

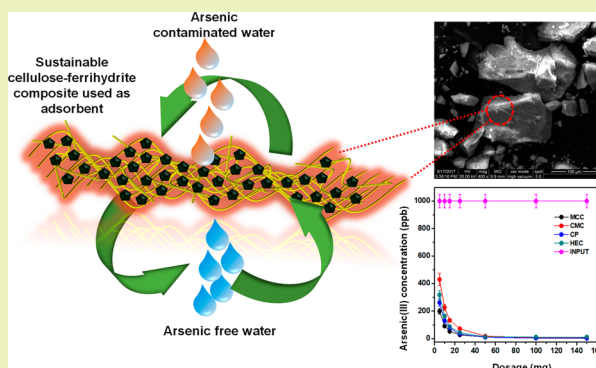
Sustainable and Affordable Composites Built Using Microstructures Performing Better than Nanostructures for Arsenic Removal

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S Supporting Information

ABSTRACT: Arsenicosis was recognized over 104 years ago. Elevated arsenic (As) concentrations in water is faced by about 200 million people worldwide and has become one of the biggest challenges in the context of water purification. Providing sustainable and affordable solutions to tackle this menace is a need of the hour. Adsorption on advanced materials is increasingly being recognized as a potential solution. Here, we report various functionalized microcellulose-reinforced 2-line ferrihydrite composites which show outstanding As(III) and As(V) adsorption capacities. Green synthesis of the composite yields granular media with high mechanical strength which show faster adsorption kinetics in a wide pH range, irrespective of the presence of other interfering ions in water. The composites and their interaction with As(III) and As(V) were studied by XRD, HRTEM, SEM, XPS, Raman, TG, and IR spectroscopy. Performance of the media in the form of cartridge reaffirms its utility for point-of-use water purification. We show that cellulose microstructures are more efficient than corresponding nanostructures for the purpose of arsenic remediation. We have also performed an evaluation of several sustainability metrics to understand the “greenness” of the composite and its manufacturing process.

KEYWORDS: Arsenic, Cellulose, Nanocomposite, Ferrihydrite, Adsorption, Sustainability metrics



INTRODUCTION

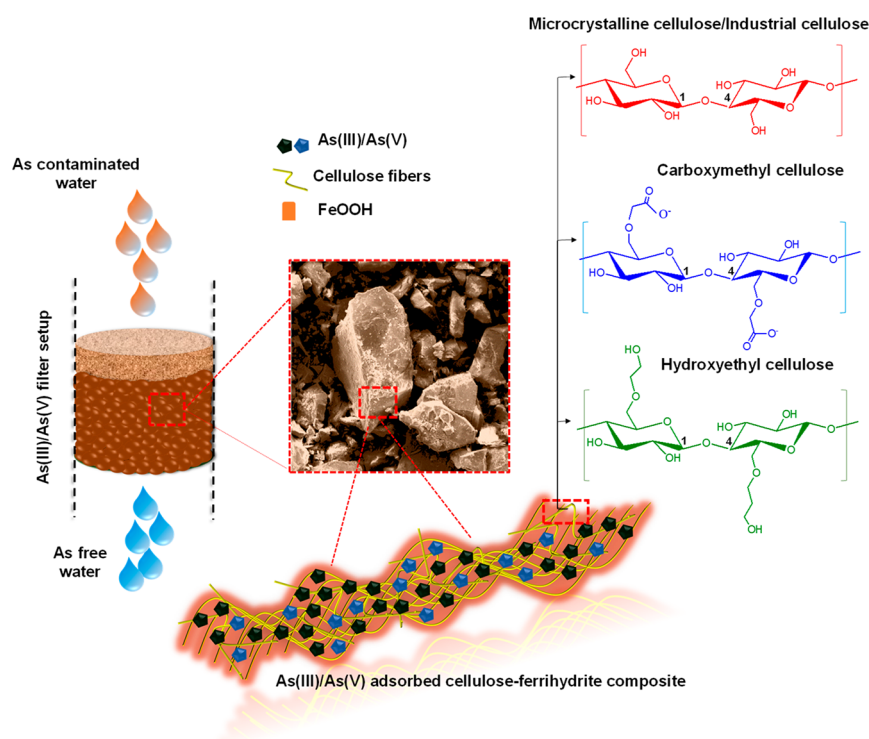
Arsenic (As), a ubiquitous metalloid occurring across the biosphere (air, soils and rocks, natural waters, and organisms), ranks 20th in the Earth's crust, 14th in seawater, and 12th in the human body in abundance.^{1,2} Despite its wide range of utilities in the field of medicine, agriculture, semiconductors, electronics, and metallurgy, As got its reputation as the “king of poisons” as a result of its very high toxicity and easy availability.^{3–5} In the natural environment, As is rarely found as the free element but rather in the form of metal arsenites/arsenates or as a part of sulfidic ores (e.g., realgar, orpiment).⁶ Mobilization of natural As to groundwater can occur through a combination of natural processes (like volcanic eruption, weathering) and/or anthropogenic activities (like mining, various industrial and agricultural activities).^{7,8} The wide impact of As contamination in drinking water and the threat it poses to global health is much more widespread than previously estimated.⁹ Arsenic gets ingested mostly through water and also through food.¹⁰ It principally exists in the +3 and +5 oxidation states in water, common species being arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) and their protonated forms, commonly referred to as As(III) and As(V), while the free element As(0) is rarely found naturally.² The species existing at pH 7 are H_3AsO_3 , $\text{H}_2\text{AsO}_4^{1-}$, and HAsO_4^{2-} . It is

now well recognized that accumulation of As, even at low levels, leads to carcinogenesis and severe dermal hazards like keratosis and neurological disorders.^{4,9,11,12} Greater than 200 million people belonging to more than 40 countries worldwide are exposed to concentrations in drinking water exceeding the World Health Organization (WHO) recommended limit of 10 $\mu\text{g/L}$.¹³ Solubility of As in groundwater is influenced by pH, speciation, redox conditions, temperature, and composition of the solution which in turn are governed by geology, climate, drainage, and topography. Desorption and dissolution are two important chemical processes that lead to As mobilization under two different physicochemical conditions. Poorly flushed aquifers having high sulfate and organic content creating highly reducing anaerobic environment are expected to present As in its reduced state, As(III), predominantly, while in alkaline aquifers in arid-to-semiarid climates, As is relatively soluble in its oxidized state, As(V).^{2,7} In general, inorganic arsenicals are more toxic than organic ones, and As(III) is 25–60 times more toxic than As(V).¹⁴

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Scheme 1. Illustration of Cellulose-Templated 2-Line Ferrihydrite Composite Used for Affordable Arsenic Removal from Water^a

^aEach of the celluloses were used in making of composites separately.

