Cellulose-Derived Nanomaterials for Affordable and Rapid Remediation of Uranium in Water

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Contents

Total number of pages: 14

Total number of figures: 9

Total number of tables: 2

Total number of equations: 8

Table of Contents

Instrumentation:

High resolution transmission electron microscopy (HRTEM): - TEM images were obtained using a JEOL 3010 instrument fitted with an ultra-high resolution (UHR) polepiece, operating at an accelerating voltage of 200 kV. For high-resolution TEM (HRTEM) analysis, the nanocomposite was first dispersed in water, and the suspension was subsequently drop-cast onto carbon-coated copper grids. The prepared grids were left to dry under ambient conditions at room temperature for imaging.

Infrared (IR) – IR spectra are collected using PerkinElmer IR instrument within the range of 400-4000 cm^{-1}.

Powder XRD – Measurements was performed by using a D8 Advance Bruker instrument, using Cu Kα as the X-ray source.

X-ray photoelectron spectroscopy (XPS) - XPS measurements were carried out using an ESCA probe TPD spectrometer from Omicron Nanotechnology. A polychromatic Al Kα source (hν = 1486.6 eV) was employed as the X-ray source. Samples were prepared as drop-cast films on a sample stub for analysis. A constant analyser energy of 20 eV was applied during data acquisition. The binding energy values were referenced to the C 1s peak at 284.8 eV. All XPS spectra were deconvoluted using CasaXPS software for detailed analysis.

Scanning electron microscope (SEM) – The surface morphology, elemental distribution, and composition were investigated using SEM coupled with energy dispersive X-ray spectroscopy (EDS) on an FEI Quanta 200 system. Samples were mounted on carbon adhesive tape, which was affixed to an aluminium sample holder for analysis.

Inductively coupled plasma mass spectrometry (ICP-MS)- Quantitative determination of uranium and other metal concentrations was conducted using a NexION 300X ICP-MS calibrated with appropriate reference standards. The ICP-MS system is equipped with an electron multiplier detector, which converts the flux of ionized analyte species into electrical signals. The intensity of these signals is directly proportional to the concentration of analyte ions present in the sample, enabling precise quantification.

Thermogravimetric analysis (TGA)- Thermogravimetric (TG) analysis was conducted on approximately 3.5 mg of the nanocomposite using a NETZSCH STA 449 F3 Jupiter system, controlled by Proteus-6.1.0 software. The experiment was carried out in a nitrogen atmosphere, with a gas flow rate of 20 mL/min. The temperature was ramped from 30°C to 900°C at a constant heating rate of 10°C/min. The sample was placed in an alumina crucible for the measurements.

Zeta potential- Zeta potential measurements were performed using a Malvern Zetasizer Nano ZSP. The surface charge of particles in suspension was determined via laser Doppler electrophoresis, with a measurable zeta potential range of -200 to +200 mV. The instrument required approximately 100 μl of sample for analysis within an electrode cell, with temperature control maintained between 1°C and 70°C during measurements.

Brunauer-Emmett-Teller (BET)- The BET surface area was determined using a Micromeritics Tri Star II. Prior to analysis, the samples were degassed under vacuum at 100°C for 6 hours and then analyzed at 77 K using ultrahigh-purity nitrogen gas.

Materials

Two distinct cellulose types, MCC and CNC were purchased from SRL Pvt. Ltd. (India) and BioPlus, respectively. NaOH, $FeCl_3 \cdot 6H_2O$, and Na_2SO_4 were obtained from RANKEM Glasswares and Chemicals Pvt. Ltd., India. Uranyl nitrate hexahydrate salt and trisodium trimetaphosphate (STMP) were procured from Thomas Baker (Chemicals) Ltd. and Sigma Aldrich, respectively. All chemicals were of laboratory grade and were utilized without additional purification. Deionized (DI) water was used for all the experiments, unless noted.

