



Efficient As(III) oxidation and removal by encapsulated BioMnO_x@Fh with ferrihydrite-promoted Mn regeneration

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ARTICLE INFO

Keywords:

Arsenic oxidation
Biogenic Mn oxides
Fe-Mn composite
Microbial regeneration
Encapsulation

ABSTRACT

Arsenic contamination, particularly the more toxic and mobile As(III), poses a significant threat to water safety. Although manganese oxides can oxidize As(III), their application is often limited by surface passivation and poor regeneration. Here, we synthesized a bio-hybrid material, BioMnO_x@Fh, via Mn(II) oxidation by *Pseudomonas putida* MnB1 in the presence of ferrihydrite (Fh), and evaluated its performance for As(III) oxidation and removal. Compared with BioMnO_x alone, BioMnO_x@Fh showed a higher Mn(IV) fraction (39.6% vs. 27.9%) and faster As(III) oxidation ($k_{ox} = 0.18 \pm 0.04 \text{ h}^{-1}$ vs. $0.080 \pm 0.013 \text{ h}^{-1}$), and $90.31 \pm 2.11\%$ dissolved total As removal under the tested conditions. Relative to abiotic MnO_x@Fh, the biogenic composite showed lower Mn(II) release and more sustained redox reactivity, consistent with biologically maintained Mn redox cycling. Fh functioned not only as a sorptive iron phase, but was also associated with the enhanced regeneration of reactive high-valence Mn species. Together, the results are consistent with a coupled treatment process in which the Fh-containing phase promotes arsenic retention, whereas the biogenic Mn oxide phase sustains oxidative transformation of As(III). Alginate encapsulation further improved material recoverability and supported short-term reuse of the composite. These results suggest that coupling ferrihydrite with biologically active Mn oxides, combined with material encapsulation, is a promising strategy for As(III) treatment.

1. Introduction

Arsenic (As) contamination in aquatic environments poses severe risks to human health and ecological security due to its high toxicity and carcinogenicity [1]. Rapid urbanization, industrial expansion and agricultural activities have intensified arsenic release into groundwater and surface water worldwide, affecting hundreds of millions of people [2–4]. In response, the development of effective and sustainable technologies for arsenic remediation remains a critical challenge in water treatment research.

In natural and engineered systems, arsenic predominantly exists as arsenite (As(III)) and arsenate (As(V)). As(III) is generally more toxic and mobile than As(V) [1], whereas As(V) exhibits stronger affinity toward mineral surfaces and is therefore more amenable to immobilization [5,6]. Consequently, oxidation of As(III) to As(V) is generally

beneficial for arsenic immobilization and is often an important step in engineered treatment systems. Among various oxidants, manganese (hydro)oxides (MnO_x), ubiquitous natural oxidants, play a pivotal role in mediating As migration and transformation through redox reactions [7,8].

However, the practical application of MnO_x for As(III) oxidation is often constrained by rapid surface passivation. During oxidation, reactive Mn(IV) sites are progressively reduced to lower-valence Mn species, while adsorbed As(V) and Mn(II) block active surfaces, leading to declining reactivity and limited oxidation capacity [9–11]. These intrinsic limitations significantly restrict the long-term effectiveness of chemically synthesized MnO_x in arsenic remediation systems.

Biogenic manganese oxides (BioMnO_x), produced by Mn(II)-oxidizing microorganisms, have attracted increasing attention as an alternative to abiotic MnO_x. Ongoing microbial Mn(II) oxidation can

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<https://doi.org/10.1016/j.cej.2026.176560>

Received 30 December 2025; Received in revised form 20 April 2026; Accepted 21 April 2026

Available online 22 April 2026

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promote the regeneration of reactive high-valence Mn species, thereby alleviating oxidant depletion and maintaining redox activity [12]. Compared with abiotic MnO_x , BioMnO_x generally exhibit greater redox sustainability and lower Mn(II) accumulation. Nevertheless, despite this regenerative advantage, BioMnO_x alone often show limited arsenic removal capacity [13], and may suffer from operational instability when used as suspended materials, which constrains their overall arsenic removal performance and practical applicability.

Iron (hydr)oxides (FeO_x), especially ferrihydrite (Fh), are widely recognized as effective arsenic-retaining phases and have been extensively investigated in arsenic treatment systems. Their interactions with As(III) and As(V), however, are strongly dependent on Fe mineral type, surface properties, and reaction conditions [14–18]. To integrate oxidation and adsorption processes, Fe–Mn binary oxide composites have been widely investigated [19–22]. In these systems, manganese oxides are generally considered to be the primary oxidizing components for As(III), whereas iron phases mainly contribute to arsenic immobilization. However, chemically synthetic Fe–Mn oxides often suffer from irreversible Mn reduction, Mn(II) leaching, and gradual loss of oxidative activity, raising concerns regarding long-term stability and the risk of secondary contamination.

Notably, most previous studies have treated iron phases primarily as adsorptive components [19,23], while their potential influence on biologically mediated Mn redox cycling has received much less attention. In particular, whether Fh can facilitate Mn regeneration in bio-mediated Fe–Mn systems, for example by modifying the local physicochemical microenvironment and thereby favoring microbial Mn(II) oxidation, remains insufficiently understood. Addressing this knowledge gap is important for developing Fe–Mn systems that combine sustained oxidation with effective arsenic immobilization.

From an application perspective, bio-oxides still face practical challenges in water treatment, particularly in solid-liquid separation, material recovery, and reuse. Therefore, alginate encapsulation was further explored here as an engineering strategy to improve the recoverability and operational applicability of the $\text{BioMnO}_x\text{@Fh}$ system [24,25].

In this study, we investigated whether incorporating Fh into a biogenic Mn-based system could enhance As(III) oxidation and removal performance and support the maintenance of reactive high-valence Mn species. To this end, $\text{BioMnO}_x\text{@Fh}$ was synthesized through Mn(II) oxidation by *Pseudomonas putida* MnB1 in the presence of Fh, and its structure, redox characteristics, and As(III) treatment behavior were systematically evaluated. Alginate encapsulation was further examined as an application-oriented extension to improve material recoverability and reuse. By examining the coupled roles of the Fe phase in arsenic adsorption and Mn redox maintenance, this work aims to provide a more mechanistically informed and application-relevant basis for developing biologically mediated Fe–Mn materials for arsenic remediation.