Several remediation technologies have come up which follow various kinds of approaches like concentration and subsequent removal, dilution and dispersion, conversion to less toxic species, or encapsulation.¹⁵ The most common technologies used previously for As removal have been coagulation with metal salts, lime softening, oxidation techniques, and iron/manganese-based removal processes.¹⁶ These techniques gradually lost their popularity due to their enhanced activity only at higher concentrations of the contaminant and inability to achieve the revised reduced drinking water standards.¹⁷ Adsorption is one of the emerging techniques which has shown high efficiency toward As removal.¹⁸ Adsorption is a phenomenon mainly driven by van der Waals and electrostatic forces causing the contaminants (adsorbate molecules and ions) to attach to the surface of a solid material (adsorbent). Adsorbents like activated carbon, activated alumina, graphene, zerovalent iron filings, zeolites, agricultural/industrial wastes, and iron oxides/hydroxides have been extensively studied and tested.^{18–22} Nanomaterials are excellent candidates for water treatment applications due to the preferred characteristics such as large surface area, high specificity, high reactivity, and catalytic potential.^{23,24} Nanoscale iron oxides, titania- or zirconia-based nanomaterials, and other metal oxides (like CuO, MgO, etc.) show high removal efficiency and have been researched widely.^{25–30} It is recognized that low-cost and simple but effective technologies that can be deployed readily at a household or community level are important.^{27,31}

In this context, biopolymers which have the characteristics like nontoxicity, biocompatibility, biodegradability, multifunctionality, and availability of adsorption sites are important to be used as reinforcing agents for nanoparticles which would act as stabilizers and prevent their agglomeration or

disintegration.³² Chitosan has been studied extensively in the context of biosorbents due to its large numbers of hydroxyl and amino groups, making it chemically reactive and hydrophilic.^{32,33} But, from a sustainability viewpoint, we cannot ignore the fact that chitosan is extracted by deacetylation of chitin which is found in the exoskeleton of crustacean shells, making it not so cheap and environmentally less enduring.

In contrast, cellulose is a plant-derived biopolymer available in nature with the highest abundance. It is a polysaccharide consisting of a linear chain of several hundred to many thousands of $\beta(1 \rightarrow 4)$ -linked D-glucose units arranged in parallel and antiparallel fashion, with a huge number of hydroxyl groups making it reactive and modifiable, apart from being renewable and inexpensive.^{34,35} Microcrystalline cellulose (MCC) is porous, ~ 10 – $50 \mu\text{m}$ in diameter, having high cellulose content, with higher crystallinity, and is composed of aggregate bundles of multi-sized cellulose microfibrils that are strongly hydrogen bonded to each other in intra-chain and inter-chain bonding configurations.³⁶ These intrachain hydrogen bonds, mostly seen as $\text{O3-H}\cdots\text{O5}$ bonds and interchain hydrogen bonding network between the $(110)_{\text{triclinic}}$ and $(200)_{\text{monoclinic}}$ planes, make cellulose a relatively stable polymer and give the cellulose fibrils high axial stiffness.³⁷ A periodic arrangement of highly ordered (crystalline) structures and disordered (amorphous-like) regions of cellulose chains coexist within the cellulose microfibrils. These smaller crystalline regions contained within the cellulose microfibrils are extracted in the process of producing cellulose nanocrystals (CNCs). The extraction process of the cellulose particles from the cellulose microfibrils may include any pretreatments or disintegration processes either mechanically or chemically. CNC production by mechanical extraction causes increased mechanical damage

leading to lesser percent crystallinity (54–88%) than the parent microfibrils (80–85%) with irregular shape and size (shown in Figure S1).³⁶ Moreover, imparting additional particle functionalities on CNCs by creating surface charges gives rise to interfibrillar repulsion. Because of all these, MCC is a mechanically and thermally more stable cellulose system for making composites for adsorption-related applications.

In this research, we have introduced micron-sized functionalized cellulose fibers-templated 2-line ferrihydrite nanocomposite for As removal from drinking water (Scheme 1). Four kinds of cellulose precursors with various functionalities, namely, carboxymethyl cellulose (CMC), microcrystalline cellulose (MCC), hydroxyethyl cellulose (HEC), and industrial grade cellulose powder (CP), have been used for making the composites to check the consistency in their adsorption performance for As removal. The individual uptake capacities of each of these composites were compared to that of the nanocellulosic (NC) composite, developed earlier by the group.³⁸ The composites have been made by a green synthetic process, and all of them show large adsorption capacity for both As(III) as well as As(V) removal. Their stability, in terms of mechanical strength and leaching-resistant properties, over a long period of time suggests the effectiveness of their use as sustainable materials for affordable point-of-use water purifiers. We compared the performance of these microstructures with the corresponding nanostructures and conducted a cost–benefit analysis of their utilization.

EXPERIMENTAL SECTION

Materials. Three types of celluloses, CMC, MCC, and HEC, were purchased from Avantor Performance Materials India Ltd., SRL Pvt. Ltd. (India), and SD Fine Chemicals India Ltd., respectively, while the fourth, CP, was purchased from the local market. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), and sodium sulfate (Na_2SO_4) were purchased from RANKEM Glasswares and Chemicals Pvt. Ltd., India. Sodium arsenite (NaAsO_2) and disodium hydrogen arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from SD Fine Chemicals Ltd. All chemicals were of laboratory grade and were used without further purification. The porous filters were procured from local suppliers. The porous clay-based particulate and iron filter was developed by CSIR-Institute of Minerals and Materials Technology (IMMT), Bhubaneswar, India, and was purchased from Watsan Envirotech Private Limited, Chennai, India. Deionized (DI) water was used throughout the experiments unless otherwise mentioned.

Methods: Synthesis of Cellulosic Composites. Cellulose-templated 2-line ferrihydrite composites were synthesized by a green synthetic route. About 0.05 g of CMC was dissolved in 10 mL of water and sonicated for about 10 min to make it a homogeneous dispersion. The pH was adjusted to 9 by using 0.2 M NaOH. After 5 min of stirring, 0.5 g of Na_2SO_4 was added, followed by another 5 min of incubation after which 10 mL of 1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added. The mixture was precipitated and brought to pH 8 using 2 M NaOH by dropwise addition. The final reaction mixture was further kept for incubation for about 12 h at ambient temperature. The resulting gel was washed with water to remove soluble salts and was dried at room temperature (around 30 °C). The composite was insoluble in water and appeared like dark brown shiny crystals. The dried solid chunks were crushed mechanically and sieved to get the granular adsorbent media. The product obtained was about 1.2 g.

Similar composites were prepared by changing the cellulose type and keeping the proportions of other reagents and conditions the same. The resulting composites were referred to as CMCFH, MCCFH, HECFH, and CPFH for the precursors CMC, MCC, HEC, and CP, respectively, where the last two letters in the former set (FH) refer to ferrihydrite. The nanocellulose–ferrihydrite composite was referred as NCFH.

Batch Adsorption Studies. In a typical batch adsorption experiment, 25 mg of the granular media was shaken with 100 mL of As(III)/As(V) spiked distilled water of 1 mg/L concentration. The water sample was collected to measure the leftover As concentration in treated water as a function of time, using inductively coupled plasma mass spectrometry (ICPMS) after acidification with 5% HNO_3 .

pH Effect. To know the pH effect on As adsorption, 25 mg of granular media was added to 25 mL of As(III)/As(V) spiked water, adjusted to the required pH by 1 M HCl/1 M NaOH, and shaken for 3 h. The treated water sample was analyzed by ICPMS.

