Supporting information

Facile and green synthesis of carboxylated cellulose nanocrystals as efficient adsorbents in wastewater treatments

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Characterization.

Field Emission Scanning Electron Microscope (FE-SEM)

The morphologies were investigated using a field emission scanning electron microscope (FE-SEM, vltra55, Carl Zeiss) and a Multimode–Nanoscope IV (Veeco, Santa Barbara, CA), equipped with an E scanner and NSC11/AIBS cantilevers (MikroMasch, Tallinn, Estonia) with a spring constant of 40 N/m. 0.01 wt% CNs were dispersed in ethanol and the suspension was sonicated in an ice bath (Model S7500, Branson, USA) for 15 minutes. The suspension was deposited on a silicon wafer, and the wafer was then dried in an oven at 60 °C.

Electron spin resonance (ESR) Spectroscopy

EPR spectra of the samples were obtained using EMX-8 / 2.7C, Bruker, Germany and Microwave Bridge (microwave frequency 9.866 GHz, conversion time, 40.96 ms, field scan 100 G, microwave power 2.016 mW, time constant 163.84 ms, number of scans, 1) 1 ml sample, immediately mixed with the capture DMPO for 2 minutes to form DMPO-OH adduct.

Fourier Transform Infrared (FTIR) Spectroscopy

FT-IR spectra were recorded on a Nicolet IS50 FT-IR spectrophotometer operating at 64 scans and 2 cm⁻¹ resolution in the region between 4000 and 400 cm⁻¹ at room temperature. CNs were mixed with KBr (1:50) and then pressed into a sheet.

X-ray diffraction (XRD) measurements

X-ray diffraction (XRD) measurements were conducted on a Thermo ARL XTRA X-ray diffractometer using Cu Ka (1.5418Å) radiation (40 kV, 40 mA) in 3° min⁻¹ steps at room temperature. The degree of crystallinity was calculated from the integrated area of crystalline and amorphous peaks using the following equation¹

$$X_c(\%) = \frac{I_{cr}}{(I_{cr} + I_{am})} \tag{1}$$

where I_{cr} , I_{am} are integrated area of the crystalline and amorphous phases.

Thermo-gravimetric Analysis (TGA).

Thermal stability of Carboxylated CNC was obtained using a thermo–gravimetric analyzer (TG209 F1, Netzsch, Germany). Under nitrogen environmental protection, the samples (5–8mg) were heated from 25 to 600 °C at a rate of 20 °C/min. The initial decomposition temperature (T_0) and maximum decomposition temperature (T_{max}) were recorded from the TGA curve.

Zeta potential analysis

The zeta potential and size distribution of CNs in water were determined using a zeta potentiometer (Zetasizer Nano series nano-ZS90, Malvern, UK). 1 mg sample was dispersed in water to prepare a 0.01% suspension. 0.1M HCl and 0.1M NaOH was used to adjust the pH of the sample.

X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical state of the elements on the surface of the sample. The XPS spectrometer used was K-Alpha (Thermo Fisher Scientific) operated in constant analyzer energy (CAE) mode with an energy step of 1 eV and an Al Ka X-ray source (1486.6 eV). The powder sample was mounted on a tape and analyzed at a typical pressure of 10-7Pa. Avantage (free software) was used for peak fitting analysis.

Determination of carboxyl content

Conductance titration was used to determine the carboxylic acid content of CNCs. Briefly, CNCs (20 mg) were dispersed in 10 mL of 0.01 M HCl and sonicated for 20 minutes to disperse the nanocrystals. It was then stirred for two hours. The CNC suspension was titrated with 0.01 M NaOH until pH = 10 at a rate of 0.1 mL/min.

Dye Absorption Kinetics for MB

The adsorption of MB dye by carboxylated CNC was investigated. For each set of experiments, 15 mL of dye and an amount of carboxylated CNC suspension were placed in a 20 mL vial and the resulting mixture was stirred at 700 rpm for 30 minutes. Then 5 mL of the mixture in a vial was placed in a small centrifuge tube and centrifuged at 7500 rpm for 10 minutes. The supernatant was removed and diluted 10 times. The absorbance of the dye in the supernatant was then measured using a UV-vis spectrophotometer (Hitachi U-3900, Japan) at 664 nm, the optimum absorption peak of MB. The dye concentration was calculated from the absorbance calibration curve of free dye molecules, and the dye uptake (q_e , mg/g) on the surface of carboxylated CNC was determined using the equation below²:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_e is the equilibrium concentration of free dye molecules in the solution (mg/L), C_0 is the initial dye concentration (mg/L), V is the volume of solution (L), and m is

the mass of carboxylated CNC (g). Three repeating tests were performed.

The dye absorption capacity at time t (mg/g, q_t) on the carboxylated CNC surface was calculated using Equation (3) below².

$$q_t = \frac{(C_0 V_0 - C_e V_t) V}{m} \qquad (3)$$

where C_t is the dye concentration (mg/L) at time t, V_t is the volume of solution (L) at time *t*.

We also analyzed the mechanism of the absorption process using the pseudo-first-order kinetic (Eq.3) and the pseudo-second-order kinetic (Eq.4) models, as shown below²:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} \times \frac{t}{q_e} \qquad (5)$$

where K_1 and K_2 are the rate constants of the pseudo-first-order and pseudo-second-order model, respectively.

Copper ion absorption studies

A certain amount of CuSO₄ was dissolved in 1 L of deionized water, and 1.5 mL of concentrated sulfuric acid was added per liter to prepare a 1g/L heavy metal ion solution. Then, a solution of $1-9 \times 10^{-2}$ g / L was diluted with a pipette, and a standard curve was measured using the inductively coupled plasma optical emission spectroscopy (ICP-OES, Plasma Quant PQ9000, Jena Analytical Instruments, Germany). 3 mg of different carboxylated CNC samples were separately added to 50 mL of a 5 mg/L heavy metal sample solution and stirred with a magnetic stirrer for 12 hours at room temperature. The adsorbent was then removed, the heavy metal ion

solution was removed and stored for ICP-OES analysis. The metal ion removal rate was calculated based on the results of the ICP-OES test.



Figure S1. FE–SEM image for MCC.

Table S1	The zeta	notential	of	CNCs-	6h	before	and	after	MB	adsor	ntion
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sample	CNCs before adsorption	CNCs after adsorption			
Zeta potential (mV)	-38.4	-14.2			

models	parameters	CNCs-2h	CNCs-4h	CNCs-6h	CNCs-8h
Pseudo-first-order	R^2	0.96995	0.91258	0.87399	0.91297
	$K_1(\min^{-1})$	0.0363	0.0371	0.0425	0.0401
	q _e (mg/g)	49.431	60.321	73.714	59.902
	R^2	0.99961	0.99976	0.99896	0.99971
Psaudo socond order	K ₂ (g/mg/min)	0.0048	0.0068	0.0079	0.0075
r seudo-second-order	q _e (mg/g)	101.01	106.268	118.765	108.225

Table S2. Absorption Kinetic Parameters for MB Absorption of CNCs.

References

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