Synthesis of phosphorylated-microcrystalline cellulose ferrihydrite (PMCCFH) and phosphorylated- cellulose nanocrystal ferrihydrite (PCNCFH) composites

A green synthetic method was employed to synthesize phosphorylated cellulose-ferrihydrite nanocomposites. The synthesis process was conducted in two stages. In the initial stage, the phosphorylation of cellulose was carried out by STMP. Later, iron oxide was incorporated into phosphorylated cellulose to synthesize a mechanically stable composite by reacting it with ferric chloride hexahydrate. Phosphorylated cellulose was synthesized using a method with slight modifications from that reported by Yawen Cai et.al.[45] The synthesis of phosphorylated cellulose (PCNC/PMCC) involved the utilization of STMP as the phosphating agent. The phosphorylation process depended on the cross-linking reaction between the ring-opened STMP and the hydroxyl (-OH) groups of cellulose in 1% NaOH solution. Using alkaline water with a pH of 12, adjusted with 2.0 M NaOH solution, a 25 mL solution containing 0.25 g of cellulose (CNC or MCC) was prepared. Subsequently, 6.25 mL of a 60% (w/v) STMP solution was added to activate the hydroxyl groups in the disaccharide units. The mixture, with its pH maintained at approximately 12.0 was gently stirred at 25 °C for 2 hours, then vigorously stirred at 65 °C for 5 hours. The resulting product was dried at 45 °C. To prepare a homogeneous dispersion, approximately 0.2 g of phosphorylated cellulose was dissolved in 40 mL of water and subjected to sonication for approximately 10 minutes. The pH of the solution was adjusted to 9 using 0.2 M NaOH. After 5 minutes of stirring, 2 g of Na_2SO_4 was incorporated, followed by an additional 5 minutes of

incubation. Subsequently, 21.6 mL of 1 M $FeCl_3 \cdot 6H_2O$ was introduced to the mixture. The resulting mixture was precipitated, and its pH was adjusted to 8 by dropwise addition of 2 M NaOH. The final reaction mixture was incubated for approximately 12 hours at room temperature. The resulting precipitate was washed with water to eliminate soluble salts and dried at ambient temperature (around 30 °C). The final composite material appeared as dark brown shiny crystals. The total weight of the product obtained was approximately 3.68 g.

Batch Adsorption Studies

To prepare 1000 mg/L uranium metal ion solutions, $UO_2(NO_3)_2 \cdot 6H_2O$ was dissolved in deionized water, and diluted to different concentrations. In a standard batch adsorption test, 25 mg of the material was mixed with 100 mL of distilled water spiked with uranium at a concentration of 1 mg/L. The water sample was subsequently collected at various time intervals to measure the concentration of remaining uranium in the solution using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Prior to analysis, the samples were acidified with 5% HNO_3 and filtered through 0.22-micron filter paper.

To investigate the impact of pH on adsorption of uranium, 25 mg of the composite was introduced to 100 mL of water, spiked with uranium. The pH of the solution was adjusted to the required level using 1 M HCl or 1 M NaOH, and the mixture was shaken for a duration of 2 hours. After following this sample preparation protocol, the treated water sample was analysed using ICP-MS.

To evaluate the impact of interfering ions on uranium adsorption, a series of heavy metal ions such as Cu(II), Cd(II), Al(III), Zn(II), Mn(II), Mg(II), Cr(III), Li(I), Co(II) and Ni(II) were taken into consideration. In one conical flask, all cations were added to 100 mL of distilled water, spiked with uranium at a concentration of 1 mg/L. On the other hand, in separate conical flasks, individual ions which are generally present in ground water such as Mg^{2+}, SO_4^{2-}, F^-, Ca^{2+}, CO_3^{2-}, HCO_3^-, K^+, PO_4^{3-}, SiO_3^{2-}, Cl^-, Na^+, and NO_3^- were introduced separately into 100 mL of water with concentrations relevant to ground water (Table S1). Input uranium concentration was 1.1 mg/L. Subsequently, the water samples were treated with 25 mg of the composite for a duration of 2 hours, followed by ICP-MS measurements.