Interfering Ions. To understand the effect of interfering ions on As adsorption, the ions of interest which generally exist in groundwater, like calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), chloride (Cl^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), nitrate (NO_3^-), silicate (SiO_3^{2-}), sulfate (SO_4^{2-}), fluoride (F^-), and phosphate (PO_4^{3-}), were spiked in 25 mL of distilled water in separate conical flasks, with concentrations relevant to groundwater. This water was treated with 25 mg of CMCFH for 3 h, and ICPMS measurements were conducted. The relevant water quality parameters are listed in Table S1, Supporting Information.

The maximum uptake of As (q_e) by cellulosic composites was calculated using eq 1 in the Supporting Information.

Details of instrumentation are presented in the Supporting Information.

RESULTS AND DISCUSSION

Characterization of CMCFH, before and after As Uptake. Figure 1A illustrates the TEM image of the granular CMCFH composite at 0.2 μm scale where homogeneously sized iron oxyhydroxide nanoparticles are embedded in the CMC matrix, confirming composite formation. The structure is largely amorphous. Iron oxyhydroxide nanoparticles are not prominently visible in the large area image due to their small

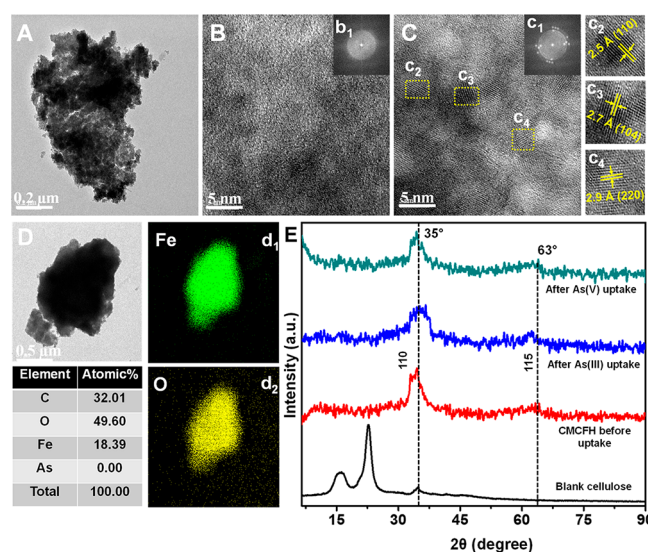


Figure 1. (A) TEM of a CMCFH aggregate. (B) HRTEM of CMCFH along with a fast Fourier-transform of the image (inset b₁). The material is largely amorphous. (C) Beam-induced crystallization of CMCFH showing crystalline regions along with a fast Fourier-transform of the image (inset c₁) and lattice-resolved images (insets c₂, c₃, and c₄) showing various crystallographic planes of CMCFH. (D) TEM image, elemental mapping images of Fe and O, respectively, of the initial CMCFH composite before As adsorption (d₁ and d₂) and their corresponding atomic compositions (C, O, and Fe). (E) Powder XRD patterns of blank cellulose, CMCFH before As adsorption and after As(III), and As(V) adsorption (bottom to top).

size but are present only within the cellulose nanoarchitecture. This analysis is further supported by the determination of surface area (BET isotherm by N_2 adsorption). The specific surface area of parent CMC was $2.44 \text{ m}^2/\text{g}$ while that of the composite was $173.31 \text{ m}^2/\text{g}$ with average pore diameter of $15.51 \text{ \AA}$. The large increase in surface area is attributed to the confinement of nanoscale iron oxyhydroxide particles in the cellulose matrix which is also responsible for superior As removal performance.³⁸ To specify the type of iron oxyhydroxide, X-ray diffraction was carried out which gives peaks at 35° (110) and 63° (115), confirming the 2-line ferrihydrite structure.³⁹ The small grain size of ferrihydrite and its relatively poor crystallinity witnessed in the composites even after As(III) and As(V) adsorption overshadow the slight crystalline nature of blank cellulose before the composite formation. The slight shift in the broad hump at 63° after As(III) adsorption indicated very strong affinity of ferrihydrite toward As(III), which is also evident from adsorption capacities and EDS values. Figure 1B clearly shows the amorphous nature of the composite in ambient conditions at 5 nm scale, with the corresponding fast Fourier-transform (FFT) pattern shown in inset b1. Beam irradiation for a few minutes gives rise to small crystalline domains (Figure 1C) upon gradual conversion of ferrihydrite to hematite (more stable form).^{40–43} These nanoscale crystalline features of the irradiated material are shown by HRTEM in the lattice-resolved images of c_2 , c_3 , and c_4 , where the lattice planes of hematite are observed. The elemental composition of CMCFH has been obtained by TEM-EDS, and mapping is shown in Figure 1D, d_1 and d_2 , which show that O and Fe are the major constituents of the composite apart from carbon present in cellulose. Excess percentage of carbon may be due to the contribution from the grid.

To investigate the morphology of the CMCFH nanocomposite, SEM images of the parent CMC fibers, CMCFH before, and after As(III) and As(V) adsorption were studied (Figure 2A–D). While the parent CMC powder showed

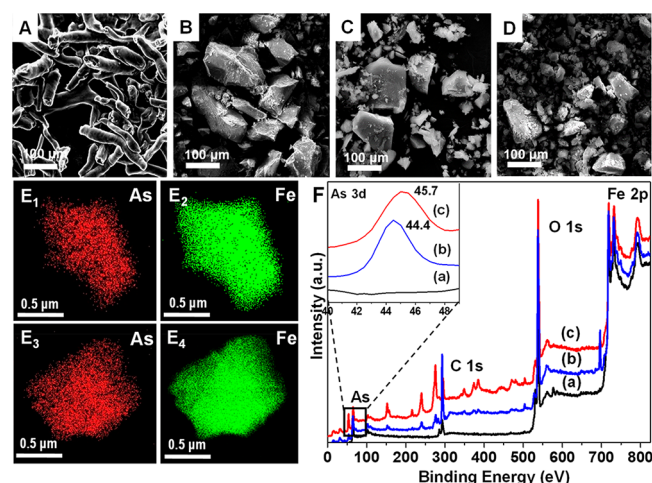


Figure 2. (A) SEM of the parent CMC fibers. (B), (C), and (D) SEM of CMCFH before, after As(III), and after As(V) adsorption, respectively. E₁, E₂, E₃, and E₄ show the EDS elemental mapping of As and Fe of CMCFH after As(III) (E₁, E₂) and As(V) (E₃, E₄) adsorption, respectively. (F) XPS survey spectra of (a) CMCFH before, (b) after As(V), and (c) after As(III) adsorption (bottom to top). Features in the As 3d region for these cases are expanded in the inset.

smooth fiberlike branched structures with cracks and visible openings, the composite showed entirely different granular structures, which resulted in a particle size in the range of 50–100 μm . No change in particle morphology was observed upon exposure to various As concentrated solutions which implies that the process of interaction is adsorption. This also implies that the composite possesses very good mechanical strength, which was confirmed by shear stress measurements in dry and wet conditions, shown in Figure S2. For the composite to be suitable in a water purification cartridge, it is important to ensure that it possesses satisfactory wet strength to retain its granular composition so that excessive pressure drop is avoided. Direct shear tests were conducted at various normal stresses to find the shear strength of the granular media. Straight-line approximation of the Mohr–Coulomb failure pattern shown in Figure S3 gave the angle of internal friction (Φ) to be 38.32° and 39.35° for dry and wet media, respectively, showing that the shear strength of prepared granular material is comparable to that of the Indian standard Ennore sand (in the range of 35 – 40° for Φ).⁴⁴ The elemental mapping shown in Figure 2E₁–E₄ illustrates the uniform distribution of As(III) and As(V) over the surface of CMCFH composite upon adsorption.

