# Supporting Information

# Precipitated Silica Agglomerates Reinforced with Cellulose Nanofibrils as Adsorbents for Heavy Metals

Aphra Agaba [a], Huan Cheng [a], Jiangbin Zhao [a], Congcong Zhang [a], Mike Tebyetekerwa [b], Liduo Rong [a], Xiaofeng Sui [a]*, Bijia Wang [a]*

[a] Key Lab of Science and Technology of Eco-textile, Ministry of Education, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, People's Republic of China

[b] Research School of Engineering, College of Engineering and Computer Science, The Australian National University, Canberra, Australian Capital Territory, 2601, Australia

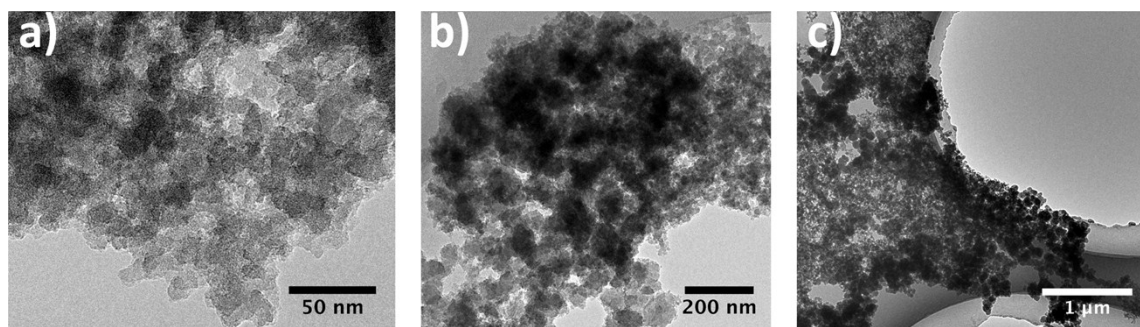Corresponding authors: *suixf@dhu.edu.cn (Xiaofeng Sui) and bwang@dhu.edu.cn (Bijia Wang)*

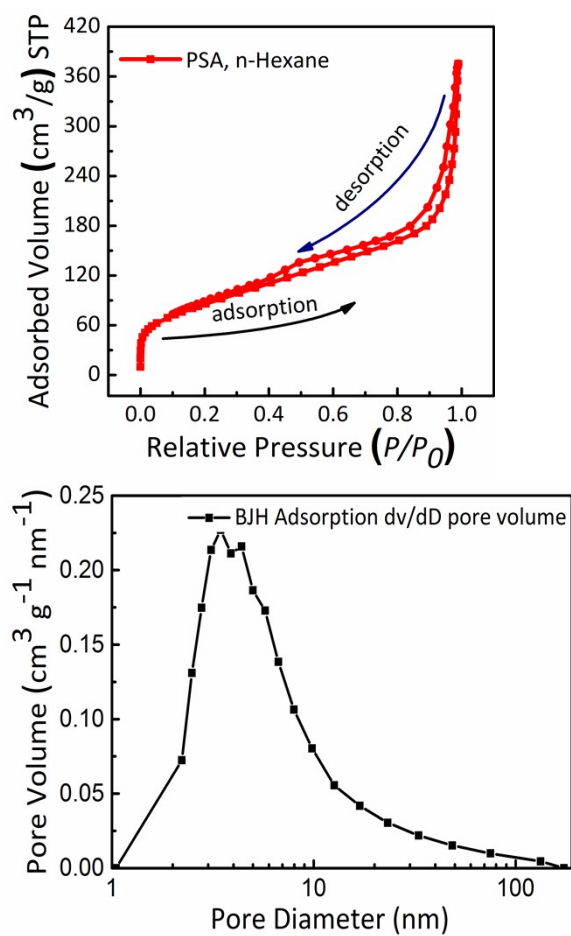**Figure S1**. TEM images of PSA at different resolutions



