Supporting Information

Arsenic (III) Removal by Nanostructured Dialdehyde Cellulose-Cysteine Microscale and Nanoscale Fibers

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Fourier Transform Infrared Spectroscopy (FTIR)

FTIR data was recorded by an ALPHA FT-IR Spectrometer (Bruker Optics Inc.). The resolution was set at 4 cm\(^{-1}\) with 16 scans over the 4000–400 cm\(^{-1}\) range. The solid samples were investigated in the attenuated total reflectance (ATR) mode.

\(^{13}\)C CPMAS Nuclear Magnetic Resonance (NMR)

Solid state \(^{13}\)C CPMAS NMR of wood pulp cellulose, MDAC, MDAC-cys complex, NDAC and NDAC-cys complex samples were carried out by a Bruker Utrashield 500WB plus (500 MHz) NMR instrument, equipped with a 2.5 mm triple resonance magic angle spinning (MAS) NMR probe, capable of spinning the sample up to 35 kHz. The resonance frequency for \(^{13}\)C was 10000 Hz, and the samples were measured at the magic angle with a spinning speed of 10 kHz.

Elemental Analysis

The elemental analysis of MDAC-sys and NDAC-sys samples was carried out using a microanalyzer instrument (Thermo Finnigan, Model FLASH EA 1112). Solid samples were
detected by this instrument.

**Thermal Gravimetric Analysis (TGA)**

The thermal stability of untreated wood pulp cellulose, MDAC, MDAC-cys, NDAC and NDAC-cys complex samples were studied by a PerkinElmer STA-6000 (Simultaneous Thermal Analyzer) instrument. The samples were run at a heating rate of 10 °C/min in the range of 25–850 °C under continuous nitrogen flow.

**Scanning Electron Microscopy (SEM) and EDS Mapping**

The morphological study of wood pulp cellulose, MDAC, MDAC-cys, NDAC, NDAC-cys samples was carried out by a Zeiss LEO 1550 SFEG-SEM system. This instrument contained the standard E-T detector, In-Lens Secondary Electron Detector and Rutherford Backscatter Electron Detector. The system was also equipped with an EDS (energy dispersive X-ray spectroscopy) unit having an EDAX detector, which provided the elemental composition information and X-ray maps of the various phases of the materials examined.

**Transmission Electron Microscopy (TEM)**
TEM measurements of two types of samples: CNF and NDAC-cys, were carried out by a FEI Tecnai G2 Spirit BioTWIN instrument, operated at an accelerating voltage of 120 kV. The instrument was equipped with a digital camera, photographic film capability, goniometer, tilt stage accessories and electron diffraction capability. For this measurement, the sample preparation scheme was as follows. 1 μL of the floc sample was diluted to 10 mL, where the resulting suspension was coated on a copper grid for the TEM analysis. To preserve the original contrast of the image, the sample was not stained.

**Atomic Force Microscopy (AFM)**

AFM measurements of CNF, NDAC and NDAC-cys samples were performed using a Bruker Dimension ICON scanning probe microscope (Bruker Corporation, U.S.A.) equipped with a Bruker OTESPA tip (the max.tip radius = 10 nm). A 10 μL of 0.005 wt % CNF, NDAC or NDAC-cys suspension was deposited on the surface of a silica plate, where the air-dried sample was measured in the tapping mode.

**BET surface area measurement**

Surface area was measured using a Quantachrome NOVA touch LX² analyzer via a multi-point
BET ((Brunauer, Emmet, and Teller) method. UHP-grade gases (N\textsubscript{2} and He) were used in measurements without further purification. The N\textsubscript{2} adsorption measurements were done at 77 K in a liquid nitrogen bath. All samples activated for 12 h at 110 °C under ultrahigh vacuum (10\textsuperscript{−8} mbar) built in the NOVA touch before processing to gas adsorption measurements.

**Wide-Angle X-ray Diffraction (WAXD)**

WAXD measurements of wood pulp cellulose, MDAC, MDAC-cys, CNF, NDAC, NDAC-cys and floc (obtained by mixing As (III) solution with MDAC-cys or NDAC-cys in suspension) samples were carried out using a Benchtop Rigaku MiniFlex 600 instrument. All samples were freeze dried first, and then cast on the glass sample holders. The Cu K\textalpha radiation was used to generate a wavelength (λ) of 0.154 nm (with 40 kV and 40 mA X-rays) and a Ni filter. The data collection was carried out using a flat sample holder in the Bragg-Brentano geometry (i.e., 5-50° at a 10 °min\textsuperscript{−1} rate).

**Atomic Fluorescence Spectrometry (AFS)**

The concentration of As(III) solution after remediation was measured by LUMINA 3300 Atomic Fluorescence Spectrometer. HCL lamp current is 100 mA, carrier gas flow is 600
mL/min (Argon), shield gas flow: 400 mL/min (Argon), reducing agent is 1.4%(w/v) NaBH4 in 0.5% (w/v) NaOH, sample medium is 15%(v/v) HCl.