The components of CMCFH and their interaction with As were also studied by X-ray photoelectron spectroscopy (XPS) as shown by the survey spectra in Figure 2F. The peaks obtained for adsorbed As(III) and As(V) correspond to the uptake during batch studies where it was observed that As(III) had higher tendency to get adsorbed on CMCFH than As(V). This was also confirmed by the TEM-EDS values shown in Figure S4.

Figure 3A shows the deconvoluted XPS spectra of C 1s, As 3d, Fe 2p, and O 1s of the parent CMCFH and after its interaction with As. The XPS spectrum of C 1s shows a characteristic peak at 284.8 eV for CMCFH which did not show any change after its interaction with As(III) and As(V). Peaks at 286.7 and 288.5 eV denote the presence of hydroxyl C–OH and carboxyl (C=O) bonds in the composite which come from cellulose. The XPS peaks corresponding to As(III) and As(V) standards appeared at 43.9 and 44.5 eV, which showed significant shift toward higher binding energies of 44.5 and 45.7 eV, respectively, after adsorption on CMCFH, suggesting that the adsorption process involves the oxidation of the As(III) species to higher oxidation states or leading to increased stabilization.⁴⁵ The shift in As(V) XPS spectra to higher binding energy can be due to the interaction of the electron-rich free arsenate ion with the ferrihydrite group leading to complexation, which may result in reduced availability of electrons in the As center and shortening of As–O bonds. Absence of shift in binding energy for Fe 2p confirms that there is no change in the oxidation state of Fe^{3+} of ferrihydrite which shows its characteristic $\text{Fe}^{3+}\text{–O}^{2-}$ peak at 709.3 eV. This suggests that the As uptake by CMCFH can occur by way of physisorption or by ligand exchange mechanism.⁴⁶ There is a slight shift toward lower binding energy in the case of O 1s for the adsorbed samples, when compared to unadsorbed CMCFH. Appearance of additional peaks at 531.9 and 531.8 eV in As(III) and As(V) adsorbed samples may be due to As–O bond formation with hydroxyl groups of cellulose.

The adsorption of As species over CMCFH was further studied by Raman spectroscopy as illustrated in Figure 3B. The Raman spectrum of an aqueous solution As(III) standard at

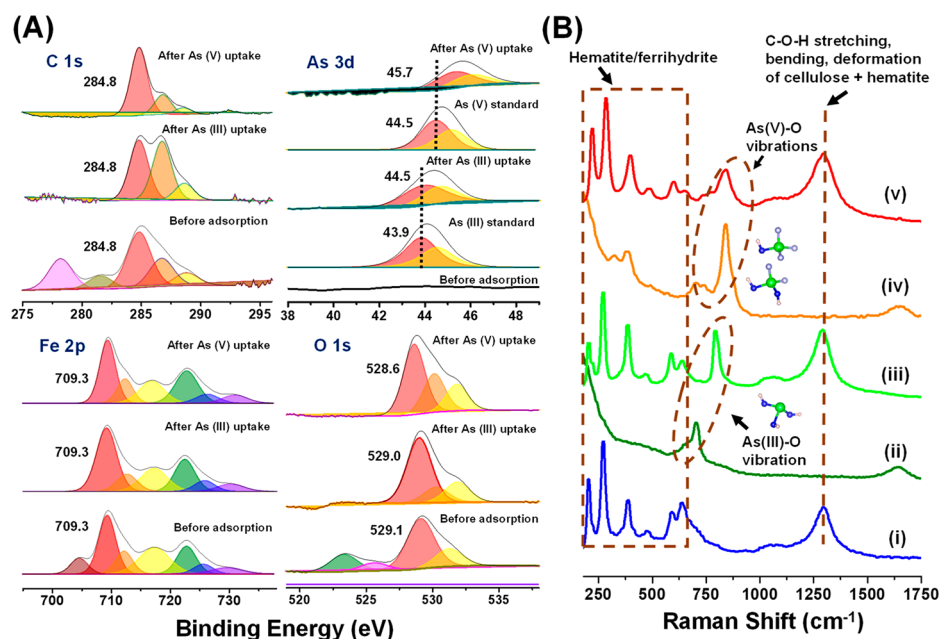


Figure 3. (A) Deconvoluted XPS spectra of C 1s, Fe 2p, O 1s, and As 3d regions of CMCFH before and after As(III) and As(V) adsorption (bottom to top). As 3d data are compared with the standards. (B) Raman spectra of (i) CMCFH solid, (iii) and (v) CMCFH before and after As(III) and As(V) adsorption, respectively; (ii) and (iv) the standard aqueous solutions of As(III) and As(V) at pH 7, respectively. Specific features are labeled. Data have been fitted with their components.

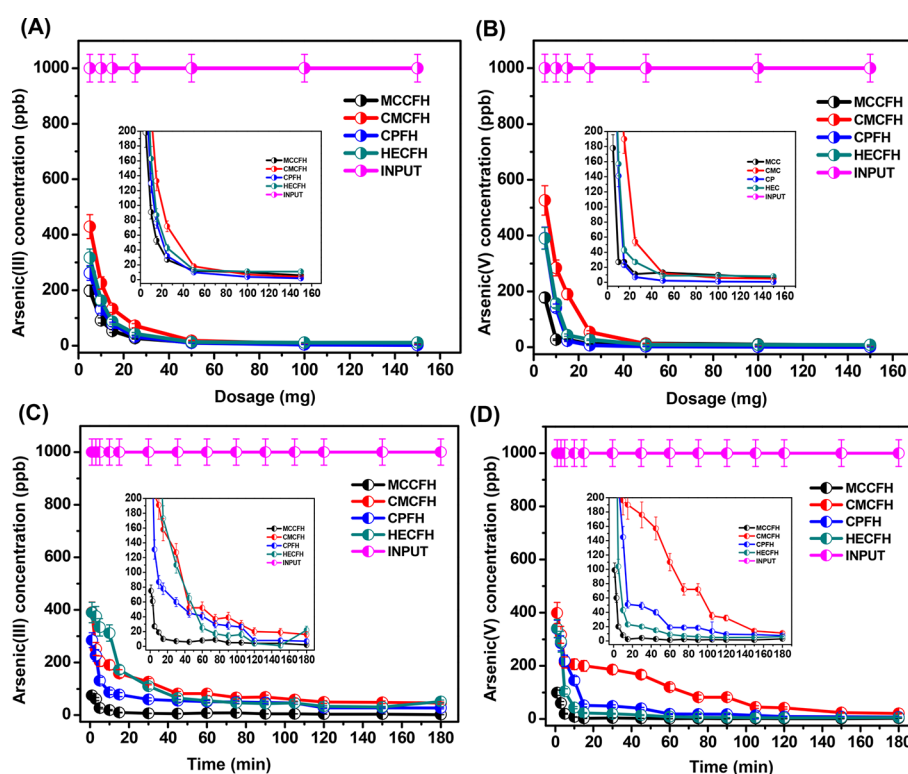


Figure 4. Batch study of the comparison of As removal performance of composites made of MCC, CMC, CP, and HEC; residual arsenite (A) and arsenate (B) concentrations as a function of dosage of composites; residual (C) arsenite and (D) arsenate concentrations as a function of contact time with the composites. Insets in each figure show the magnified images in low concentration region, for clarity.