2. Materials and methods

2.1. Chemicals and microbial cultivation

All chemicals used were of at least analytical grade. N-(2-hydroxyethyl)piperazine-N'-ethanesulfonic acid (HEPES, $\geq 99.5\%$), 2-morpholinoethanesulfonic acid monohydrate (MES, $\geq 99.5\%$), polyethylene glycol (average molecular weight 8000 Da, PEG 8000, BioUltra grade), sodium alginate (SA, biochemical grade, derived from brown algae), xanthan gum (XG, $> 85\%$) and Tween® 80 (polysorbate 80, $\geq 98\%$), were purchased from Sigma-Aldrich (USA). All other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Pseudomonas putida strain MnB1 (ATCC® 23483™), a Gram-negative Mn(II)-oxidizing bacterium originally isolated from an Mn oxide-encrusted pipeline [26], was obtained from American Type Culture Collection (ATCC, USA). The strain was activated in 30 mL of tryptic soy

broth (TSB) at 26 °C with shaking (220 rpm) for 12 h until the logarithmic growth phase was reached [27]. Cells were then harvested by centrifugation (5000 $\times g$, 10 min, 4 °C) and washed three times with 10 mM HEPES-NaOH buffer (pH 7.0 $\pm$ 0.05, containing 0.85% NaCl) to remove residual medium. The resulting cell pellet was resuspended in the same buffer, and the cell density was adjusted to an optical density at 600 nm (OD_{600}) of 0.5 using a spectrophotometer (Agilent Technologies Cary 8454).

2.2. Preparation of BioMnO_x and $\text{BioMnO}_x\text{@Fh}$

For BioMnO_x production, the cell suspension was inoculated (5%, v/v) into a sterile liquid growth medium [28] (composition shown in Table S1). Stock solutions of trace elements, glucose, HEPES-NaOH buffer (pH 7.0 $\pm$ 0.05; final concentration, 10 mM), and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (final Mn(II) concentration, 1 mM) were sterilized through 0.22 μm PES membranes and then aseptically added to the autoclaved medium (121 °C, 20 min). The cultures were incubated at 26 °C with shaking at 220 rpm for 3 d until complete Mn(II) removal was achieved. To preserve the reactivity associated with retained biological activity, the harvested BioMnO_x was washed three times with 10 mM HEPES-NaOH buffer (pH 7.0 $\pm$ 0.05), resuspended in the same buffer, and stored at 4 °C. In this study, the term “ BioMnO_x ” refers to the combined suspension of Mn(II)-oxidizing cells and the biogenic manganese oxides formed by MnB1, which have been reported to develop through a cell-associated exopolymer matrix [26,29].

For the synthesis of $\text{BioMnO}_x\text{@Fh}$ series with different Mn loadings under fixed Fh input, ferrihydrite (Fh) was added to the cell suspension at a fixed final concentration of 10 $\text{g} \cdot \text{L}^{-1}$, followed by pre-incubation on a rotary shaker (26 °C, 220 rpm) for 12 h. $\text{BioMnO}_x\text{@Fh}$ was then produced using initial Mn(II) concentrations of 0.25, 0.5, 1, and 2 mM, following the same procedure as described above for BioMnO_x . Unless otherwise stated, $\text{BioMnO}_x\text{@Fh}$ prepared with 1 mM Mn(II) was used in the standard experiments. To evaluate the contribution of biological activity to As(III) oxidation and removal, a portion of the prepared bio-oxides was thermally inactivated in a water bath (65 °C, 4 h) to suppress microbial viability. Chemically synthesized MnO_x and $\text{MnO}_x\text{@Fh}$ were also prepared for comparison with bio-oxides; the detailed procedures are provided in Supplementary Text S2.

The Mn concentration in each oxide suspension was quantified by atomic absorption spectroscopy (AAS; Agilent 200 series). Specifically, an aliquot of the suspension was mixed with an equal volume of concentrated hydrochloric acid (HCl) to completely dissolve the oxide phase. The dissolved Mn concentration was then measured, and this molar concentration was used to define the concentration of the oxide suspension on an Mn-equivalent basis. Based on this normalization, suspended BioMnO_x and $\text{BioMnO}_x\text{@Fh}$ were applied at 0.2 mM Mn-equivalent in the following batch experiments described below, except for the Fe/Mn composition effect experiments.

2.3. As(III) oxidation and removal by suspended bio-oxides

Batch experiments were conducted in 150 mL conical flasks containing 100 mL of bio-oxides suspension and agitated at 25 °C and 300 rpm. To evaluate As(III) oxidation and removal performance, the bio-oxides were dosed at 0.2 mM on an Mn-equivalent basis and reacted with 10 $\text{mg} \cdot \text{L}^{-1}$ As(III) for 2 d. The reaction pH was maintained at 7.0 using 10 mM HEPES-NaOH buffer. At predetermined time intervals, a 2 mL aliquot was withdrawn and divided into two 1 mL portions for parallel analysis. One portion was filtered through a 0.22 μm membrane, and the filtrate was acidified with concentrated HCl to a final concentration of 1% (v/v) prior to analysis. The other portion was mixed with 4 mL of 1 M NaOH and shaken for 1 h to desorb surface-associated As(V) [30]. The mixture was then centrifuged (12,000 $\times g$, 1 min), and the supernatant was collected for analysis. At the end of the reaction, the solids were collected by centrifugation (10,000 $\times g$, 5 min) and

thoroughly washed with deionized water to remove residual dissolved ions. Control experiments included buffered arsenic solution without solids, a cellular material suspension, an Fh suspension, and an Fh suspension with adsorbed cellular material (Fh-CM).

Additional batch experiments were conducted to assess the effect of pH (pH 5.0–8.0) and Fe/Mn composition in $\text{BioMnO}_x\text{@Fh}$, selected coexisting ions (Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , SiO_2 , and phosphate), natural organic matter (NOM), and simulated groundwater/surface-water/challenge-water matrices on the As(III) oxidation and removal performance of $\text{BioMnO}_x\text{@Fh}$. Detailed procedures, matrix compositions, and results are provided in Texts S3–S5 and Table S2.

