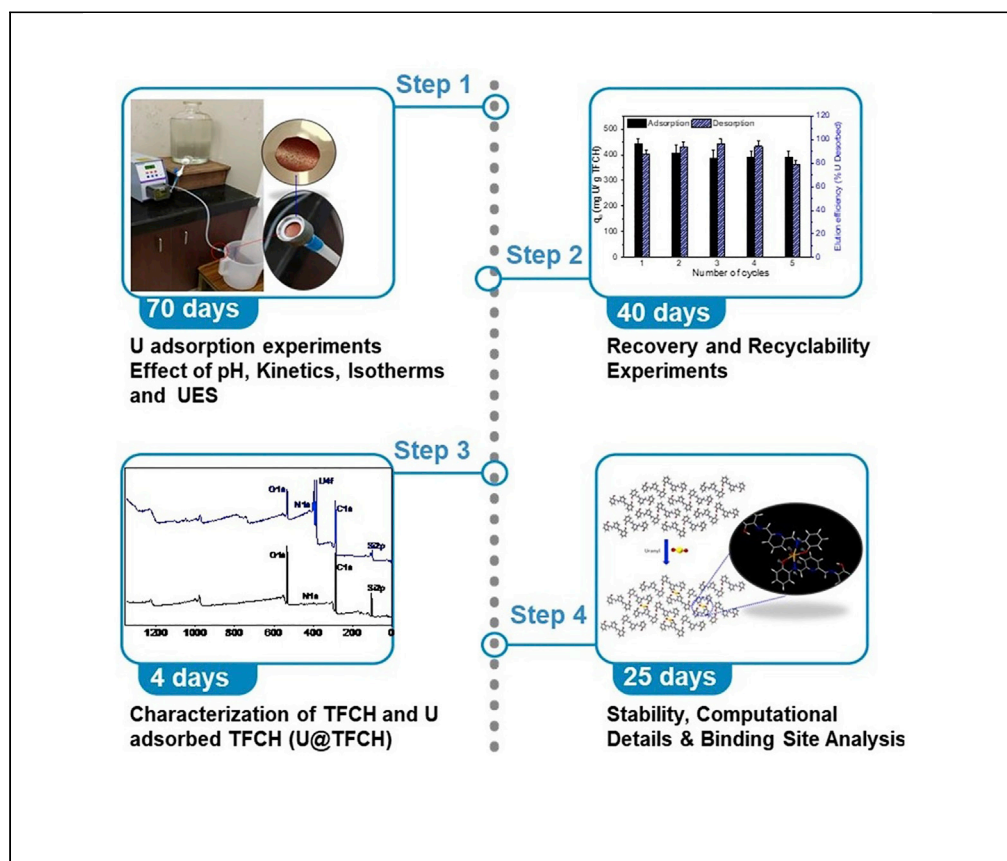


Protocol

Protocol for extraction, characterization, and computational analysis of uranium from seawater



Here, we present a protocol for uranium extraction from seawater (UES) and its characterization and computational-based structure analysis. We describe formulating batch adsorption experiments for adsorptive separation of uranium using thin film (TFCH) of Hydrogen-bonded Organic Framework (CSMCRIOF-1). We then detail the recovery of uranium using eluent mixtures and the steps to regenerate TFCH for recyclability studies. Finally, we describe the spectroscopic characterizations of TFCH and uranium adsorbed TFCH, followed by computational analysis of the structures and binding sites.

Publisher's note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.

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Highlights

Evaluation of uranium adsorption isotherm and kinetics using porous TFCH

Strategy to recover uranium and regenerate TFCH for assessing recyclability

Determination of adsorption mechanism by post-UES spectroscopic characterizations

Detailed analysis of binding sites for uranium selective adsorption

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Protocol

Protocol for extraction, characterization, and computational analysis of uranium from seawater

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SUMMARY

Here, we present a protocol for uranium extraction from seawater (UES) and its characterization and computational-based structure analysis. We describe formulating batch adsorption experiments for adsorptive separation of uranium using thin film (TFCH) of Hydrogen-bonded Organic Framework (CSMCRIHOF-1). We then detail the recovery of uranium using eluent mixtures and the steps to regenerate TFCH for recyclability studies. Finally, we describe the spectroscopic characterizations of TFCH and uranium adsorbed TFCH, followed by computational analysis of the structures and binding sites.

For complete details on the use and execution of this protocol, please refer to Kaushik et al. (2022).¹

BEFORE YOU BEGIN

Prompted by energy and environmental perspective uranium extraction from seawater (UES) has emerged as a daunting challenge, due to the lean Uranium concentration in seawater.² Adsorption is an efficient, facile, low cost, simple and energy efficient method. Implementation of suitable design strategy for U selective materials as adsorbents is required for separation and recovery of Uranium from seawater. This initiated early work on adsorbent technologies involving inorganic materials, like Mg-Al bimetallic oxides (Mg/Al-BOs),³ amidoximated silver-silica core-shell nanoparticle (Ag@SiO₂-AO),⁴ magnetic nanoparticles,⁵ mesoporous silica materials.⁶ The developmental stage of UES is dominated by oxime functionalized materials, i.e., polymeric materials (OxF),⁷ porous organic polymers (POPs),⁸ porous aromatic frameworks (PAFs),⁸ synthetic organic polymers,⁹ biopolymers,¹⁰ porous carbonaceous adsorbents,¹¹ ionic liquids,¹² graphene oxides,¹³ grafted fibers¹⁴ etc.

Innumerable examples from the material library been tested and touted for their UES performance are polyamidoxime-based composite hydrogels,¹⁵ polysaccharide based amidoxime-functionalized konjac glucomannan (AO-KGM) sponge,¹⁶ β-cyclodextrin/sodium alginate/diatomite (CSD) hydrogel beads,¹⁷ ion-crosslinked supramolecular Zn²⁺ poly(amidoxime) (PAO) hydrogel,¹⁸ poly (amidoxime) (PAO) hydrogel membrane fabricated by sunlight polymerization,¹⁹ plant-mimetic directional-channel poly(amidoxime) (DC-PAO) hydrogel.²⁰ Further, various approaches using different materials in combination with electrochemically or photo-chemically driven processes have been utilized to advance UES, like electrochemical method based on poly (brilliant cresyl blue),²¹



electrodeposited polypyrrole/biomass-derived carbon composite electrodes,²² covalent organic frameworks (COFs),²³ and metal organic frameworks (MOFs).²⁴

These benchmark sorbent material's design have the scope of improvement to attain the economic feasibility criterion for UES. The material design needs work on maximizing the adsorption capacity, degree of functional groups, surface area, kinetics, U binding affinity, and water/chemical stability. A paradigm shift has been observed in the last decade, mainly in the material design from micro- to nano- to nano-porous materials (fibers, beads, films etc) with U selective binding sites.¹ This led to an increase in porosity, diffusion rate, and surface area, which ensued the utilization of more number of active sites. This strategy yielded improved material design resulting in maximized UES adsorption capacity.¹ The hydrogen bonded organic frameworks (HOFs) are a developing class of materials with excellent physical properties desired for UES. HOFs can be post-functionalized with ease, they have maximized surface area, tailorable porosity, chemical/hydrolytic stability, ease in processability and regeneration via mere recrystallization. This led us to development of CSMCRI-HOF-1 with robust stability and U selective binding sites and its downsized thin film (TFCH) to obtain maximized surface area and applicability in large area UES.¹

Institutional permissions

A PRIS number (CSIR-CSMCRI-210/2022) has been assigned for this manuscript.

Preparation of the reagents and equipment

A complete list of reagents and equipment can be found in the “[key resources table](#)” and “[materials and equipment](#)”.

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Uranyl nitrate hexahydrate (reagent grade) 99%	Suvidhinath Laboratories, India	CAS NO: 13520-83-7
Sodium hydroxide AR grade (98%)	Research Lab Fine Chem Industries, India	CAS NO: 1310-73-2
Nitric acid ER, (69%–72%)	Thermo Fisher Scientific India Private Limited	CAS NO: 7697-37-2
Sodium carbonate anhydrous extrapure AR (99.9%)	Sisco Research Laboratories Pvt Ltd	CAS NO: 497-19-8
Hydrogen peroxide, extra pure, >6%w/v, 20 volumes, SLR	Thermo Fisher Scientific India Private Limited	CAS NO: 7722-84-1
Sulfuric acid (98%) LR grade	Qualikems Fine Chem Pvt Ltd	CAS NO: 7664-93-9
Potassium permanganate (LR grade) 99.0%	Ranbaxy Fine Chemicals Ltd	CAS NO : 7722-64-7
Hydrochloric acid ER (36.5%–38.0%)	Thermo Fisher Scientific India Private Limited	CAS NO: 7647-01-0
Nylon membrane filter	Axiva Slichem Biotech, India	SFNY13RB
Silicon wafer	University Wafer, Boston, USA	590
25 L Storage glass jar	Glassco Laboratory Equipment Pvt Ltd	Custom made
Stainless steel syringe port	Axiva	
Fabric support	Nordlys-TS100, Polymer Group Inc., France	NA
O Ring	Custom made	
Milli-Q Water (18.2 MOhm)	CSIR-CSMCRI, Bhavnagar, India	Electro-deionization unit (US 2015/0298116A1)
ICP multi-elements standard solution VIII. (24 elements in dilute nitric acid).	Merck	
Vanadium ICP standard (V SRM) NH4VO3 in 2%–3% HNO3.	Merck	
Uranium ICP standard (U SRM) in 2%–5% HNO3	Reagecon	

(Continued on next page)

