Supporting Information

Adsorption behavior of ionic liquid from aqueous solutions by functional corncob-cellulose nanocrystals

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1. Characterization

The surface morphologies of adsorbents were observed by a field emission scanning electron microscope (SEM, NOVA NanoSEM450, USA) equipped with an energy dispersive X-ray spectroscopy (EDS) and an atomic force microscope (5500AFM/SPM). Fourier-transform infrared (FT-IR) spectra of the samples were carried out on a VERTEX 70 spectrometer in transmittance mode by the use of KBr pellets at room temperature. Powder X-ray diffraction (XRD) patterns were acquired at a rate of 6° min^{-1} over the range of 5-60° (2θ) on Bruker D8 Advance X-ray diffract meter equipped with Cu Kα radiation (40 kV, 40 mA).

2. Equilibrium adsorption capacity calculation

The equilibrium adsorption capacity (q_e, mmol g^{-1}) of [Bmim]Cl was calculated according to the equation evaluated of Eq. S1:

$$qe = \frac{C0 - Ce}{m} \times V \quad S1)$$

Co and Ce (mmol/L) are the initial and equilibrium concentration of [Bmim]Cl, respectively, m (g) is the mass of the adsorbent, and V (L) is the volume of solution.

3. Determination of oxygen-containing function groups on CNGD and CNGS

The oxygen-containing function groups content of the CNGD was determined through retro-titration. 0.10 g CNGD was suspended in 100 mL NaOH solution (0.010 mol L^{-1}) and then stirred for 2 h at 45 ^{o}C. The solid was separated by filtration and 25.0 mL supernatant fluid was treated by HCl solution (0.010 mol L^{-1}). The experiment was carried out in parallel three times. The concentration of the carboxylic

function was calculated by Eq. S2:

$$C_{COOH} = \frac{(C_{NaOH} \times V_{NaOH} - 4 \times C_{HCl} \times V_{HCl})}{m_{CNM}} \quad (S2)$$

where C_{NaOH} and C_{HCl} are the concentrations of hydroxide and acid (mol L^{-1}), V_{NaOH} and V_{HCl} are the volumes of initial hydroxide and hydrochloric acid (mL) used in the titration of the excess non-reacted NaOH solution (L), m_{CNM} (g) is the mass of CNM.

The sulfonic acid groups and carboxyl groups on CNGS were measured by the same theory above. From the structural we will see, sulfonic acid group content is equal to the content of carboxyl group, which is half of the consumption of NaOH amount.

4. The kinetic models

Two kinetics models (i.e., pseudo-first-order and pseudo-second-order models) were employed to evaluate the [Bmim]Cl adsorption mechanism by CNGD and CNGS. Their linearized rate equations are expressed as follows [1]:

Pseudo-first-order model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (S3)$$

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}} + \frac{1}{q_e} t$$

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where k_1 is the rate constant of pseudo-first-order (h^{-1}), k_2 (g $mmol^{-1}$ h^{-1}) is the pseudo-second-order adsorption rate constant; q_e (mmol g^{-1}) and q_t (mmol g^{-1}) are the amounts of [Bmim]Cl adsorbed at equilibrium and at time t (h), respectively.

5. Adsorption isotherm models

The Langmuir isotherm equation (Eq. S5) assumes that monolayer coverage of the adsorbate over a structurally homogenous adsorbent surface and a saturated adsorption capacity is expected due to limited adsorptive sites on the surface[2].

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \quad \text{(S5)}$$

where q_e (mmol g^{-1}) is the equation adsorption capacity; C_e (mmol L^{-1}) is the equilibrium concentration of [Bmim]Cl in solution. q_m (mmol g^{-1}) is the maximum adsorption capacity; K_L (L $mmol^{-1}$) represents the Langmuir adsorption constant, associated with the adsorbing energy.

The Freundlich equation is employed to describe heterogeneous systems, which both mono-layer and multiple-layer adsorptions occur in the adsorption process. The equation in logarithmic form is expressed as (Eq. S6)[3]:

$$q_e = K_F C_e^{\frac{1}{n}} \quad \text{(S6)}$$

where K_F denotes the Freundlich constant and 1/n is the heterogeneity factor of the adsorbent, associated with the surface heterogeneity of adsorbent.