**Determination of Aldehyde Content**

The aldehyde content of the varying sample was determined using by the following procedure. 0.25 M hydroxylamine hydrochloride solution was first prepared where the pH value of the solution was adjusted to 4.5 by HCl and NaOH, where 1 or 2 drops of methyl orange was then added into the solution as an indicator. 0.1 g of dried mass (e.g. MDAC and NDAC) was added to 40 ml (excess) of hydroxylamine hydrochloride solution and reacted overnight at room temperature. As the reaction occurred, pH would go down and the solution color would turn pink. Subsequently, 0.05 M – 0.1 M of NaOH solution was used to titrate the suspension until the pH value returned back to 4.5 (the suspension was equilibrated for 1 hr to make sure the pH value remained constant). The consumption of the NaOH solution was directly related to the aldehyde content.

**Determination of Carboxyl Content**

The carboxyl content of CNF, NDAC and NDAC-cys samples were measured by the
conductometric titration method. In this measurement, 20 ml of sample with known concentration was diluted into 220 ml (the final concentration of each sample is shown in Table S2). 0.05M HCl solution was subsequently added to the sample suspension dropwise until the pH value became lower than 2.5. The resulting suspension was then titrated with 0.01 M NaOH solution. The titration curves (Figure S1) were used to determine the carboxyl content. In specific, the degree of oxidation (DO) was calculated using the following equation:

\[
DO = 162 \left( \frac{V_2 - V_1}{c} \right) \left( w - 36 \left( \frac{V_2 - V_1}{c} \right) \right)^{-1}
\]

where \( V_1 \) and \( V_2 \) are the volume of NaOH in liter as shown in Figure 1S, \( c \) is the NaOH concentration (mol/L) and \( w \) is the weight of oven-dried sample (g).
Figure S1 Conductimetric titration curves of CNF, NDAC and NDAC-cys.
**Figure S2** SEM image and element mapping of MDAC-cys-As(III)-500 (prepared with 500 ppm of AS(III) solution).
Figure S3 SEM image and element mapping of NDAC-cys-As(III)-500 (prepared with 500 ppm of AS(III) solution).
Figure S4 BET surface adsorption of MDAC and NDAC

Langmuir isotherm of MDAC-cys-As (50-250 ppm)

Langmuir isotherm of MDAC-cys-As (500-2500 ppm)
**Figure S5** Langmuir adsorption isotherm model fitting for MDAC-cys and NDAC-cys in 50-250 ppm and 500-2500 ppm.
**Table S1.** The results from the hydroxylamine hydrochloride titration method to determine aldehyde content in MDAC and NDAC.

|                      | MDAC  | NDAC  |
|----------------------|-------|-------|
| Mass of sample (g)   | 0.1006| 0.0149|
| $C_{NaOH}$ (mol/L)   | 0.0973| 0.0973|
| $V_{initial NaOH}$ (ml) | 0.84  | 5.00  |
| $pH_{initial}$       | 1.79  | 3.46  |
| $V_{end NaOH}$ (ml)  | 12.45 | 6.11  |
| $pH_{end}$           | 4.50  | 4.50  |
| $V_{consumption}$ (ml)| 11.61 | 1.11  |
| Content of aldehyde groups (mmol/g) | 11.23 | 7.25  |

*Content of aldehyde groups (mmol/g) = $C_{NaOH} * V_{consumption} / M_{MDAC}$*
Table S2 The results from the conductimetric titration method to determine carboxyl content in CNF, NDAC and NDAC-cys samples.

|        | Concentration (wt %) | Weight of sample (g) | $V_2-V_1$ (ml) | $C_{NaOH}$ (mol/L) |
|--------|----------------------|----------------------|----------------|--------------------|
| CNF    | 0.291                | 0.6402               | 10.58          | 0.0973             |
| NDAC   | 0.087                | 0.1914               | 1.91           | 0.0973             |
| NDAC-cys | 0.142              | 0.3124               | 2.42           | 0.501              |
Table S3 $^{13}$C CPMAS NMR peaks in wood pulp, MDAC and MDAC-cys samples.

|                | Wood pulp (ppm) | MDAC (ppm) | MDAC-cys (ppm) |
|----------------|-----------------|------------|----------------|
| $C_1$          | 105             | 100        | 100            |
| $C_4$          | 89              | 92         | 92             |
| $C_2, C_3, C_5$| 72, 75, 83      | 69, 78, 86 | 67, 72, 78     |
| $C_6$          | 66              | 65         | 64             |
| -CHO           | ------          | 201        | ------         |
| -COOH          | ------          | ------     | 173            |
| Other peaks in |                 |            |                |
| cysteine       | ------          | ------     | 31, 58         |
Table S4 Summary of the TGA and DTG profiles.