Continued

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Ultrapure Water	Wasser Agua Eau. Merck	
Sodium chloride (NaCl), ultra dry, 99.998% (metal basis)-10 Mesh Beads, ampouled under argon	Alfa Aesar	
Ultra-pure nitric acid (67%–70%) (Trace Metal Grade)	Thermo Fisher Scientific	
Vanadium pentoxide (V ₂ O ₅) 99.5% pure	Sisco Research Laboratories Pvt. Ltd.	CAS No. 1314-62-1
Ferrous chloride tetrahydrate (FeCl ₂ ·4H ₂ O) 98% pure	Sisco Research Laboratories Pvt. Ltd.	CAS No.13478-10-9
Cobalt sulfate heptahydrate (CoSO ₄ ·7H ₂ O)	Sisco Research Laboratories Pvt. Ltd.	CAS No. 10026-24-1
Nickel chloride hexahydrate (NiCl ₂ ·6H ₂ O)	Qualigens 97%	CAS No. 7791-20-0
Copper sulfate pentahydrate (CuSO ₄ ·5H ₂ O)	SRL, 99.5% extrapure AR	CAS No. 7758-99-8
TFCH	Kaushik et al. ¹ , Marvaniya et al. ²⁵	(Thin Film of ^{CSMCR} HOF-1)

Software and algorithms

Microsoft Excel	Microsoft	Excel 2013 (v15.0)
CasaXPS software	Casa Software Ltd	Version 2.3.25
XPSPEAK41	Raymund Kwok.XPSPeak	Version 4.1.0.0
Gaussian	Carnegie Mellon University Gaussian, Inc.	Version 09

Other

Digital pH meter	Eutech, with ATC Probe PH5TEMB01P, EUTECH INSTRUMENTS
Plate Shaker	Tarsons SPINX-Orbital Shaker MC-02
Peristaltic pump with silicone rubber tubing	PARISA TECHNOLOGY
Fourier transform-infrared spectrometer (FT-IR)	PerkinElmer, Spectrum GX
Inductively coupled plasma mass spectrophotometer	Thermo iCAP QICP-MS
Powder X-ray diffraction	Philips X'pert MPD System
Scanning electron microscopy	Jeol, JSM-7100F
Transmission electron microscopy	JEOL, JEM-2100
XPS spectrometer	Thermo Fisher Scientific Instruments UK, K ALPHA +
Brunauer-Emmett-Teller	Micromeritics, ASAP 2010

MATERIALS AND EQUIPMENT

2% background sodium chloride (NaCl) salt solution

- Prepare the standard solution of 20% (w/v) NaCl salt solution. In order to prepare it, add 10 g NaCl to 50 mL measuring flask and make the volume up to 50 mL with Milli-Q water. The solution is then further diluted to make 2% NaCl salt solution.

Note: For standard preparation, use ultrapure sodium chloride (NaCl) salt for matching the sample matrix.

- Then, prepare 2 ppb, 5 ppb, 10 ppb, 20 ppb, 50 ppb, 100 ppb, 200 ppb, 500 ppb with ME Elements, U SRM, V SRM, diluted in 2% NaCl solution for a volume of 35 mL each.

Note: All standard background salt matrix is same i.e., 2% (w/v) NaCl.

- Add 350 μ L HNO₃ (Trace Metal Grade) to each solution (1% (v/v)) to store the samples in acidic condition before analysis, this prevents precipitation and biomass growth.
- Dilute all standards with 2% NaCl solution.

Note: For sample preparations, clean all the lab wares thoroughly by boiling with concentrated hydrochloric acid for one hour followed by rinsing with distilled water and 3 times using

Milli-Q water. Rinse the plastic equipment with 10% nitric acid solution and afterward wash with distilled water and 3 times using Milli-Q water.

Uranyl nitrate spiked seawater

- Prepare two different sets of 16 ppm and 32 ppm uranyl nitrate spiked seawater solution separately.
- To prepare 16 ppm and 32 ppm uranyl nitrate spiked seawater solution, collect uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), vanadium pentoxide (V_2O_5), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) chemical compounds.
- To prepare 16 ppm uranyl nitrate spiked seawater solution, weigh and add 33.75 mg, 57.07 mg, 56.96 mg, 76.45 mg, 67.83 mg, 62.86 mg chemical compounds respectively in 1 L conical flask and dissolve them.
- Adjust the pH of the solution to 5 (at pH 5, some salts can precipitate).
- Filter the precipitate, again measure the concentration of metal ions using ICP-MS.
- After filtration, the concentration of metal ions is less than the actual concentration, which is considered to be the initial concentration for further experiments.
- To prepare 32 ppm uranyl nitrate spiked seawater solution, weigh and add 67.504 mg, 114.13 mg, 113.92 mg, 152.901 mg, 135.671 mg, 125.73 mg chemical compounds respectively in 1 L conical flask and dissolve them.
- Adjust the pH of the solution to 5 (at pH 5, some salts can precipitate).
- Filter the precipitate, again measure the concentration of metal ions using ICP-MS.
- After filtration, the concentration of metal ions is less than the actual concentration, which is considered to be the initial concentration for further experiments.

16 ppm uranyl nitrate spiked seawater solution (1 Ltr) (Storage condition: 25°C, for max. 1 month)

Reagent	Final concentration	Amount
Uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)	16 ppm	33.75 mg
Vanadium pentoxide (V_2O_5)	16 ppm	57.07 mg
Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$)	16 ppm	56.96 mg
Cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$)	16 ppm	76.45 mg
Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	16 ppm	67.83 mg
Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	16 ppm	62.86 mg

32 ppm uranyl nitrate spiked seawater solution (1 Ltr) (Storage condition: 25°C, for max. 1 month)

Reagent	Final concentration	Amount
Uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)	32 ppm	67.504 mg
Vanadium pentoxide (V_2O_5)	32 ppm	114.13 mg
Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$)	32 ppm	113.92 mg
Cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$)	32 ppm	152.901 mg
Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	32 ppm	135.671 mg
Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	32 ppm	125.73 mg

- Prepare 16 ppm and 32 ppm uranyl nitrate spiked seawater solution separately in 1 L.
- Weigh the exact weight in mg with the help of weighing balance that gives accurate and precise reading in mg scale.

△ **CRITICAL:** Uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) exposure can cause health hazards such as acute, chronic, cancer, reproductive and other long term effects. To

reduce direct and mixed exposure, workplace controls and practices must be followed strictly.

STEP-BY-STEP METHOD DETAILS

Part 1: Adsorption studies

Ⓞ Timing: 70 days

Ⓞ Timing: 24 h for step 3

Ⓞ Timing: 4 days for step 4

Ⓞ Timing: 4 days for step 5

Ⓞ Timing: 30 days for step 6

Ⓞ Timing: 30 days for step 7

This section describes the laboratory scale batch mode adsorption experiments with natural and spiked seawater, monitoring the metal ion concentrations for pre and post adsorption samples, using optimized Argon Dilution kit (AGD-KED mode) in ICP-MS. Determination of effect of pH, time, and concentration of adsorbate on adsorption of U from spiked solutions and natural seawater are included in this section.

1. Batch Analysis.

- a. Perform the adsorption experiment in batch mode.

Note: Small scale experiment from the batch study is favored at laboratory scale investigation as only small amount of material is required and it is less time consuming. Study of adsorption by equilibrium in batch mode enables the prediction of performance of adsorbent before application in larger scale.

- b. Measure the residual concentration of U (indirect method) and by acid digestion of U adsorbed samples (direct method) using the argon dilution method (AGD-KED mode) on inductively coupled plasma mass spectrophotometer (ICP-MS).
- c. Collect the natural seawater for the adsorption experiments and measure its pH (for the adsorption studies, the natural seawater was collected from the Alang coast of Gujarat, India. The pH value of this seawater was measured to be 8.1).
- d. Measure the average concentration of metal ions present in the natural seawater using ICPMS with AGD-KED mode as shown in the [Table 1](#).
- e. Perform the calibration each time prior to the sample analysis with standards prepared in 2% background salt concentration to match the seawater matrix.
- f. Measure the amount of U adsorbed (Q_e mg/g) onto TFCH in the following way,

$$Q_e = \frac{(C_i - C_e)}{m} \quad \text{(Equation 1)}$$

Where, C_i = Initial concentration of metal ion in mg/L.

C_e = Equilibrium concentration equilibrium concentration of metal ion in mg/L.

m = Mass of adsorbent in g/L.

q_e = Amount of metal ion adsorbed per gram of adsorbent.

- g. Average the data from three parallel experiments to obtain each experimental result.

