

Surface-engineered naturally-derived xerogel for boosting chelation of refractory contaminants: From low-temperature hydrochar strategies, characterization probes to underlying mechanisms

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Abstract

Conventional filtration results in secondary pollution due to poor degradability and disposal challenges. We established a protocol for synthesizing a metal-free Xerogel Infiltration Matrix (XIM) from banana via low-temperature HTC reactions via soft control of carbon-rich hydrochar. To address sustainability gaps, main signature of synthesis was the use of natural precursors and solvents unlike chemically driven high temperatures routes. XIM dominated by turbostratic configuration and intense C1s and O1s XPS signals pointed oxygenated organic hybrid surfaces. Structurally, matrix contained a condensed carbonaceous core with a moderate fraction of thermally labile species facilitating relaxation, secondary crystallization, and reactive transitions. Raman primary peaks identified D (disorder-induced) and G band (graphitic configuration), while carbon-iodine showed additional features that were absent in pristine or carbon-chromium spectral signatures. XIM deployment circumvented prerequisites of inert environments, decarbonated water, or pH regulations. Chelation was rate-regulated by chemisorption and intraparticle diffusion, while energetics confirmed spontaneous, endothermic, and entropy-driven process across moderate to high temperatures. Contaminant chelating models demonstrated that surface engineering could achieve significant sequestration. In comparison to widely used commercial activated carbon, XIM demonstrated superior functional performance in the treatment of contaminated waters containing carcinogenic chromium and in capture g iodine from amphiphilic (polar and non-polar) environments. Xerogel maintained efficacy across ionic strengths, pH levels, and co-occurring metal interferences. Synergistic enhancement observed with Fe^{3+} ; conversely, inhibition variability detected in presence of Cu^{2+} , Pb^{2+} , Ag^{+} and As^{5+} . Xerogel exhibited stability, supported by leaching test and aging deployments. Information provided will improve underlying local mechanisms on naturally-derived xerogel that optimizes both separation effectiveness and degradability.

Keywords: Xerogel, Low-temperature HTC, Contaminants, Raman spectra

1. Introduction

Chromium-dependent sectors must navigate the critical dichotomy between sustaining economic viability and mitigating profound biological and environmental stressors [1]. Hexavalent chromium, a primary vector in drinking water contamination has been linked to the emergence of ‘cancer villages’ in specific region of China [2]. Tremendous applications lead to their discharge deliberately or accidentally into the environment [3]. Intriguingly, chromium has been categorized from essential trace element to a recalcitrant toxin [4]. Trivalent species are considered non-toxic and have a crucial role as a trace element in metabolism of insulin, glucose, and lipid [5, 6]. Conversely, hexavalent chromium is harmful with carcinogenic characteristics, which penetrates skin and mucous membrane, leading to mutagenic effects on lungs, kidneys, and gastrointestinal tract [7-10]. A higher-order of water solubility of hexavalent chromium compared to trivalent forms triggers their increased bioavailability and a spike in the pollution burden, resulting in adverse effects on environment and human health [5, 11]. Nevertheless, drinking water guidelines for safe level of chromium have discrepancies over ‘total chromium’, ‘trivalent chromium’ and ‘hexavalent chromium’[12]. Maximum permissible limit of total chromium is 50 µg per litre by World Health Organization (WHO) [13] and is 100 µg per litre by the US Environmental Protection Agency (USEPA), not specifically for more toxic hexavalent chromium [14, 15]. An understanding of each species rather than overall chromium concentration is essential for accurately assessing the toxicological impacts. Conventional approaches to remove and recover chromium from environmental matrices are precipitation [16], electrochemical precipitation [17], ion exchange [18], reduction [19-21], membrane filtration [22], reverse osmosis [23], ultrafiltration [24] and ion exchange [25]. Majority of approaches fall short of the criteria set by the United Nations Sustainable Development Goals, particularly Goal 6 (Clean Water and Sanitation), Goal 7 (Affordable and Clean Energy), and Goal 9 (Industry, Innovation and Infrastructure). They are characterized by prohibitive costs, energy-intensive operations, and secondary pollution risks, moreover, they generate significant wastewater and prove ineffective when treating low-concentration contaminants [26-28].

Another contaminant of interest, iodine mainly occurs in molecular (I_2), iodide (I^-) and iodate (IO_3^-) forms, depending on pH and redox waters. Iodine is moderately to highly soluble species impacting their mobilization in water. Iodine can be a toxic radionuclide and persists in environment, their release, mainly ^{129}I and ^{131}I [29, 30] occur during nuclear fuel reprocessing. As an example, the Fukushima disaster (Japan, 2011) released radioiodine that spread through watercourses beyond geographical boundaries. Thus, wide occurrence, high volatility, and chronic exposure can impact adverse effects on human health [31, 32]. Chlorine, hydrogen peroxide, and ozone serve as water disinfectants and sanitizers that eliminate harmful microorganisms; notably, iodide anions are oxidized by these strong oxidants, resulting in toxic iodinated disinfection byproducts (I-DBPs) compared to chlorinated and brominated DBPs [33-35]. This highlights the overlooked potential of DBPs, which subsequently releases iodine into water. Thus far, derivation of iodine guideline on basis of information on its effects is inappropriate. Australia has established a drinking water guideline for iodide at 500 $\mu g/L$, whereas Canada utilizes a contaminant limit (screening value) of 240 $\mu g/L$ [36, 37]. The USEPA, WHO, and EU lack definitive regulatory standards for iodide. These regulatory disparities are likely attributable to daily dietary intake, tolerable daily intake, and adult consumption rates. Based on available data and Recommended Dietary Allowances (RDA), remediation should be considered for groundwater iodine concentrations at $>300 \mu g/L$ [32, 38]. Activated carbon [39], metal-organic framework, covalent organic framework [40, 41], and aerogel [42] have been considered for iodine uptake, either in solid or liquid form. However, concerns of chemical techniques are at risk of further contamination by addition of chemical agents.

In this context, bioprivileged materials represent a strategic complement to established methodologies. The rational design of natural scavengers through surface engineering addresses a longstanding demand for systems that balance efficient filtration alongside necessary degradability. Characterized by operational simplicity, physicochemical stability, and the elimination of hazardous solvents, these natural precursors provide superior, sustainable alternatives aligned with circular economy frameworks [43, 44]. Investigations into environmental dimension, naturally-derived xerogels for pollutant removal started with synthesis of silica xerogel from bagasse ash [45]. A xerogel is a solid structure derived from a hydrogel—a 3-D network of hydrophilic polymer chains dispersed in water. The synthesis involves the transition from a viscoelastic gel to a solid state via evaporative or convective drying at ambient

temperatures [46]. This process removes the liquid phase while maintaining the underlying network architecture. A critical challenge in xerogel synthesis is the significant, irreversible shrinkage of the gel network as solvent evaporates. The unavoidable contractions induce stress, leading to formation of cracks and fractures within material matrix. Consequently, to preserve structural integrity of xerogel, a slow and controlled drying protocol is implemented to mitigate these stresses [47, 48], thereby preserving the structural fidelity of the hydrogel precursor as much as possible.

Xerogels represent a burgeoning class of materials due to a combination of advantageous properties that distinguish them from hydrogel and aerogel. Compared to aerogel, xerogel typically possesses a higher skeletal density and enhanced mechanical robustness, coupled with streamlined synthetic pathway [49]. Xerogel characteristics are affected by precursor chemistry, solvent-mediated drying dynamics, and specific liquid-vapor interface [50]. The removal of solvent under ambient conditions creates an interconnected network with tunable characteristics, rendering these materials highly effective for the sequestration of fluid-phase contaminants via physisorption, chemisorption, or a combination of these mechanisms. Furthermore, xerogels exhibit superior mechanical stability compared to aerogels; the inherent fragility and friability of the latter frequently preclude their application in aqueous environments with extreme pH environments or high-flow gas streams. For such demanding environments, an alternative additional approach involves, such as embedding active sorbent material within a more robust, passive matrix [51]. Moreover, a significant constraint in production of aerogel is the requirement of critical point drying and supercritical fluids [52], a step that often involves complex and costly procedures. These requirements can be circumvented in xerogel production through low-temperature hydrothermal reactions followed by drying under ambient conditions (this study). Xerogels are emerging research domain for environmental applications, though they are still in their infancy. These matrices present a sustainable alternative to aerogel or hydrogel that are often derived from tedious routes, chemical-based precursors or those containing metals. In this work, modification on banana (genus *Musa*) demonstrated a promising surface engineered infiltration matrix. Controlled hydrothermal reaction conditions yielded a pristine carbon-rich hydrochar and self-organized hierarchical microstructure developed into a tunable green xerogel. Efficiency and outcome of hydrothermal carbonization (HTC), a thermochemical process that converts wet biomass into carbonaceous product, are tuned by controllable parameters, primarily

reaction medium, residence time, and temperature [53, 54]. This offers a distinct advantage over traditional high-temperature carbonization and pyrolysis. Utilizing water as benign and an inexpensive universal solvent, HTC operates under moderate temperatures, typically within the range of 150-250°C. In contrast, conventional pyrolysis and carbonization techniques occur at substantially higher temperatures, often exceeding >300°C, and require an energy-intensive pre-drying of feedstocks [55, 56]. At elevated hydrothermal temperatures, the removal of organic linkers further modulates morphology and properties of resulting xerogel. Fundamental HTC mechanism involves a series of reactions, including hydrolysis, dehydration, decarboxylation, and aromatization, which progressively increase carbon contents of the organic framework. Residence time, referring to the duration the biomass is held at desired temperature, impacts on the degree of carbonization and the properties of resulting organic gel. In such hydrothermal system, HTC products require three main modulators: a source of hydrothermal energy, the presence of water, and the permeability of the precursor. Superheated water and steam become entrapped in the fractured network of matrix tissue that is initially impermeable. This procedure promotes circulation of hydrothermal fluids and interaction with organic precursors, aiding in the formation of carbon-rich deposits.

To test our findings, we demonstrated this research to (1) synthesize Xerogel Infiltration Matrix from banana via carbon-rich hydrochar; (2) investigate sequestration at interface demonstrating interaction forces between xerogel layers and specific contaminants, namely Cr(VI) and iodine; (3) determine impact of water quality under natural and environmentally relevant conditions and compared against commercial purification material; (4) elucidate underlying mechanisms and physicochemical characteristics, i.e. the local environment profile. Intriguingly, the new green chemicals rely solely on plentiful supply of edible fruits that are widely consumed around the world, thus achieving a balance between technological innovation and environmental safety. Synthesis of work broadens the mechanistic knowledge on tailoring of natural xerogels and highlights green scavengers of contaminants with multiple benefits.

2. Materials and methods

Descriptions of the procedures including materials used, experiments, and data analyses are provided in the *Supporting Information (SI), sections S1-S3*.

2.1 Spectroscopy, imaging, and analysis techniques

Surface morphologies were examined using a Field Emission Scanning Electron Microscope (FESEM, JEOL, JSM-7900F) at 5 -20 kV accelerating voltage. Before imaging, powder samples were platinum-coated (30 s) while being mounted onto a carbon tape on an aluminium stub using a standard sputtering technique. In JFC2300HR coating unit, a multi-angle planetary-rotation stage exposed the sample surfaces during the coating cycle. Coating uniformity during the deposition process was done under argon gas pressure. A coupled energy-dispersive X-ray (EDX) established the compositional details of target material. For transmission electron microscopy (TEM) imaging (Hitachi High-Tech HT7700), a droplet of diluted XIM sample was mounted on carbon-coated copper grid and the sample was dried at room temperature to visualize surface morphology and structure of material. Powder X-ray diffraction (PXRD) diagrams of crystalline structures were obtained with a D8 Discover Bruker Diffraction System, using nickel-filtered Cu-K α radiation ($\lambda = 0.15418$ nm) operated at 40 mA and 40 kV, with a scan speed of 3°/min having set the 2 θ angle 5° to 80°. State of topmost layers of xerogel was characterized using X-ray photoelectron spectroscopy (XPS) (Thermo Fisher, USA). Spectra of surface functional groups were obtained using a Fourier transform infrared (FTIR) spectrometer, VERTEX 70 FTIR (Bruker optik GmbH), with a resolution of 4 cm⁻¹ and accumulation of 32 scans between 4000 to 400 cm⁻¹ on ATR mode. In electrokinetic measurements, electrical charge of material particles in water were analysed by ζ -potential, recorded using a zeta-potential analyzer (Malvern Zetasizer nano series, Nano-ZS). Differential scanning calorimetry and thermogravimetric analysis (DSC/TGA) (Q200 instrument, TA Instruments) were performed to detect thermal changes and stability of samples.