The concentrations of dissolved As(V) and dissolved total As in the filtrate were determined using the molybdenum blue colorimetric method [31]. The dissolved As(III) concentration was calculated as the difference between dissolved total As and dissolved As(V). For the NaOH-desorbed samples, As(III) and total As were measured by atomic fluorescence spectrometry (AFS; Kylin S12) according to the national standard method (GB/T 5009.11–2003), and desorbed As(V) was calculated by subtraction. The reliability of this difference-derived speciation approach was verified by explicit quality-control procedures, including calibration linearity, method detection and quantification limits, matrix-spike recovery, precision, matrix-effect evaluation, and short-term preservation/stability tests under the adopted sample-handling conditions, as detailed in Supplementary Text S6. Dissolved Mn was quantified using the formaldoxime colorimetric method [32].

As(III) oxidation and removal were treated as two distinct response variables and fitted independently using pseudo-first-order models. As(III) oxidation was defined as the generation of As(V), whereas As(III) removal was defined as the decrease in dissolved As(III) concentration in the filtrate. The corresponding kinetic expressions are given in Eqs. (1) and (2):

$$[\text{As(V)}]_{\text{gen},t} = [\text{As(III)}]_0 \cdot (1 - \exp.(-k_{\text{ox}} \cdot t)) \quad (1)$$

$$[\text{As(III)}]_{\text{aq},t} = [\text{As(III)}]_0 \cdot \exp.(-k_{\text{rm}} \cdot t) \quad (2)$$

where $[\text{As(V)}]_{\text{gen},t}$ ($\text{mg} \cdot \text{L}^{-1}$) is the generated As(V) concentration at time t (h), $[\text{As(III)}]_{\text{aq},t}$ ($\text{mg} \cdot \text{L}^{-1}$) is the residual dissolved As(III) concentration at time t , $[\text{As(III)}]_0$ ($\text{mg} \cdot \text{L}^{-1}$) is the initial As(III) concentration, and k_{ox} and k_{rm} (h^{-1}) are the apparent pseudo-first-order rate constants for As(III) oxidation and As(III) removal, respectively.

2.4. Characterization

The synthesized bio-oxides and post-reaction solids were characterized to determine their morphology, crystalline structure, and elemental oxidation states. Samples were prepared either by washing with deionized water followed by freeze-drying, or by chemical fixation when preservation of bacterial structural integrity was required.

Morphological features and elemental distributions were examined using field-emission scanning electron microscopy coupled with energy-dispersive spectroscopy (FESEM-EDS), and nanoscale morphology and crystallographic features of BioMnO_x and $\text{BioMnO}_x\text{@Fh}$ were further examined by transmission electron microscopy (TEM) and selected area electron diffraction (SAED). Crystalline phases were identified by X-ray diffraction (XRD). Surface functional groups were analyzed by Fourier transform infrared spectroscopy (FTIR). The oxidation states of key elements, including Mn and As, were analyzed by X-ray photoelectron spectroscopy (XPS).

Detailed sample preparation procedures, instrument models, and operating conditions for all characterization methods are provided in Supplementary Text S7.

2.5. Preparation of alginate capsules

Alginate capsules containing BioMnO_x or $\text{BioMnO}_x\text{@Fh}$ were

prepared based on the method reported by Zvulunov and Radian [25] with minor modifications. Briefly, the bio-oxides, thickening agent, and divalent cross-linking cations were mixed to form the core solution. The core solution was dripped into a stock solution consisting of 1% (w/v) sodium alginate and 0.1% (w/v) Tween® 80, thereby forming an ionically cross-linked alginate shell at the liquid–liquid interface and generating stable capsules. Two core formulations were used to provide sufficient viscosity for capsule formation: (1) 0.2% (w/v) xanthan gum (XG) with 20% (v/v) glycerol, and (2) 10% (w/v) PEG 8000 with 20% (v/v) glycerol. Detailed preparation procedures are provided in Supplementary Text S8. Capsule morphology and size were examined using an optical microscope.

2.6. As(III) treatment by encapsulated BioMnO_x and $\text{BioMnO}_x\text{@Fh}$

The As(III) treatment performance of encapsulated BioMnO_x and $\text{BioMnO}_x\text{@Fh}$ was evaluated at a dosage matched to the corresponding suspended systems on an Mn-equivalent basis. The final dosage was 0.2 mM Mn-equivalent, and batch experiments were carried out according to the procedure described in Section 2.3. Temporal profiles of dissolved As(III), dissolved As(V), and dissolved total As were determined to evaluate both oxidation and removal behavior.

For reuse experiments, the capsules were incubated in 10 mM HEPES-NaOH buffer solution (pH 7.0 ± 0.05) containing $5 \text{ mg} \cdot \text{L}^{-1}$ As(III) at 26°C and 200 rpm for 12 h in each cycle. At predetermined time intervals, 1.2 mL aliquots were withdrawn, acidified with concentrated HCl to a final concentration of 1% (v/v), and analyzed for dissolved arsenic species and the corresponding As(III) removal efficiency. After each cycle, the capsules were recovered using a sieve with a mesh size of 2 mm, rinsed several times with deionized water, gently blotted dry, weighed, and then transferred to the next cycle. The capsule mass remained essentially unchanged over the five reuse cycles. In addition, a separate long-term cyclic test was further performed in 10 mM HEPES-NaOH buffer solution (pH 7.0 ± 0.05) containing $1 \text{ mg} \cdot \text{L}^{-1}$ As(III) at 26°C and 200 rpm for 15 successive cycles, with each cycle lasting 6 h. The dissolved As(III) concentration was determined at the end of each cycle. The concentrations of Fe, Mn, Ca, and Ba released into the solution were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES, 5110VDV, Agilent).

2.7. Statistical analysis

Data are presented as mean $\pm$ standard deviation unless otherwise stated. Unless otherwise stated, batch experiments were performed in duplicate; experiments used for statistical comparisons were conducted in biological triplicate. Apparent pseudo-first-order rate constants for As(III) oxidation and removal were obtained by independent fitting of the kinetic models described in Section 2.3. Statistical differences among treatments were evaluated by one-way analysis of variance (one-way ANOVA), followed by Tukey's honestly significant difference (HSD) test for multiple comparisons. Differences were considered significant at $p < 0.05$.