Regeneration of adsorbent

The regeneration of the adsorbent holds paramount importance for any cost-effective technology. In this study, 25 mg of adsorbent were introduced into a 20 mL solution containing 1 ppm of uranium (VI). Adsorption was followed by desorption conducted with varying concentrations of

HNO$_3$ solution, while maintaining a constant volume of solution, namely 20 mL. Optimal desorption outcomes were observed with 0.01 M HNO$_3$, within 90 minutes of agitation. Quantitative assessment of uranium uptake was conducted by ICP-MS. Subsequently, the uranium removal percentage was calculated, and the experiment was repeated up to four cycles.
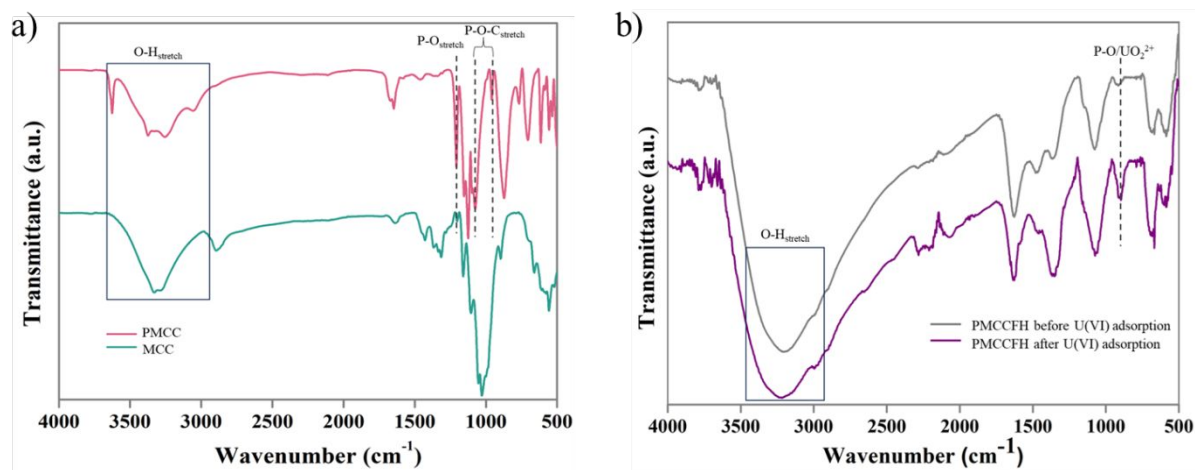

Figure S1. (a) Comparative FTIR spectra of phosphorylated MCC and blank MCC. (b) FTIR spectra of PCNCFH before and after U(VI) adsorption.
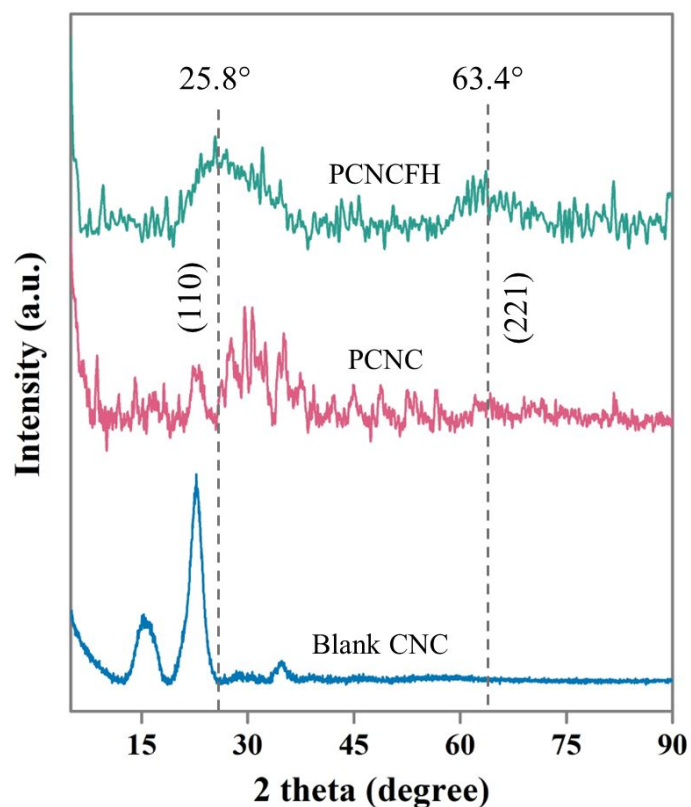
Figure S2. Powder XRD patterns of blank cellulose nanocrystal (CNC), Phosphorylated CNC and PCNCFH.
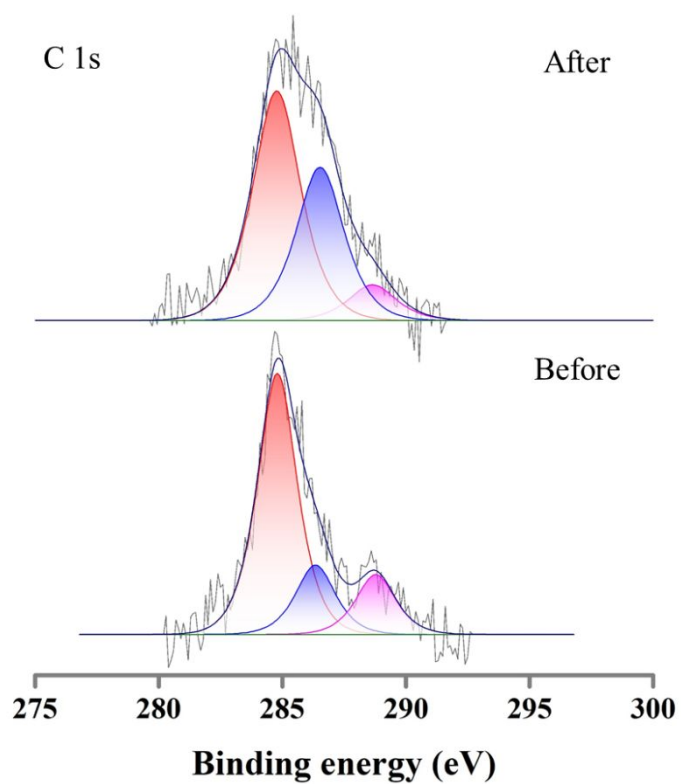
Figure S3. Deconvoluted XPS spectra of C 1s of PCNCFH before and after U(VI) adsorption.