A Raman spectrometer (Thermo Scientific DXR3xi Raman Imaging Microscope) utilized to examine molecular structure by illuminating with a DXR 532 nm laser on the sample. Spectra obtained using the OMNICxi Raman Imaging Software for analysis and acquisition. A tiny quantity of powder sample was positioned on the microscope slide. Microscope was set-up for reflected light bright field (BF) illumination. Laser power (ranged from 1-3 mW), exposure duration (ranged from 0.2-2 sec), number of scans (100) and aperture (50 micron slit) parameters modified to obtain the spectral quality of xerogel. Maximum laser power option was utilized that did not burn the sample and reducing exposure time settings could enhance the spectral quality. Multiple scans were averaged. A confocal pinhole slit of 50 micron enabled the highest Raman energy to reach the detector.

2.2 Synthesis of xerogel (XIM)

Core strategy underlying the xerogel synthesis is schematically described in **Figure 1**. Ripe banana (*Musa* sp.) pulp was utilized as a natural precursor without the use of chemical additives. Fresh fruit samples were procured from local markets in Patna, India, during the summer season (April–May) and transported to the laboratory in sealed plastic bags within 2 hours. For each sample, pristine soft pulp (flesh) was separated from peel and cut into equidimensional cylindrical sections (height = diameter = 2.0 cm; 16.8 g). For the hydrothermal synthesis, the prepared pulp was submerged in 25 mL of ultrapure water (resistivity 18.2 M Ω ·cm) and sealed within a hydrothermal synthesis reactor (100 mL capacity (screw sealing) equipped with outer stainless steel jacket and inner Teflon liner/chamber). The reactor was then kept in a muffle furnace at 175°C for 8 hours, followed by natural cooling to room temperature. Supernatant liquid was decanted, and the resulting solid monolith was washed thoroughly with ultrapure water to remove surface impurities. Soft control over hydrothermal carbonization (HTC) reaction, medium, residence time and temperature regulated the reaction equilibrium between heterogeneous phases to yield an organic hydrochar with a self-organized hierarchical microstructure. Following the reaction, the crude carbonaceous hydrochar was dried in a hot air oven at 45°C for 24 hours until a constant mass was achieved. The final product, labeled XIM (0.69 g), corresponded to a mass reduction of approximately 96% attributed to the elimination of hydrothermal fluids (volatiles and moisture) via low temperature HTC (<200°C) coupled with controlled drying. XIM stored in an amber bottle to ensure stability and product quality at room temperature.

3. Results and discussion

Representing a shift toward cleaner production, green chemical serves as a sustainable alternative to conventional methods, engineered to optimize contaminant removal while maintaining stability within liquid matrices. Tuning banana into XIM to control chromium and iodine addresses the critical challenge of combining filtration effectiveness with natural degradability. XIM outperforms commercialized standard activated carbon. Performance metrics, supported by robust physicochemical characterization probes combined with mechanistic analysis, underscore the ability of xerogel for sustainable water treatment.

3.1 Underlying mechanism and characterizing tools

3.1.1 TEM and SEM-EDX investigation

Electron microscopic investigations showed a surface modification of unique growth pattern of the spherofibrillar network formation that self-assembled into a spherical or sphere-like morphology, as in **Figure 2(a-d)**. Material exhibited mechanical properties relative to their load-bearing capacity (strength-to-weight ratio). XIM achieved strength through interlocked fibers, intricate cellular structures, and domain structure distributed stress of fibers balancing minimal weight with significant load support. As illustrated in **Figure 1(a-viii)**, XIM was also light enough to rest on delicate flower petals (like Bougainvillea and Lily). EDX and elemental mapping verified presence of chromium (~0.2 wt%) and iodine (~39 wt%) when compared to pristine material, as in **Figure 2(e)**. Carbon peak appeared at an energy level of around 0.3 keV and oxygen peak appeared at an energy level around 0.5 keV. Presence of oxygen indicated C-O, C-OH, >C=O containing groups (see subsequent sections). Among major peaks, C (44 wt%) and O (33 wt%) observed relatively high peaks, indicating their significant presence in XIM.

3.1.2 Raman peaks analysis

The image shows overlaid Raman spectra for three XIM samples: pristine carbon (*red labeled*), carbon loaded with chromium (*blue labeled*), and carbon loaded with iodine (*black labeled*), as shown in **Figure 3(a)**. Each spectrum exhibited characteristic D and G bands of carbon with notable changes in intensity and additional features after metal/halogen incorporation. Pristine carbon spectrum displayed two prominent peaks in 1000–2000 cm^{-1} region. First intense band near $\sim 1350 \text{ cm}^{-1}$ corresponded to D band, associated with disordered or defect-rich carbon domains. Second peak around $\sim 1580\text{--}1600 \text{ cm}^{-1}$ was G band, arising from the in-plane stretching vibration of sp^2 -bonded carbon in graphitic structures. The relative intensities and sharpness of these two peaks suggested a partially ordered carbon framework with a measurable degree of structural disorder. For carbon-chromium spectrum, Raman profile retained the characteristic D and G bands of carbon but with clear modifications in intensity and background. D band near $\sim 1350 \text{ cm}^{-1}$ became more intense and broader compared with pristine carbon, indicating an increase in structural disorder (defect density) in carbon matrix after chromium incorporation. G band around $\sim 1580\text{--}1600 \text{ cm}^{-1}$ also showed enhanced intensity and slight broadening, reflecting changes in the graphitic domains and possible charge-transfer interactions between chromium species and carbon framework. The overall elevated baseline and higher signal over the 600–3200 cm^{-1} range implied stronger light–matter interaction and additional vibrational

contributions from Cr–O or Cr–C coordination environments superimposed on carbon background, even though distinct sharp chromium specific Raman modes were not individually resolved at this scale. Carbon-iodine spectrum differed markedly, with lower absolute intensity and several additional narrow peaks at lower wavenumbers. Carbon D and G bands were still visible near $\sim 1350\text{ cm}^{-1}$ (D) and $\sim 1580\text{--}1600\text{ cm}^{-1}$ (G), but they appeared broader and less intense relative to background, suggesting modification of sp^2 domains and increased structural heterogeneity upon iodine loading. Multiple sharp peaks observed below 800 cm^{-1} ; these low frequency bands could be attributed to iodine-related vibrations (I–I stretching or C–I modes) and interaction with carbon lattice, indicating load of iodine species on XIM carbon surface. Combination of broadened carbon bands and superimposed iodine-associated modes possibly pointed to formation of charge-transfer complex and iodine chemisorption on carbon matrix.

3.1.3 FTIR analysis

FTIR analysis (comparison before and after chromium and iodine uptake) is illustrated in *SI, Figure S1*. A broad and strong stretching of –OH bands occurred between $3250\text{ and }3100\text{ cm}^{-1}$. The $1280\text{--}990\text{ cm}^{-1}$ segment was due to contributions from C–O and C–C vibrational stretches, and C–O stretching of the alcohol bands appeared at $1050\text{--}1010\text{ cm}^{-1}$ in native and chromium and iodine-loaded scans. A strong intense band centered at $\sim 1190\text{ cm}^{-1}$ could be C–O stretch of ether/alcohol group, C–N stretching in the overlapped peak regions ($1000\text{--}1350\text{ cm}^{-1}$) and strong band at $\sim 1660\text{--}1600\text{ cm}^{-1}$ could be assigned to carbonyl $>\text{C}=\text{O}$ stretch in sample scans. Presumably, oxygen containing functional groups from XIM stabilized the contaminants and kept their homogeneity intact. FTIR data after uptake of chromium or iodine showed no significant changes in vibrational frequencies, except for a slight shift in functional group peaks. Chromium and iodine may have had a relatively minor effect at the studied concentrations compared to presence of other groups within XIM, as indicated by spectra.

3.1.4 Powder X-ray diffractogram

The image represents a PXRD pattern of XIM, plotted as intensity vs. diffraction angle 2θ (degrees) in range of 5° to 80° (**Figure 3b**). The pattern indicated a predominantly amorphous or poorly crystalline material with a broad diffraction feature rather than sharp Bragg peaks. Diffractogram showed a steep rise in intensity at low angles, followed by a broad maximum centered near $23\text{--}26^\circ 2\theta$ and then a gradual monotonic decay in intensity toward higher angles. The most significant feature was a wide hump, peaking at $24\text{--}26^\circ 2\theta$, where intensity reached its

maximum. This broad peak was characteristic of short-range order, typical of amorphous phase or highly disordered (nano)structured material, such as an amorphous carbon, rather than well-resolved reflections from a crystalline lattice. Beyond about 30° 2θ , intensity decreased smoothly at 80° 2θ with no distinct sharp peaks superimposed. Absence of narrow, high-intensity Bragg reflections over 30 – 80° range further supported the interpretation that sample XIM lacked long-range crystalline order and was dominated by an amorphous structural arrangement. In combination with imaging data and spectroscopic analysis, XIM turbostratic carbon layers showed internal bonding and in-between fibre structures that stacked randomly without a fixed, ordered pattern, unlike perfect graphite where layers align neatly.

3.1.5 XPS data

The image presents a wide scan (survey) XPS spectrum coupled with XRD (**Figure 3b**). Spectrum revealed surface composition and distinct photoelectron peaks superimposed on a relatively low background, characteristic of a clean surface with well-defined elemental signals. Three intense peaks dominated the spectrum - C1s, O1s, and N1s. The C1s peak appeared at a binding energy around 285 eV and exhibited high intensity, indicating that carbon was a major surface constituent, typically associated with graphitic, C–C/C–H, or functionalized carbon species. The O1s peak occurred at 530–535 eV with the highest intensity in spectrum, implying oxygen-containing functionalities, or metal-oxygen bonds on surfaces. The N1s peak was located near 400 eV with moderate intensity, signifying incorporation of nitrogen species in material from natural precursors in forms of small nitrogen environments depending on higher resolution scans. A smaller peak labeled Na1s was observed in higher binding energy region around 1070–1085 eV. This peak was likely arising from residual salts, exchangeable cations, or sodium-containing functional groups introduced inherently. However, combination of strong C1s and O1s signals indicated a carbonaceous or organic hybrid surface enriched with oxygenated functionalities.

3.1.6 TG–DTG analysis

As illustrated in **Figure 4(a)**, at the beginning of run, sample mass was normalized to 100%, and TG curve (*green labeled*) remained almost horizontal up to 60–65 min, indicating negligible mass loss and high thermal stability in this initial region. A minor early mass change of 1–2% marked near 5–10 min, which could be attributed to desorption of surface moisture or very weakly bound species. Beyond 65–70 min, TG curve showed a pronounced downward slope,

corresponding to a major decomposition event with mass change of 31-32%, after which the curve stabilized at a residual mass of 68-70% at the end of run. DTG curve (*black labeled*) oscillated around zero in early part of experiment, confirming that no significant decomposition occurred during initial isothermal or low-temperature period. A broad, sharp negative DTG peak appeared between 75 and 90 min, reaching a minimum rate near $-3\% \cdot \text{min}^{-1}$, which reflected main degradation step responsible for large mass loss observed in TG curve. A smaller DTG feature toward the end of time-scale suggested a minor secondary process, possibly slow oxidation or further structural rearrangement of the remaining char or inorganic residue. Overall, combined TG-DTG data indicated that material is thermally stable up to a threshold time (or corresponding temperature) where a major decomposition step occurred, removing one-third of initial mass and leaving a substantial thermally stable residue. Small initial mass loss and large final residue fraction implied that sample likely contained a significant condensed carbonaceous component, with only a moderate proportion of thermally labile organic or volatile species.