3. Results and discussion

3.1. Characterization of bio-oxides

3.1.1. BioMnO_x characterization

BioMnO_x produced by strain MnB1 consisted of nanoparticles closely associated with the cell surface and forming agglomerated, flocculent filamentous aggregates (Fig. 1b, d, f, g, S1b, S1e, and S2a–c). EDS mapping showed a homogeneous distribution of C, O and Mn throughout the bio-oxide aggregates (Fig. 1d), indicating intimate association between the biogenic Mn phase and the cellular matrix. XRD analysis showed only weak diffraction peaks (Fig. 1f), and the corresponding SAED pattern displayed diffuse rings (Fig. S2c), together

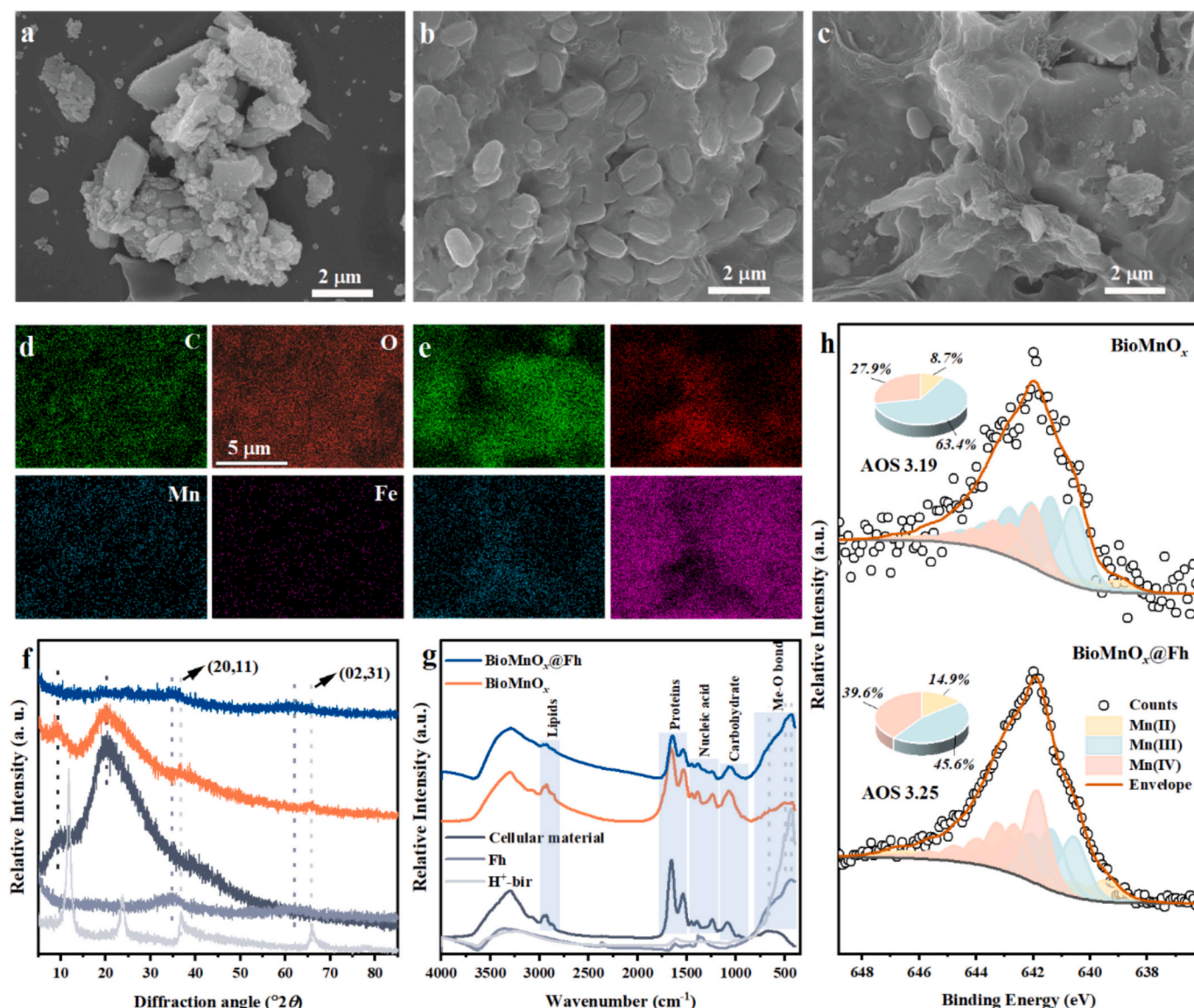


Fig. 1. FESEM micrographs of (a) ferrihydrite (Fh), (b) BioMnO_x , and (c) $\text{MnO}_x@\text{Fh}$; Multi-element EDS mapping images of (d) BioMnO_x and (e) $\text{MnO}_x@\text{Fh}$; (f) XRD patterns and (g) FTIR spectra of BioMnO_x and $\text{MnO}_x@\text{Fh}$; (h) Mn $2p_{3/2}$ XPS spectra deconvolution for BioMnO_x and $\text{MnO}_x@\text{Fh}$. Reference spectra in XRD and FTIR analyses included the cellular material of *Pseudomonas putida* MnB1, Fh, and acid birnessite ($\text{H}^+\text{-bir}$).

indicating low crystallinity. Two broad peaks at 9.4° and 20.2° (2θ) were attributed to cellular organic components, whereas two minor peaks at 36.5° and 65.8° (2θ) corresponded to the (20,11), and (02,31) planes of synthetic acid birnessite ($\text{H}^+\text{-bir}$, PDF #01-073-4155). The absence of (001) and (002) reflections suggested a turbostratic hexagonal birnessite-like structure [33]. FTIR analysis further supported the coexistence of cellular material and $\text{H}^+\text{-bir}$ -like phase in BioMnO_x (Fig. 1g; peak assignments are listed in Table S3). Semi-quantitative EDS analysis indicated that cellular material constituted the dominant component of BioMnO_x (C: 71.88 wt%; Mn: 3.41 wt%; Fig. S1h), which was consistent with the O 1s XPS deconvolution results (Fig. S3a). This high organic content is consistent with substantial surface masking and may explain the very low measured BET specific surface area of BioMnO_x ($0.94 \text{ m}^2 \cdot \text{g}^{-1}$; Table S4). Semi-quantitative deconvolution of the Mn $2p_{3/2}$ XPS spectrum showed Mn(II), Mn(III), and Mn(IV) fractions of 8.7%, 63.4%, and 27.9%, respectively, corresponding to an average Mn oxidation state (Mn AOS) of 3.19 (Fig. 1h). Overall, BioMnO_x was characterized as a poorly crystalline, cell-associated $\text{H}^+\text{-bir}$ -like Mn phase embedded within an organic-rich matrix.