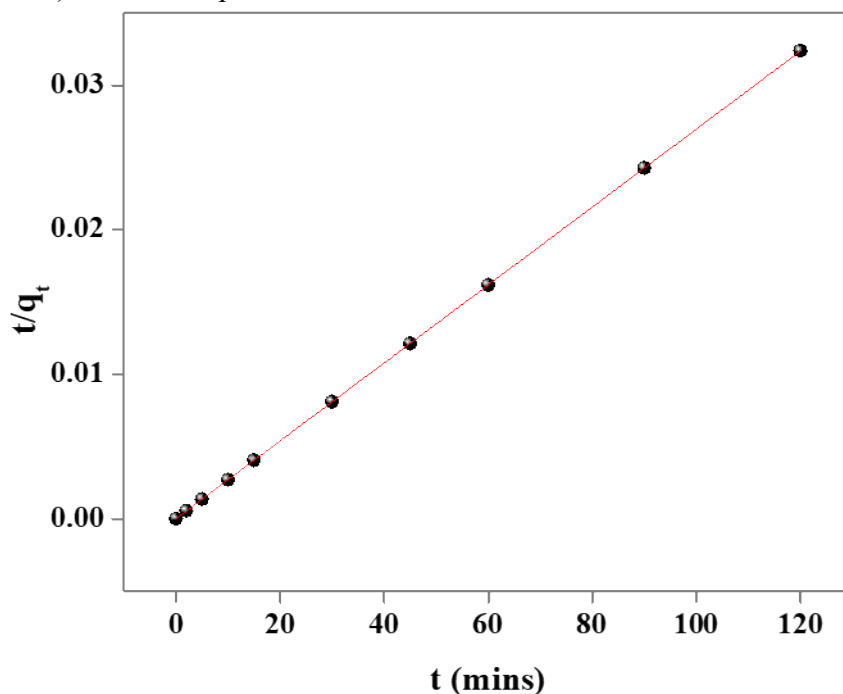| Element	Weight%
C	6.04
O	24.29
P	13.65
Fe	47.96
U	8.07
Total	100
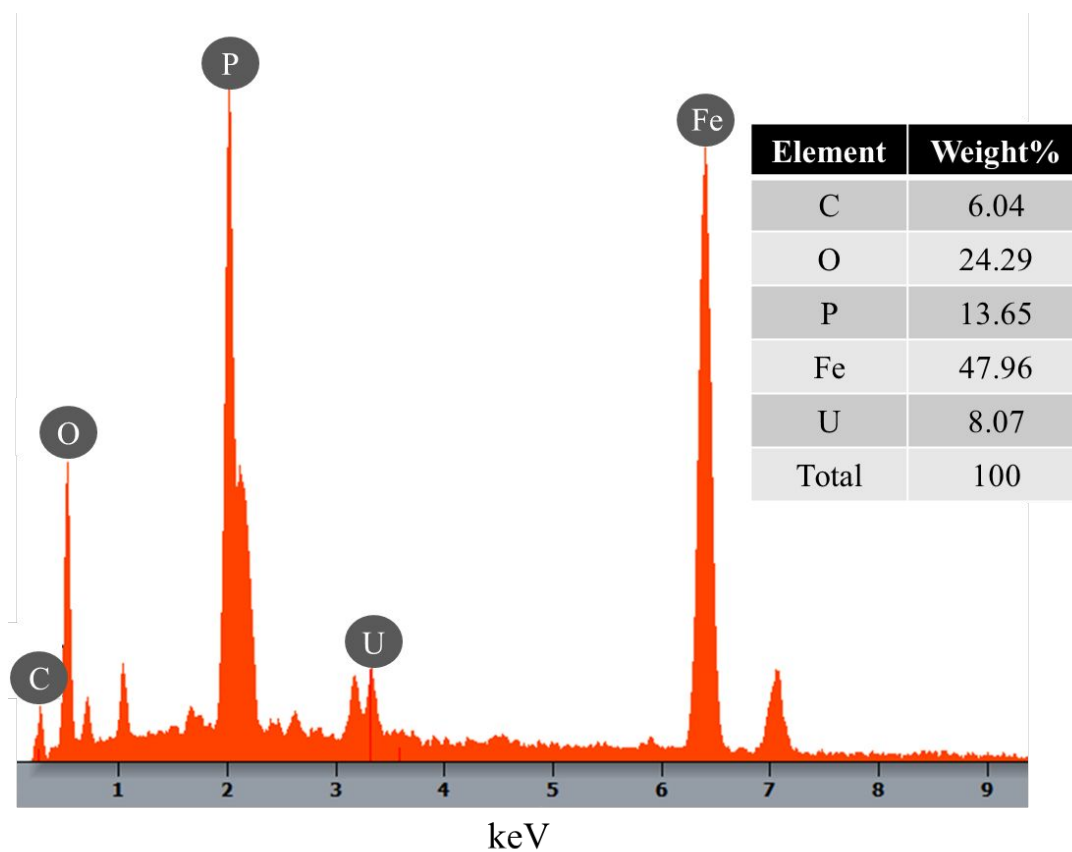
Figure S4. SEM-EDS of PCNCFH after U(VI) adsorption with weight percentage of elements.