3.1.7 DSC data

DSC thermogram of material matrix showed heat flow (DSC, in mW) as a function of temperature ($^{\circ}\text{C}$), as in **Figure 4(b)**. Immediately after run started, curve stood sharply and then formed a broad exothermic complex peak with a maximum near $40\text{--}50^{\circ}\text{C}$. This low temperature complex peak typically corresponded to release of (ad)sorbed species, relaxation of physically bound water, and low temperature structural rearrangement (rather than true melting), because exothermic features in this range indicated ordering or curing phenomena. After this event, baseline returned close to a nearly constant level, indicating that material was thermally stable with no major enthalpic transitions up to $150\text{--}160^{\circ}\text{C}$. Around $180\text{--}200^{\circ}\text{C}$, a smaller complex event marked on curve, visible as a slight downward deflection from baseline. Such subtle exothermic features in this temperature interval were associated with secondary crystallization, further crosslinking, or stepwise condensation reactions within material matrix. A further complex peak was annotated at $220\text{--}230^{\circ}\text{C}$, again exothermic, indicating a distinct kinetic process such as additional curing, ordering of remaining amorphous domains, or reaction of residual functional groups. Relatively small peak height suggested a modest enthalpy change compared with low temperature complex event. From about 300°C up to nearly $500\text{--}550^{\circ}\text{C}$, DSC trace remained close to a flat baseline with only minor fluctuations. No large enthalpy phase transitions such as melting or glass transition with high heat capacity change occurred in

this regime. Beyond 500°C, signal gradually drifted upward and became more irregular, which was consistent with onset of slow exothermic decomposition, oxidation, or structural rearrangement of remaining material, processes that typically produced broad, poorly defined DSC features rather than sharp peaks. These data allowed multiple thermal events of material such as relaxation, secondary crystallization, and reaction processes.

3.2. Investigations on water chemistry conditions

pH modulators and zeta potential

The pH modulators alter microenvironments, significantly affecting chemical reactions and material surfaces. So, aqueous matrix pH is a critical parameter governing both the physicochemical surface properties and the ionic speciation of target contaminants [57]. Uptake of Cr(VI) was evaluated across a pH range of 2.1-9.8(± 0.2) at 298K. As illustrated in **Figure 5a**, surface behavior of XIM is pH-dependent. Without adjusting solution pH, the maximum uptake of oxyanions reached 90% at pH 5.6 in comparison to a higher acidic or basic end values. Both XIM and the popular purification material - Powdered Activated Carbon (PAC), exhibited maximum uptake in acidic pH range. While uptake capacity declined for both materials as conditions became more alkaline, xerogel consistently demonstrated superior removal efficiency compared to PAC throughout experiments. Notably, initial pH values (2.1–9.8) resulted in a narrower range of final pH (3.2–5.8), suggesting buffering stabilization by material matrices (*SI, Figure S2*). As illustrated in chromium speciation diagram (*SI, Figure S3*), speciation primarily yields HCrO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, and HCr_2O_7^- in aqueous solutions and is determined by pH and metal concentration. HCrO_4^- predominates under acidic conditions at low concentrations, whereas CrO_4^{2-} is the dominant species at pH levels >7 [58]. So, enhanced sequestration from solutions was attributed to the high concentration of protons (H^+), which protonated surface functional groups; this facilitated uptake of chromium oxyanionic species via abundant hydroxyl and oxygen-containing moieties. In contrast, under alkaline conditions, high concentration of hydroxyl ions (OH^-) could compete with CrO_4^{2-} species for active surface sites, thereby inhibiting adsorption. Additionally, surface charge depends on solution pH and its point of zero charge (pH_{PZC}), which is the pH value at which the net surface charge is zero. As illustrated in **Figure 5(b)**, electrokinetic analysis of ζ -potential revealed distinct surface behaviors. Negative zeta potential attributed to acidic surface functional groups, promoting stability and preventing aggregation in aqueous solutions [59]. XIM maintained a negative charge (-35 to -5 mV), PAC

demonstrated amphoteric behavior (-31 to +11 mV) across the pH range of 2.1–10.5, with a pH_{PZC} at 4.2. Consequently, PAC surface was protonated (positive) below pH 4.2 and deprotonated (negative) above it. The observation of zeta potential magnitudes $>|30\text{ mV}|$ suggested high suspension stability, a factor anticipated to promote the formation of surface complexes with Cr(VI).

Effect of ionic strength

Electrolyte levels (as NaCl, ranging from 7-800 mM), mimicking usual freshwater/river water (~7-10 mM), seawater (~400 mM) to wastewater (~1M or greater) affected the solution phase equilibrium between contaminant and XIM. Data revealed a distinct inverse correlation between electrolyte concentration and Cr(VI) uptake. Specifically, removal efficiency was approximately 90 % at 7 mM ionic strengths, with suppression observed at elevated levels upto ~800 mM (43%) (**Figure 5c**). Ionic strength of solution could have a strong influence on conformation of surface groups [60]. Change in such conformation impacted an effect on accessibility of surface sites, which in turn affected solid-solution interface between chromium species and XIM layers. Presumably, presence of spectator ions (Na^+ and Cl^-) caused to decrease solubility of chromium ions with aqueous solvent. High concentration of background ions likely caused electrostatic screening of surface charges, effectively shielding active sites and preventing chromium-binding.

Effect of metal interferences

Co-existing heavy metals in water matrices may exert synergistic, antagonistic, or neutral effects on target contaminant. As illustrated in **Figure 5(d)**, influence of co-existing metal ions (Fe^{3+} , Cu^{2+} , Pb^{2+} , Ag^+ = 5 mg/L, As^{5+} = 1 mg/L) on Cr(VI) by XIM was evaluated. Among them, presence of Fe^{3+} induced a synergistic effect, significantly enhancing capture of Cr(VI). XIM demonstrated higher efficiency (~99%) compared to PAC (~88%) in presence of trivalent iron. This noteworthy enhancement is attributed to the hydrolysis of Fe^{3+} species ($pK_a \sim 2.2$), which releases hydronium ions (H_3O^+), thereby lowering solution pH (H^+ - H_2O) and favoring chromium uptake in synergy with iron [61]. Conversely, other tested metal ions inhibited chromium uptake. Divalent copper (Cu^{2+}) reduced capacity to moderate 64% (PAC 51%) due to co-precipitation of mixed metals. A higher inhibition occurred in presence of Pb^{2+} (44%) (PAC 26%), Ag^+ (42%) (PAC 34%) and As^{5+} (27%) (PAC 20%). Lead and silver ions exhibited comparable inhibitory effects through competitive binding at surface sites. Maximum inhibition was observed in presence of pentavalent arsenic (AsO_4^{3-}), likely due to their oxyanionic

competition with chromium species. Hence, XIM proved to be a viable alternative to conventional PAC benchmark when treating multi-component heavy metal co-existing solution matrices.

Leaching test and aging impact

XIM was equilibrated with Cr(VI), achieving a steady-state uptake efficiency of ~90% under uncontrolled pH conditions. Extended leaching tests conducted over a 96-hour static interval showed a plateau in (ad)sorption capacity, with no statistically significant release of chromium back into the solution at 14, 24, 48, or 96 hours. This was contrast with commercial PAC, which demonstrated fluctuations (<5%) in (ad)sorbate stability (**Figure 5e**). These data confirmed that equilibrium was established within 14 hours and that the resulting Cr(VI)-XIM complex remained chemically stable. Absence of secondary leaching suggested high surface affinity and stability, critical metrics for long-term deployments. Hence, to assess shelf-life of XIM, samples were stored at ambient temperature for up to 9 months (time points: 7 days, 1, 3, 6, and 9 months) (**Figure 5f**). Quantitative analysis revealed no significant deviation in Cr(VI) capture efficiency between fresh and aged samples. The structural integrity (in terms of surface functional active centres) of products was maintained meticulously, with no evidence of auto-oxidation of surface groups (alcoholic/hydroxyl moieties) or possible formation of degradation byproducts at ambient temperature. Thermodynamic stability and availability of active binding sites remained intact with no loss in performance. Thus, XIM allowed long-term storage without matrix deterioration and reduction in remediation capacity within 9 months of deployment time.

Chromium uptake mechanism

Interplay between XIM layers and contaminant were important governing the fate of dissolvable Cr(VI). Kinetic, isotherm, and thermodynamic examinations thus verified the experimental data by varying contact time, initial metal concentration, and temperature. Details of adsorption parameters are provided in *SI, section S2*.

Isotherm surface response

Maximum metal monolayer uptake capacity (Q_m) for chromium on XIM was determined as 41.4 mg/g using the Langmuir data (**Figure 6a** and *SI, Table S1*), a contaminant attachment model of environmental significance. However, interface complexity of sorbate-sorbent indicated that heterogeneous interactions could also be influential. Langmuir data could not define complex models considering surface heterogeneity or interaction between the (ad)sorbing molecules.

Notably, it defines the equilibrium attachment onto homogeneous monolayer surfaces and is contrary to the Freundlich model which describes multilayer heterogeneous depositions. Despite the only Langmuir and Freundlich fits, the superior performance of the Sips isotherm (a three-parameter model) indicated that XIM matrix facilitated uptake through a complex mechanism involving both monolayer deposition and heterogeneous surface interactions ($Q_m=60.7$ mg/g). Consequently, the Sips isotherm—which converges to Freundlich behavior at low concentrations ($C_e \rightarrow 0$ or when term $k_{lf}C_e$ is small) and Langmuir behavior at high concentrations ($C_e \rightarrow \infty$, n (or $1/n$) = 1) —was applied to account for surface heterogeneity. A statistical comparison confirmed the optimal fit order as Sips ($R_{adj}^2=0.9747$) > Freundlich ($R_{adj}^2=0.9571$) > Langmuir ($R_{adj}^2=0.9401$), indicating that the XIM surface possessed both heterogeneous and homogeneous binding sites.

Kinetically-controlled reactions and thermodynamic energetics

Kinetic fractionation of Cr(VI) immobilization on XIM sites evaluated to elucidate the underlying mechanisms of chemical reaction control and mass transfer over time. Pseudo-first-order regression yielded a rate constant of 0.30 min^{-1} . Material demonstrated initial rapid kinetic uptake, achieving >14% efficiency within first 15 min, rising to 24% at 30 min, and reaching near-quantitative removal (90%) at equilibrium (14 hours). Consequently, this was established as the optimal contact period. Such kinetic pattern could predict the Weber-Morris intraparticle diffusion (IPD) [62]. Mechanistic analysis of IPD $\sqrt{t}$ plots revealed a tri-phasic profile. Initial phase included swift external surface diffusion, followed by a gradual rate-limiting linear phase attributed to diffusion into pores, and concluding with a saturation-driven equilibrium plateau where IPD appeared to decline due to active site saturation by chromium, indicating minimal metal concentrations remaining in solution (adsorption-desorption equilibrium) (**Figure 6b**). Multilinearity of the plot and their deviation from origin (non-zero intercept) indicated that the reaction rate did not govern solely by IPD but rather by a mixed-control mechanism involving external diffusion (film diffusion) and surface chemical reactions. To verify this, a combined modeling approach elucidated pseudo-second-order (PSO) kinetically-controlled uptake of Cr(VI). PSO model provided a superior statistical fit ($R_{adj}^2=0.9726$) compared to the pseudo-first-order model ($R_{adj}^2=0.9443$; **Figure 6c** and *SI, Table S2*). High F-value, low χ^2 metric, and good concordance between calculated and experimental q_e suggested interfacial complexation and chemical reactions were rate-controlling steps between chromium and surface

functional groups. Regression analysis demonstrated that PSO minimized the error function (χ^2) and maximized the correlation coefficient compared to the first-order model. Statistical validation of PSO model confirmed that immobilization governed principally by chemisorption mechanisms, driven by formation of an intensive covalent or ionic immobilization network between Cr(VI) and XIM sites.