Table 1. Concentration of various metal ions in natural seawater from the coast of Hathab village, Bhavnagar, Gujarat, India

Metal ions	Concentration in ppm
Li	0.136 ± 0.003
Mg	1129.604 ± 6.778
Al	0.005 ± 0.001
Ca	130.314 ± 1.173
Ba	0.024 ± 0.001
Pb	0.003 ± 0.001
Zn	0.212 ± 0.005
Sr	7.784 ± 0.047
V	0.013 ± 0.001
Fe	0.015 ± 0.001
Ni	0.005 ± 0.0001
Co	0.002 ± 0.0001
Cu	0.016 ± 0.0001
U	1.3 ± 0.0001

h. Use the values of correlation coefficients (r) and standard deviation (SD) to compare the models.

$$r = \frac{(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}} \quad \text{(Equation 2)}$$

2. ICPMS sample analysis using Argon dilution kit.

- a. Initiating AGD-KED mode.
 - i. Check all basic parameters such as knob of argon gas and helium gas cylinder, exhaust, sampler chiller, air conditioner, computer etc. before running AGD-KED mode.
 - ii. Check argon gas (cylinder and knob should be on).
 - iii. Check helium gas (it should be always on).
 - iv. Check additional argon gas (whenever needed) for AGD-KED mode.
 - v. Switch on the exhaust.
 - vi. Switch on the auto sampler.
 - vii. Fill the rinse solution for washing (1% HNO₃ in ultrapure water).
 - viii. Fix the sample tube & drain tube.
 - ix. Switch on chiller (the temperature should be 19°C–20°C).
 - x. Check vacuum of the instrument.
 - xi. Switch on air conditioner (AC) and keep the temperature at 22°C–24°C.
 - xii. Switch on the computer (double click on the instrument control software).
 - xiii. Put the probe in rinse solution (before igniting the plasma).
 - xiv. Now, switch on plasma (watch the plasma chamber if orange flame appears then rotate plasma chamber handle clock wise and then take second attempt).
 - xv. After some times, check drain solution.
 - xvi. Ignite plasma and allow it to warm-up for 20–30 min with rinse solution (1% HNO₃ in ultrapure water).
 - xvii. After plasma ignition (15–20 min warm-up for stabilization of plasma & instrument), place the tune solution and check the counts of elements (Co, Li, In, Bi, Ba, U).
 - xviii. Now, go for tuning & performance in both mode STD & KED with tune solution.
- b. Tuning & Performance of Instrument.
 - i. Check all elements counts (Co, Bi, Li, U, V, Se etc.) just before tuning and performance in STD and KED mode.
 - ii. Match the counts with SOP and then go for tuning and performance.

- iii. First, check tuning in STD & KED, tuning will pass then go for performance in both mode with the solution of 1 ppb of Ba, Bi, Ce, Co, In, Li, U in 2.5% (v/v) HNO₃ and 0.5% (v/v) HCl.
- iv. After passing tuning & performance with good counts, instrument is ready for AGD-KED mode.

Note: Tuning and performance is carried out as a sensitivity test to ensure data accuracy and reproducibility.

- c. Optimization of AGD-KED mode.
 - i. First, switch on AGD-KED kit.
 - ii. Then, select gas panel followed by selecting gas flow (make sure additional argon line is empty and additional argon knob is off) because of when normal mode STD/KED is switched to AGD-KED that time additional argon flow is on so argon flow increases automatically high then plasma suddenly goes off.
 - iii. Opt for optimization after completing tuning and performance.
 - iv. Go in software instrument controller, switch to STD/KED to AGD-KED mode.

Note: Plasma is not affected because of still additional argon knob is off and additional argon line is empty.

- v. Now, select gas panel then select additional gas flow.
Set the additional gas flow to zero and switch additional argon gas knob on.
- vi. Now, additional argon gas flow increases slowly (0.1, 0.2, 0.5, 0.8...1, 2, 5...to nearby 50.00) depends on the counts/method/analysis plan (additional argon is used in dilution for aerosol).
- vii. Now, place tune solution then run in AGD-KED mode for checking counts.
- viii. Then, check counts of elements with 1 ppb of Ba, Bi, Ce, Co, In, Li, U in 2.5% (v/v) HNO₃ and 0.5% (v/v) HCl.
- ix. If the counts match with the SOP, then instrument sensitivity is good in AGD-KED.
- x. Now, AGD-KED mode ready for the analysis.

- d. AGD-KED Analysis Method.
 - i. Prepare the sample in aqueous medium and in 2% salt. Now, prepare the lab book.
 - ii. Double click on the 'Qtegra' software.
 - iii. Fill the REQ number.
 - iv. Select elements for analysis.
 - v. Then set all different parameters (interference correction, measurement mode, dwell time, washing time, sample intake time etc.).
 - vi. After setting all parameter, set sequence wise standards and samples.
 - vii. Then, go for the analysis. For, sake of understanding, refer [Figure 1](#) which demonstrates different parts of ICP-MS instrument and sample preparation.

3. Batch experiments to determine the optimal pH and its effect on adsorption.
 - a. Define the optimal pH for maximum adsorption of uranium by varying the initial pH of the 8 mg/L U spiked seawater in the range of pH 1–10.
 - b. To study the effect of pH, conduct the batch adsorption experiments separately.
 - c. Take 25 mL 8 mg/L uranyl spiked seawater in 30 separate 100 mL stoppered glass bottles.
 - d. Adjust the pH of 8 mg/L spiked seawater from pH 1–10 using 0.1 M NaOH and/or HNO₃ in triplicate.
 - e. Add 2 mg of TFCH in all the glass bottles containing 8 mg/L uranyl spiked seawater with adjusted pH.
 - f. Agitate the bottles at 25°C on a plate shaker at 100 rpm for 24 h.
 - g. At the end of 24 h, acidify the suspensions using 2% HNO₃ and filter using 0.22-µm nylon membrane filter.



Figure 1. Different parts of ICP-MS instrument and sample preparation demonstration

- h. Analyze the filtrate for residual concentration of U (C_e mg/L) using the AGD-KED mode in ICP-MS.
- i. Calculate the amount of U adsorbed on TFCH and its standard deviation (SD) using the [Equations 1 and 2](#).

△ CRITICAL: Run parallel set of blank (8 mg/L U spiked seawater without addition of TFCH) for each pH at 0 and 24 h to define actual initial concentration of U (C_i mg/L).

4. Batch experiments to determine the optimal time and adsorption kinetics.
 - a. Examine the mode of adsorption/mechanism with respect to variation in time.
 - b. Implicate the well-established models, i.e., pseudo 1st order, and pseudo 2nd order kinetics to derive the rate determining and adsorption driving steps.
 - c. Take 500 mL of 16 and 32 mg/L uranium spiked seawater each in three different 1 L stoppered glass bottles.
 - d. Adjust the pH of uranium spiked seawater to pH 8 using 0.1 M NaOH and/or HNO₃.
 - e. Withdraw 500 μ L sample from each bottle to measure the actual initial concentration (C_i), as concentration of the prepared solutions differs the actual concentration due to speciation of added metals at pH 8.
 - f. Carefully weigh and add 5 mg TFCH to each bottle.
 - g. Place the bottles on an orbital plate shaker and allow shaking of solutions at 120 rpm at room temperature 25 C.
 - h. Withdraw 500 μ L sample from each bottle at varied time intervals (0 time to 4 days).
 - i. Preserve the samples instantly by adding 2% nitric acid followed by filtration using 0.22- μ m nylon membrane filter.
 - j. Replenish 500 μ L fresh pH adjusted uranium spiked seawater in each bottle.
 - k. Monitor the M^{n+} concentrations of all the samples withdrawn at different time intervals using ICP-MS (AGD-KED mode).
 - l. Adopt the [Equation 4](#) for pseudo 1st order kinetic model and evaluate fitting of adsorption data,

where, t (min) = contact time,

k_1 (min^{-1}) = 1st order rate constant,

q_t (mg/g) = amount of uranium adsorbed at the particular contact time.

q_e (mg/g) = amount of uranium adsorbed at the equilibrium time.

Table 2. Fitting parameters for U adsorption kinetics on TFCH

Kinetics	Units	16 ppm spiked sea water (SSW)	32 ppm spiked sea water (SSW)
EXP q_e	(mg/g)	780.43	1201.12
PS1	q_e (mg/g)	766.34	1229.39
Pseudo 1 st Order	k_1 (min ⁻¹)	0.158	0.051
	r^2	0.986	0.989
PS2	q_e (mg/g)	726.714	1137.075
Pseudo 2 nd Order	k_2 (g.min/mg)	0.002	9.17E-05
	r^2	0.945	0.936

- m. Adopt the Equation 5 for pseudo 2nd order kinetic model and evaluate fitting of adsorption data,

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (\text{Equation 5})$$

where, t (min) = contact time.

k_2 (g.min/mg) = 2nd order rate constant.

q_t (mg/g) = amount of uranium adsorbed at the particular contact time.

q_e (mg/g) = amount of uranium adsorbed at the equilibrium time.

- n. Solve the equations and define unknown fitting parameters (Table 2) for non-linear function using the Solver function in Microsoft Excel.

Note: Define the potential rate controlling steps associated with U adsorption by fitting the adsorption kinetics experimental data of 16 and 32 ppm spiked seawater (SSW) to pseudo 1st order kinetics (PS1), and pseudo 2nd order (PS2) kinetics using the non-linear fitting models.

5. Batch experiments to determine the optimal concentration and adsorption isotherm.
- Perform the adsorption experiments at pH ~8.0 for 30 min, for a wide range of initial concentrations of U spiked in DI water (0.5 mg/L to 30 mg/L) and seawater (0.5 mg/L to 40 mg/L), with a dose of 2 and 10 mg/L TFCH respectively.
 - Monitor the initial concentrations also using ICP-MS (AGD-KED mode), as concentration of the prepared solutions differs the actual concentration due to speciation effect at pH 8.
 - For the analysis of adsorption processes using two and three-parameter isotherm models, solve all the equations for two and three-parameter isotherm models and define unknowns for non-linear function using the Solver Function in Microsoft Excel.
 - Use two parameter isotherm models, Langmuir and Freundlich for the studies.

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (\text{Equation 6})$$

$$q_e = k_f C_e^{1/n} \quad (\text{Equation 7})$$

where,

C_e (mg/L) = Residual concentration of uranium in the solution.

k_L (L/mg) = Langmuir equilibrium constant.

k_f ((mg/g)(L/mg)^{1/n}) = Freundlich equilibrium constant.

1/n = Heterogeneity factor.

q_m (mg/g) = Maximum amount of uranium adsorbed.

q_e (mg/g) = Maximum amount of uranium adsorbed at equilibrium time.