Ho's pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

q_t (mg/g) and q_e (mg/g) are the amount of adsorbed uranium at particular time t and equilibrium, respectively.

k_2 (g mg^{-1} min^{-1}) is the adsorption rate constant.

Figure S5. Pseudo second-order reaction kinetics plot for adsorption of uranium on PCNCFH.

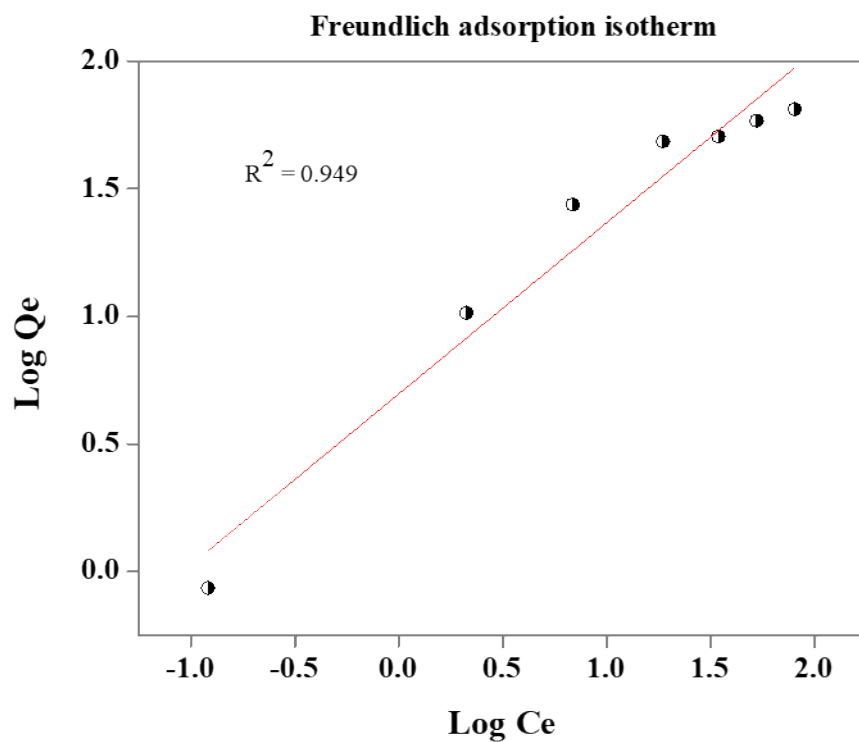**Freundlich adsorption isotherm:**

The Freundlich isotherm model can be expressed as follows:

$$\text{Log } Q_e = \text{Log } K_F + (1/n) \log C_e$$

where Q_e is the experimental adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L); K_F represents the equilibrium constant in Freundlich equation (L/mg), n signifies the Freundlich constant associated with adsorption intensity.
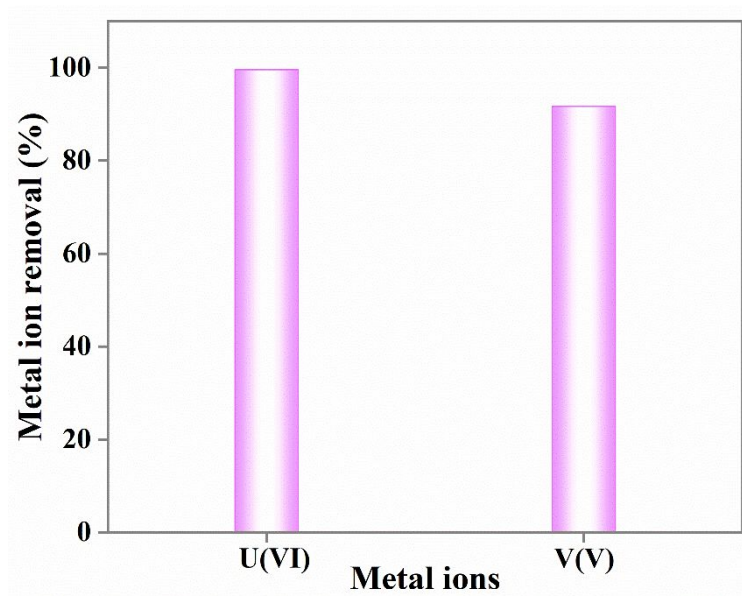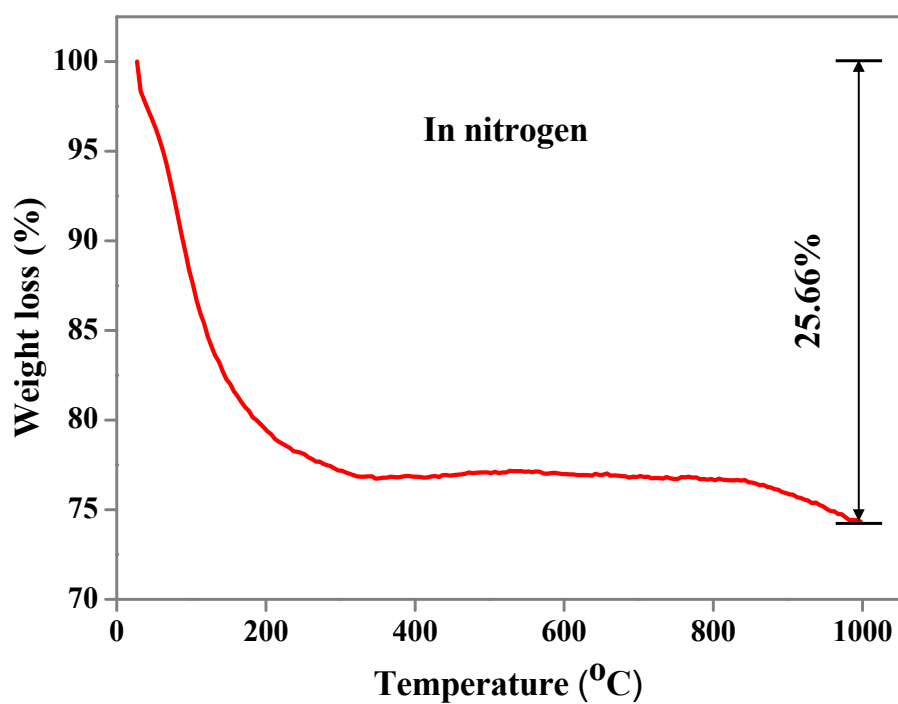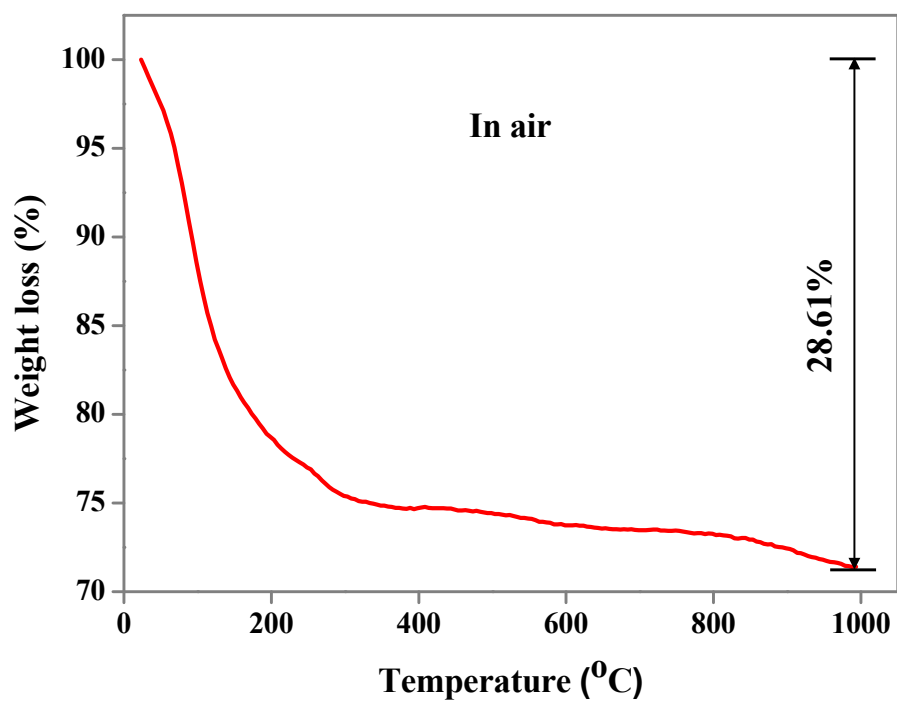
Figure S6. Freundlich adsorption isotherm model showing the correlation coefficient for uranium adsorption on PCNCFH.
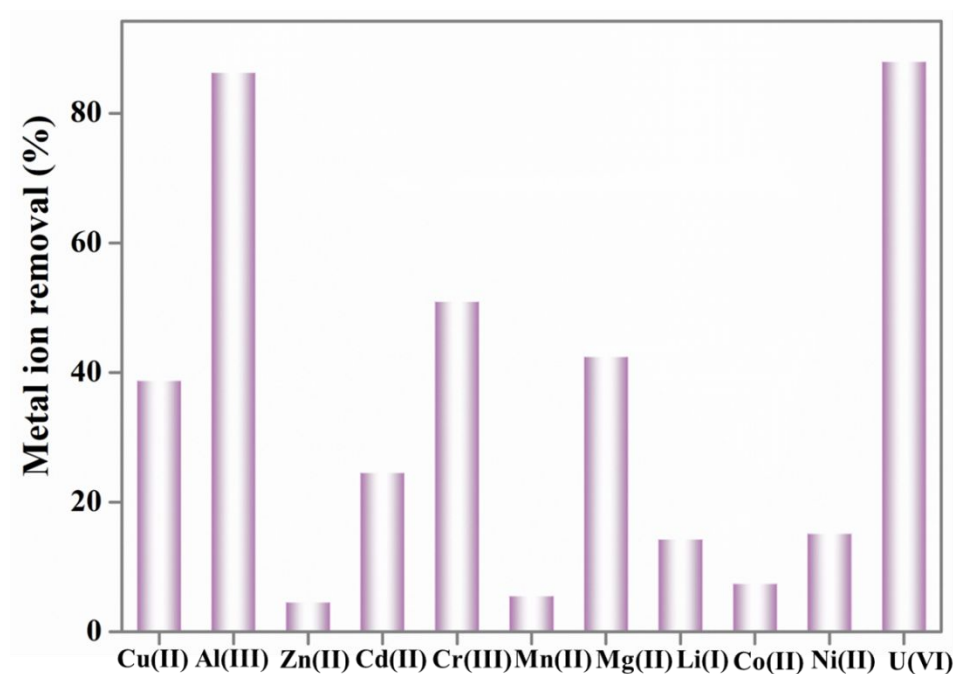
Figure S7. Selectivity of adsorption of PCNCFH for multiple metals.