Furthermore, XIM indicated a thermal energy-dependent mechanism. The standard Gibbs free energy (Eq. 1) and the van't Hoff relationship (Eq. 2) were employed to evaluate thermodynamic feasibility by determining Gibbs free energy (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) [63]. By applying van't Hoff equation, ΔH^0 and ΔS^0 calculated from slope and intercept, respectively, of regression line obtained from plotting equilibrium constant and temperature ($\ln K_c$ vs. $1/T$) (**Figure 6d**).

$$\Delta G^{\circ} = -RT \ln K_c \quad (1)$$

$$\ln K_c = -(\Delta H^{\circ})/RT + (\Delta S^{\circ})/R \quad (2)$$

where R represents the gas constant (8.314×10^{-3} kJ/mol·K), T indicates the absolute temperature (K), and K_c denotes the equilibrium constant. Cr(VI) removal efficiency exhibited a positive correlation with temperature, rising from 51% at 277K to 99% at 313K. The process was determined to be spontaneous and endothermic. ΔG^0 values were negative and became increasingly favorable with temperature (-0.58 to -6.4 kJ/mol between 277–313K). Positive ΔH^0 (+43.98 kJ/mol) confirmed the endothermic reaction, suggesting activation of XIM binding sites at elevated temperatures. Positive ΔS^0 (+0.16 kJ/mol.K) indicated increased randomness at solid-solution interface, driving feasibility of reactions across the tested thermal range. Thus, XIM remained active from moderate to higher temperature on sequestration of chromium. Overall uptake occurred aligning the key thermodynamic parameters as: $\Delta G^0 < 0$, $\Delta H^0 > 0$, $\Delta S^0 > 0$ (*SI, Table S3*). In a nut shell, energetics showed a feasible uptake reaction, higher temperatures facilitated activation of XIM binding sites, and process was driven by an increase in interfacial disorder.

3.3. Iodine capture

Iodine capture was evaluated by suspending 1.25 g/L of XIM in initial 1 mM iodine-hexane and iodine-water solutions. A comparative testing in amphiphilic environments of polar and non-polar phases established the material's broad applicability, as in **Figure 7(a–b)**. Solution displayed a characteristic dark color of dissolved iodine initially ($t=0$) and later became

noticeably lighter, reflecting reduction in iodine concentration with time progression, as illustrated in *insets of Figure 7(a-b)*. A control blank was monitored simultaneously under identical conditions to ensure experimental accuracy. Iodine sequestration efficiency in water; $[I_2]_w$ system reached ~75% within the first 0.5 hours, increasing to ~80% at 6 hours and 94% by 24 hours. In contrast, hexane-mixed solutions; $[I_2]_h$ system exhibited slower kinetics, with efficiencies of ~23%, >62%, and 77% at 0.5, 6, and 24 hours, respectively. Although presence of hexane retarded the initial uptake, sequestration demonstrated a sustained increase over the 24-hour period. The accelerated initial capture ascribed to readily accessible, unoccupied active sites on XIM surfaces, which facilitated swift interaction and binding of iodine molecules. As these high-affinity sites progressively became occupied, the driving force for further (ad)sorption declined. Rate of iodine uptake gradually slowed, indicating a transition towards a more diffusion- or equilibrium-controlled regime. Kinetic pattern observed a typical IPD, i.e. the intraparticle diffusion and process showed as a multi-linear curve, indicating that multiple physical mechanisms controlled reaction rates at different times (**Figure 7c**). Reactions were governed by a three-stage process that facilitated transitions from surface attachment (fast) to pore diffusion (slow/linear) to final equilibrium (stopped). Slope of the plot were declined and eventually flattened (slope $\approx$ 0). This referred to reduction in diffusion rate as surface pores became saturated, preventing further ingress of iodine molecules. Results showed that removing contaminants from water (aqueous phase) was more effective than removing them within organic solvents. XIM possessed a significant number of active sites, a portion of them could be located in less accessible regions, requiring longer contact times for iodine molecules to diffuse and interact effectively.

Iodine data were fitted to pseudo-first-order and PSO (pseudo-second-order) models for chromium sequestration from water matrices (**Figure 7d**; *SI, Table S2*). PSO yielded a significantly higher correlation coefficient ($R_{adj}^2=0.9369$) compared to pseudo-first-order model ($R_{adj}^2=0.9268$). In contrast to physisorption, statistical fit (F-value and χ^2) suggested that iodine molecules onto XIM primarily mediated by active surface functional sites, identifying chemisorption as the principal driver. XIM proved effective from distinct solvents, demonstrating versatility in liquid-phase extraction. These findings, therefore, validated XIM as an effective infiltration matrix for remediation of iodine species in both polar and non-polar environments.

3.4 Material performance in natural waters

To demonstrate practical viability and address the demand for effective water remediation, this study benchmarked the performance of XIM against commercial PAC using real-world water matrices. Samples obtained from three distinct locations in Saran, Bihar, India, were utilized to assess the impact of environmental matrix interferences on the sequestration of chromium and iodine. Field samples were collected, comprising surface water from a Ganga River tributary (25°44'16"N, 84°57'34"E), a local pond (stagnant water body), and groundwater from a potable hand pump source (25°45'01"N, 85°00'49"E). Baseline analysis indicated no detectable natural chromium or iodine. Analysis measurements showed that chromium-contaminated mixed waters at concentrations of 360 µg/L, while, iodine-contaminated mixed water at concentrations of 890 µg/L. Hexavalent chromium and iodine spiked assays were performed, as illustrated in **Figure 8**. With control over material dosing, XIM matrix significantly outperformed commercial PAC across all tested environments. Both materials demonstrated (ad)sorption stability across diverse environmental matrices. XIM achieved chromium removal efficiencies of 88–90% (vs. 49–51% for PAC) and iodine removal of 90–94% (vs. 89–93% for PAC) across river, pond, and groundwater samples. Final concentrations of chromium were determined to be below the maximum permissible limits (< 50 µg/L) based on XIM data, making them suitable for drinking water use. PAC exhibited lower efficacy under identical conditions. Minimal variation in performance of XIM relative to PAC validated its resilience to matrix effects across diverse surface, groundwater sources, and engineered water environments either at low or high concentrations of contaminants. Unmodified activated carbon (powder or granular activated carbon) suffers from non-specific binding, metal's properties, its concentration, and water matrix interferences. PAC is not effective for all metal ions showing minimal impact on sequestration unless their tedious, costlier, and chemical modifications [27, 64-67]. On the other hand, xerogel derivatives validate potential for recovery of metals in concentrated forms across a wide concentration range. XIM prototype constitutes a viable green solution, complying with strict environmental standards while eliminating secondary pollution.

4. Conclusions and future perspectives

Emergence of bioprivileged material has catalyzed a paradigm shift in water purification strategies, offering a streamlined and efficacious framework that addresses the limitations of

established synthetic protocols. As a proof of concept, we report a metal-free Xerogel Infiltration Matrix (XIM) synthesized from banana precursors for scavenging carcinogenic chromium and capturing iodine from polar and non-polar environments. Underlying mechanisms plausibly elucidated using characterizing tools of Raman spectroscopy, electron microscopy (TEM and SEM), XPS, XRD, zetasizer, IR, and TGA/DSC. Natural precursor at a low-temperature HTC soft control exhibited a turbostratic carbon structure and an oxygen-rich organic hybrid surface, as evidenced by prominent C1s and O1s XPS spectral features, signifying enhanced filtration with intrinsic degradability. XIM indicated a condensed carbon component together with thermally labile species prone to relaxation, stepwise condensation, and reactive transitions. Raman spectra identified D band, attributed to lattice disorders, and G band, indicative of graphitic structures. Additional spectral features emerged upon iodine capture unlike pristine carbon or carbon-chromium spectra. Reaction pathways established pseudo-second-order driven by intraparticle diffusion mechanisms. Thermodynamic functions yielded a spontaneous, endothermic, and entropy-driven energetics. Contaminant attachment models demonstrated that surface-engineered XIM could achieve significant sequestration under conditions relevant to natural waters. In contrast to popular commercial Activated Carbon, XIM demonstrated enhanced functional performance unperturbed by environmental variables, including varying pH, ionic strengths, and co-occurring metal interferences. Material exhibited stability via leaching test and aging deployments with no loss in performance. These findings position XIM xerogel as a net-zero compatible, minimal-footprint solution for specific applications. Scaling the production can offer a viable workflow for chelation of metals under similar environmental dimensions. Specific coordination between carbon types and inorganic metal requires further elucidation on resolving atomic-level interactions within local aquatic environments. Pilot-scale studies are recommended to assess the dynamic control of mixed metals in complex systems. Future investigations will advance knowledge of metal(loid)-organic frameworks and the lasting environmental fate of metallic species to validate their safety and effectiveness in diverse environmental scenarios.

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Declaration

On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- [1] X. Wang, L. Li, X. Yan, X. Meng, Y. Chen, Processes of chromium (VI) migration and transformation in chromate production site: A case study from the middle of China, *Chemosphere* 257 (2020) 127282.
<https://doi.org/https://doi.org/10.1016/j.chemosphere.2020.127282>.
- [2] L. Zhang, B. Li, Z. Jiang, H. Xu, C. Li, Y. Wei, H. Wang, Enhanced Cr(VI)-removal mechanism of nano MgO recycled from high-magnesium slag by titanium synergy, *Separation and Purification Technology* 382 (2026) 135938.
<https://doi.org/https://doi.org/10.1016/j.seppur.2025.135938>.
- [3] S.B. Wilbur, Toxicological profile for chromium, (2000).
- [4] E. Vaiopoulou, P. Gikas, Regulations for chromium emissions to the aquatic environment in Europe and elsewhere, *Chemosphere* 254 (2020) 126876.
<https://doi.org/https://doi.org/10.1016/j.chemosphere.2020.126876>.
- [5] A. Monga, A.B. Fulke, D. Dasgupta, Recent developments in essentiality of trivalent chromium and toxicity of hexavalent chromium: Implications on human health and remediation strategies, *Journal of Hazardous Materials Advances* 7 (2022) 100113.
<https://doi.org/https://doi.org/10.1016/j.hazadv.2022.100113>.
- [6] A. Swaroop, M. Bagchi, H.G. Preuss, S. Zafra-Stone, T. Ahmad, D. Bagchi, Chapter 8 - Benefits of chromium(III) complexes in animal and human health, in: J.B. Vincent (Ed.), *The Nutritional Biochemistry of Chromium (III)* (Second Edition), Elsevier 2019, pp. 251-278.
<https://doi.org/https://doi.org/10.1016/B978-0-444-64121-2.00008-8>.
- [7] S.S. Wise, A.E.-M. Aboueissa, J. Martino, J.P. Wise Sr, Hexavalent chromium-induced chromosome instability drives permanent and heritable numerical and structural changes and a DNA repair-deficient phenotype, *Cancer research* 78(15) (2018) 4203-4214.
- [8] T.L. DesMarias, M. Costa, Mechanisms of chromium-induced toxicity, *Current Opinion in Toxicology* 14 (2019) 1-7. <https://doi.org/https://doi.org/10.1016/j.cotox.2019.05.003>.

