Electronic Supplementary Material (ESI) for RSC Advances.

Phosphonate-Functionalized Cellulose Fibres for the Recovery of Uranium from Seawater

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Supplementary Information

Description of Synthesis Procedure

The functionalization procedure involved loading about 1.2 g of Sisal twine into 45 mL PTFE-lined autoclaves, adding 20 mL of 0.10 M of each phosphonate (V/m = 16.7) and reacting at a defined temperature under autogeneous pressures in a fan-forced oven for 16 h. The samples are denominated ATMP-Sisal-*x* and GLY-Sisal-*x* where *x* is the temperature used for the hydrothermal treatment. W-Sisal-*x* and WE-Sisal-*x* represent samples treated hydrothermally in water and water-ethanol (50%) solutions. The pH of the ATMP solution prior to use was 1.31 and that of the GLY was 4.87. The filtrates after hydrothermal reaction at 150 ^{o}C had pH values of 1.42 and 3.82 for ATMP and GLY respectively and had the intense brown coloration characteristic of lignins indicating that significant quantities of lignins had been stripped from the fibres during the process.

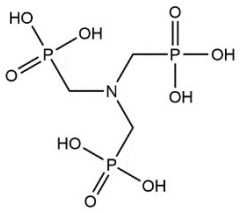
After the initial filtration, the twine was washed with copious amounts of water and dried at 60 ^{o}C on a hot plate. Prior to use the twine was allowed to equilibrate at ambient temperature and humidity. The phosphorus loading was determined my measuring the phosphorus content of the phosphonic acid solution before after hydrothermal reaction. In general the loading was found to be between 10 and 20 mg P/g. Fibres reacted at greater than 120 ^{o}C in 0.10 M ATMP solution were found to have been cleaved while the fibres reacted with GLY could be heated up to 180 ^{o}C without any perceptible cleavage. The difference is probably more a result of the acidity of the phosphonates rather than the type of phosphonate. The P content of the fibres themselves gave similar values for the amount of P grafting. Batch contact uranium sorption experiments were undertaken as described in the supplementary materials section.

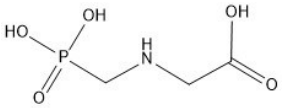
Batch Sorption Procedure

Batch contact uranium sorption experiments were undertaken by agitating 0.20 g of Sisal and functionalized-Sisal fibres for 24 or 48 h with 20 mL seawater whose U concentration had been raised to either 4 or 10 ppm to facilitate measurement. For the 4 ppm seawater solution, UO_2SO_4 was used. Since the pH remained close to that of seawater (pH 8.2) no pH adjustment was necessary. In the case of the 10 ppm seawater solution, $UO_2(NO_3)_2$ was used and the pH adjusted by the addition of Na_2CO_3

solution. The uranium content was analysed using the Total Reflection X-ray Fluorescence (TXRF) technique using Ga as the internal standard.

Molecular Structures of ATMP and Glyphosate





XRD Patterns of Acid Treated Sisal

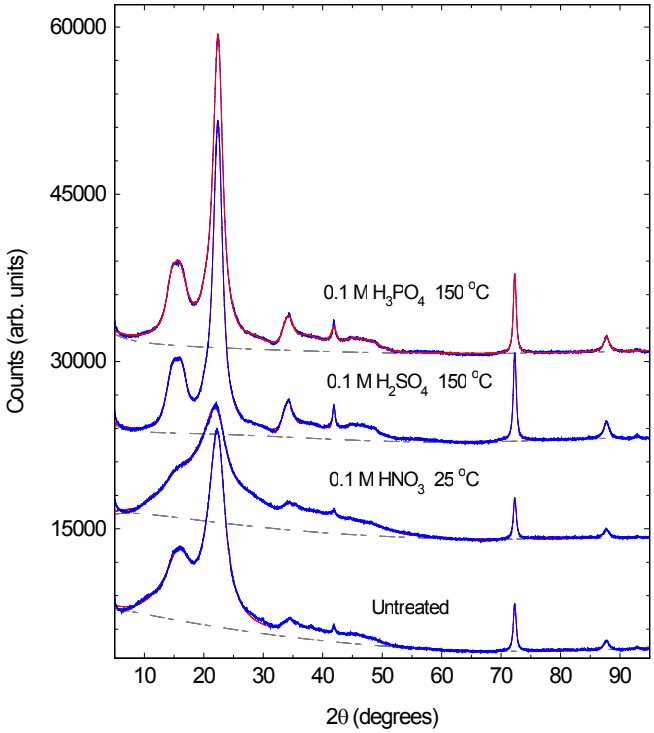


Figure S1. Fitted X-ray powder diffraction patterns of untreated Sisal fibres and Sisal fibres treated with different acids at different temperatures.