| Entry     | $T_{\text{onset}}$ (°C) | $T_{\text{max}}$ (°C) | Residual % at 800 °C |
|-----------|-------------------------|------------------------|----------------------|
| Wood pulp | 243                     | 357                    | 8.3                  |
| MDAC      | 170                     | 199 and 262 (broad)    | 17.5                 |
| MDAC-cys  | 115                     | 146 and 160            | 13.4                 |
| NDAC      | 154                     | 187, 306 and 422       | 2.5                  |
| NDAC-cys  | 101                     | 161, 249 (broad) and 324 | 1.2                  |
**Table S5** The As (III) adsorption results by MDAC-cys.

| Original As(III) conc (ppm) | Original As(III) conc, AFS (ppb) | Equilibrium As(III) conc, AFS (ppb), Ce | Adsorption efficiency | Ideal adsorption capacity (mg/g) | Experimental adsorption capacity (mg/g), Qe |
|-----------------------------|----------------------------------|----------------------------------------|----------------------|---------------------------------|----------------------------------------|
| 10                          | 10                               | 2.3                                    | 0.77                 | 5                               | 3.85                                   |
| 20                          | 20                               | 6.6                                    | 0.67                 | 10                              | 6.7                                    |
| 50                          | 50                               | 9.1                                    | 0.818                | 25                              | 20.45                                  |
| 100                         | 100                              | 20                                     | 0.8                  | 50                              | 40                                     |
| 125                         | 125                              | 26                                     | 0.792                | 62.5                            | 49.5                                   |
| 250                         | 250                              | 57                                     | 0.772                | 125                             | 96.5                                   |
| 500                         | 500                              | 103                                    | 0.794                | 250                             | 198.5                                  |
| 1000                        | 1000                             | 181                                    | 0.819                | 500                             | 409.5                                  |
| 1500                        | 1500                             | 303                                    | 0.798                | 750                             | 598.5                                  |
| 2000                        | 2000                             | 430                                    | 0.785                | 1000                            | 785                                    |
| 2500                        | 2500                             | 536                                    | 0.7856               | 1250                            | 982                                    |
Table S6 The As (III) adsorption results by NDAC-cys

| Original As(III) conc (ppm) | Original As(III) conc, AFS (ppb) | Equilibrium As(III) conc, AFS (ppb), Ce | Adsorption efficiency | Ideal adsorption capacity (mg/g) | Experimental adsorption capacity (mg/g), Qe |
|-----------------------------|----------------------------------|-----------------------------------------|----------------------|----------------------------------|-----------------------------------------|
| 10                          | 10                               | 4.1                                     | 0.59                 | 5                                | 2.95                                    |
| 20                          | 20                               | 3.7                                     | 0.815                | 10                               | 8.15                                    |
| 50                          | 50                               | 8.6                                     | 0.828                | 25                               | 20.7                                    |
| 100                         | 100                              | 16                                      | 0.84                 | 50                               | 42                                      |
| 125                         | 125                              | 21                                      | 0.832                | 62.5                             | 52                                      |
| 250                         | 250                              | 51                                      | 0.796                | 125                              | 99.5                                    |
| 500                         | 500                              | 101                                     | 0.798                | 250                              | 199.5                                   |
| 1000                        | 1000                             | 171                                     | 0.829                | 500                              | 414.5                                   |
| 1500                        | 1500                             | 243                                     | 0.838                | 750                              | 628.5                                   |
| 2000                        | 2000                             | 387                                     | 0.8065               | 1000                             | 806.5                                   |
| 2500                        | 2500                             | 478                                     | 0.8088               | 1250                             | 1011                                    |
Table S7 The Langmuir model fitting results of the adsorption data (50-250 ppm)

|                  | MDAC-cys-As(III) | NDAC-cys-As(III) |
|------------------|------------------|------------------|
| Entry            |                  |                  |
| K                | 6.66             | 7.77             |
| Qm (mg/g)        | 344.82           | 357.14           |
| R²               | 0.943            | 0.815            |

Table S8 The Freundlich model fitting results of the adsorption data.

|                  | MDAC-cys-As(III) | NDAC-cys-As(III) |
|------------------|------------------|------------------|
| Entry            |                  |                  |
| K_f              | 9.561            | 9.535            |
| n                | 0.987            | 0.974            |
| R²               | 0.999            | 0.998            |

Reference
1. Kumari, S.; Chauhan, G. S. New Cellulose–Lysine Schiff-Base-Based Sensor–Adsorbent for Mercury Ions. *ACS Appl. Mater. Interfaces* 2014, 6, 5908-5917.
2. Saito, T.; Kimura, S.; Nishiyama, Y.; Isogai, A. Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation of Native Cellulose. *Biomacromolecules* 2007, 8, 2485-2491.