References

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2. W. Song, B. Gao, T. Zhang, X. Xu, X. Huang, H. Yu and Q. Yue, *Bioresour. Technol.*, 2015, **190**, 550-557.
3. M. Cobas, A. S. Danko, M. Pazos and M. A. Sanroman, *Bioresour. Technol.*, 2016, **213**, 2-10.

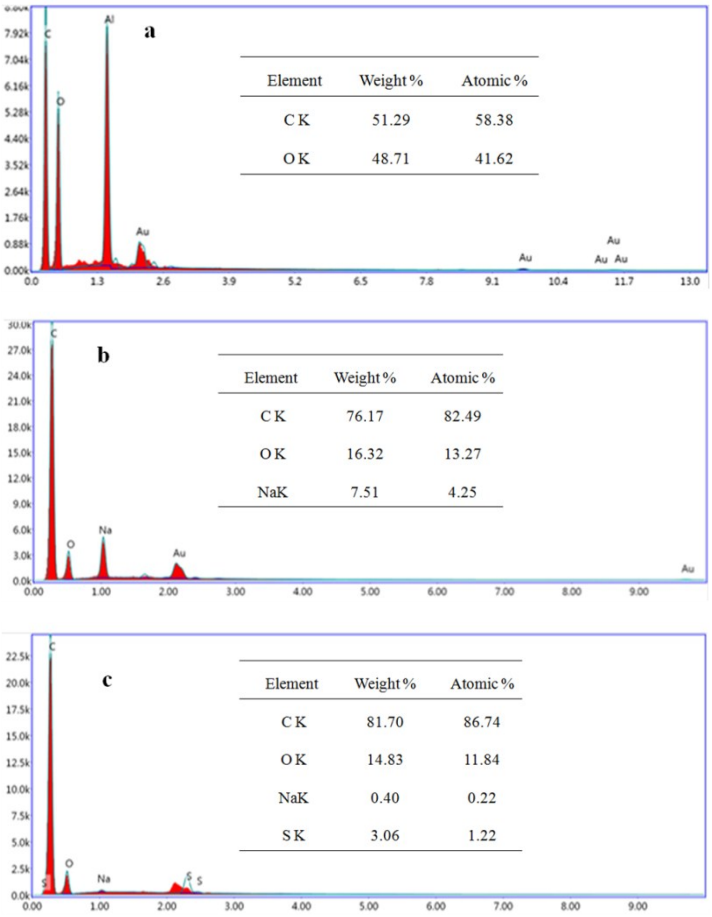

Fig. S1 EDS analysis of (a) CNCs (b) CNGD (c) CNGS

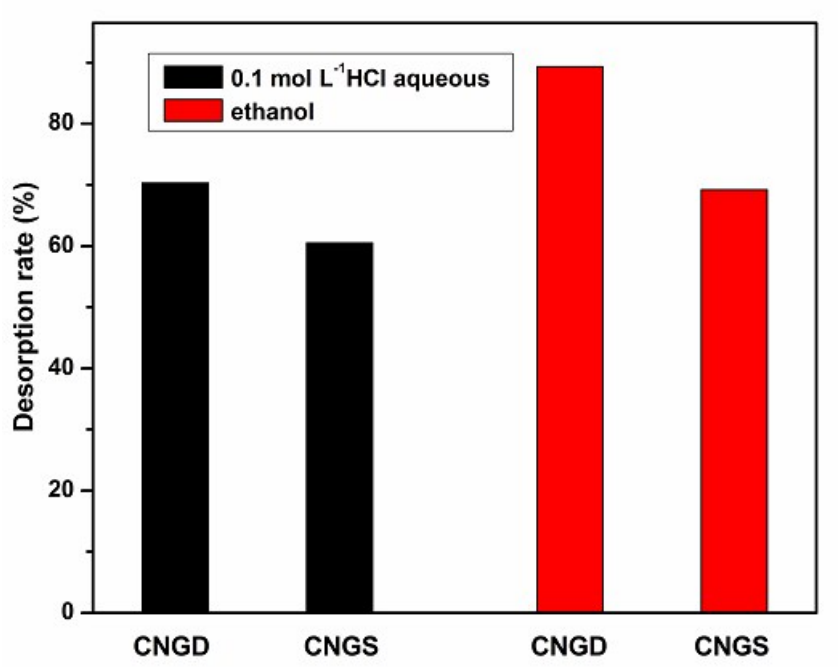

Fig. S2 Desorption of [Bmim]Cl by HCl aqueous solution and ethanol.