3.1.2. $\text{BioMnO}_x@\text{Fh}$ characterization

Pristine Fh exhibited an aggregated nanospherical morphology (Figs. 1a and S1g) with a high BET specific surface area of $314.54 \text{ m}^2 \cdot \text{g}^{-1}$ (Table S4). Given its well-documented arsenic adsorption capacity [14,34], Fh was introduced as the sorptive Fe phase in $\text{BioMnO}_x@\text{Fh}$. During synthesis, MnB1 cells readily associated with the Fh surface while maintaining intact cellular morphology (Fig. S1d). In the presence of Fh, MnB1-mediated BioMnO_x formation was enhanced, as indicated by greater Mn(II) depletion and increased Mn oxide production relative to the Fh-free treatment (Fig. S4). By contrast, the Fh-only control showed no measurable Mn(II) oxidation under the tested conditions, and only approximately 14% of Mn(II) was removed from solution via adsorption (Fig. S4). Transcriptomic analysis further showed that Fh treatment upregulated genes involved in secretion-related processes, flagellar/surface-response functions, and respiration-associated electron-transfer pathways in MnB1, changes that may have favored Mn(II) oxidation (Text S9; Figs. S5–S7; Table S5–S7). This interpretation is consistent with previous studies showing that Mn(II) oxidation in *Pseudomonas* is associated with secretion pathways, flagellar-mediated surface responses, and respiratory electron-transfer components

[26,35,36].

The resulting $\text{BioMnO}_x\text{@Fh}$ composite retained the poorly crystalline, filamentous H + -bir-like characteristics associated with MnB1 cells (Fig. 1f, g, S1f, and S2d–f), while also incorporating a substantial Fe fraction. EDS mapping showed co-localization of Mn with C, whereas the spatial association between Mn and Fe was comparatively weaker (Fig. 1e). This elemental distribution suggests that BioMnO_x deposition was more closely associated with biomass than with co-precipitation on the Fh phase, supporting the view that Mn oxide formation remained primarily linked to biological Mn(II) oxidation. SAED analysis further showed that the bio-mineral formed in the Fh-containing system exhibited more diffuse diffraction rings than that formed in the Fh-free system (Fig. S2f), indicating a lower degree of crystallinity. Semi-quantitative EDS further indicated that Fe accounted for 40.88 wt% of the composite (Fig. S1i), and the BET specific surface was $136.29 \text{ m}^2\cdot\text{g}^{-1}$ (Table S4), markedly lower than that of pristine Fh. This decrease is likely attributable to partial masking of the Fh surface by the cell-associated organic fraction and to the accumulation of BioMnO_x within the composite, which reduced the accessible surface area.

Semi-quantitative Mn $2p_{3/2}$ XPS analysis further showed that $\text{BioMnO}_x\text{@Fh}$ contained a higher proportion of Mn(IV) and a slightly higher Mn AOS than BioMnO_x formed in the absence of Fh (39.6% vs. 27.9% Mn(IV); AOS 3.25 vs. 3.19; Fig. 1h). For comparison, the corresponding abiotic MnO_x and abiotic $\text{MnO}_x\text{@Fh}$ controls are described in Text S10 and Figs. S8–S9. Unlike the biological system, the introduction of Fh into the abiotic system lowered both the apparent crystallinity and the Mn AOS of the Mn-containing phase (Mn AOS 3.38 vs. 3.12). This contrast indicates that the increase in Mn AOS observed in $\text{BioMnO}_x\text{@Fh}$ was unlikely to result from simple Fh addition alone, but was instead associated with the Fh-promoted MnB1-mediated mineralization process. These structural differences are consistent with the distinct As(III) treatment behaviors observed in the subsequent experiments.

3.2. As(III) oxidation and removal by suspended bio-oxides

3.2.1. As(III) oxidation and removal kinetics by BioMnO_x

No spontaneous As(III) oxidation or removal was observed in the 10

mM HEPES buffer control (pH 7.0) (Fig. 2a). The cellular material of MnB1 showed negligible As(III) removal capacity and no detectable oxidative activity (Fig. 2b). In contrast, Fh exhibited rapid As(III) removal, with an apparent removal rate constant of $1.84 \pm 0.14 \text{ h}^{-1}$ (Fig. 2c; Table S8), but no detectable As(III) oxidation. When Fh was pre-associated with MnB1 cellular material to form the Fh-CM composite, the apparent As(III) removal rate decreased to $0.85 \pm 0.092 \text{ h}^{-1}$ (Fig. 2d; Table S8), while no detectable As(III) oxidation was observed. These results indicate that, under the tested conditions, neither Fh nor the bacterial cellular components alone promoted As(III) oxidation. As a Gram-negative bacterium, MnB1 has a net negatively charged cell surface [37]. Pre-association of cellular material with Fh likely modified the accessible surface properties of Fh, leading to a lower apparent As(III) removal rate, although substantial total As removal was still maintained ($93.54 \pm 1.43\%$ vs. $96.19 \pm 0.61\%$ of pure Fh, Table S8), consistent with the strong arsenic affinity of Fh [15].