pH 7 gave a characteristic peak due to the A_1 mode of H_3AsO_3 (C_{3v} symmetry) at 703 cm^{-1} , while after its adsorption on CMCFH, the peak of interest corresponding to As(III)-O vibrations was shifted to 789 cm^{-1} . In the case of As(V) adsorption, the characteristic peak corresponding to As(V)=O symmetric stretching vibrations of $H_2AsO_4^{1-}$ and $HAsO_4^{2-}$

species at 838 cm^{-1} was shifted to 842 cm^{-1} in the adsorbed sample. A weak peak at 588 cm^{-1} and a hump at 1050 cm^{-1} are due to ferrihydrite ($FeOOH$), while the sharp peaks at 202, 272, 391, and 637 cm^{-1} are due to the characteristic Raman features of hematite ($\alpha\text{-Fe}_2\text{O}_3$), which were also observed in the Raman spectra of CMCFH in each case. This suggests

thermal transformation of ferrihydrite to more stable hematite (through the maghemite phase, with a peak at 1293 cm⁻¹) with increasing laser power.^{47,48} This transformation has been confirmed by the XRD pattern of CMCFH, after annealing at 900 °C, shown in Figure S5.⁴⁹ The broad peak around 1300 cm⁻¹ also contains stretching and bending frequencies of C–O–H bonds of the cellulose skeleton.

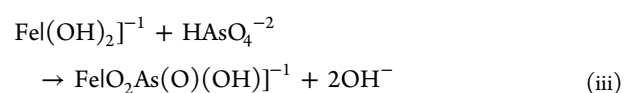
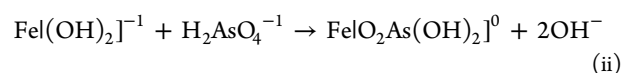
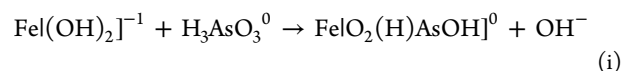
Infrared spectroscopic investigation also provides qualitative insight regarding the As uptake by the composite as shown in Figure S6. Ferrihydrite mainly interacts with the hydroxyl groups of cellulose, which gives the 1420 cm⁻¹ peak attributed to free –OH bending vibrations of parent cellulose. This gets shifted to 1385 cm⁻¹ in the composite. The appearance of a distinct peak at 613 cm⁻¹ in the composite due to ferrihydrite, over the broad feature around 600 cm⁻¹ in the parent cellulose, assigned to H-bonding of free hydroxyl groups, indicates the interaction between the two. Apart from the characteristic cellulosic peaks shown by CMCFH alone at 3430 (–OH stretching), 2920 (C–H asymmetric stretching and tensile vibration in the pyranoid ring), 1387 (–OH bending), and 1058 cm⁻¹ (asymmetric C–O–C vibration), As–O stretching peaks were also shown at 785 and 1122 cm⁻¹ by pristine NaAsO₂. These latter features were red-shifted to 790 and 1211 cm⁻¹ after As(III) adsorption on CMCFH. Similarly, Na₂HAsO₄·7H₂O shows peaks at 814 and 1109 cm⁻¹ due to As–O stretching vibrations, which were also red-shifted to 825 and 1163 cm⁻¹ after interaction with the composite.⁵⁰

Batch Studies of As Adsorption on Cellulosic Composites. Figure 4 represents the comparative performance of various composites prepared with MCC, CMC, HEC, and CP from batch studies, as reported for As(III) and As(V) adsorption, separately. It is observed that MCCFH nano-composite exhibited superior performance where 100 mL of 1 mg/L As spiked water was treated with different dosages of adsorbent composites ranging from 5 to 150 mg, as shown in Figure 4A and B for As(III) and As(V), respectively. Less than 50 mg of any composite is sufficient for bringing down the As concentration below 10 µg/L in 100 mL of water within 3 h of exposure time.

Figure 4C and D show the fast uptake kinetics of the composites where initial 1 mg/L concentration of As(III) and As(V), respectively, was rapidly reduced to 100 µg/L within 60 min of incubation, by virtue of availability of maximum number of free surface sites. At the end of 3 h, the residual concentration of As(III) and As(V) decreased further to 10 µg/L, following a relatively slower kinetics, due to high surface coverage. In order to understand the system better, the kinetic data were initially analyzed using two reaction models: Lagergren's pseudo-first-order and Ho's pseudo-second-order.⁵¹ Mathematical representations of these models and the kinetic plots generated by them are given in the Supporting Information (Figures S7 and S8). The kinetic parameters obtained from these model fits are summarized in Table 1. The plots of t/q_t against time for adsorption of arsenite and arsenate followed the pseudo-second-order model with the values of the correlation coefficients close to 1 (>0.997), indicating that the availability of number of surface sites for adsorption also plays an important role in overall rate determination. This also suggests that the adsorption of As(III) and As(V) may be occurring in a ligand exchange fashion on the ferrihydrite. At pH ≥ 7, the following equations may be contributing to the overall rate of adsorption.⁵²

Table 1. Estimated Pseudo-First-Order and Second-Order Kinetic Parameters for the Adsorption of As(III) and As(V) by CMCFH

Species	Model	k (1/h) or (g/mg h)	q_e (mg/g)	R^2
As(III)	pseudo 1st order	0.0214	3.838	0.9381
As(V)	pseudo 1st order	0.0205	3.946	0.9667
As(III)	pseudo 2nd order	0.4535	3.838	0.9998
As(V)	pseudo 2nd order	0.3965	3.946	0.9979



(The symbol “ $]$ ” as in $\text{Fe}(\text{OH})_2]^{-1}$ used in the chemical equations denote a surface bidentate complex of ferrihydrite.)

The reactions suggest that complexation with iron oxy-hydroxides was driven by the ligand exchange mechanism, which led to the formation of Fe–O–As bonds at neutral pH. As the ferrihydrite composite is exposed to water, it acquires more hydroxyl groups accessible to As species. Two kinds of adsorption geometries are possible in this case.^{53,54} 1. Physical adsorption which occurs due to physical interaction of the As species with the surface groups by means of hydrogen bonding, leading to outer sphere complexes. 2. Chemical adsorption of As species to ferrihydrite groups leading to more stable inner sphere complexes. Different kinds of inner sphere complexes are monodentate mononuclear, bidentate binuclear corner sharing, and bidentate mononuclear/binuclear edge sharing. Transformation of outer sphere complex to inner sphere complex is often observed depending upon the pH of the solution.⁴⁶ The stabilities of the complexes are in the following order: bidentate binuclear ($>(\text{FeO})_2\text{AsOH}$) > monodentate mononuclear ($>(\text{FeO})-\text{As}(\text{OH})_2$) > physical adsorption. Moreover, to have further insight into the mechanism, various isotherm models like Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) were evaluated (Figure S9).^{55,56} While Freundlich showed correlation coefficient (R^2) of 0.90, which is lower than the obtained R^2 value of Langmuir fit, D–R isotherm yielded adsorption energy (E) value of 3162 kJ/mol. The large E value and higher correlation with Langmuir isotherm suggest a dominant chemisorption pathway for the As species.