**Figure S2.** BET surface area of PSA and pore-size distribution plot of PSA calculated from the adsorption isotherm by BJH technique.
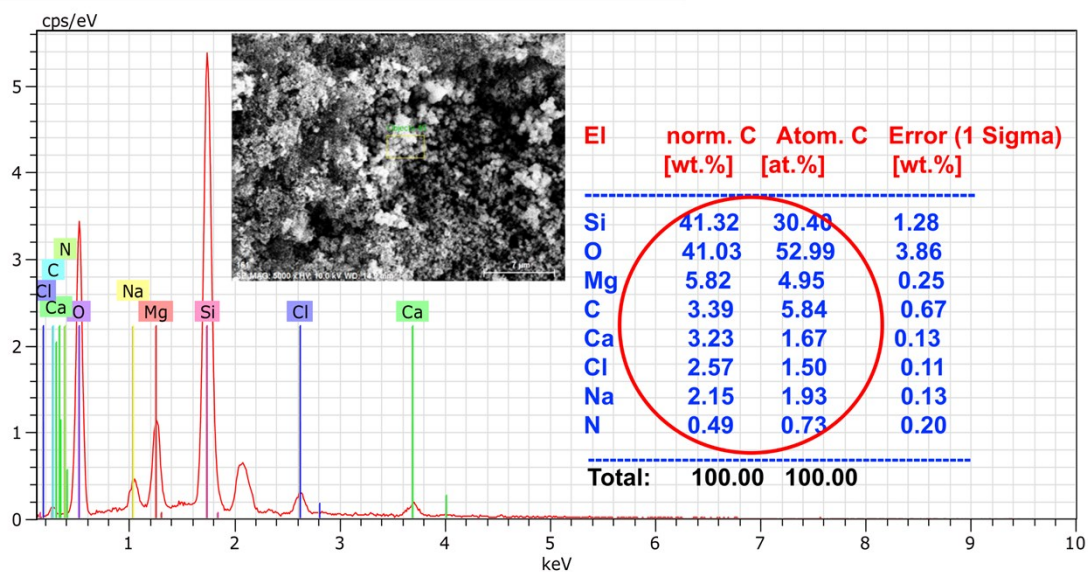
**Figure S3**. EDX, Chemical composition of PSA in relation to Sodium silicate precipitated with 1.5 M Ca-and or Mg-Chloride (35:65) dispersed in n-Hexane before APD.

EDX point analysis was also conducted on the area indicating the presence of oxygen and silicon. The atomic percentage of Si and O confirms the stoichiometric ratio of silica, despite a small excess of oxygen from the hydroxyl branch of PSA.