- e. Imply the three parameter isotherm models, Redlich Peterson and Sips (Langmuir-Freundlich) as depicted in Equations 8 and 9,

Table 3. Parameters for different isotherm fitting for U adsorption on TFCH

Isotherms		Spiked MQ water (SMW)	Spiked seawater (SSW)
Langmuir	Q_m (mg/g)	2161.972	1284.369
	k_L (L/mg)	10.316	1.039
	ΔG	-5823.5	-96.611
	r^2	0.859	0.892
Freundlich	n	2.535	2.179
	k_f ((mg/g)(L/mg) ^{1/n})	847.674	351.007
	r^2	0.625	0.946
RP	k_{RP} (L/g)	6.662	22.819
	α_{RP} (L/mg)	14312.24	9576.741
	β	0.986	0.616
	r^2	0.847	0.955
Langmuir-Freundlich	Q_m (mg/g)	2356.864	3272.128
	k_s (L/mg)	6.981	0.022
	n	0.844	0.519
	r^2	0.857	0.962

$$q_e = \frac{k_{RP} C_e}{1 + \alpha_{RP} C_e^\beta} \quad (\text{Equation 8})$$

$$\frac{q_e}{q_m} = \frac{(k_s C_e)^n}{1 + (k_s C_e)^n} \quad (\text{Equation 9})$$

where, C_e (mg/L) = Equilibrium concentration of uranium in the solution.

k_{RP} (L/g), α_{RP} (L/mg), β = Redlich-Peterson equilibrium constants.

k_s (L/mg) = Sips equilibrium constant.

n = Heterogeneity factor.

q_m (mg/g), q_e (mg/g) = Maximum amount of uranium adsorbed.

q_e (mg/g) = Maximum amount of uranium adsorbed at equilibrium time.

- f. Fit the parameters for different isotherm for U adsorption on TFCH as depicted in [Table 3](#).
6. U extraction from natural seawater (UES).
 - a. Collect the natural seawater first.
 - b. Determine the initial concentration of various metal ions in the natural seawater by ICP-MS (AGD-KED mode) against standard calibration performed in ~2% salt water to resemble the seawater matrix.
 - c. Conduct the lab-scale UES experiments using a simplified set-up ([Figure 2](#)) of a flow through assembly in batch recirculation mode.
 - d. In this set-up, connect a 25 L storage glass jar to a stainless steel syringe port containing the adsorbent bed of 1 cm² area TFCH onto a fabric support, fitted with the help of a O-ring.
 - e. Pump the natural seawater stored in the glass jar continuously using a peristaltic pump through the TFCH with a flow rate adjusted to 0.5 mL/min.
 - f. Run the experiment continuously for 30 days.
 - g. Monitor the samples for the remaining concentration of U, at a predefined interval.
 - h. Evaluate the adsorption kinetics using the pseudo 1st order, and pseudo 2nd order models for the batch adsorption from natural seawater with respect to time intervals (day 1 to day 30).
 - i. Solve all the equations and define unknowns for the non-linear function in [Equations 4](#) and [5](#) using the Solver function in Microsoft Excel.
 - j. Present the kinetic parameters evaluated as shown in the [Table 4](#).

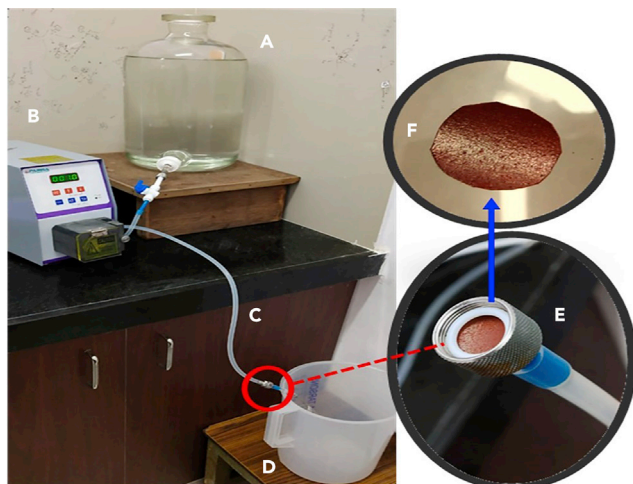


Figure 2. Laboratory-scale experimental set-up for the Uranium Extraction from Seawater

- (A) 25 L storage glass jar.
- (B) Peristaltic pump.
- (C) Silicon rubber tubing.
- (D) Plastic jug (5 L).
- (E) O ring assembly.
- (F) TFCH on fabric support.

- k. After the completion of 30 day experiment with natural seawater, characterize the surface of the thin films with the help of SEM and EDAX to check if there is any growth of bio fouling or not, as represented in the [Figure 3](#).
7. Direct measurement of adsorbed U after 30 days of adsorption from natural seawater.
 - a. Perform the direct measurement for adsorbed U, by using the US EPA method 3031.²⁶
 - b. Digest the U@TFCH samples with conc. acids and KMnO_4 with stirring.
 - c. Homogenize and weigh the sample, place in a beaker.
 - d. Add potassium permanganate in 1:1 ratio with respect to the sample.
 - e. Add 1.0 mL of concentrated H_2SO_4 dropwise and stir with stirring rod.
 - f. Add 1.0 mL of concentrated HNO_3 and stir.
 - g. Add 2 mL of concentrated HCl and stir.
 - h. Heat the beaker containing sample and acid mixtures to digest the organic content, till there is no further gas evolution.
 - i. Repeat the addition of acids and heating until complete digestion indicated by clear yellow digestate with black or dark reddish-brown precipitates.
 - j. Carefully wash the beakers, cover and sides with deionized water and then filter the residue and collect the filtrate.
 - k. Allow the filtrate to cool and quantitatively transfer to a volumetric flask and bring it to a specified volume (10 mL).

Note: This reaction is highly exothermic and needs to be performed with very much caution.

- l. Collect the residue with centrifuge and wash with hot conc. HCl .
- m. Collect the washings containing the adsorbed U digested from the U@TFCH and make up to 10 mL.
- n. Further, take 0.1 mL sample and dilute with 10 mL Milli-Q water for the analysis of extracted U using ICP-MS with an optimized Argon dilution method.
- o. Calculate the amount using the formula, and report the result as shown in [Table 5](#).

Table 4. Parameters for the Kinetics models fitted to adsorption experimental data with natural seawater

Kinetics		Units	Natural seawater
EXP	q_e	(mg/g)	17.915
PS1 Pseudo 1 st Order	q_e	(mg/g)	18.0811
	k_1	(min ⁻¹)	0.18114
	r^2		0.965
PS2 Pseudo 2 nd Order	q_e	(mg/g)	21.275
	k_2	(g.min/mg)	0.011
	r^2		0.953

$$[C \text{ (mg/L)} * (DF)*V \text{ (L)}]/m \text{ (mg)}.$$

Where, C = Measured concentration for extracted U.
m = U@TFCH taken.
DF = Dilution factor.

Part 2: Recovery and recyclability experiments

⌚ Timing: 4 days

This section deals with the experimentation details of recovery and recyclability study of TFCH. Recovery of U using eluent mixtures and procedure to regenerate TFCH and study its recyclability using Fourier Transform Infra-Red (FTIR) analysis.

- Conduct separate experiments for the recovery and recyclability experiment of TFCH.
- Prepare U adsorbed TFCH (U@TFCH) samples first, by allowing the adsorption of U onto TFCH.
- Take (2 mg) for 24 h from 8 ppm spiked seawater (25 mL SSW) at room temperature.
- Isolate the U adsorbed U@TFCH samples from the solutions by filtration.
- Rinse thoroughly with MQ water and air-dry it.
- Recover the U from the dried U@TFCH (2 mg) rapidly using well reported 10 mL eluent mixture (1.0 M Na₂CO₃ + 0.1 M H₂O₂), within 60 min.

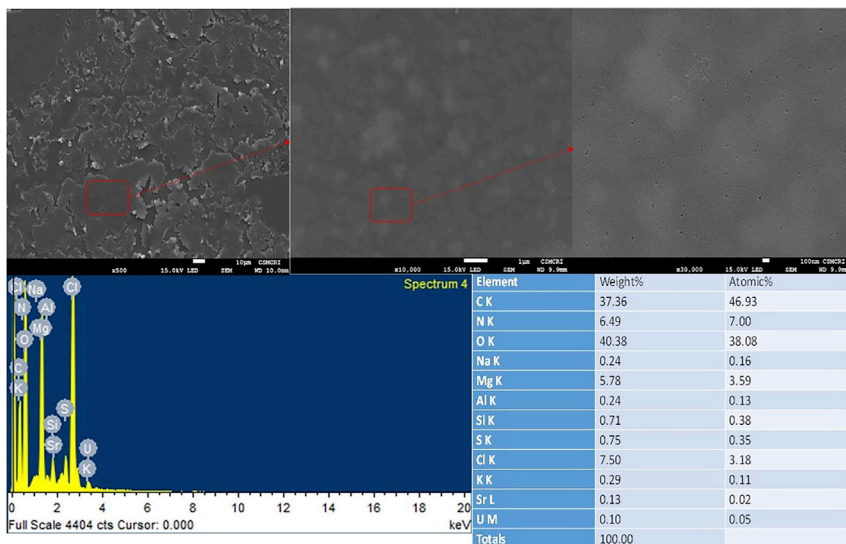


Figure 3. SEM and EDX of elements in U@TFCH, after 30 days of Uranium extraction from natural seawater

Table 5. Direct measurement of U adsorbed with ICP-MS acid digestion method

ICP-MS concentration	Digested U@TFCH		
	R ₁	R ₂	R ₃
Concentration average	17.803 ppb	17.807 ppb	17.893 ppb
Concentration per Run 1	17.801 ppb	17.801 ppb	17.911 ppb
Concentration per Run 2	17.812 ppb	17.812 ppb	17.897 ppb
Concentration per Run 3	17.798 ppb	17.808 ppb	17.872 ppb
Concentration RSD	0.50%	0.40%	1.40%

- Estimate the amount of U adsorbed and desorbed by continuous monitoring of the U concentration in the residual solution of U adsorbed from 8 ppm SSW and the eluent solutions after 60 min contact, respectively using the AGD-KED mode in ICP-MS and applying the Equation 1.
- Confirm the recyclability of TFCH by FTIR analysis before and after adsorption and desorption as shown in Figure 4.
- Further, immerse TFCH (TFCH_Pristine) and samples in seawater for 30 days (^{CSMCRI}HOF-1_30d and TFCH_30d).
- Regenerate TFCH after 2 cycles (each adsorption cycle of 30 days) of adsorption-desorption to confirm the recyclability of the material.
- Study the regeneration of TFCH for U extraction from natural seawater for 2 adsorption-desorption cycles with 30 days adsorption followed by desorption as shown in Figure 5.
- Characterize the uranium concentration from residual solution using ICPMS.