- [9] Y. Zhigalenok, A. Tazhibayeva, S. Kokhmetova, A. Starodubtseva, T. Kan, D. Isbergenova, F. Malchik, Hexavalent chromium at the crossroads of science, environment and public health, *RSC Advances* 15(27) (2025) 21439-21464. <https://doi.org/10.1039/D5RA03104D>.
- [10] R. Chakraborty, K. Renu, M.A. Eladl, M. El-Sherbiny, D.M.A. Elsherbini, A.K. Mirza, B. Vellingiri, M. Iyer, A. Dey, A. Valsala Gopalakrishnan, Mechanism of chromium-induced toxicity in lungs, liver, and kidney and their ameliorative agents, *Biomedicine & Pharmacotherapy* 151 (2022) 113119. <https://doi.org/10.1016/j.biopha.2022.113119>.
- [11] B.D. Kerger, D.J. Paustenbach, G.E. Corbett, B.L. Finley, Absorption and elimination of trivalent and hexavalent chromium in humans following ingestion of a bolus dose in drinking water, *Toxicology and applied pharmacology* 141(1) (1996) 145-58. <https://doi.org/10.1006/taap.1996.0271>.
- [12] A. Vengosh, R. Coyte, J. Karr, J.S. Harkness, A.J. Kondash, L.S. Ruhl, R.B. Merola, G.S. Dywer, Origin of Hexavalent Chromium in Drinking Water Wells from the Piedmont Aquifers of North Carolina, *Environmental Science & Technology Letters* 3(12) (2016) 409-414. <https://doi.org/10.1021/acs.estlett.6b00342>.
- [13] WHO2020, World Health Organization (2020). Chromium in drinking-water. Background document for development of WHO Guidelines for drinking-water quality. Geneva, World Health Organization (WHO/HEP/ECH/WSH/2020.3).
- [14] USEPA2025, U.S. Environmental Protection Agency (updated on Feb 20, 2025). Chromium in Drinking Water. <https://www.epa.gov/sdwa/chromium-drinking-water> (accessed 16.11.2025).
- [15] NPDWR2024, National Primary Drinking Water Regulations (updated on December 12, 2024). <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations> (accessed on 16.11.2025).
- [16] A. Misganaw, B. Akenaw, S. Getu, Determination of the level of chromium (III) and comparison of chemical precipitating agents to recover and reuse it from tannery waste water, *Desalination and Water Treatment* 317 (2024) 100150. <https://doi.org/10.1016/j.dwt.2024.100150>.
- [17] J. Xiong, X. Yang, L. Xiao, S. Song, L. Cao, M. Xia, P. Wu, Y. Shi, K. Pi, G. Qiu, Enhanced electrochemical reduction and precipitation removal of Cr(VI) by a confined

crystallization inducing cathode structure, *Desalination* 616 (2025) 119408.

<https://doi.org/https://doi.org/10.1016/j.desal.2025.119408>.

[18] Y. Fan, X. Wang, M. Wang, Separation and recovery of chromium and vanadium from vanadium-containing chromate solution by ion exchange, *Hydrometallurgy* 136 (2013) 31-35.

<https://doi.org/https://doi.org/10.1016/j.hydromet.2013.03.008>.

[19] Y. Qiu, Q. Zhang, B. Gao, M. Li, Z. Fan, W. Sang, H. Hao, X. Wei, Removal mechanisms of Cr(VI) and Cr(III) by biochar supported nanosized zero-valent iron: Synergy of adsorption, reduction and transformation, *Environmental Pollution* 265 (2020) 115018.

<https://doi.org/https://doi.org/10.1016/j.envpol.2020.115018>.

[20] M. Hori, K. Shozugawa, M. Matsuo, Reduction process of Cr(VI) by Fe(II) and humic acid analyzed using high time resolution XAFS analysis, *Journal of Hazardous Materials* 285 (2015) 140-147. <https://doi.org/https://doi.org/10.1016/j.jhazmat.2014.11.047>.

[21] B. Jiang, Y. Gong, J. Gao, T. Sun, Y. Liu, N. Oturan, M.A. Oturan, The reduction of Cr(VI) to Cr(III) mediated by environmentally relevant carboxylic acids: State-of-the-art and perspectives, *Journal of Hazardous Materials* 365 (2019) 205-226.

<https://doi.org/https://doi.org/10.1016/j.jhazmat.2018.10.070>.

[22] J. Wen, W. Cheng, Y. Zhang, Y. Zhou, Y. Zhang, L. Yang, Highly efficient removal of Cr(VI) from wastewater using electronegative SA/EGCG@Ti-SA/PVDF sandwich membrane, *Journal of Hazardous Materials* 459 (2023) 132073.

<https://doi.org/https://doi.org/10.1016/j.jhazmat.2023.132073>.

[23] H. Mohammadi, M. Gholami, M. Rahimi, Application and optimization in chromium-contaminated wastewater treatment of the reverse osmosis technology, *Desalination and Water Treatment* 9(1) (2009) 229-233. <https://doi.org/https://doi.org/10.5004/dwt.2009.808>.

[24] K. Roa, A. Boulett, E. Oyarce, J. Sánchez, Removal of Cr(VI) by ultrafiltration enhanced by a cellulose-based soluble polymer, *Journal of Water Process Engineering* 51 (2023) 103478.

<https://doi.org/https://doi.org/10.1016/j.jwpe.2022.103478>.

[25] S. Kocaoba, G. Cetin, G. Akcin, Chromium removal from tannery wastewaters with a strong cation exchange resin and species analysis of chromium by MINEQL+ *Scientific Reports* 12(1) (2022) 9618. <https://doi.org/10.1038/s41598-022-14423-3>.

- [26] B.J. Singh, A. Chakraborty, R. Sehgal, A systematic review of industrial wastewater management: Evaluating challenges and enablers, *Journal of Environmental Management* 348 (2023) 119230. <https://doi.org/https://doi.org/10.1016/j.jenvman.2023.119230>.
- [27] A.D. Dwivedi, R. Permana, J.P. Singh, H. Yoon, K.H. Chae, Y.-S. Chang, D.S. Hwang, Tunichrome mimetic matrix, its perspective in abatement for carcinogenic hexavalent chromium and specific coordination behavior, *Chemical Engineering Journal* 328 (2017) 629-638. <https://doi.org/https://doi.org/10.1016/j.cej.2017.07.078>.
- [28] A.D. Dwivedi, M. Lahtinen, S.P. Dubey, R.S. Varma, Transformation of carcinogenic hexavalent chromium and nitrophenol isomers in aqueous media using leftover vegetable peels, *Clean Technologies and Environmental Policy* 27(10) (2025) 5895-5906. <https://doi.org/10.1007/s10098-024-03008-5>.
- [29] J. Yang, W. Tai, F. Wu, K. Shi, T. Jia, Y. Su, T. Liu, P. Mocilac, X. Hou, X. Chen, Enhanced removal of radioactive iodine anions from wastewater using modified bentonite: Experimental and theoretical study, *Chemosphere* 292 (2022) 133401. <https://doi.org/https://doi.org/10.1016/j.chemosphere.2021.133401>.
- [30] H. Zhu, Y. Qin, Y. Guo, Z. Shen, M. Imran, M. Asim Mushtaq, Z. Zhang, C. Ni, Y. Chen, Y. Ding, H. Gul, J. Zou, P. Tsiakaras, H.-Y. Hsu, J. Zhao, Covalent organic polymers for efficient removal of iodine from gas- and liquid-phase environments, *Chemical Engineering Journal* 484 (2024) 149739. <https://doi.org/https://doi.org/10.1016/j.cej.2024.149739>.
- [31] ATSDR2004, Toxicological profile for iodine. Agency for Toxic Substances and Disease Registry.
- [32] R. Ma, M. Yan, P. Han, T. Wang, B. Li, S. Zhou, T. Zheng, Y. Hu, A.G.L. Borthwick, C. Zheng, J. Ni, Deficiency and excess of groundwater iodine and their health associations, *Nature Communications* 13(1) (2022) 7354. <https://doi.org/10.1038/s41467-022-35042-6>.
- [33] H. Dong, Z. Qiang, S.D. Richardson, Formation of Iodinated Disinfection Byproducts (I-DBPs) in Drinking Water: Emerging Concerns and Current Issues, *Accounts of Chemical Research* 52(4) (2019) 896-905. <https://doi.org/10.1021/acs.accounts.8b00641>.
- [34] S.D. Richardson, F. Fasano, J.J. Ellington, F.G. Crumley, K.M. Buettner, J.J. Evans, B.C. Blount, L.K. Silva, T.J. Waite, G.W. Luther, A.B. McKague, R.J. Miltner, E.D. Wagner, M.J. Plewa, Occurrence and Mammalian Cell Toxicity of Iodinated Disinfection Byproducts in

Drinking Water, *Environmental Science & Technology* 42(22) (2008) 8330-8338.

<https://doi.org/10.1021/es801169k>.

[35] Y. Yang, Y. Komaki, S.Y. Kimura, H.-Y. Hu, E.D. Wagner, B.J. Mariñas, M.J. Plewa, Toxic Impact of Bromide and Iodide on Drinking Water Disinfected with Chlorine or Chloramines, *Environmental Science & Technology* 48(20) (2014) 12362-12369.

<https://doi.org/10.1021/es503621e>.

[36] NHMRC2011, National Water Quality Management Strategy. Australian Drinking Water Guidelines 6. Version 3.5 Updated August 2018. National Health and Medical Research Council (NHMRC), Canberra. Available at: <https://www.Nhmrc.Gov.au/about-us/publications/australian-Drinking-Water-Guidelines>.

[37] CanadaReport2022, Drinking water screening value for Iodide – Technical Summary. <https://www.canada.ca/en/services/health/publications/healthy-living/drinking-water-screening-value-iodide-technical-summary.html>

[38] IOM2001, Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium and Zinc. U.S. National Institute of Medicine, Available at: www.nap.edu/read/10026/chapter/1.

[39] C.-C. Chien, Y.-P. Huang, W.-C. Wang, J.-H. Chao, Y.-Y. Wei, Efficiency of Moso Bamboo Charcoal and Activated Carbon for Adsorbing Radioactive Iodine, *CLEAN – Soil, Air, Water* 39(2) (2011) 103-108. <https://doi.org/10.1002/clen.201000012>.

[40] X. Zhang, I. da Silva, R. Fazzi, A.M. Sheveleva, X. Han, B.F. Spencer, S.A. Sapchenko, F. Tuna, E.J.L. McInnes, M. Li, S. Yang, M. Schröder, Iodine Adsorption in a Redox-Active Metal–Organic Framework: Electrical Conductivity Induced by Host–Guest Charge-Transfer, *Inorganic Chemistry* 58(20) (2019) 14145-14150.

<https://doi.org/10.1021/acs.inorgchem.9b02176>.

[41] J. Wang, S. Zhuang, Covalent organic frameworks (COFs) for environmental applications, *Coordination Chemistry Reviews* 400 (2019) 213046.

<https://doi.org/10.1016/j.ccr.2019.213046>.

[42] K.S. Subrahmanyam, D. Sarma, C.D. Malliakas, K. Polychronopoulou, B.J. Riley, D.A. Pierce, J. Chun, M.G. Kanatzidis, Chalcogenide Aerogels as Sorbents for Radioactive Iodine, *Chemistry of Materials* 27(7) (2015) 2619-2626.

<https://doi.org/10.1021/acs.chemmater.5b00413>.