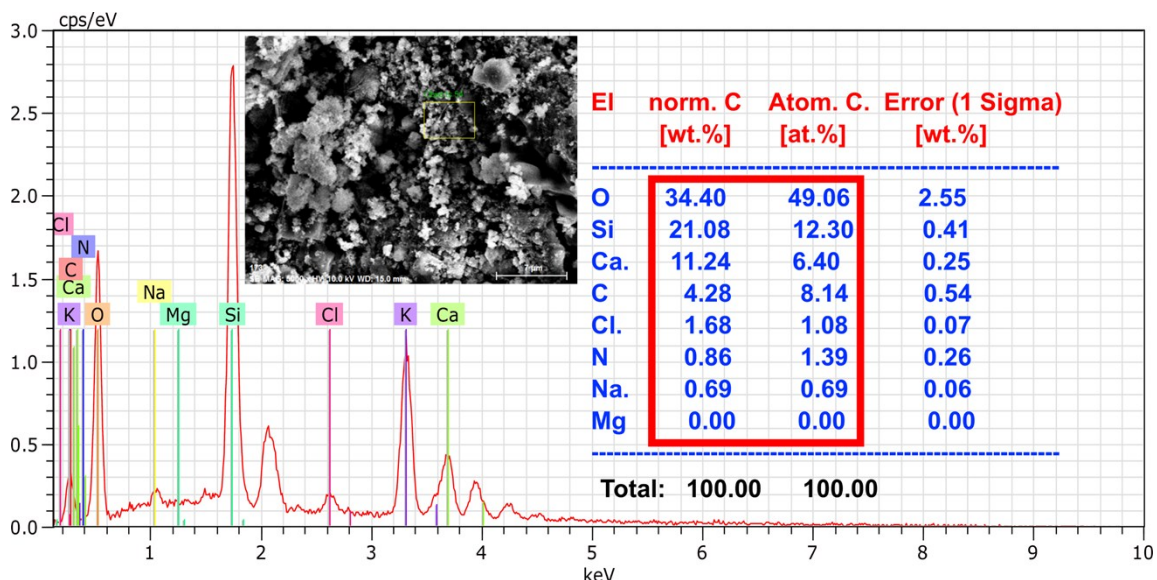**Figure S4.** EDX, Chemical composition of PSA in relation to sodium silicate (1.5 M $SiO_2$) precipitated with 1.5 M Ca-and or Mg-Chloride (0:100) modified with KI and KOH before APD. This implies that PSA can be customized to attach functional groups
