Supplementary information

Pyridine based cross-linked chitosan: a biopolymer adsorbent for the green removal of toxic metals from water

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**Materials and instrumentations**

Pyridine-2,6-dicarboxylic acid (PDC) and chitosan (obtained from crab shell) were acquired from Sigma-Aldrich. Cr(NO3)3·9H2O, MnCl2·4H2O, NiCl2, CdCl2·H2O, (CH3COO)2Pb·3H2O and Cu(NO3)2·2.5H2O which were used as the source of the metal ions were of analytical reagent grade likewise other substances.

Chitosan and 2,6-pyridinedicarboxylic acid cross-linked chitosan (PDC-CCS) have been characterized using the following instrumental analysis: 1H NMR, 13C NMR, UV-visible spectroscopy, FT-IR spectroscopy, elemental analysis, powdered x-ray diffraction spectroscopy, BET, scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

The 1H NMR spectra of chitosan and PDC-CCS were recorded on a 500MHz Bruker Avance spectrometer.

UV-vis spectra were collected on a Shimadzu UV-1800 spectrophotometer while FTIR analysis of chitosan and PDC-CCS was performed using a Shimadzu IRAffinity-1S.

A Thermo Scientific FLASH 2000 organic elemental analyzer (CHNS-O ANALYZER) was used for the elemental analysis. The carbon to nitrogen ratio was used to confirm crosslinking.

Bradford assay was performed to determine the extent of crosslinking of chitosan where the number of the free amino functional groups in chitosan before crosslinking (Cb) and after crosslinking (Ca) is expected to be a function of the solution absorbance. The percentage degree of cross-linking was calculated from the equation:

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| $$\%Crosslinking index= \frac{C\_{b}-C\_{a}}{C\_{b}}×100\%$$ |  |  |

Where Cb is a measure of the number of the free amino functional groups before crosslinking chitosan and Ca is a measure of the number of the free amino groups in crosslinked chitosan.

X-ray diffraction patterns for chitosan and cross-linked chitosan were analyzed with a Rigaku MiniFlex 600 diffractometer (Cu-Kα, 40 KV, 40 mA, λ = 1.5406 Å) at diffraction angle of 2θ = 4 – 60º

METTLER TOLEDO DSC822e and SDTQ600 thermogravimetric analyzer were used to study the thermal behavior and weight changes of the samples.

A Micromeritics ASAP 2460 was used for the porosity and surface area analysis. Before the analysis, streams of N2 gas were passed at 90 ℃ for about 6 h to degas the samples. Brunauer-Emmett-Teller (BET) technique was used for the surface area determination while the Barret-Joyner-Halenda (BJH) technique was employed in the determination of pore size and pore size distribution.

The surface morphology of the samples was confirmed using Tescan Vega 3 LMH Scanning electron microscopy (SEM).