Figure S8. Effect of V(V) on U(VI) adsorption on PCNCFH.

Figure S9. Thermogravimetric analysis (TGA) of PCNCFH at air and nitrogen atmospheres from room temperature to 900^{0}C with 10 mins scan rates.

Equations used

Equation (1): The removal percentage of uranium is calculated using the equation mentioned below:

$$\text{Removal \%} = [(C_o\text{-}C_e)/C_o]*100$$

where C_o and C_e represent the initial and equilibrium concentrations of the metal ions, respectively.

Equation (2): The maximum uptake of uranium (q_e) by nanocomposites was determined using the following equation:

$$q_e = (C_o\text{-}C_e)*V/m$$

where q_e represents the amount of U(VI) adsorbed per gram of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of uranium in the bulk solution (mg/L), C_o is the initial concentration of uranium (mg/L), V is the volume of the solution (L), and m is the mass of the adsorbent (g).

Equation (3): The linearized form of Langmuir equation used in this work is defined as,

$$C_e/q_e = C_e/q_{max} + 1/bq_{max}$$

where q_e is the amount of adsorption at the surface of the adsorbent (mg/g), C_e is the equilibrium concentration of the solution (mg/L), q_{max} is the maximum surface density at monolayer coverage and b is the Langmuir adsorption constant (L/mg) related to the free energy of adsorption and $1/q_{max}$ and $1/bq_{max}$ are the Langmuir constants.

Equations used for evaluating sustainability metrics

Equation (4):

$$\text{Mass intensity, or process mass intensity} = \frac{\text{Total mass used in a process excluidng water}}{\text{Mass of product}} \text{(kg/kg)}$$

Equation (5):

$$\text{Water intensity} = \frac{\text{Mass of all water used in a process}}{\text{Mass of product}}\text{(kg/kg)}$$

Equation (6):

$$\text{Reaction mass efficiency} = \text{For a particular reaction A+B} \longrightarrow \text{C,}$$

$$\frac{\text{Mass (C)}}{\text{Mass (A) + Mass (B)}} * 100\%$$

Equation (7):

$$\text{Energy intensity} = \frac{\text{Total process energy}}{\text{Mass of the final product}} \text{ KW.h/kg}$$

Equation (8):

$$\text{E factor} = \frac{[\text{kg(raw materials)} - \text{kg(desired product)}]}{\text{kg(total product including water)}}$$

Table S1. Composition of synthetic tap water.

Types of ions	Concentration of ion used in ppm
Mg^{2+}	15
SO_4^{2-}	33
F^-	0.6
Ca^{2+}	29
CO_3^{2-}	100
HCO_3^-	100
K^+	2.5
PO_4^{3-}	55.83
SiO_3^{2-}	16
Cl^-	87
Na^+	53.74
NO_3^-	1.9

Table S2.

Sustainability metrics evaluation for the synthesis of PCNC.

Material	Mass intensity (MI) (kg/kg)	Solvent intensity (SI) (kg/kg)	Reaction mass efficiency (RME) %	E - factor
PCNC	1.42	10.72	70.40	0.03