BioMnO_x exhibited substantially greater As(III) oxidation than abiotic MnO_x , approaching near-complete oxidation within 24 h under the tested conditions (Fig. 2e), whereas the abiotic MnO_x system achieved less than 40% oxidation after 48 h (Fig. 2f). The initial oxidation process in both systems could be described by pseudo-first-order kinetics. The apparent As(III) oxidation rate constant of BioMnO_x ($0.080 \pm 0.013 \text{ h}^{-1}$) was close to that of abiotic MnO_x ($0.074 \pm 0.012 \text{ h}^{-1}$; Table S9), indicating that the fitted initial oxidation kinetics were similar, even though the overall oxidation extents differed markedly. In other words, the similar k_{ox} values mainly reflect comparable apparent early-stage kinetics, whereas the large difference in final oxidation extent indicates divergence in sustained reactivity over time.

Despite the similar apparent oxidation rate constants, BioMnO_x reached a much higher final oxidation extent than abiotic MnO_x . Based on the current results, this difference is plausibly related to two factors. First, the abiotic MnO_x system showed approximately stoichiometric Mn(II) release during As(III) oxidation ($\text{As(V):Mn(II)} \approx 1:1$; Fig. S10b), consistent with progressive consumption of reactive Mn species through direct redox reactions. By contrast, the BioMnO_x system showed negligible Mn(II) release during As(III) oxidation (Fig. S10a), which is consistent with continued biologically mediated re-oxidation of reduced

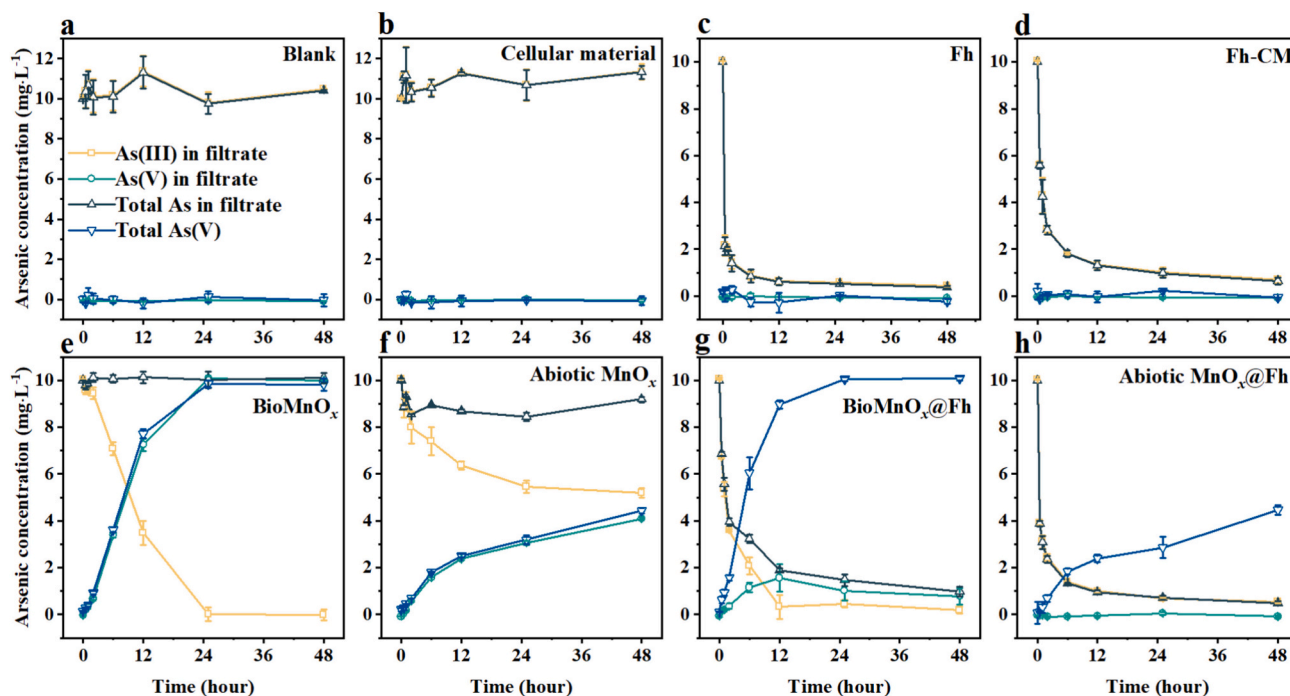


Fig. 2. Temporal variations in As(III), As(V), total As in filtrate, and total As(V) generation in suspension during removal experiments: (a) Blank control (buffer solution); (b) cellular material; (c) Fh; (d) Fh with adsorbed cellular material (Fh-CM); (e) BioMnO_x ; (f) Abiotic MnO_x ; (g) $\text{BioMnO}_x\text{@Fh}$; (h) abiotic $\text{MnO}_x\text{@Fh}$.

Mn species by associated MnB1 cells [12,38]. This process would help maintain the pool of reactive high-valence Mn species. Second, abiotic MnO_x retained $8.09 \pm 0.17\%$ of total As through surface adsorption (Fig. 2f; Table S8), which may have contributed to progressive blocking of reactive sites [9]. In comparison, BioMnO_x showed no measurable arsenic removal (Fig. 2e). The absence of appreciable arsenic retention in the BioMnO_x system may therefore have minimized accumulation of surface-bound arsenic species and helped preserve oxidative reactivity over time.

3.2.2. As(III) oxidation and removal kinetics by $\text{BioMnO}_x\text{@Fh}$

The Fe-containing biogenic composite, $\text{BioMnO}_x\text{@Fh}$, showed markedly improved overall As(III) treatment performance relative to BioMnO_x alone and relative to the corresponding abiotic Fe—Mn composite (Fig. 2g, h). Under the tested conditions, $\text{BioMnO}_x\text{@Fh}$ exhibited faster As(III) oxidation than BioMnO_x alone, as indicated by its higher apparent oxidation rate constant ($0.18 \pm 0.04 \text{ h}^{-1}$ vs. $0.08 \pm 0.013 \text{ h}^{-1}$; Fig. 2g; Table S9). This difference is likely related to the higher Mn(IV) fraction and slightly higher Mn AOS of $\text{BioMnO}_x\text{@Fh}$ (Fig. 1h), together with its lower crystallinity (Fig. S2). Moreover, the observed promotion of Mn(II) re-oxidation by Fh may have contributed to sustaining reactive Mn oxide phases (Fig. S11), which could further enhance As(III) oxidation.