Note: The Figure 4 clearly shows, ~17.6 mg/g adsorption efficiency with ~10% reduction in UES efficiency in consecutive cycle with natural seawater, which is fitting close to the criterion for techno-economical viability of UES.

Part 3: Characterization of TFCH and U adsorbed TFCH (U@TFCH)

⊙ Timing: 4 days

- X-Ray Photoelectron Spectroscopic (XPS) Analysis.

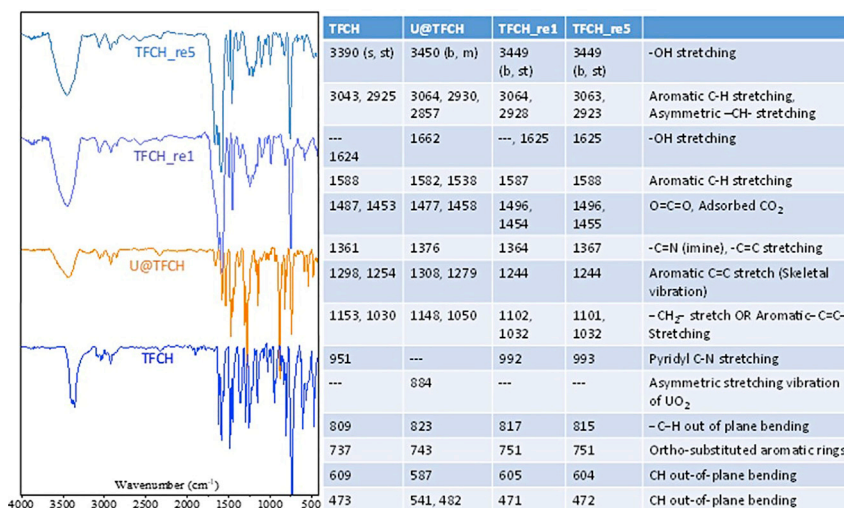


Figure 4. FTIR spectra and table for the changes in frequency before/ after adsorption of U, and after 1st/ 5th regeneration cycle in TFCH and U@TFCH

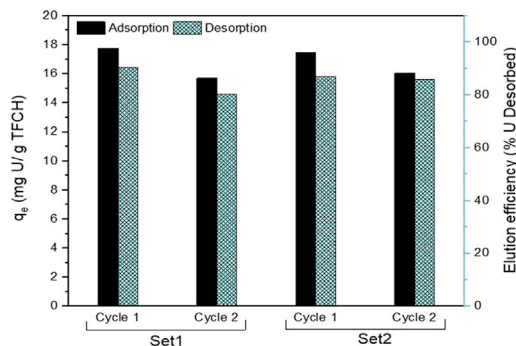


Figure 5. Recycling capability of TFCH in 2 different sets, adsorption of U from natural seawater (Cycle 1 in mg/g), followed by desorption (Cycle 1 in %), repeated the cycle for 2nd time with regenerated TFCH for adsorption-desorption (Cycle 2 adsorption in mg/g, and desorption in %)

This part describes XPS analysis, FTIR analysis of pristine TFCH and U adsorbed U@TFCH samples. SEM imaging and EDX analysis followed by elemental mapping using STEM and EDX are important characterizations that reveal the structural and morphological information.

- a. Perform the X-ray Photoelectron Spectroscopic (XPS) studies for defining the quantitative composition of TFCH and its bonding pattern.
 - b. Grow the TFCH with 30 mM/L ^{CSMCRI}HOF-1, in 24 h, at 25°C.
 - c. Place in 8 ppm U spiked seawater.
 - d. Filter after 60 min.
 - e. Wash with MQ water and analyze with high resolution XPS.
 - f. Deconvolute the U 4f7/2 and U 4f5/2 peaks in high resolution XPS spectra (U4f) of TFCH and U@TFCH into two non-stoichiometric peaks, on a Shirley background using XPSPEAK41 software.
 - g. Analyze the U4f7/2 and U4f5/2 peaks with respect to the satellite peak from XPS as depicted in Table 6 and report the results as shown in Figure 6.
21. Fourier –Transform Infrared Spectroscopic (FT-IR) Analysis of TFCH and U@TFCH.
 - a. Perform the Fourier-Transform Infrared Spectroscopic (FT-IR) analysis of TFCH and U@TFCH to study changes in the frequencies.
 - b. Grow the TFCH with 30 mM/L ^{CSMCRI}HOF-1, in 24 h, at 25°C.
 - c. Place in 8ppm U spiked seawater.
 - d. Filter after 60 min.
 - e. Wash with MQ water.
 - f. Analyze with FT-IR and report the result as shown in Figure 7.
 22. SEM and EDX mapping of elements in TFCH and U@TFCH.
 - a. Grow the TFCH with 30 mM/L ^{CSMCRI}HOF-1, in 24 h, at 25°C.
 - b. Prepare the samples by picking the crystalline TFCH from the air liquid interface at different time intervals onto silicon wafer and air dry, followed by thin layer gold coating for FESEM.
 - c. Perform the SEM imaging and EDX mapping of TFCH and U@TFCH and present the result as depicted in Figure 8.
 23. STEM and EDX mapping of elements in TFCH and U@TFCH.
 - a. Grow the TFCH with 30 mM/L ^{CSMCRI}HOF-1, in 24 h, at 25°C.
 - b. Perform the STEM imaging and EDX mapping of elements in TFCH and U@TFCH and report the result as shown in the Figure 9.

Table 6. XPS analysis for the U 4f 7/2 and 5/2 peaks with respect to the satellite peak

U 4f peaks	Main peak	4f peak separation	Satellite peak	Distance from satellite peak
U4f 7/2	382.73	10.83	386.15	3.42
U4f 5/2	393.56		396.64	3.08

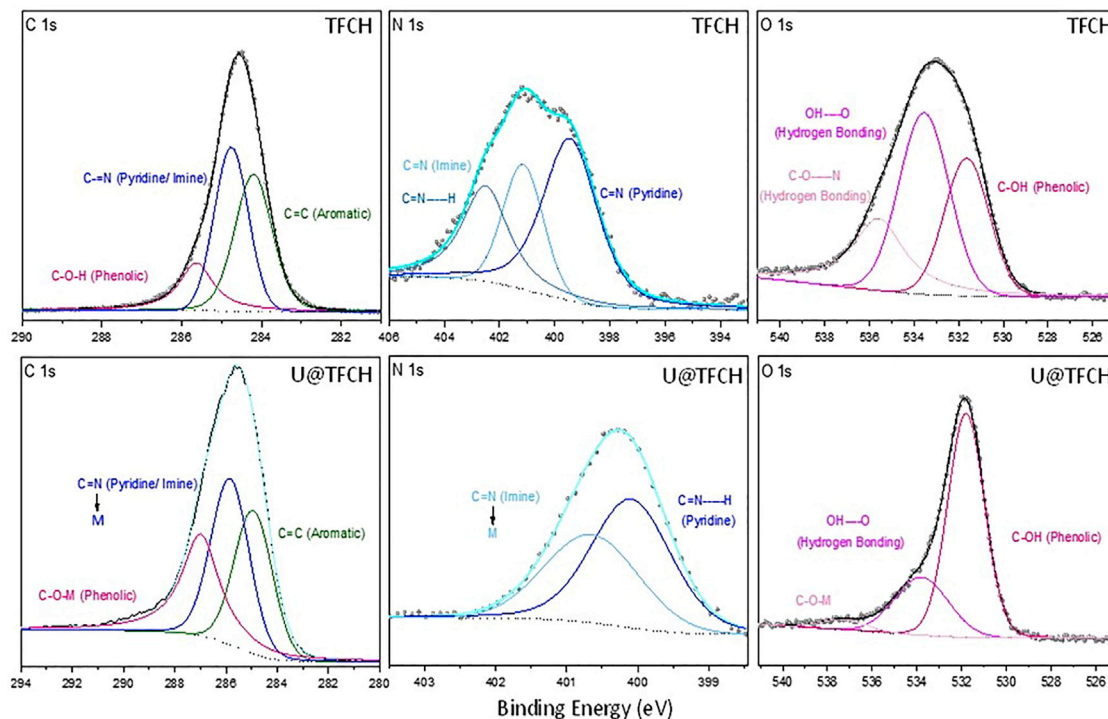


Figure 6. The high resolution C1s, N1s, O1s XPS spectra of TFCH and U@TFCH

Part 4: Computational details and binding site analysis

⊙ Timing: 20 to 25 days depending upon the geometry optimization/conversion

This part describes the computational methodology used for energy minimization and geometry optimization of the structures for probable U/TFCH interactions, using Density Functional Theory (DFT). Further the comparative study of TFCH binding sites with Oxime based ligands is performed to understand the feasibility of adsorption thermodynamics.