The uptake performance shown by MCCFH in the batch studies was the best among the four composites, attributed to the finer crystalline structure of MCC, as compared to other forms. The uptake efficiencies of the composites prepared by different kinds of celluloses were also tested under different pH conditions. All the composites were found to be working with excellent efficiency in a broad pH region of pH 4–10, as shown in Figure 5A and B. Analysis of the histograms give us insight regarding the possible reasons behind CMCFH showing relatively lesser As(V) uptake than other cellulosic composites in higher pH conditions, like pH 10. To understand this further, zeta potentials of aqueous As(V) solutions at pH 5 and 9 using buffers were studied. As the pH condition was shifted from lower to higher, zeta potential varied from +14 mV (pH

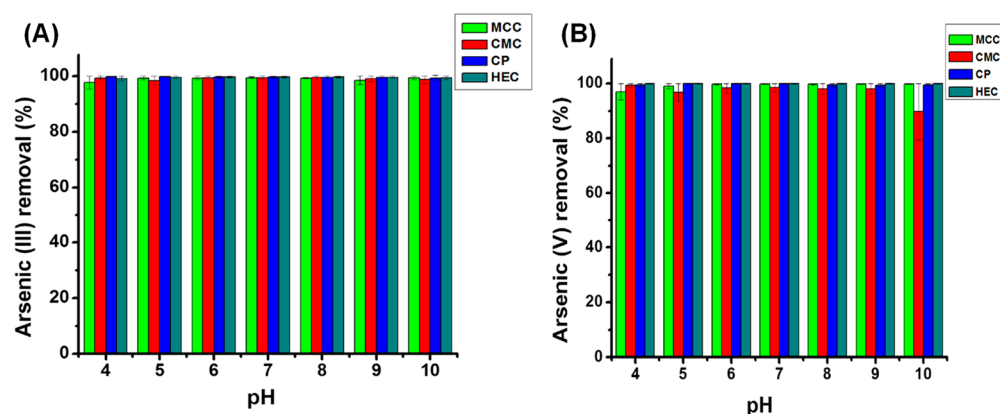


Figure 5. Batch study of the comparison of As removal performance of composites made of MCC, CMC, CP, and HEC for (A) arsenite and (B) arsenate removal over a pH window of 4–10.

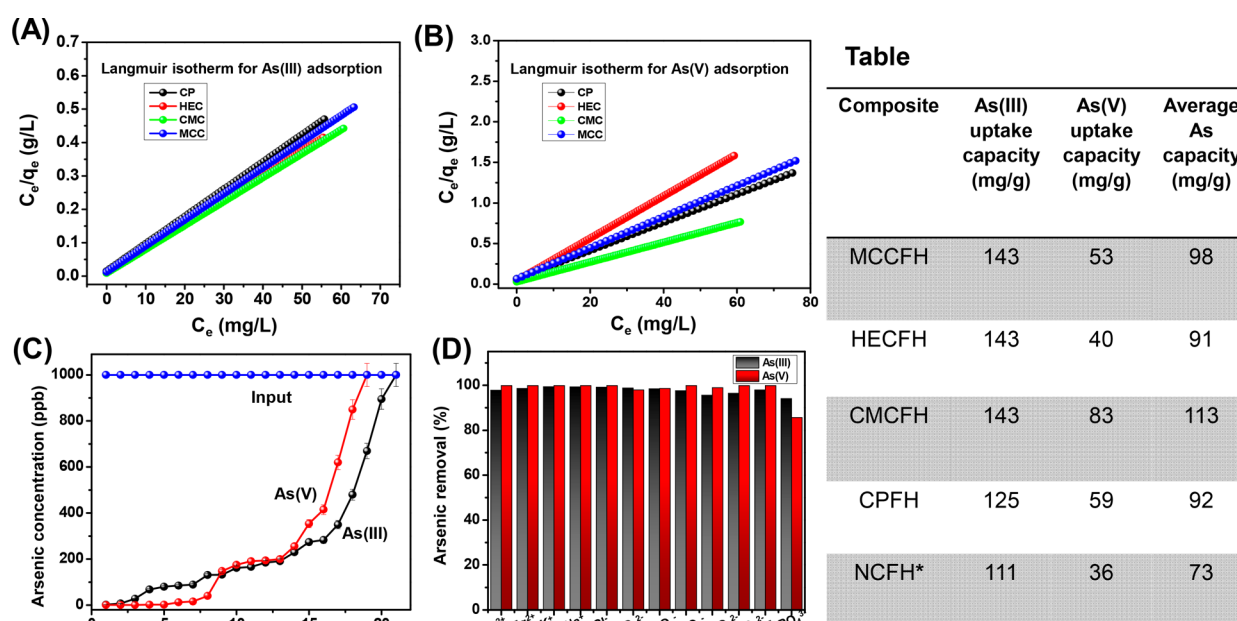


Figure 6. Langmuir adsorption isotherms of various composites prepared by MCC, CMC, CP, and HEC for the comparison of maximum uptake capacities of (A) As(III) and (B) As(V). (C) Batch adsorption studies for number of cycles of As(III) and As(V) adsorption by CMCFH. (D) Uptake of As(III) and As(V) in the presence of other competing ions (cations and anions) which are generally present in groundwater by CMCFH; table shows the As uptake capacities of various composites. *Data from ref 38.

5) to -22 mV (pH 9). Due to the presence of the anionic carboxylate (COO^-) group on CMC skeleton at higher pH and the overall negative surface charge on the solid composite, CMCFH particles experience greater electrostatic repulsion from HAsO_4^{2-} , which is the species existing for As(V) at pH 10. This is responsible for lower As(V) adsorption in alkaline medium.⁵⁷

To investigate the maximum adsorption capacity, a series of arsenite and arsenate solutions with initial As concentration from 1 to 200 mg/L were shaken with the composite CMCFH for 24 h at neutral pH. To account for the effect of equilibrium concentration on the adsorption capacity, evaluation was done with the Langmuir isotherm model.⁵⁸ The model assumes that localized adsorption occurs at specific homogeneous adsorption sites on the surface of the adsorbent with no lateral interaction between the adsorbed species giving rise to a saturated monolayer at equilibrium. The plots of C_e/q_e versus C_e give straight lines using the linearized form of the Langmuir

equation (Supporting Information, eq 2) for various composites, as shown in Figure 6A and B. The values of q_{max} and b can be calculated from the slope and intercept of the plots, respectively. The maximum adsorption capacities for all the composites made of microstructural celluloses were calculated and compared to that of nanocrystalline cellulose templated FeOOH composite (NCFH),³⁸ as shown in the table. A linear plot of C_e/q_e versus C_e along with a high value of correlation coefficient, i.e., $R^2 > 0.99$ in each case, indicates that the Langmuir isotherm provides a better fit of the equilibrium data. CMCFH was observed to have the highest average As uptake capacity of 113 mg/g, higher in comparison to other composites, while NCFH showed the lowest adsorption capacity. The higher capacity of microstructured materials over nanostructured materials is unconventional and nonobvious as nanostructured materials are considered superior in the field of adsorption, catalysis, etc., and the origin of this needs architectural investigation. Figure 6C