The apparent As(III) removal rate constant by $\text{BioMnO}_x\text{@Fh}$ ($0.66 \pm 0.096 \text{ h}^{-1}$) was also markedly higher than that of BioMnO_x alone ($0.080 \pm 0.013 \text{ h}^{-1}$; Table S8), indicating substantially faster depletion of dissolved As(III) from solution. This behavior is consistent with a coupled process in which rapid initial uptake of As(III) by the Fe-containing phase is followed by continued oxidation in the Mn-containing phase (Text S11). Correspondingly, the dissolved As(V) concentration in the supernatant first increased and then decreased over time (Fig. 2g), and the system achieved $90.31 \pm 2.11\%$ dissolved total As removal under the tested conditions (Table S8). Under circumneutral conditions, the stronger affinity of Fh for As(III) than for As(V) [39] may facilitate this behavior by enriching As(III) at the Fe-containing surface, after which oxidation can occur at adjacent reactive Mn sites and the generated As(V) can subsequently redistribute between the solid and aqueous phases.

In contrast, the abiotic $\text{MnO}_x\text{@Fh}$ system showed a higher initial As(III) removal rate ($1.90 \pm 0.35 \text{ h}^{-1}$ vs. $0.66 \pm 0.096 \text{ h}^{-1}$; Table S8), but its As(III) oxidation capacity was much lower (Fig. 2h). Thus, dissolved As(III) depletion in the abiotic Fe—Mn system was governed primarily by adsorption rather than sustained oxidative transformation, and the system did not achieve the same extent of oxidative conversion as $\text{BioMnO}_x\text{@Fh}$. In addition, because the abiotic system lacked biological Mn regeneration, the Mn-containing phase was progressively reduced during reaction, accompanied by greater Mn(II) release (Fig. S10a). Although part of the released Mn(II) may have remained associated with the solid phase, the abiotic composite still showed a higher risk of Mn release and a greater decline in oxidative performance over time.

Additional experiments showed that the performance of $\text{BioMnO}_x\text{@Fh}$ was influenced by both pH and Fe/Mn composition. $\text{BioMnO}_x\text{@Fh}$ remained effective over pH 5–8, although acidic conditions suppressed Mn-mediated oxidation and alkaline conditions weakened As(V) removal, consistent with the distinct roles of the Mn- and Fe-containing phases in the composite (Text S3; Fig. S12). In addition, increasing the relative Mn loading accelerated As(III) oxidation but did not proportionally improve dissolved As removal, indicating a trade-off between reactive Mn-associated oxidation capacity and Fh-associated arsenic retention (Text S4; Fig. S14). Coexisting solutes had differential effects on $\text{BioMnO}_x\text{@Fh}$ performance (Text S5; Fig. S15). While Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and HCO_3^- caused only minor changes, SiO_2 , phosphate, NOM, and the more complex challenge-water matrix more clearly suppressed arsenic removal, consistent with competitive occupation of reactive sites in the composite [40–42].

3.2.3. Solid-phase characterization after reaction

Post-reaction solid-phase analyses further supported the distinct As(III) treatment behaviors of the four oxide systems. The As 3d spectra (Fig. 3) were deconvoluted into spin-orbit doublets ($3d_{3/2}$ and $3d_{5/2}$) using a fixed splitting energy of 0.69 eV and a fixed 2:3 area ratio. The As $3d_{5/2}$ binding energies at 44.2–44.4 eV and 45.0–45.2 eV were assigned to As(V) and As(III), respectively [43]. For BioMnO_x and abiotic MnO_x , As 3d signals were not clearly resolved by XPS (Figs. 3a, c), consistent with their limited arsenic removal in the solution-phase results. In contrast, both $\text{BioMnO}_x\text{@Fh}$ and abiotic $\text{MnO}_x\text{@Fh}$ showed clear post-reaction As 3d signals (Figs. 3b, d), confirming that incorporation of the Fe-containing phase substantially increased arsenic adsorption on the solids. Semi-quantitative fitting further indicated that the surface arsenic retained on $\text{BioMnO}_x\text{@Fh}$ was dominated by As(V) (70.8% peak-area fraction), whereas the corresponding abiotic $\text{MnO}_x\text{@Fh}$ solid showed a lower relative As(V) fraction (36.9%; Figs. 3b, d). This difference is consistent with the stronger oxidative conversion observed for the biogenic composite in the kinetic experiments.

FTIR and XRD analyses of the post-reaction solids provided additional evidence for coupled oxidation and Mn-phase transformation (Fig. 4). In BioMnO_x , no detectable phase changes were observed (Figs. 4a, b), indicating that the overall crystalline framework, including the H^+ -bir-like structure, remained largely preserved during reaction. However, semi-quantitative deconvolution of the Mn $2p_{3/2}$ XPS spectra showed an increase in the Mn(IV) fraction (from 27.9% to 37.8%) and Mn AOS (from 3.19 to 3.28) after reaction (Figs. 1h, S16a; Table S10). This apparent contrast between XRD and XPS can be rationalized by their different information depths: XRD mainly reflects bulk crystallographic features, whereas XPS is more sensitive to the near-surface region. Therefore, the observed Mn valence evolution likely occurred primarily at the particle surface. Taken together, these results are consistent with continued redox turnover in BioMnO_x during reaction, which may progressively enrich higher-valence Mn species at reactive surface sites.

In abiotic MnO_x , FTIR showed a weak band at 800–950 cm^{-1} (Fig. 4c), attributable to As—O stretching vibrations [44], consistent with its limited arsenic removal in the batch experiments (Fig. 2f). No major new crystalline phase was detected by XRD (Fig. 4d), indicating that the bulk mineral structure remained broadly similar over the reaction period. XPS analysis also showed only minor changes in Mn valence state (Figs. S8c, S16c; Table S10), suggesting that the abiotic MnO_x phase mainly underwent partial reductive consumption rather than extensive structural transformation under the tested conditions. The weakened diffraction intensity, particularly near 7.4 Å and 3.7 Å, may reflect partial Mn reduction during reaction (Fig. 4d).