24. Computational Details.

Note: The DFT calculations follow a step-by-step instruction to perform the structure optimization calculations. Before going to optimize the structure, construct the geometry in the XYZ coordinate format or Z-matrix coordinate by using the Gauss View or Chem-Craft.

Note: The aim of geometry optimization is to find the configuration of minimum energy of the molecule.

Note: Following the completion of the wave function and energy calculations at the initial geometry, the technique continues on to the next step, which is the search for a new geometry with a lower energy.

Note: This process is performed numerous times until the geometry with the least amount of energy is discovered.

- a. DFT calculation set up: Perform DFT calculation by using the Gaussian 09 programs.²⁷

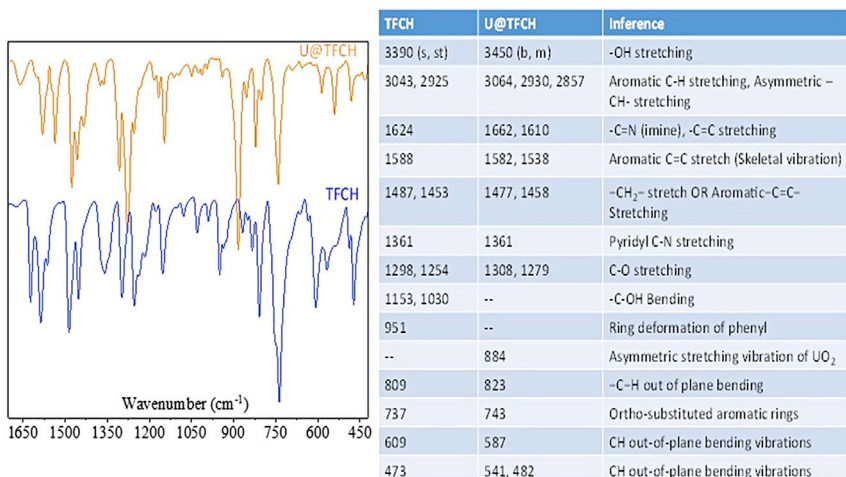


Figure 7. FTIR spectra and table for the changes in frequency before and after adsorption of U, in TFCH and U@TFCH

- Apply the generalized gradient approximation GGA functional which is composed of the Becke 1988 exchange functional and Perdew 86 correlational functional (GGA-BP86).^{28–30}
- A basis set known as split valance polarization (SVP) was utilized for the atoms that were not metals.
- Employed the Stuttgart/Dresden small core RECP (relativistic effective core potential) plus valence double- ζ -basis set (SDD) for Uranium (U) atom.³¹
- To validate that each stationary point is a local minimum, calculate frequency at the same level. Negative frequencies suggest molecular instability or potential energy surface geometry. Stable molecules contain no imaginary frequencies. Multiple imaginary frequencies indicate molecular geometry issues.

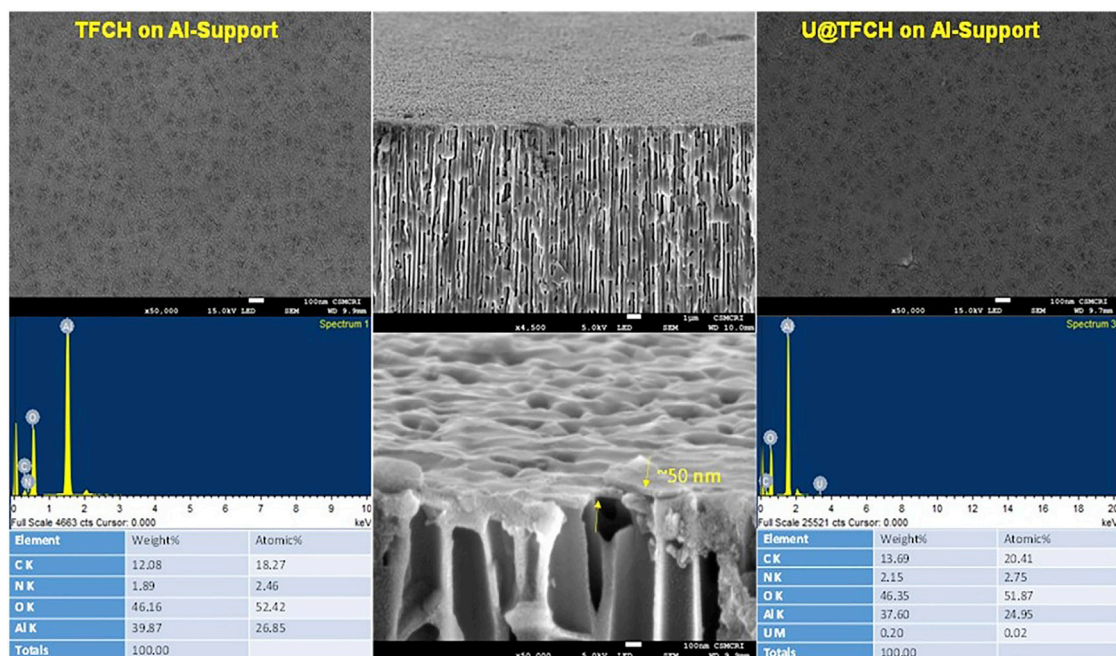


Figure 8. SEM and EDX mapping of elements in TFCH and U@TFCH (8 ppm U spiked MQ water)

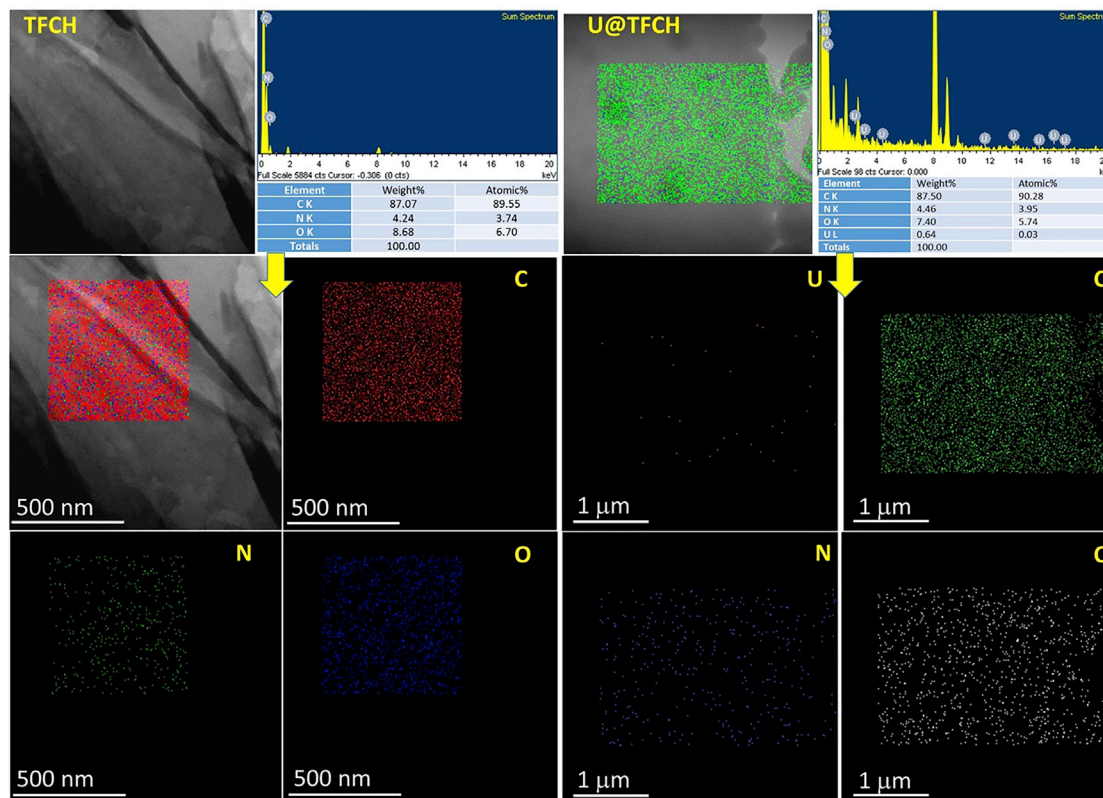
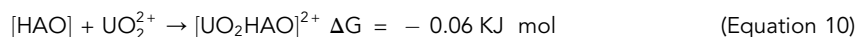
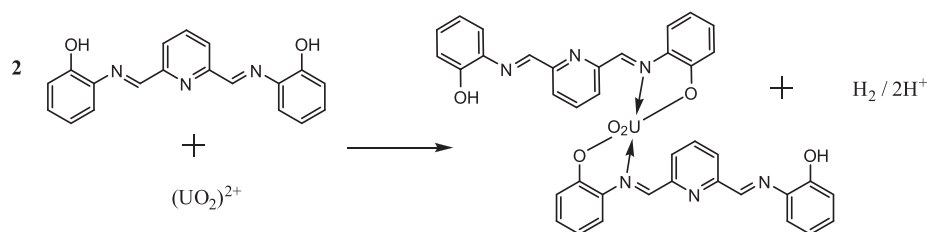
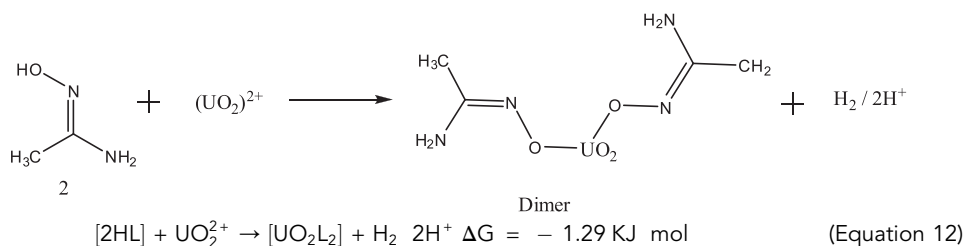
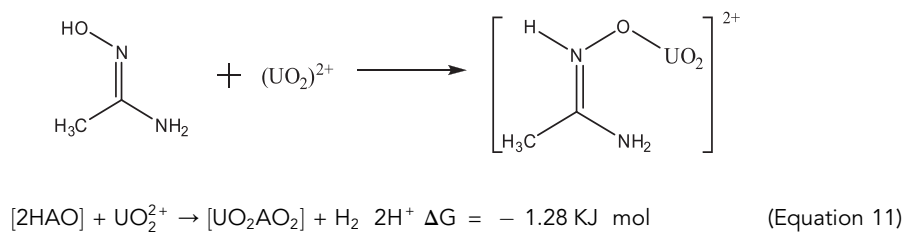