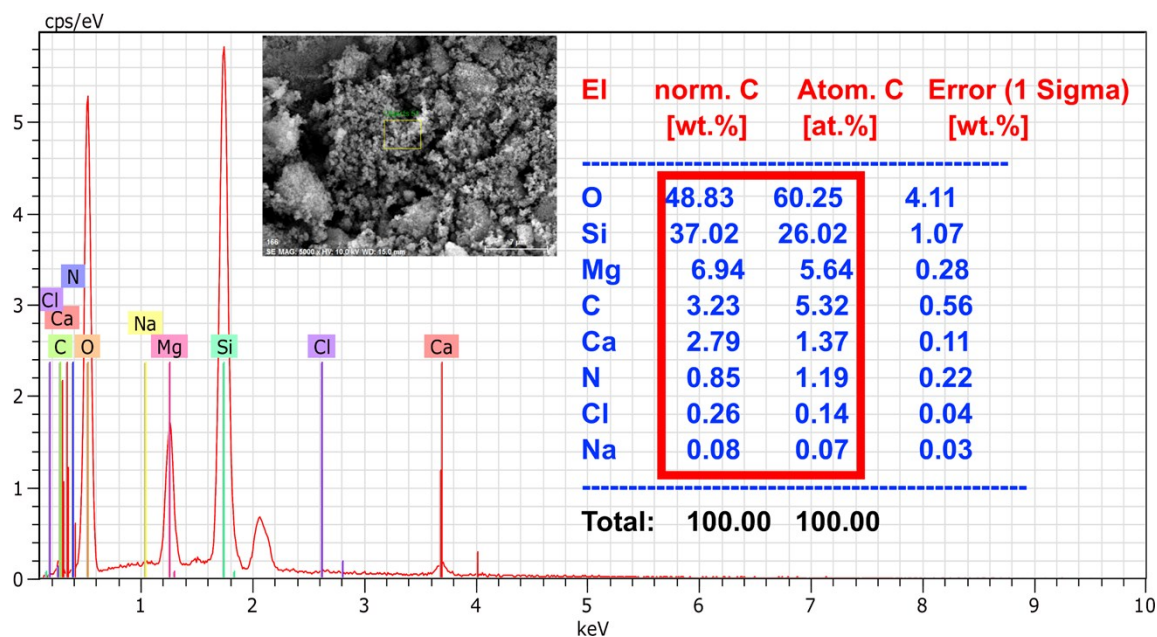
**Figure S5**. EDX, Chemical composition of plain PSA in relation to sodium silicate (1.5 M SiO$_2$) precipitated with 1.5 M Ca-and or Mg-Chloride (35:65)
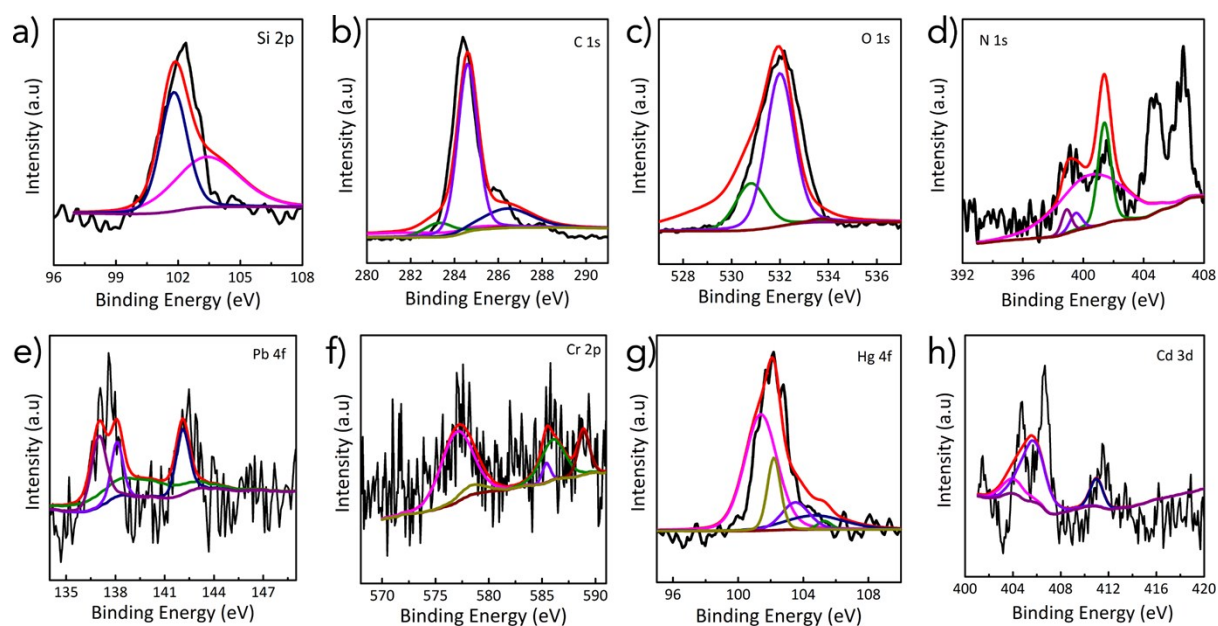