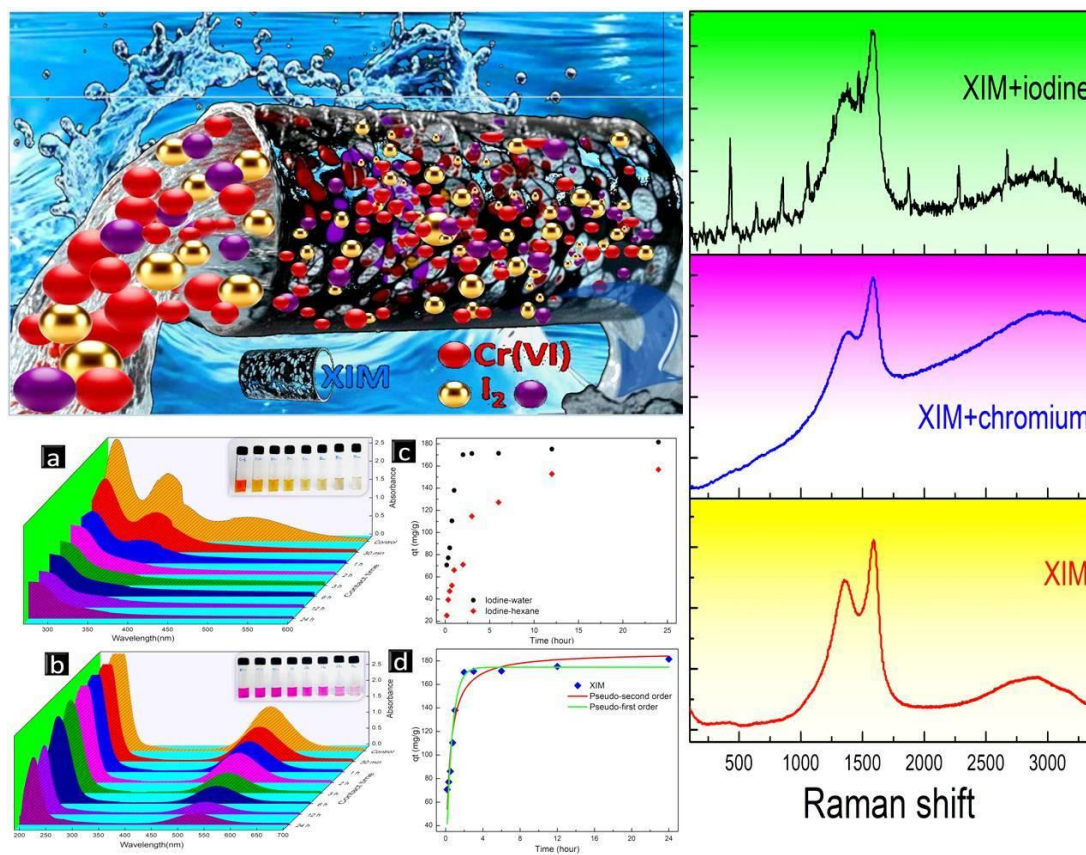
- [43] S.P. Dubey, K. Gopal, Application of natural adsorbent from silver impregnated *Arachis hypogaea* based thereon in the processes of hexavalent chromium for the purification of water, *Journal of Hazardous Materials* 164(2) (2009) 968-975.
<https://doi.org/https://doi.org/10.1016/j.jhazmat.2008.08.111>.
- [44] A.D. Dwivedi, U. Kumar, K. Roy, L. Kumar, S. Hokkanen, S.P. Dubey, Naturally derived infiltration matrix using *Cyperus articulatus* to control iodine and improvised elimination of methylene blue, *Industrial Crops and Products* 232 (2025) 121326.
<https://doi.org/https://doi.org/10.1016/j.indcrop.2025.121326>.
- [45] S. Affandi, H. Setyawan, S. Winardi, A. Purwanto, R. Balgis, A facile method for production of high-purity silica xerogels from bagasse ash, *Advanced Powder Technology* 20(5) (2009) 468-472. <https://doi.org/https://doi.org/10.1016/j.appt.2009.03.008>.
- [46] C.U. Kemas, N.C. Ngwuluka, N.A. Ochekepe, E.I. Nep, Starch-based xerogels: Effect of acetylation on Physicochemical and rheological properties, *International Journal of Biological Macromolecules* 98 (2017) 94-102.
<https://doi.org/https://doi.org/10.1016/j.ijbiomac.2017.01.101>.
- [47] T. Metzger, A. Léonard, W. Jomaa, H. Tamon, Understanding and Preventing Structural Changes during Drying of Gels, *Modern Drying Technology* 2014, pp. 155-229.
<https://doi.org/https://doi.org/10.1002/9783527631728.ch18>.
- [48] K. Czarnobaj, Preparation and characterization of silica xerogels as carriers for drugs, *Drug delivery* 15(8) (2008) 485-92. <https://doi.org/10.1080/10717540802321495>.
- [49] E.L. Holthoff, F.V. Bright, Molecularly Imprinted Xerogels as Platforms for Sensing, *Accounts of Chemical Research* 40(9) (2007) 756-767. <https://doi.org/10.1021/ar700087t>.
- [50] R.A.M. Barros, R.O. Cristóvão, S.A.C. Carabineiro, M.C. Neves, M.G. Freire, J.L. Faria, V.C. Santos-Ebinuma, A.P.M. Tavares, C.G. Silva, Immobilization and Characterization of L-Asparaginase over Carbon Xerogels, *BioTech* 11(2) (2022) 10.
- [51] B.J. Riley, D.A. Pierce, J. Chun, J. Matyáš, W.C. Lepry, T.G. Garn, J.D. Law, M.G. Kanatzidis, Polyacrylonitrile-Chalcogel Hybrid Sorbents for Radioiodine Capture, *Environmental Science & Technology* 48(10) (2014) 5832-5839.
<https://doi.org/10.1021/es405807w>.

- [52] B.J. Riley, S. Chong, Environmental Remediation with Functional Aerogels and Xerogels, Global challenges (Hoboken, NJ) 4(10) (2020) 2000013.
<https://doi.org/10.1002/gch2.202000013>.
- [53] K. Wiedner, C. Naisse, C. Rumpel, A. Pozzi, P. Wieczorek, B. Glaser, Chemical modification of biomass residues during hydrothermal carbonization – What makes the difference, temperature or feedstock?, Organic Geochemistry 54 (2013) 91-100.
<https://doi.org/https://doi.org/10.1016/j.orggeochem.2012.10.006>.
- [54] Q. Xu, Q. Qian, A. Quek, N. Ai, G. Zeng, J. Wang, Hydrothermal Carbonization of Macroalgae and the Effects of Experimental Parameters on the Properties of Hydrochars, ACS Sustainable Chemistry & Engineering 1(9) (2013) 1092-1101. <https://doi.org/10.1021/sc400118f>.
- [55] A. Funke, F. Ziegler, Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering, Biofuels, Bioproducts and Biorefining 4(2) (2010) 160-177. <https://doi.org/https://doi.org/10.1002/bbb.198>.
- [56] Ž. Knez, E. Markočič, M.K. Hrnčič, M. Ravber, M. Škerget, High pressure water reforming of biomass for energy and chemicals: A short review, The Journal of Supercritical Fluids 96 (2015) 46-52. <https://doi.org/https://doi.org/10.1016/j.supflu.2014.06.008>.
- [57] H.C. Vu, A.D. Dwivedi, T.T. Le, S.-H. Seo, E.-J. Kim, Y.-S. Chang, Magnetite graphene oxide encapsulated in alginate beads for enhanced adsorption of Cr(VI) and As(V) from aqueous solutions: Role of crosslinking metal cations in pH control, Chemical Engineering Journal 307 (2017) 220-229. <https://doi.org/https://doi.org/10.1016/j.cej.2016.08.058>.
- [58] W.S.W. Ngah, A. Kamari, S. Fatinathan, P.W. Ng, Adsorption of chromium from aqueous solution using chitosan beads, Adsorption 12(4) (2006) 249-257. <https://doi.org/10.1007/s10450-006-0501-0>.
- [59] M. Niksirat, R. Sadeghi, J. Esmaili, Removal of Mn from aqueous solutions, by activated carbon obtained from tire residuals, SN Applied Sciences 1(7) (2019) 782.
<https://doi.org/10.1007/s42452-019-0797-5>.
- [60] P.R. Wittbrodt, C.D. Palmer, Effect of Temperature, Ionic Strength, Background Electrolytes, and Fe(III) on the Reduction of Hexavalent Chromium by Soil Humic Substances, Environmental Science & Technology 30(8) (1996) 2470-2477.
<https://doi.org/10.1021/es950731c>.

- [61] G.V. Motuzova, I.P. Makarichev, M.I. Petrov, The effects of iron, mercury, and copper ions on the acid-base properties of aqueous soil extracts, *Moscow University Soil Science Bulletin* 66(4) (2011) 157-162. <https://doi.org/10.3103/S0147687411040041>.
- [62] J. Wang, X. Guo, Rethinking of the intraparticle diffusion adsorption kinetics model: Interpretation, solving methods and applications, *Chemosphere* 309 (2022) 136732. <https://doi.org/https://doi.org/10.1016/j.chemosphere.2022.136732>.
- [63] F. Zhao, E. Repo, D. Yin, Y. Meng, S. Jafari, M. Sillanpää, EDTA-Cross-Linked β -Cyclodextrin: An Environmentally Friendly Bifunctional Adsorbent for Simultaneous Adsorption of Metals and Cationic Dyes, *Environmental Science & Technology* 49(17) (2015) 10570-10580. <https://doi.org/10.1021/acs.est.5b02227>.
- [64] L. Qiu, C. Suo, N. Zhang, R. Yuan, H. Chen, B. Zhou, Adsorption of heavy metals by activated carbon: effect of natural organic matter and regeneration methods of the adsorbent, *Desalination and Water Treatment* 252 (2022) 148-166. <https://doi.org/https://doi.org/10.5004/dwt.2022.28160>.
- [65] R. Baccar, J. Bouzid, M. Feki, A. Montiel, Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions, *Journal of Hazardous Materials* 162(2) (2009) 1522-1529. <https://doi.org/https://doi.org/10.1016/j.jhazmat.2008.06.041>.
- [66] A.D. Dwivedi, N.D. Sanandiya, J.P. Singh, S.M. Husnain, K.H. Chae, D.S. Hwang, Y.-S. Chang, Tuning and Characterizing Nanocellulose Interface for Enhanced Removal of Dual-Sorbate (AsV and CrVI) from Water Matrices, *ACS Sustainable Chemistry & Engineering* 5(1) (2017) 518-528. <https://doi.org/10.1021/acssuschemeng.6b01874>.
- [67] Z. Guo, J. Zhang, H. Liu, Y. Kang, Development of a nitrogen-functionalized carbon adsorbent derived from biomass waste by diammonium hydrogen phosphate activation for Cr(VI) removal, *Powder Technology* 318 (2017) 459-464. <https://doi.org/https://doi.org/10.1016/j.powtec.2017.06.024>.

Table of content (TOC)

Tuning hydrochar technique, unravelling underlying local mechanisms together with characterization probes where material interacts with contaminants are demonstrated; xerogel from banana fruit is designed via surface engineering as boost up green chelator of chromium and iodine.



Captions for Figures

Figure 1: Schematics showing synthetic approach **(a)** low-temperature HTC reactions and XIM activation (i-viii), and present work illustration; **(b)** boost up water treatment application; and **(c)** characterization probes

Figure 2: SEM observations of surface morphologies: scale bars **(a)** 50 μm ; **(b)** 10 μm ; **(c)** 2 μm of XIM; and **(d)** TEM micrograph (scale bar 0.2 μm); **(e)** energy-dispersive X-ray elemental mapping showing pristine and post-treated (after chromium and iodine) observations in XIM xerogel

Figure 3: **(a)** Raman spectra for XIM samples: pristine carbon (*red labeled*), carbon loaded with chromium (*blue labeled*), and carbon loaded with iodine (*black labeled*); **(b)** PXRD diffractogram (5-80° 2 θ) coupled with survey XPS spectrum (combination of strong C1s and O1s signals of a carbonaceous organic hybrid surface)

Figure 4: **(a)** TG/DTG profile (TG trace is plotted in *green* as percentage mass (TG / %) on the left Y-axis, while the DTG trace is plotted in *black* as rate of mass loss (DTG / %·min⁻¹) on the right Y-axis); **(b)** DSC curve: *(a)* low temperature region (upto 120°C); *(b)* intermediate temperature events (160–260°C); *(c)* high temperature region (> 300°C) (Y-axis is labeled with exothermic heat flow in the downward direction, and X-axis spans from room temperature to about 600°C. Peak annotations with onset, peak, and endset parameters indicates deconvolution (peak-fitting) analysis, enabling quantitative estimation of enthalpy changes and transition widths for DSC events)

Figure 5: **(a)** Operational pHs on chromium sequestration onto XIM and PAC (material doses = 0.5 g/L, [Cr]₀ = 10 mg/L, reaction time = 14 hours, temperature = 298K); **(b)** electrokinetic measurement showing ζ -potential plot; **(c)** ionic strengths on Cr(VI) uptake efficiency (7-800 mM as NaCl, material doses = 0.5 g/L, [Cr]₀ = 10 mg/L, time = 14 hours); **(d)** co-occurring metal interferences (Fe³⁺, Cu²⁺, Pb²⁺, Ag⁺ = 5 mg/L, As⁵⁺ = 1 mg/L) onto XIM and PAC (material doses = 0.5 g/L, [Cr]₀ = 10 mg/L, time = 14 hours); **(e)** leaching test of exhausted materials