Figure 9. STEM and EDX mapping of elements in TFCH and U@TFCH (8 ppm U spiked seawater)

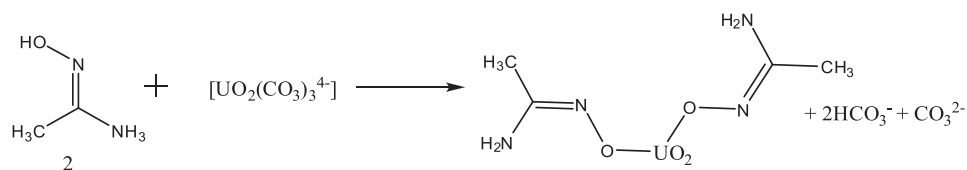
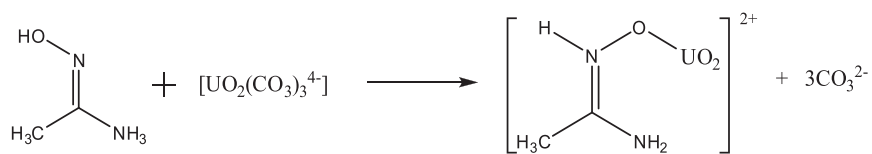
- f. To refine the computed energy, the single point calculations were performed, but with a larger basis set or a more accurate method than is possible with the basis set and method used to optimize the geometry. Herein, perform single-point calculations using M06 functional³² and extended Def2-TZVPP basis set.
 - g. Employ the self-consistent reaction field (SCRf) method with the SMD continuum solvation model for all structures.³³
 - h. Finally calculate the Gibbs free energies using the equation below.
 - i. $\Delta G = \Delta E + \Delta ZPE - T \Delta S$.
 - j. Where ΔE , ΔZPE and ΔS are the energy of reaction, the zero-point energy contribution, and entropy change, respectively.
25. Binding Site Analysis.
- a. Perform the thermodynamic feasibility analysis with the help of Density Functional Theory to draw the comparison of U binding with the Oxime ligands (HAO Equations 10 and 11) and at the molecular binding sites of TFCH (HL Equation 12).

Note: Here the formation energies must be negative in all the three assumptions, suggesting that the binding is thermodynamically feasible. As, in Equations 11 and 12 the free energy for binding U is almost equivalent ($[\text{UO}_2\text{AO}_2]$ -1.28 kJ/mol and $[\text{UO}_2\text{L}_2]$ -1.29 kJ/mol), further ascertaining the thermodynamic feasibility of U binding at the molecular binding sites.





26. Comparison of electronic parameters and thermodynamic feasibility of U coordination at the molecular binding sites of TFCH (HL) and AO.
- Calculate the formation energies for the binding of UO₂ with AO and HL, suggesting that the Uranyl coordination is feasible even with the presence of UO₂(CO₃)₃⁴⁻.
 - Follow the expressions used in the [Equations 13–15](#).
 - Define the electron distribution in HOMO-LUMO orbitals of AO and HL to define and establish their electronic properties.



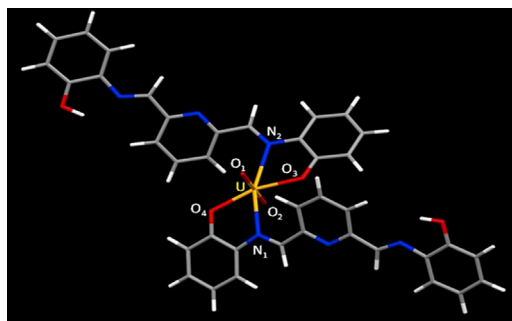
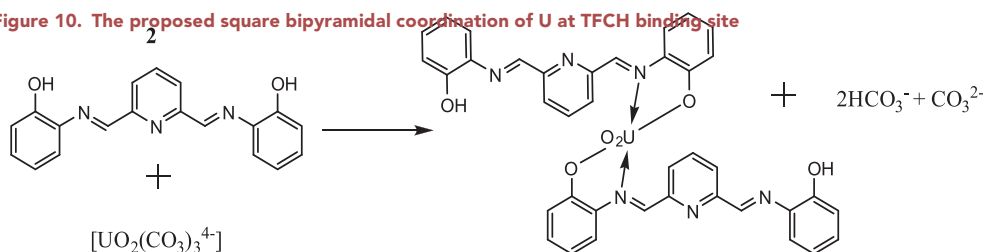


Figure 10. The proposed square bipyramidal coordination of U at TFCH binding site



27. U@TFCH binding analysis.

- a. Carry out this analysis to get the insight of the binding pocket in TFCH that it is comprised of two monoanionic bidentate [N: & O-] chelating sites from individual PMAP module.
- b. Each UO_2 must get coordinated to the TFCH binding site in a distorted square bipyramidal geometry (Figure 10), by forming covalent bonds with two O-TFCH and coordinate covalent bonds with NTFCH.

28. Uranyl Binding Analysis, Theoretical versus Experimental Binding Site Utilization.

- a. Based on the structural analysis after adsorption in and thermodynamic evaluation of uranyl binding using DFT calculations, suggested 2:1 binding as shown in the Figure 11.
- b. Calculate the theoretical maximum adsorption efficiency based on the U adsorption at probable binding site in TFCH.

EXPECTED OUTCOMES

This protocol demonstrates the application of thin film (TFCH) of hydrogen-bonded organic framework (^{CSMCR1}HOF-1) for effective and selective recovery of energy mineral uranium from seawater via adsorptive mechanism. The expected outcomes can be presented as follows.

Expected pH for optimum adsorption capacity

The optimum pH for uranium adsorption from spiked seawater using TFCH is found to be above pH 4 with maximum adsorption capacity achieved at pH 7 ($Q_e = 401 \pm 4.01$ mg/g, after 24 h). The freestanding TFCH exhibited an excellent uptake capacity (>55% U uptake) over a broad pH range pH 4 – pH 10 ($q_e \sim 354 \pm 3.89$ – 390 ± 3.94 mg/g), due to the reduced competition of H^+ ions and deprotonation of the binding sites OH_{TFCH} and N_{TFCH} on the adsorbent surface to attract and bind the uranyl ions efficiently. TFCH continued to exhibit equivalent capacity at pH ~ 8 ($Q_e = 393 \pm 1.97$ mg/g, after 24 h), indicating that use of TFCH is promising for U extraction from seawater.

Expected adsorption kinetics

The adsorption suggests speedy uptake of U attaining saturation within 20 min for 16 ppm spiked seawater ($q_e = \sim 777 \pm 38.8$ mg/g); and 45 min for 32 ppm spiked seawater ($q_e = \sim 1185 \pm 34.41$ mg/g).

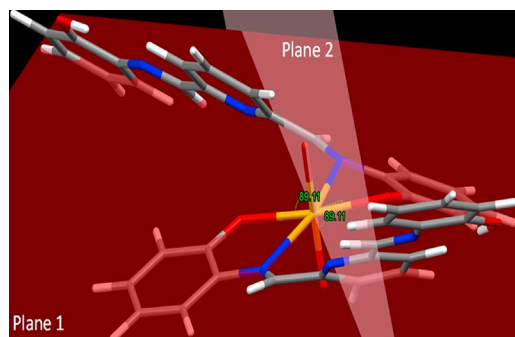


Figure 11. Uranyl adsorption at TFCH binding pocket in a square bipyramidal manner, Plane 1 (Red) defines the equatorial chelation and Plane 2 (Pink) has axial oxygen of uranyl

The experimental data were fitted to pseudo 1st order kinetics (PS1), and pseudo 2nd order (PS2) kinetics using the non-linear fitting using the Solver function in Microsoft Excel. The non-linear fitting of both models to the experimental data provided a satisfactory fitting with correlation coefficient $r^2 > 0.93$ (Table 4). The excellent fitting ($r^2 = 0.986$ for 16 ppm SSW; $r^2 = 0.989$ for 32 ppm SSW) and corroboration of the adsorption capacities with the PS1 kinetics is suggesting the rate of reaction is diffusion controlled. Although, the fitting to the PS2 kinetics provided underestimated values of the adsorption capacity ($q_e = 726.714$ mg/g for 16 ppm; and $q_e = 1137.075$ mg/g for 32 ppm) indicating the less availability of active binding sites. Whereas, fitting of PS2 kinetics towards equilibrium has improved and moving relatively closer to the true adsorption capacity indicating the involvement of valence forces to attain equilibrium.

Here, the adsorption of U onto TFCH is diffusion controlled and occurs in two steps, i.) dissociation reliant diffusion of uranyl ions through the TFCH channels and pores to maximize the availability of active binding sites, ii.) followed by the adsorption of U involving complexation, coordination and/or chelation to attain the equilibrium.