**Figure S6**. High resolution core-level XPS spectra of (a, b, c and d) Si 2p, O 1s, N 1s, C 1s and heavy metals (e, f, g and h) Pb 4f, Cr 2p, Hg 4f and Cd 3d electrons after treatment with TO-CNF PSA.

XPS was conducted to determine the surface composition of TO-CNF PSA before and after adsorption of the selected metal ions. Four remarkable peaks (C 1s, O 1s, N 1s Si 2p) are shown in the XPS pattern of TO-CNF PSA. XPS has often been used to identify the mechanism

of heavy metal sorption because the interaction between metal ions functional groups may change the distribution of electrons around the corresponding atoms.[1] No change can be observed for the peak at 531.5 eV (C–O–H) whereas other peaks changed a little. This implies that the carboxylate groups on the surface of TO-CNF PSA were involved in the adsorption process. Deconvolution of N 1s spectrum shows peaks at 399.1 and 400.8 eV for the nitrogen in amine groups.[2] C 1s was deconvoluted at 286.4, 293.9 and 283.3 eV conforming to C=O, C–O and C–N respectively. There is a visible decrease in C=O peak, implying that the amine groups in TO-CNF PSA played a crucial role in reduction of metal ions. The peak of O 1s was tailored to peaks at 530.1 and 530.8 eV attributed to C–O and C=O groups. A decrease in the proportion of amine groups implies that the amine groups acted as electron donors for reducing Pb (II), Hg (II), Cr (III) and Cd (II) ions. Cd 3d displays 2 peaks at 411.7 and 405eV indicating Cd (II) is in ionic form [1] . The peak of Hg 4f was attained at 100.8 and 104.6 eV. The spectrum displays two broad peaks at 575.9 and 585.4 eV assigned to Cr 2p. On the basis of the aforementioned results, the negatively charged surface properties of TO-CNF PSA generated electrostatic interactions. These interactions definitely aided Pb (II), Hg (II), Cr (III) and Cd (II) ions to rapidly form complexes and bind onto abundant amine and active sites of the adsorbent.
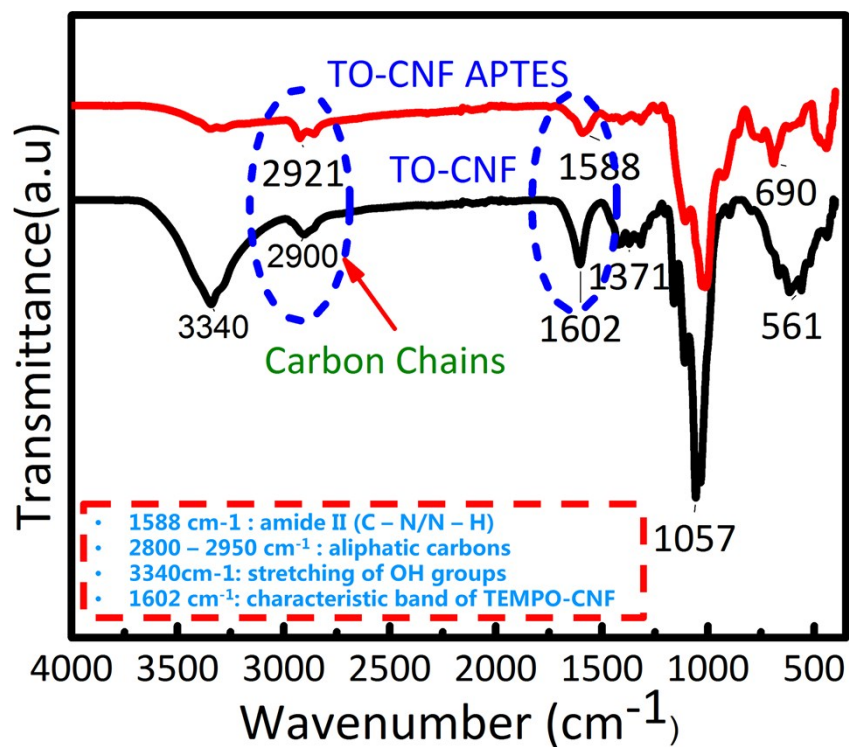
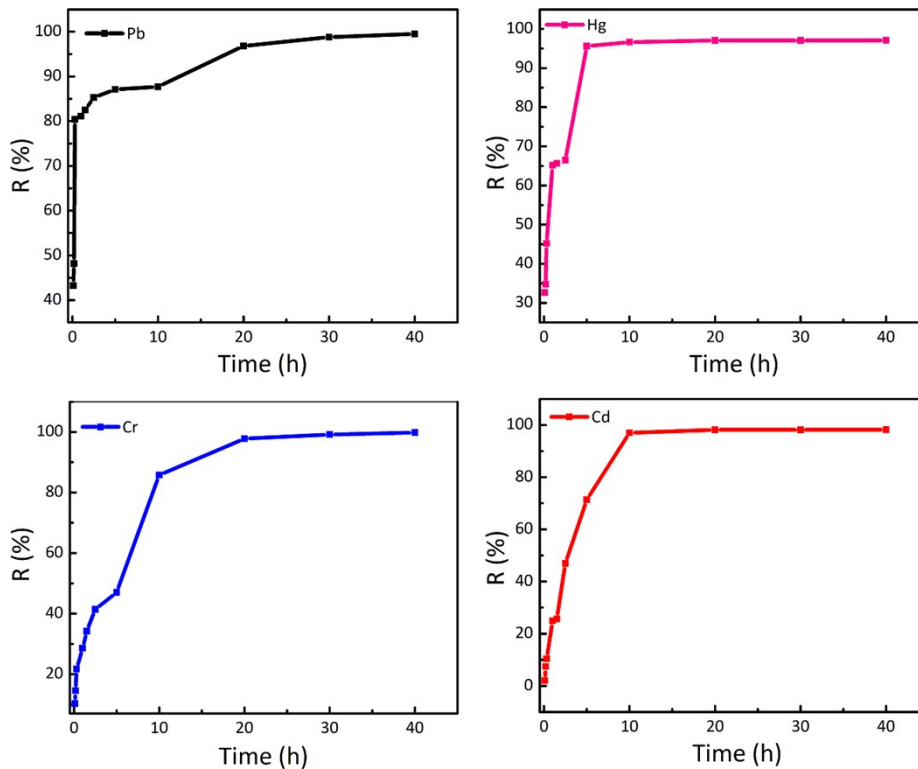**Figure S7.** FT-IR image of TO-CNF/APTES and TO-CNF confirming successful attachment of APTES