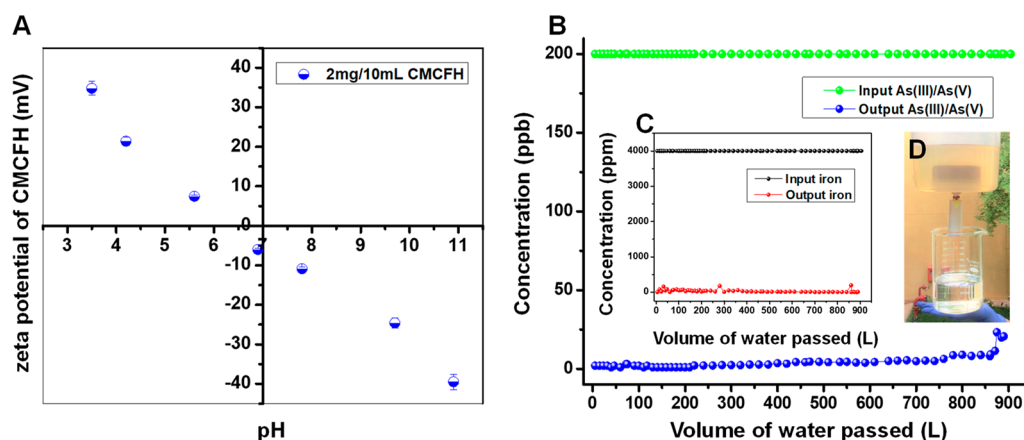


Figure 7. (A) Zeta potential vs pH (pH window 3–11) for CMCFH particles in water (2 mg in 10 mL). (B) As concentration in the water using a 40 g cartridge with the input of 200 $\mu\text{g/L}$ As(III)/As(V) and 4 mg/L 1:1 $\text{Fe}^{2+}/\text{Fe}^{3+}$ mixture. (C) Iron output for the same input. (D) Photograph of the setup used for filtration containing arsenic and iron contaminated water using a cartridge comprised of CMCFH, along with a porous clay prefilter.

illustrates the reuse performance of the CMCFH composite by batch adsorption, as a function of number of cycles. The material was not desorbed, but each time the material was recovered by centrifugation to prevent any weight loss. CMCFH can be reused for greater number of cycles for As(III) removal than As(V) which is in agreement with its higher As(III) uptake than As(V), also shown by SEM-EDS and elemental mapping (Figure S11).

To understand this preference in adsorption, we need to consider the speciation of arsenite and arsenate in water according to varying pH conditions. Depending on the pH, predominant species of arsenate existing in water medium are as follows: H_3AsO_4 (pH < 2), $\text{H}_2\text{AsO}_4^{1-}$ (pH 2–7), HAsO_4^{2-} (pH 7–11), and AsO_4^{3-} (pH > 12), while those of arsenite are H_3AsO_3 (pH < 9), $\text{H}_2\text{AsO}_3^{1-}$ (pH 9–12), HAsO_3^{2-} (pH 12–13), and AsO_3^{3-} (pH > 13), respectively. Also, the change in the surface charge of CMCFH particles according to pH variation was studied by zeta potential measurements, shown in Figure 7A. It suggests that the particles possess an overall negative surface charge at pH ≥ 7 . Thus, pH is a key factor which influences the speciation of As in solution and the surface charge of the solid particles significantly. Since most of the adsorption procedures were carried out at pH 7 or greater, As(III) species are neutral as compared to negatively charged As(V) species and they do not exhibit as much repulsion, and as a result, As(III) was adsorbed in greater amount by CMCFH at pH 7 and also in a wide pH range. This justification can also be supported by the fact that points of zero charge (PZCs) of iron oxides occur in the pH range 6–8. Hence, the surface of CMCFH particles are expected to be positively charged when the equilibrium pH values are below pH_{PZC} , but the positively charged sites are expected to decrease with increasing pH, making electrostatic interaction with various As species, an important factor explaining higher As(III) removal than As(V).⁵⁸

One of the unique advantages associated with the use of CMCFH as an active adsorbent is that it does not show any significant drop in the performance of As(III) and As(V) removal even when used with water spiked with other interfering ions like calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), chloride (Cl^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), nitrate (NO_3^-), silicate (SiO_3^{2-}), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), and fluoride

(F^-) with concentrations relevant to tap water. The removal % of As was calculated using the equation mentioned (eq 3, Supporting Information). While a slight decrease in As(III) uptake (maximum decrease up to 95%) was witnessed in the presence of anions like NO_3^- , HCO_3^- , SiO_3^{2-} , and SO_4^{2-} , As(V) uptake was fairly consistent (maximum decrease up to 98%) in the presence of most potential interfering ions, as shown in Figure 6D. Interference by phosphate is seen as it competes with arsenate to get adsorbed. Cations hardly showed any effect on the adsorption behavior of CMCFH.⁵⁹ Other cellulosic composites (MCCFH, HECFH, and CPFH) also show high As removal efficiency ($\geq 95\%$) in the presence of interfering ions in water as shown in Figure S10.

The toxicity characteristic leaching protocol (TCLP) studies as per the USEPA standard SW-846 Test Method 1311 were conducted using the saturated composite CMCFH to know the possible leaching of adsorbed As. The test showed a leaching of 2.2 mg/L. TCLP regulatory limit set by United States Environmental Protection Agency (USEPA) for As is 5.0 mg/L. For cellulose, the total organic carbon (TOC) detected in the leachate was 1.6 mg/L, while the acceptable USEPA limit for TOC in drinking water is 4.0 mg/L. Deionized water showing a TOC of 0.3 mg/L was used for the experiments.

Thermal stability of CMCFH was checked by thermogravimetric analysis (TGA) in air and in nitrogen atmosphere (Figure S12). The composite loses 23.7% and 27.6% of its initial weight as it was heated from room temperature to 900 $^\circ\text{C}$ in air and nitrogen atmosphere, respectively. The composite begins to lose water loosely adhering to the interior and the exterior of its surface up to 100 $^\circ\text{C}$, which explains the initial weight loss. By the time the temperature reaches 250–300 $^\circ\text{C}$, major thermal degradation of the cellulosic skeleton takes place. Beyond 300 $^\circ\text{C}$, FeOOH starts getting converted to more stable forms of iron oxides after getting dehydrated yielding $\alpha\text{-Fe}_2\text{O}_3$ at a temperature between 600 and 750 $^\circ\text{C}$, from XRD analysis (Figure S5).^{60–62}

After the performance of the composites in batch experiments was evaluated, a prototype filter consisting of a water purification cartridge (diameter, 35 mm; height, 11 cm) along with an iron remover was developed as shown in Figure 7D. The experiment was done for iron and arsenic together as they coexist in natural environment in the affected regions. About

40 g of CMC FH (72 mesh) was packed, and a porous clay based particulate and iron filter was attached with it, assembled in an antigravity fashion. In Figure 7D, we show the prototype through which over 900 L of water was passed with a flow rate of 8–15 mL min⁻¹ under gravity. The input water contains 200 µg/L of a mixture of As(III) and As(V) in 1:1 ratio along with 4 mg/L of Fe, keeping the pH at 7.5. The output water samples were tested by ICPMS and were found to have total As and Fe levels well below the WHO permissible limits for drinking water as shown in Figure 7B and C, respectively.