Expected adsorption isotherm

The rapid uptake during the initial range of U concentration from ~ 7 ppm to 30 ppm SSW showed a steady increase in adsorption capacity, getting saturated at 30 ppm indicating the saturation of available binding sites. The analysis of adsorption processes using two and three-parameter isotherm models showed better fitting to the spike seawater adsorption isotherms ($r_{LF}^2 > r_{RP}^2 > r_F^2 > r_L^2$) as compared to spiked milliQ water adsorption isotherms ($r_{LF}^2 \sim r_{RP}^2 \sim r_F^2 > r_L^2$). The Langmuir-Freundlich three-parameter model provided the best fit to the U adsorption isotherms, but overestimated the maximum adsorption capacities and evaluated value of $n < 0.8$ suggested adsorption of ~ 1 uranyl molecule per free adsorbent site. The Redlich-Peterson equilibrium constant $\beta \cong 1.0$ suggested the Langmuir type monolayer adsorption with a hybrid of homogeneous and heterogeneous adsorbent surface. The fitting parameters of Freundlich model indicates multilayer adsorption is feasible which could be due to the adsorption of other ions onto TFCH. The non-linear fitting to the Langmuir model provided better approximation of maximum adsorption capacities with moderate correlation coefficients. The fitting of Langmuir model supports our hypothesis, that uranyl molecules have diffused through TFCH and allowed monolayer adsorption on the finite number of identical sites of TFCH, this further ascertains the fitting of pseudo 1st order adsorption kinetics, showing the U adsorption onto TFCH is diffusion-controlled.

Expected U extraction from natural environmental seawater

Lab-Scale UES experiments using such a simplified set-up of flow through assembly in batch recirculation mode utilizing 1 cm² area TFCH onto a fabric support, with continuous pumping of natural seawater from the storage glass jar for a span of 30 days and studying the fitting parameters of pseudo 1st and pseudo 2nd order models indicates that this is a diffusion controlled physisorption process.

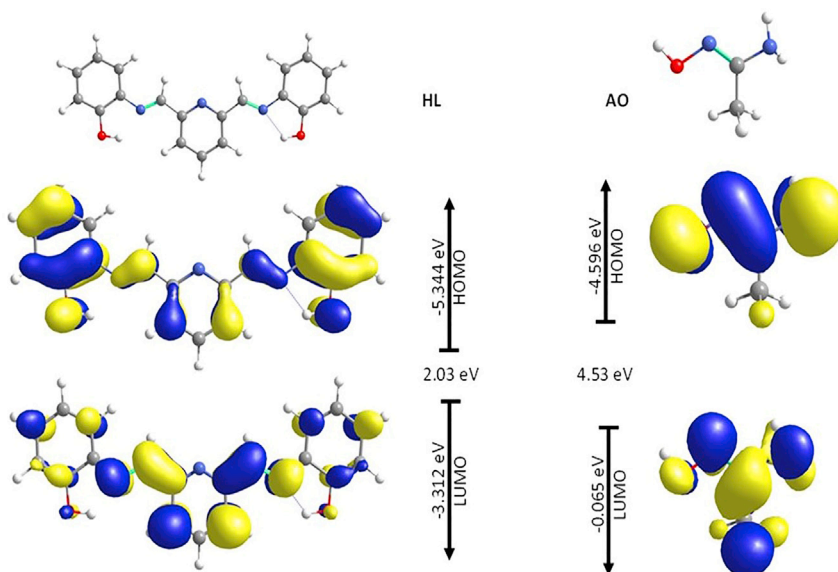


Figure 12. Electron distribution in HOMO-LUMO orbitals of AO and HL

Expected recovery and recyclability test

The recovery of U from dried U@TFCH was recovered using the reported 10 mL eluent mixture and analyzed using ICPMS. The spectroscopic characterizations were performed on regenerated TFCH for its recyclability. The FTIR, XPS and UV-Visible analysis confirmed the stability of TFCH up to 5 consecutive adsorption-desorption cycles from spiked seawater under batch mode. The recyclability of TFCH was further ascertained with two consecutive adsorption-desorption cycles with natural seawater. The TFCH is found to retain the 17.6 mg/g adsorption efficiency with 10% reduction in efficiency in ultimately fits close to the techno-economical extraction from seawater.

Expected quantitative composition and bonding pattern in TFCH

In context to the characterizations of the TFCH and U adsorbed TFCH, XPS analysis divulged the correct phenolic, imine, aromatic and U attached to TFCH peaks. FTIR – Spectra revealed that changes in frequency before and after adsorption of U took place, and –OH stretching shifted to $3,450\text{ cm}^{-1}$ from $3,390\text{ cm}^{-1}$ upon U binding. SEM image and EDX mapping of elements in TFCH and U@TFCH was in accordance with the expected result.

Expected binding pattern assisted by computational support

Density Functional Theory (DFT) was used to analyze the thermodynamic feasibility of TFCH binding sites and the contemporary Oxime ligands. Negative value of Gibb's free energy suggested a thermodynamically favorable and feasible event to occur (Figure 12). See Table 7 below, which prop up bonding pattern to play into computational support.

For TFCH, theoretical adsorption capacity was found to be 418 mg/g and experimental adsorption capacity as 393 mg/g, this indicates the 94% utilization of adsorption binding sites perfectly suiting for physicochemical adsorption phenomenon. We compared the theoretically calculated vs true experimental adsorption efficiency as reported as shown in Table 8.

LIMITATIONS

Handling of huge number of ICPMS samples, and the mechanical strength of the TFCH.

Table 7. U@TFCH binding analysis

Bond length (angstrom)		Bond angle (theta)		Torsion angle	
U-O ₁ (Axial U-O _{Ax})	1.80 (1.79)	O1-U-O2	175.11	N2-U-N1-C	-172.75
U-O ₂ (Axial U-O _{Ax})	1.80 (1.79)	O3-U-N1	131.77	N2-U-O4-C	170.30
U-O ₃ (Equatorial U-O _{Eq})	2.24 (2.28)	O3-U-O4	162.86	O3-U-O4-C	165.79
U-O ₄ (Equatorial U-O _{Eq})	2.23 (2.28)	O4-U-N2	131.77	O3-U-N1-C	-172.06
U-N1	2.431	N1-U-N2	161.52	NA	NA
U-N2	2.259	NA	NA	NA	NA

Values in Parenthesis in bold are obtained from ref.²³

Expected Practicality to Utilize TFCH as an Adsorbent for U Extraction.

TROUBLESHOOTING

Problem 1

Estimation of true adsorption efficiency at such low concentrations (Part 1).

The measurement of remaining concentration of metal ions from the spiked or un-spiked seawater using ICPMS is an indirect method to calculate the adsorption efficiency. ICPMS is highly sensitive technique but it requires careful analysis at various steps as mentioned in the method. One such problem is that seawater contains microbial biomass and that can grow further upon utilization of natural organic matter present in seawater. This biomass can grow and rapidly adsorb metal ions in the isolated samples of ICPMS, if left for a period of 2–3 days.

Potential solution

For every 10 mL sample isolated at predefined interval should be added with 100 μ L HNO₃ (1% nitric acid) to prevent the precipitation of metal ions by forming the poly-nuclear species, followed by filtration through the 0.2 micron nylon syringe filters to remove the microbial content. The acidic medium along with filtration inhibits any growth of biomass.

Problem 2

The preparation of metal salts spiked seawater (Part 1).

Usually seawater is at pH \sim 8.2, which allows the metal ion speciation into poly-nuclear species and precipitation. Hence, the calculated initial concentration differs from the actual initial concentration of metal ions.

Potential solution

The spiked seawater is prepared by adding the calculated amount of metal salts as per the initial concentrations and allowed to equilibrate overnight. After 24 h of equilibration, the precipitated salts were removed by filtration. The concentration of metal ions in the filtrate was determined using ICP-MS. This measured concentration, which is of course less than the actual spiked concentration is considered the initial concentration of spiked seawater.

Problem 3

Cross-verification of metal ion concentration and adsorption efficiency (Part 1).

Potential solution

The residual concentration of uranium was measured using the argon dilution method (AGD-KED mode) on sophisticated inductively coupled plasma mass spectrometer (ICP-MS) by direct method and indirect method as well. The indirect method involves the back calculation from remaining concentration, measured as such without any enrichment procedure, while the direct method involves acid digestion of U adsorbed sample.

Table 8. Uranyl binding analysis, theoretical versus experimental binding site

Sr. No.	Material	Source of U	Theoretical adsorption capacity	Experimental adsorption capacity	Utilization of adsorption sites	Method of UES	Reference
1.	TFCH	8 ppm spiked seawater	418 mg/g	393 mg/g	94%	Physicochemical adsorption	This work
2.	MISS-PAF-1		253 mg/g	82 mg/g	32.4%		25
3.	PPA@MISSPAF-1		208 mg/g	49 mg/g	23.4%		25
4.	TFCH	Natural Seawater	418 mg/g	17.9 mg/g (30 days)	4.2%		This work
5.	MISS-PAF-1		253 mg/g	6.4 mg/g (56 days)	2.3%		26
6.	PPA@MISSPAF-1		208 mg/g	13.5 mg/g (56 days)	6.4%	Electrochemically assisted adsorption	25

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Ashish Maurya (ashish.csmcri22j@acsir.res.in).

Materials availability

All materials generated in this study are available from the [lead contact](#) without restriction.

Data and code availability

This study did not generate any datasets.

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AUTHOR CONTRIBUTIONS

A.M., methodology, drafting protocol; K.M., P.D., reviewing, editing; N.C., performing the ICPMS analysis, optimizing, drafting the AGD-KED method; M.M. for drafting the computational analysis section; K.P., S.K., investigation, supervision.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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