(reaction time = 14-96 hours; ambient temperature); and **(f)** aging impact on XIM derivatives for Cr(VI) (time points = 7 days to 9 months) ($[\text{Cr}]_0 = 10 \text{ mg/L}$, XIM/PAC doses = 0.5 g/L , time = 14 hours)

Figure 6: Interphase behaviour for chromium sequestration onto XIM xerogel **(a)** isotherm curves; **(b)** IPD $\sqrt{t}$ plot; **(c)** rate kinetic plots (pseudo-second order vs. pseudo-first order); **(d)** thermodynamic energetics (a constant material dosing of 0.5 g/L was maintained, chromium concentrations ($1\text{-}50 \text{ mg/L}$) were used to obtain isotherm relationships at equilibrium, reaction kinetics examined from 0.25 to 24 hours, thermodynamic parameters examined over a temperature range of $277\text{-}313\text{K}$, with chromium concentration held constant (10 mg/L), and an equilibrium time of 14 hours)

Figure 7: Sequestration of molecular iodine from amphiphilic environments **(a)** in water ($[\text{I}_2]_w = 1 \text{ mM}$; material dosing = 2.5g/L ; contact time = 24 hours); **(b)** in n-hexane ($[\text{I}_2]_h = 1 \text{ mM}$) (*insets reflecting reduction in iodine concentrations with time progression*); **(c)** IPD $\sqrt{t}$ plots for $[\text{I}_2]_w$ and $[\text{I}_2]_h$; and **(d)** rate kinetics (pseudo-second-order vs. pseudo-first-order) for $[\text{I}_2]_w$ system

Figure 8: Performance metrics of XIM xerogel and PAC (commercial purification material) in river, pond, and groundwater samples: for Cr(VI) treatment (reaction conditions: $[\text{Cr}]_0 = *360 \text{ }\mu\text{g/L}$, uncontrolled pH, material dosing = 0.5 g/L , time = 14 hours, temperature = 298K); for iodine treatment (reaction conditions: $[\text{I}]_0 = *890 \text{ }\mu\text{g/L}$, uncontrolled pH, material dosing = 2.5 g/L , time = 24 hours, temperature = 298K)

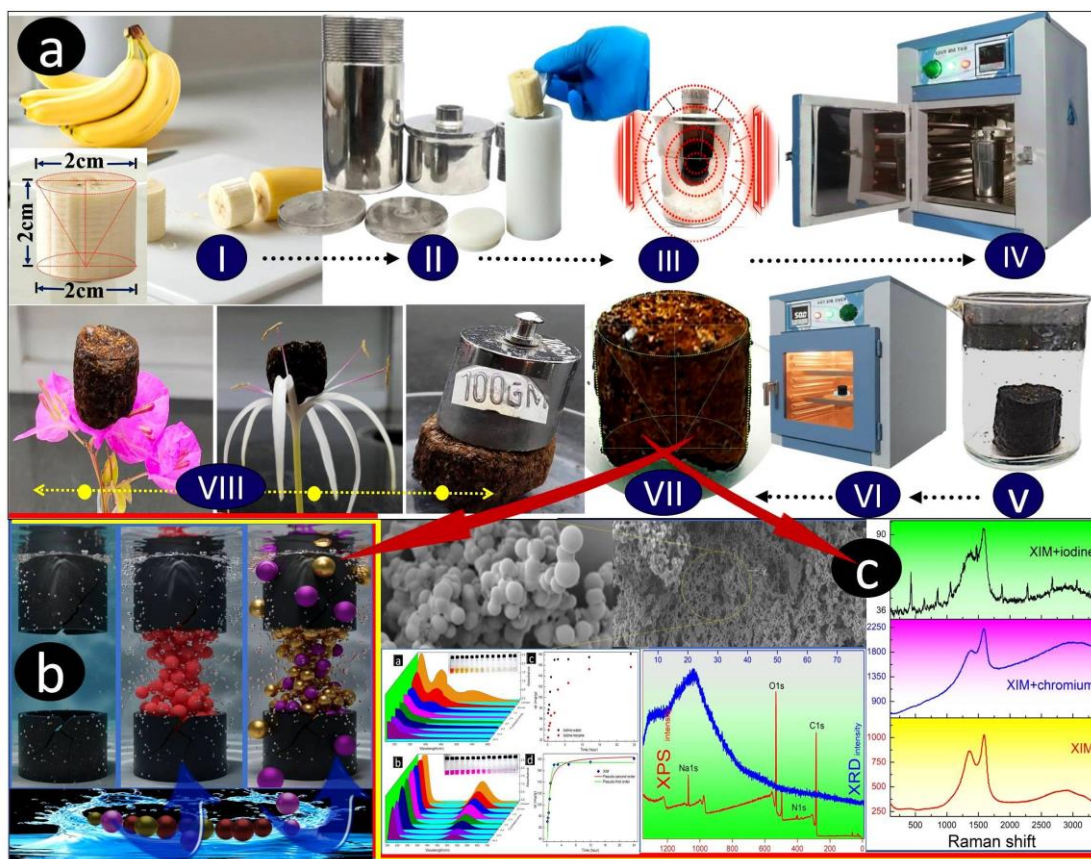


Figure 1

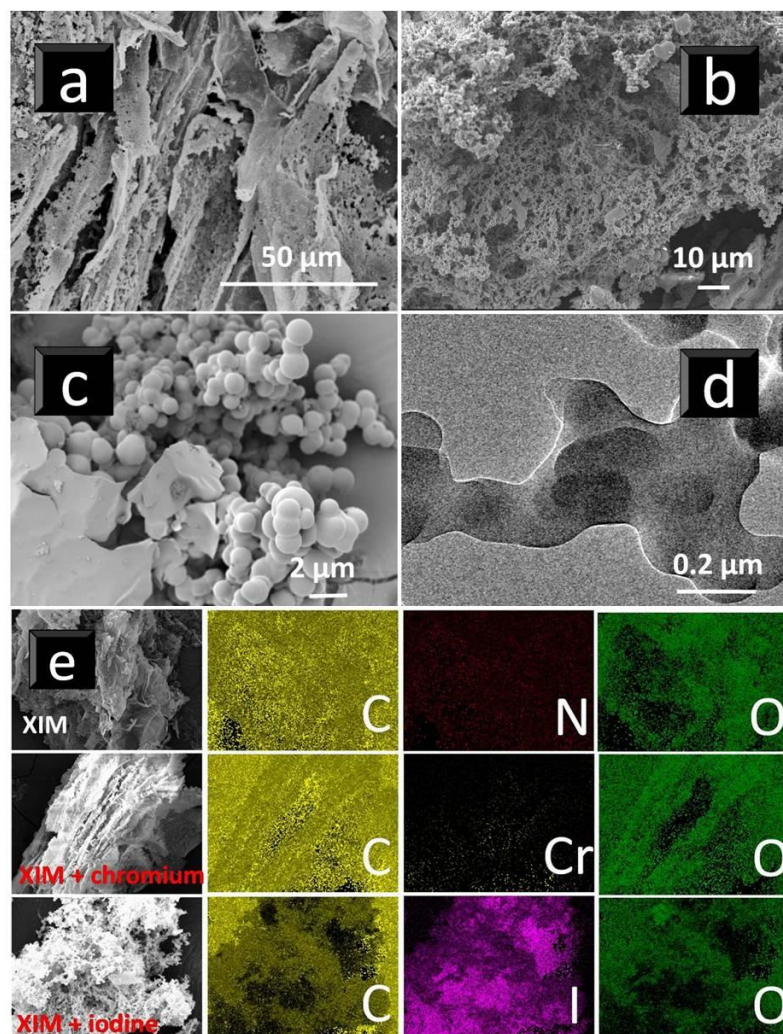


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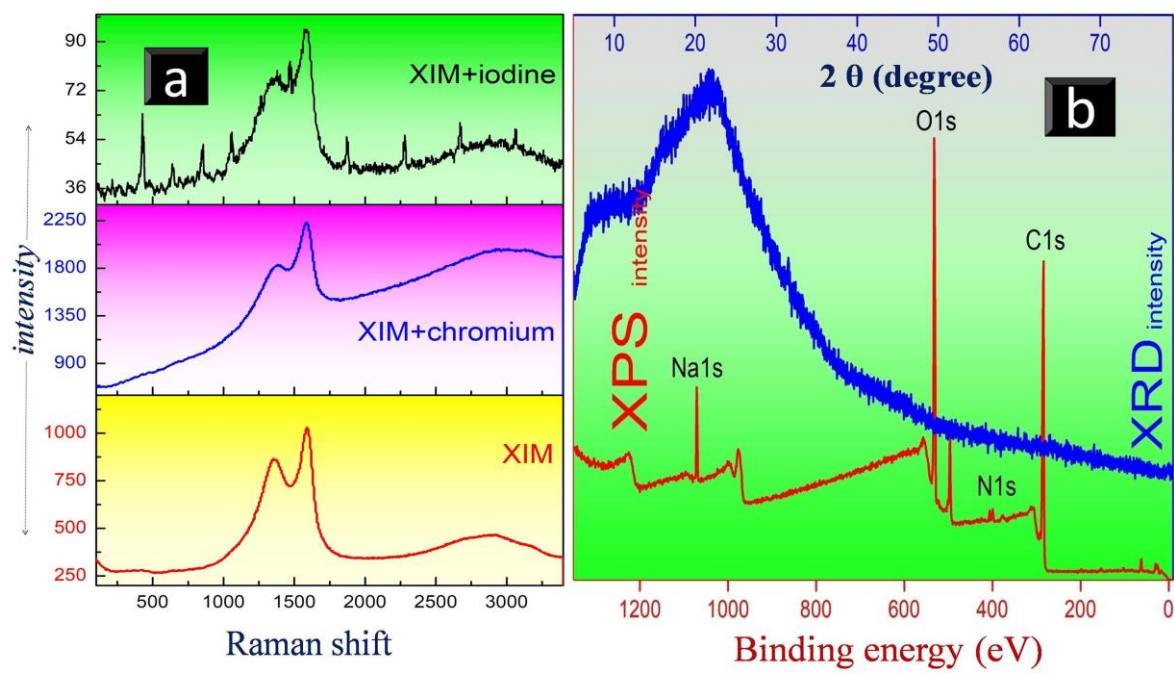


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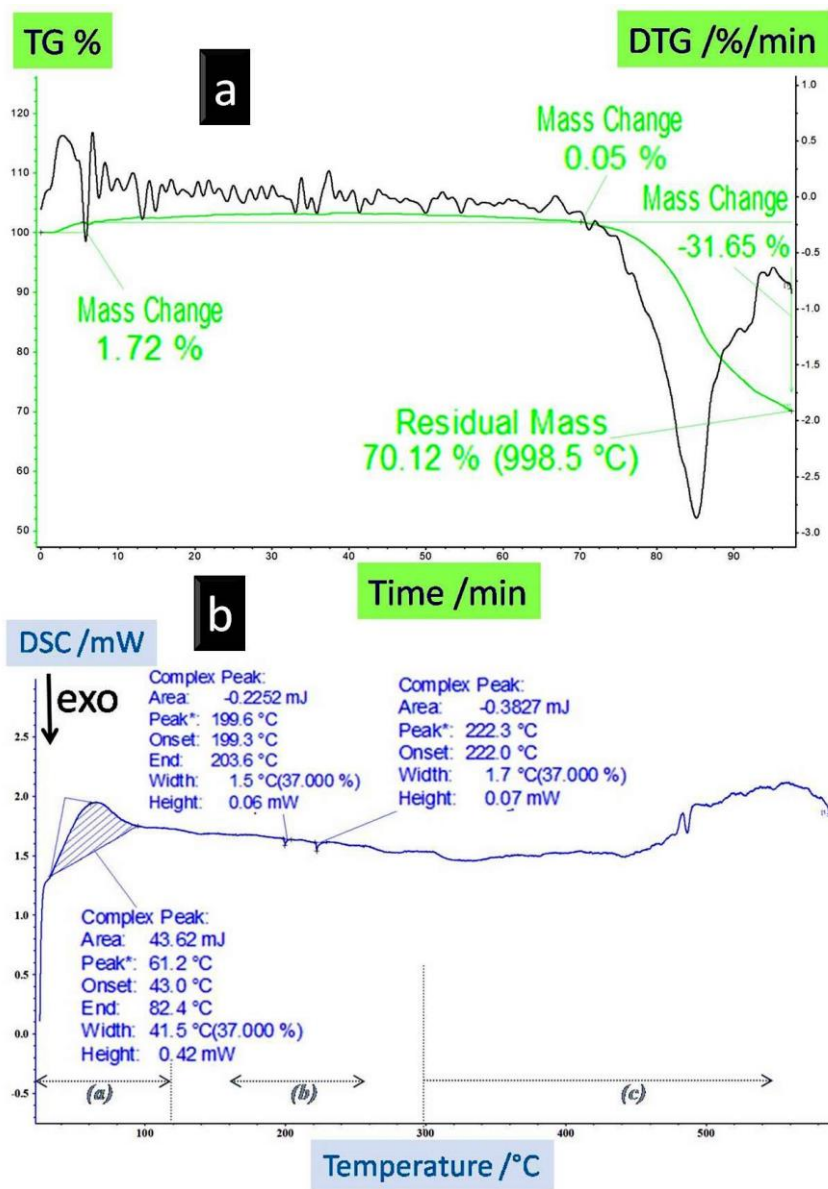