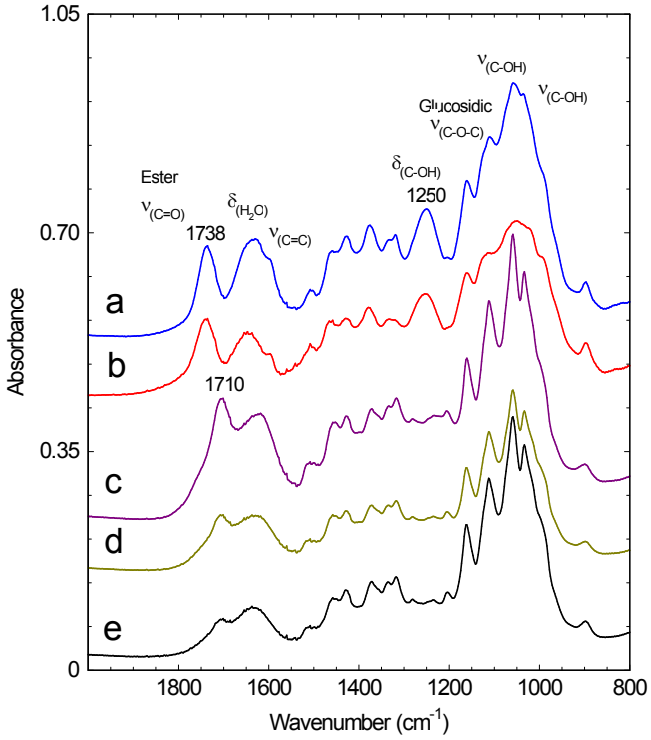


Figure S2. FTIR showing the effect of increasing ATMP concentration in solution. **(a)** as received Sisal, **(b)** Sisal washed with 0.1 M HNO_3 and Sisal reacted with **(c)** 0.1, **(d)** 0.3 and **(e)** 0.5 M ATMP solution.

SAXS Measurements

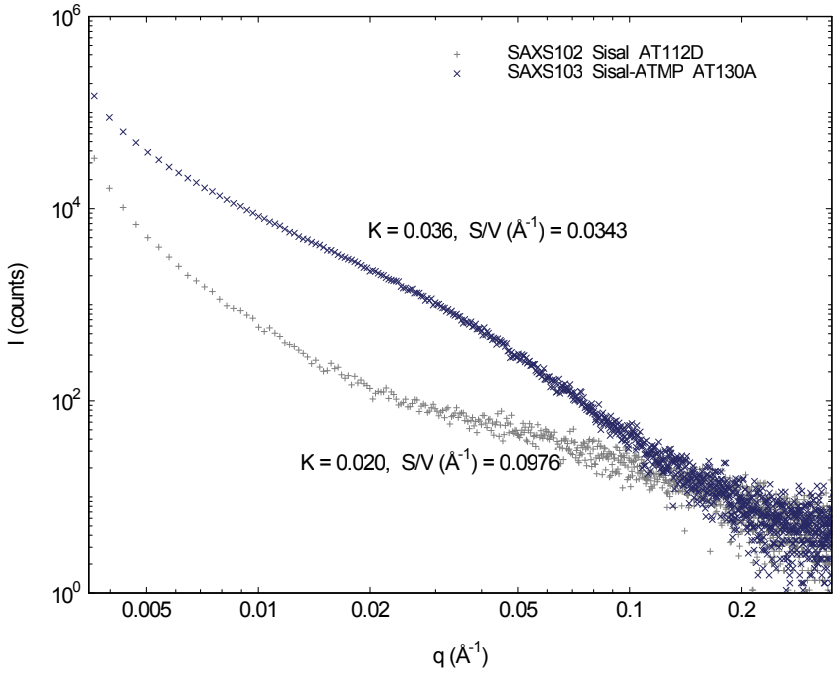


Figure S3. SAXS curves for untreated Sisal and ATMP-Sisal-150.