**Figure S8.** Removal percentages of Pb (II), Hg (II), Cr (III) and Cd (II) performed longer for 48 h.

**Table S1.** Textural properties of Precipitated Silica Agglomerates, TO-CNF PSA

| Sample | BET S.A ($m^2/g$) | Average Pore Diameter (nm) | Pore Volume ($cm^3/g$) |
|---|---|---|---|
| n-Hexane- PSA | 378.98 | 4.69 | 0.44 |
| TO-CNF | 8.83 | 28.91 | 0.06 |
| TO-CNF-PSA | 13.66 | 13.00 | 0.04 |

**Table S2.** Pseudo-First-Order and Pseudo-Second-Order Adsorption Kinetics Fitting Results for Pb (II), Hg (II), Cr(III) and Cd (II) Ions Adsorption on TO-CNF PSA.

| | Pseudo-first order model | | | Pseudo-second- order model | | |
|---|---|---|---|---|---|---|
| Metals | $k_l$ | $q_{e,cal}$ (mg/g) | $R^2$ | $k_2$ (g/mg) | $q_{e,cal}$ (mg/g) | $R^2$ |
| Pb (II) | 0.289 | 6.128 | 0.93614 | 1.059 | 2.265 | 0.99912 |
| Hg (II) | 0.285 | 7.123 | 0.82676 | 0.729 | 2.068 | 0.99741 |
| Cr (III) | 0.458 | 17.359 | 0.97035 | 0.022 | 2.378 | 0.99604 |
| Cd (II) | 0.320 | 19.248 | 0.97433 | 0.092 | 2.072 | 0.97931 |

**Table S3.** Thermodynamic parameters for the adsorption of Pb (II), Hg (II), Cr (III) and Cd (II) by TO-CNF PSA.

| Metal | T(K) | $\Delta G°$ (kJ mol$^{-1}$) | $\Delta S°$ (J mol$^{-1}$K$^{-1}$) | $\Delta H°$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| Pb (II) | 298 | -1.4 | 154.2 | 44.5 |
| | 308 | -2.9 | | |
| | 318 | -4.5 | | |
| | 328 | -6.0 | | |
| | 338 | -7.6 | | |
| Hg (II) | 298 | -2.3 | 206.5 | 59.3 |
| | 308 | -4.3 | | |
| | 318 | -6.4 | | |
| | 328 | -8.4 | | |
| | 338 | -10.5 | | |
| Cr (III) | 298 | -4.1 | 67.7 | 16.4 |
| | 308 | -4.4 | | |
| | 318 | -5.1 | | |
| | 328 | -5.8 | | |
| | 328 | -6.4 | | |
| Cd (II) | 298 | -0.9 | 40.1 | 11.0 |
| | 308 | -1.3 | | |
| | 318 | -1.7 | | |
| | 328 | -2.1 | | |
| | 338 | -2.5 | | |

**Table S4.** Kinetic parameters for metal adsorption and re-adsorption onto TO-CNF PSA during the repeat adsorption-desorption cycles.

| Metal | Adsorption | Re-adsorption |
|---|---|---|

| | $q_e$ pseudo-second order (mg/g) | $R^2$ | $q_e$ cycle 1 (mg/g) | $q_e$ cycle 2 (mg/g) | $q_e$ cycle 3 (mg/g) | $q_e$ cycle 4 (mg/g) |
|---|---|---|---|---|---|---|
| Pb (II) | 2.265 | 0.99912 | 1.999 | 1.998 | 1.985 | 1.991 |
| Hg (II) | 2.068 | 0.99741 | 1.898 | 1.872 | 1.868 | 1.824 |
| Cr (III) | 2.378 | 0.99604 | 2.272 | 2.254 | 2.242 | 2.219 |
| Cd (II) | 2.072 | 0.97931 | 1.573 | 1.563 | 1.556 | 1.545 |

## References.

1.  J. Ma, G. Zhou, L. Chu, Y. Liu, C. Liu, S. Luo and Y. Wei, *ACS Sustain Chem Eng*, 2016, **5**.
2.  Z. Y. Sui, Y. Cui, J. H. Zhu and B. H. Han, *ACS Appl. Mater. Interfaces*, 2013, **5**, 9172.