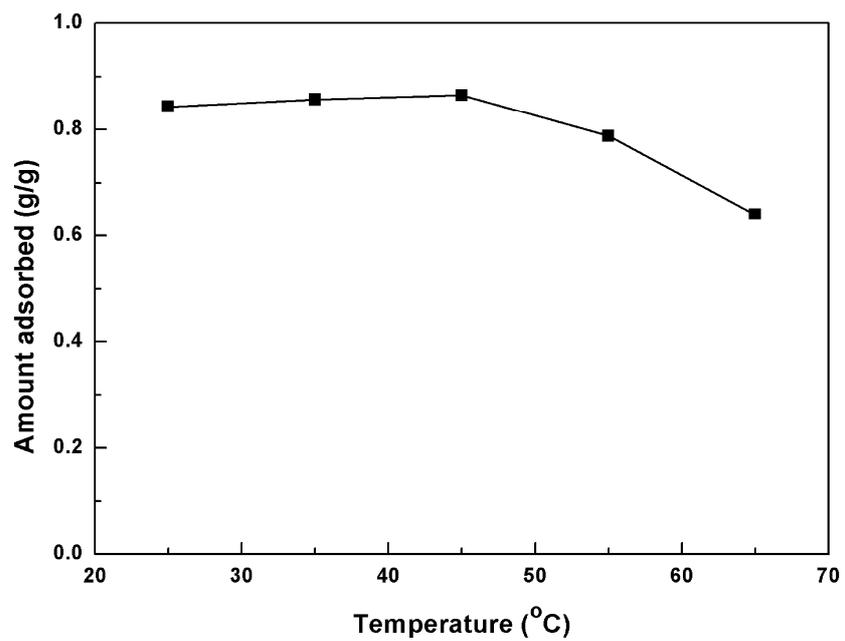


Fig. S6. The effect of temperature of the solution on the adsorption performance of C/MMT.

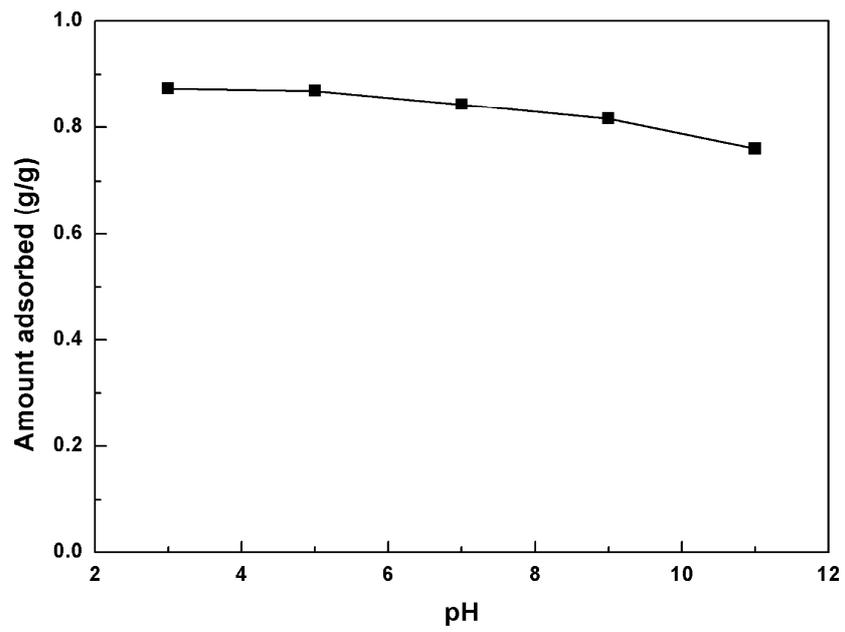


Fig. S7. The effect of pH value of the solution on the adsorption performance of C/MMT.

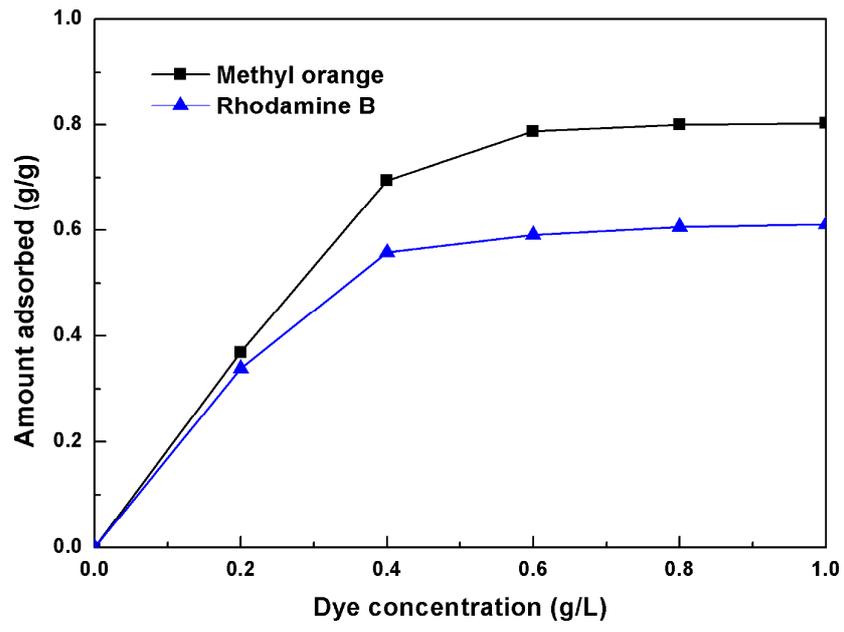


Fig. S8. The adsorption performance of C/MMT for Rhodamine B and methyl orange.

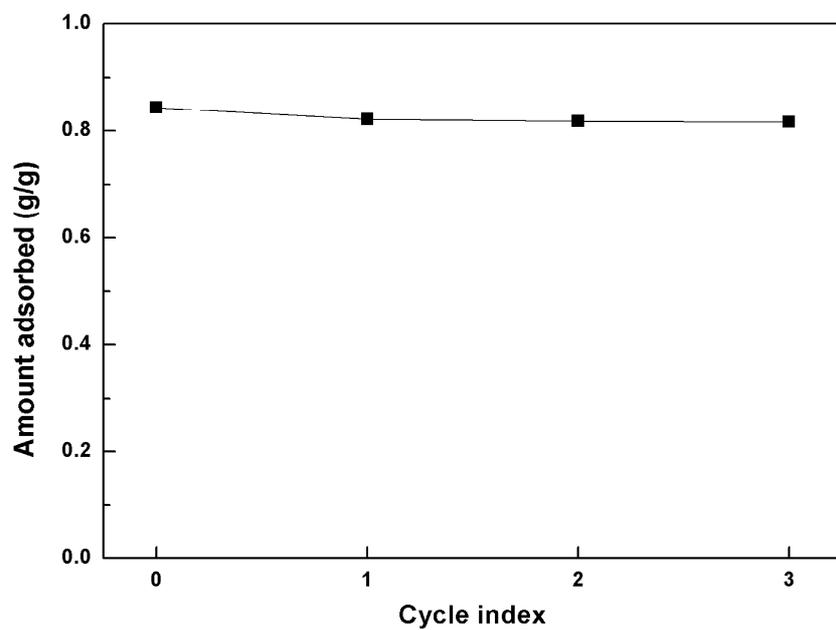


Fig. S9. The cycle adsorption performance of C/MMT for Congo red.