Microstructures Perform Better than Nanostructures. As far as the performance and uptake capacity of a material are concerned, they depend not only upon the porosity and the surface area (responsible for physisorption) but also on the chemical functionalization of the material (facilitating chemisorption). In microcellulose fibers with diameter in the micrometer range, maximum available hydroxyl groups may be used for anchoring of ferrihydrite nanoparticles which act as the active adsorption sites, responsible for better interaction with the As species. Microcellulose is subjected to lesser pretreatment and extraction processes which keep the microfibrils more stable mechanically and chemically, as compared to cellulose nanocrystals (CNC). Thus, it gives rise to a more efficient, stable, and stronger composite showing better performance than CNC-based composites. These structural aspects are speculative at present as precise data on the composite structure are not available.

Economic Analysis. Arsenic affected population in India is around 70 million.⁶³ We are aware that the number will differ substantially depending on the tolerance limit chosen. We assumed that 10 L of clean water is needed for cooking and drinking per person per day. Assuming an average As concentration of 200 µg/L in the accessible water in the affected communities,⁴⁵ and assuming that all of them are served with this technology for As remediation, it is necessary to have 1.02 million kg of the composite having a removal capacity of 50 mg/g to remove 51100 kg of arsenic from 255.5 billion liters of drinking water needed for a year. The amount of cellulose required to produce this composite media is about 42.5 tons per year. We have considered a reduced adsorption capacity of 50 mg/g in field conditions although the measured capacity is 100 mg/g in the lab. Assuming industrial prices, this quantity of cellulose amounts to \$ 0.09 million. Current industrial production of cellulose in India is about 15 million tons, by paper and pulp industry alone. Since cellulose production and processing are integral parts of the paper and pulp, textile, food processing, and pharmaceutical industries, we can estimate the annual cellulose production by observing output capacities of the aforementioned industries. Hence our cellulose requirement as a raw material can be met easily. Other raw materials are also available in bulk. This evaluation suggests that arsenic menace in India can be handled affordably with such materials.

Preliminary Sustainability Assessment. This technology was assessed based on the economic and environmental aspects by qualitatively and quantitatively evaluating some of the relevant sustainability parameters to determine the extent of its “greenness”.^{64–66} The formulas referred to for calculating the sustainability metrics are listed as eqs 4–8, Supporting Information.

Raw Materials. Major raw materials include cellulose which is renewable and biodegradable. Processing of cellulose usually involves mechanical extrusion and chemical treatment by

strong acid/alkali. Those manufacturers who use mild processing techniques for lignocellulosic fibers should be preferred for supply of the raw material. Iron salts and alkali were used in less quantities which are nontoxic. Water was used as the solvent. The mass intensity (excluding water) was calculated to be 1.9, while the water intensity (W_p) came as 29.2. Reaction mass efficiency was 52%. The mass intensity can be brought down to 1 by avoiding loss of the composite during filtration and washing. The method of preparation of the composite is water positive by 2–3 orders of magnitude; i.e., it produces 700 L of clean water for every 1 L of water consumed for its production.

Energy Consumption. Electricity was used for stirring, vacuum filtration, and drying. No energy consumption was involved in the operation of the technology. Energy intensity was calculated to be 2.3 kW·h/kg of the composite, according to the lab-scale synthesis setup. The energy intensity can be reduced effectively by increasing the scale of production. Large-scale iron and steel and aluminum industries consume 10 and 15 kW·h/kg of product, respectively.^{67,68} However, our energy consumption value is comparable with microfibrillated cellulose manufacturing industries which have an average energy intensity about 2.8 kW·h/kg.⁶⁹

Resulting Emissions. No harmful solvents/fumes or side products were discharged during the synthesis of the composite. The *E* factor (environmental factor) was observed to be 0.3, indicating negligible amount of emission of harmful byproducts. The discharged water after washing containing salts can be largely recycled and reused by using a reverse osmosis setup (which will increase energy consumption by 0.8 kW·h/kg).

Toxicity Potential. As per European Chemicals Agency (ECHA), FeCl₃ and NaOH have been classified as skin sensitizer and corrosive, respectively. But they are nonflammable and stable at room temperature. FeCl₃ and NaOH show acute oral toxicity (LD50) at 900 and 280–680 mg/kg in mice, respectively. Manufacturing process therefore has to be undertaken with some simple precautionary measures.⁷⁰

Disposal of Waste. Arsenic-loaded composites were subjected to multiple regenerations for subsequent adsorption cycles by acid/base treatment. They could be finally disposed in leach-free landfills. TCLP suggests safe disposal of the adsorbent after saturation loading.

Affordability. This technology can provide arsenic and iron free water under \$ 0.3/1000 L of clear water.

CONCLUSIONS

We report a green method for preparing highly efficient and sustainable cellulose-based composites for the removal of As(III) and As(V) from drinking water. The 2-line ferrihydrite nanoparticles incorporated in the biopolymeric confinement of microcellulose act as active sites for As(III) and As(V) adsorption. TEM, SEM, and XPS studies ensure that the physical and chemical properties of CMC FH remain intact even after As exposure until saturation, while TCLP and TOC suggest it to be free from leaching. Moreover, the composite works equally well in a wide range of pH with fast kinetics of adsorption. The maximum adsorption capacity of CMC FH by batch studies was 143 and 83 mg/g for As(III) and As(V), respectively. The CMC FH packed cartridge showed arsenic removal (according to WHO standards) for about 1000 L of water with an average flow rate of 12 mL/min without any regeneration of material, confirming it to be an excellent

candidate for an industrially feasible and green material for delivering affordable water in As-affected communities worldwide. Lastly, evaluation of sustainability metrics provided further insights into the socio-economic benefits as well as environmental impact of the manufacturing process of the nanocomposite.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b05157.

Instrumentation; equations used in main text; SEM images of cellulose nanocrystals; plot of horizontal shear stress vs horizontal displacement of CMCFH; Mohr–Coulomb failure pattern (shear stress vs normal stress) of CMCFH; HRTEM and EDS of CMCFH after As(III) and As(V) adsorption; XRD of CMCFH annealed up to 900 °C; IR spectra of CMCFH before and after As(III)/As(V) adsorption, corresponding to IR of As standards; pseudo-first-order reaction kinetic plots for the adsorption of As(III) and As(V) on ferrihydrite; pseudo-second-order reaction kinetic plots for the adsorption of As(III) and As(V) on ferrihydrite; As(III) adsorption on MCCFH for Freundlich and Dubinin–Radushkevich isotherm models; effect of interfering ions (cations and anions) for MCCFH, CPFH, and HECFH; SEM-EDS and elemental mapping of CMCFH before and after As(III)/As(V) adsorption; thermogravimetric analysis (TGA) of CMCFH at air and nitrogen atmospheres; physicochemical characteristics of influent natural drinking water (PDF)

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Notes

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