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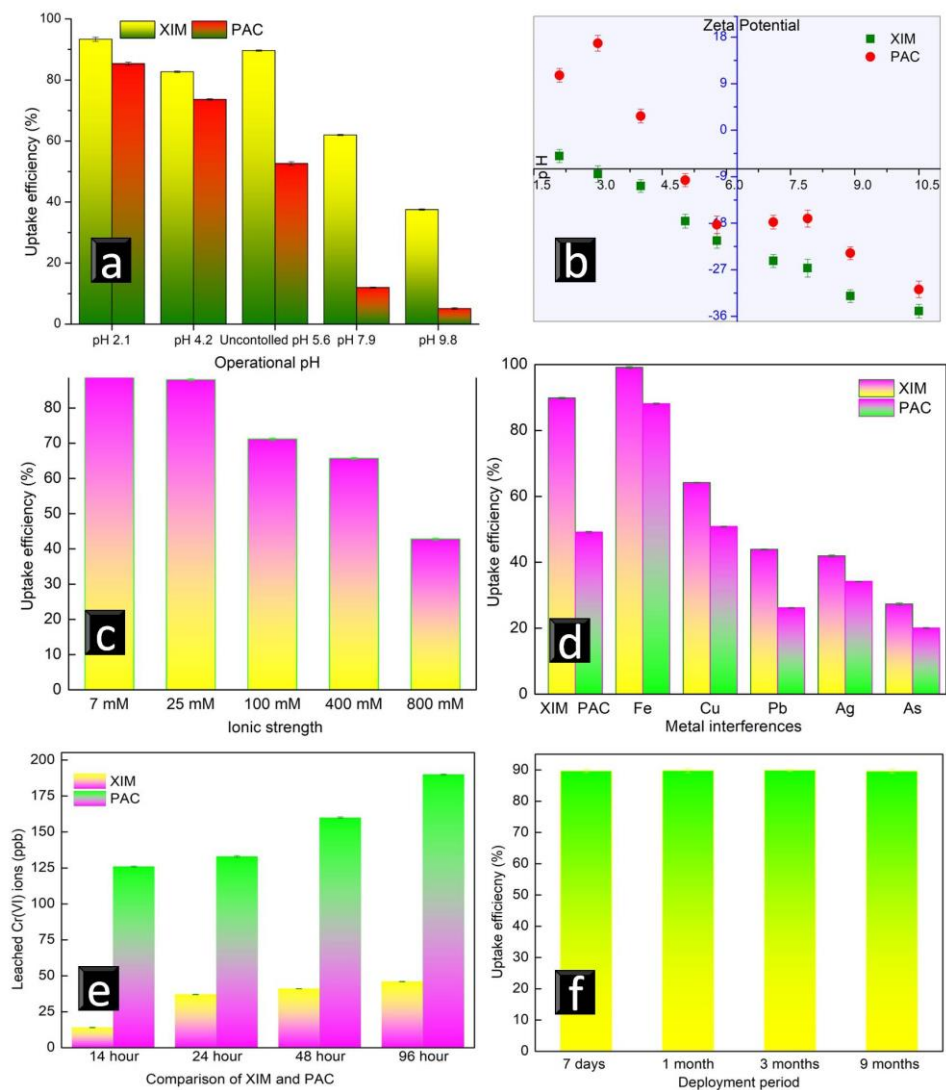


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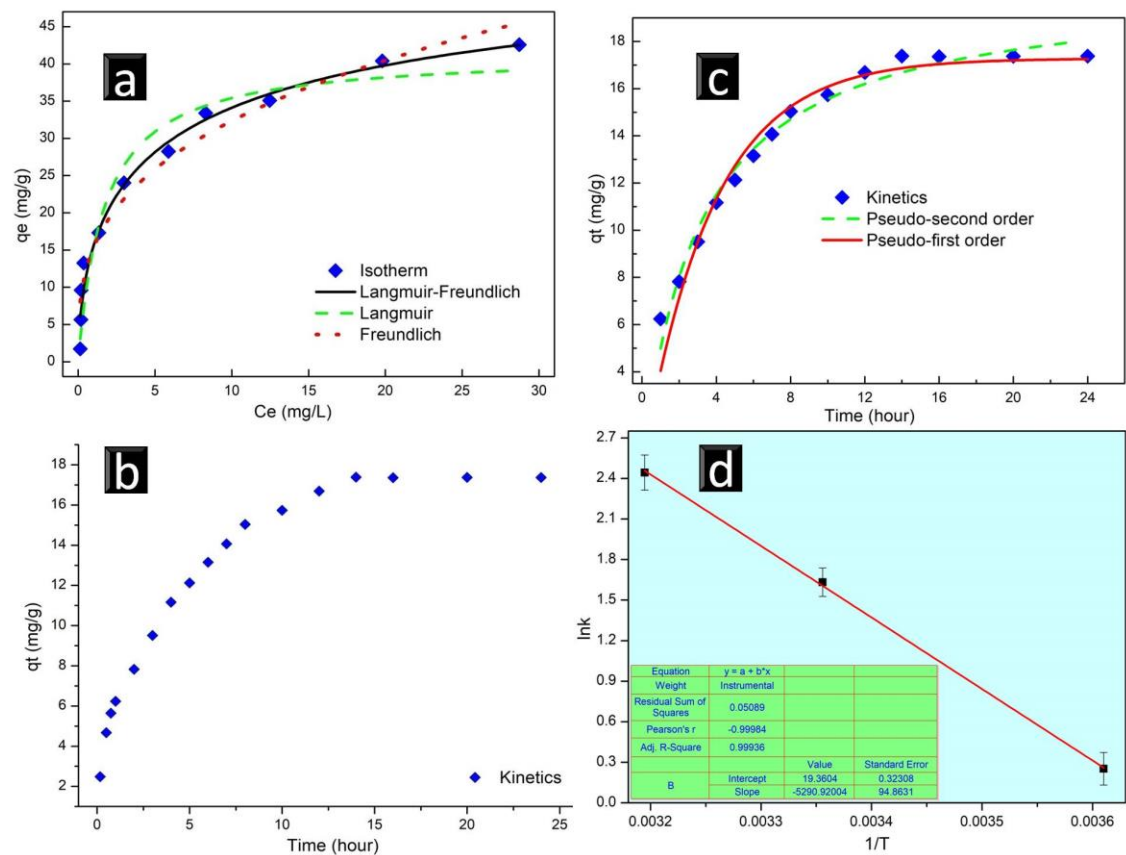


Figure 6

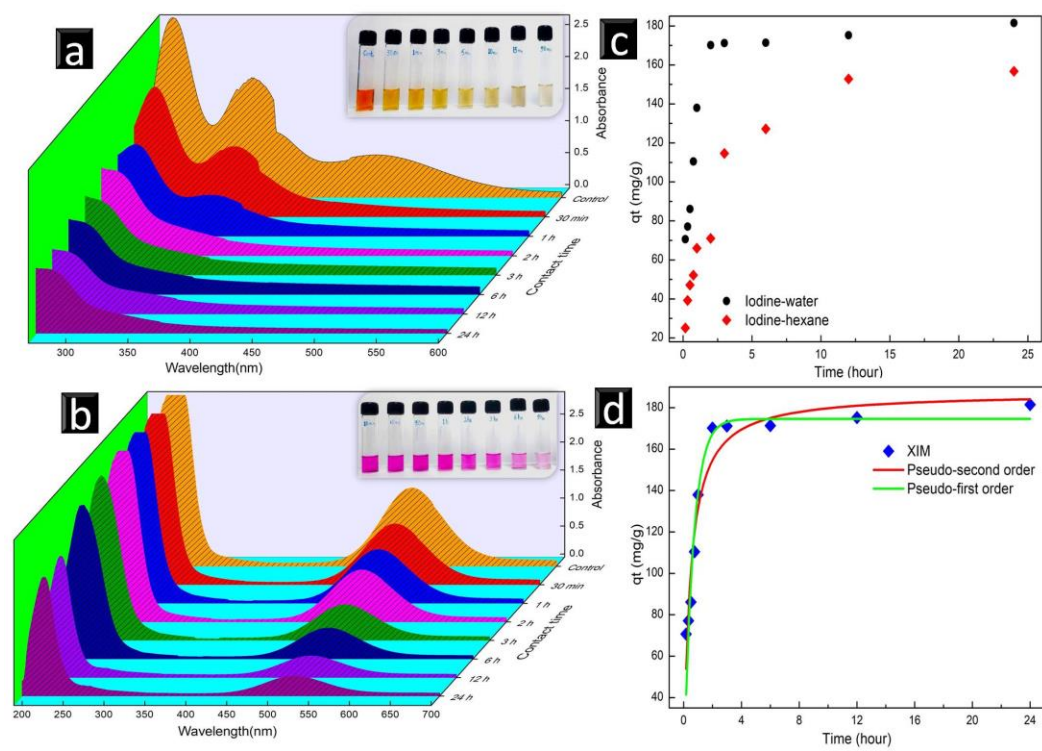


Figure 7

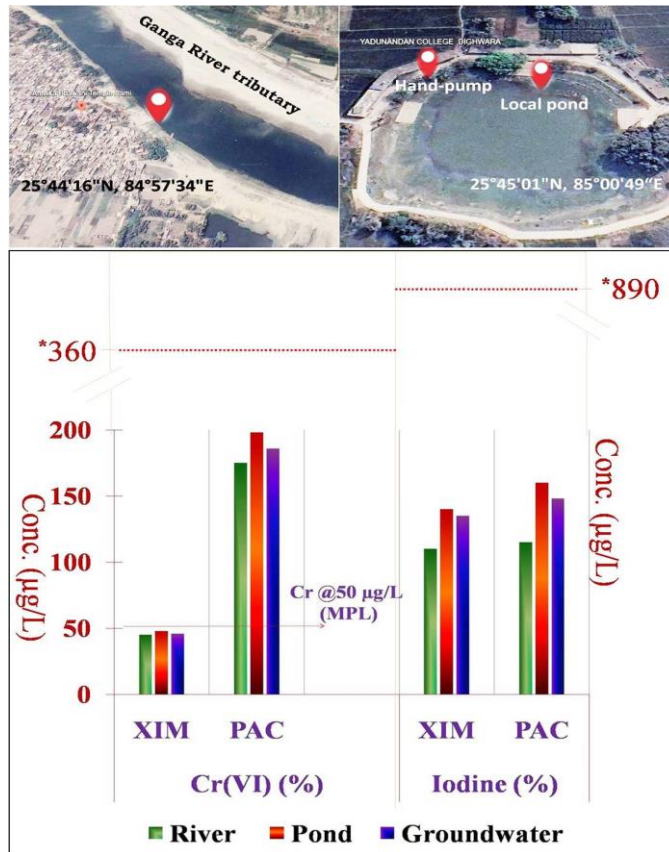


Figure 8

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