pH Dependence of Adsorption

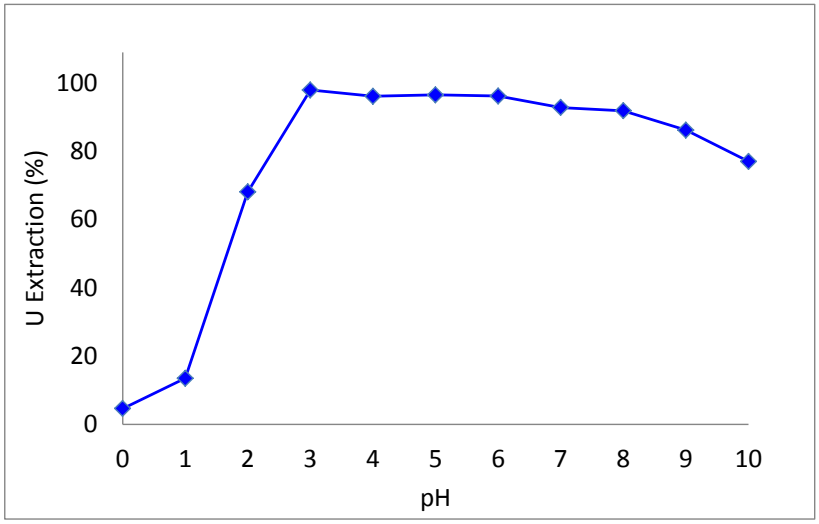


Figure S4. pH dependence of adsorption of U on ATMP-Sisal-150.

Nitrogen Adsorption-Desorption Isotherms

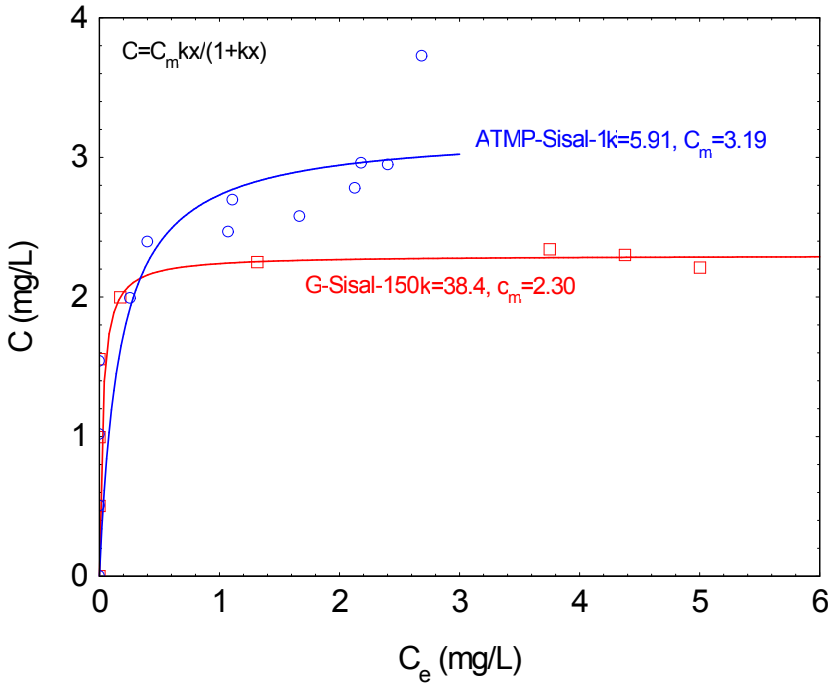


Figure S5. Sorption isotherms for U on ATMP-Sisal-150 and G-Sisal-150.

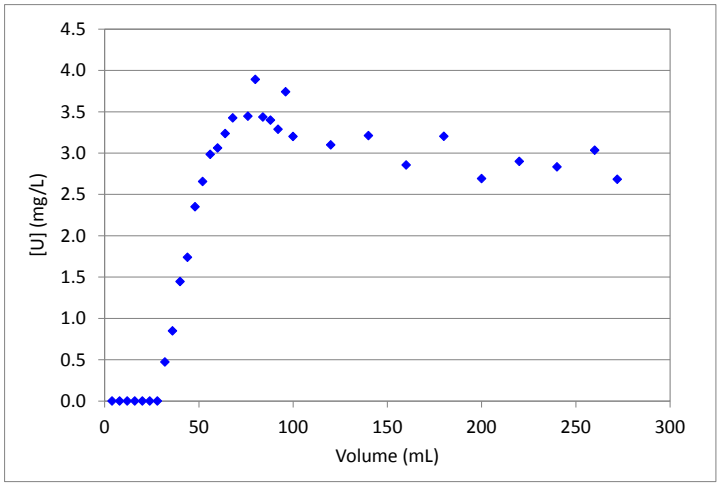


Figure S6. Column breakthrough curve for ATMP-Sisal-150 in seawater. [U]initial = 2.86 mg/L; flow rate 0.20 mL/min.

Table S1. Elemental analysis of seawater used in study.

Element	conc. (ppm)
Na	10869
Mg	1255
K	389
Ca	445
Fe	0.58
Zn	0.037
S	741
Sr	6.8
Cl	17121
Br	68
U	0.0043