For the post-reaction biotic and abiotic Fe—Mn binary oxides (Figs. 4e, g), two distinct FTIR bands appeared at 810 and 876 cm^{-1} within the 800–950 cm^{-1} region and were assigned to As—O stretching vibrations of adsorbed As(V) [44,45]. These bands are consistent with oxidation of As(III) to As(V), followed by adsorption of the resulting As(V) on the Fe-containing solids. Additional bands at 1040, 1086, and 1151 cm^{-1} were assigned to hydroxyl-related vibrations in MnOOH -like phases [46], and a new diffraction peak at 4.9 Å appeared in the XRD patterns of both binary systems, consistent with formation of hausmannite-like lower-valence Mn phases (Figs. 4f, h). Together, these results indicate that the Mn oxide components in both Fe-containing systems underwent partial transformation toward lower-valence Mn phases during reaction.

Notably, despite the appearance of these lower-valence Mn phases in both binary systems, their overall Mn redox evolution differed. In abiotic $\text{MnO}_x\text{@Fh}$, Mn AOS decreased slightly after reaction (Figs. S8c, S16d; Table S10), consistent with a net loss of reactive high-valence Mn species. In contrast, $\text{BioMnO}_x\text{@Fh}$ showed an increase in Mn AOS after reaction (Figs. 2h, S16b; Table S10), resembling the trend observed for BioMnO_x . This difference suggests that, although partial reductive transformation occurred in both Fe-containing systems, the biogenic

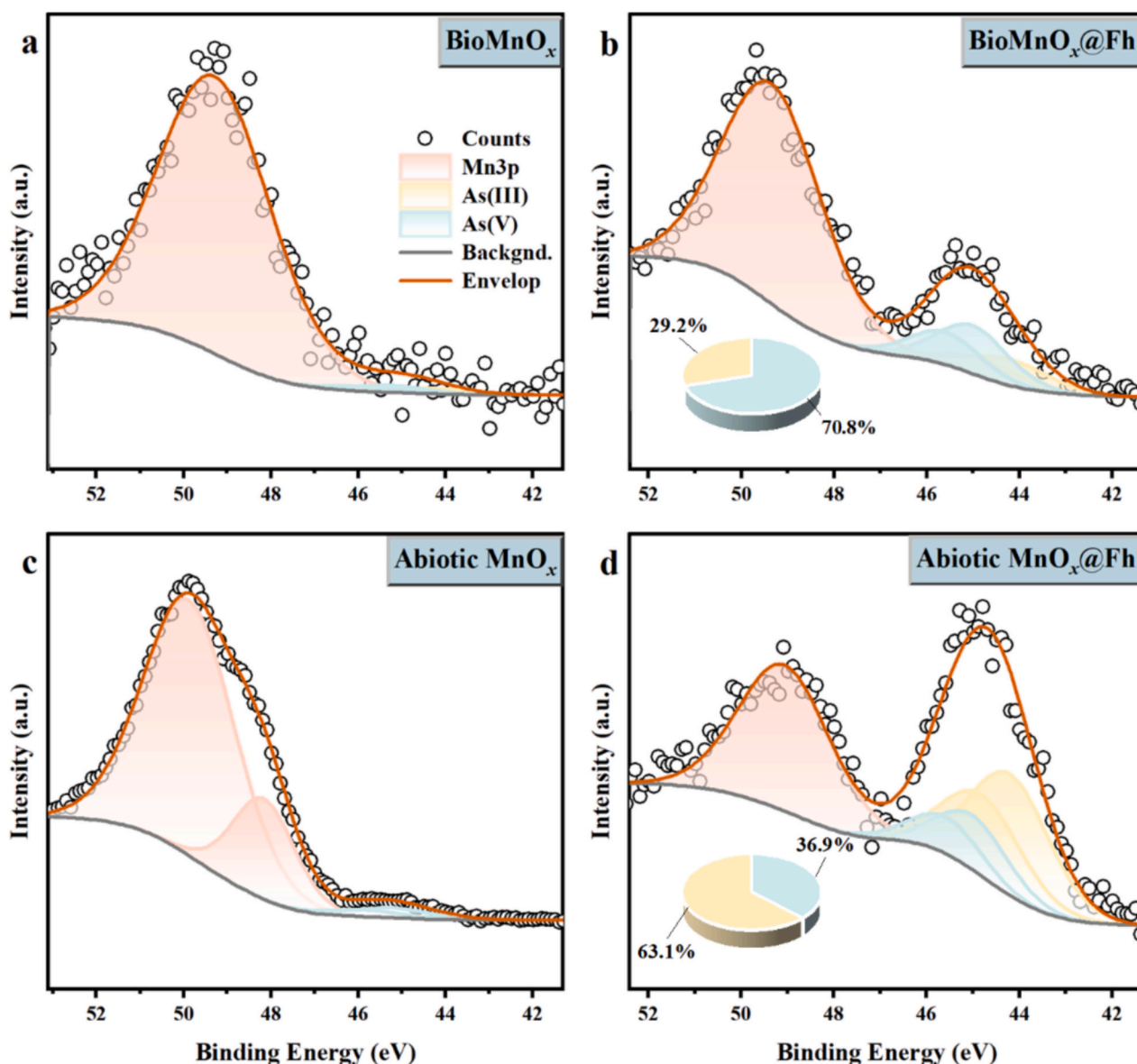


Fig. 3. Fitted As 3d XPS spectra of solid samples after As(III) removal: (a) BioMnO_x; (b) BioMnO_x@Fh; (c) Abiotic MnO_x; (d) Abiotic MnO_x@Fh.

composite retained a stronger capacity to maintain or regenerate higher-valence Mn species during reaction. This interpretation is consistent with the lower Mn(II) accumulation and stronger As(III) oxidation observed in BioMnO_x@Fh system. Overall, the post-reaction solid-phase results support the conclusion that the superior performance of BioMnO_x@Fh arose from coupled arsenic adsorption by the Fh-containing phase and more sustained redox activity in the biogenic Mn-containing phase.

3.3. Contribution of retained biological activity

To probe the contribution of retained biological activity to the performance of BioMnO_x and BioMnO_x@Fh, both biogenic materials were subjected to thermal treatment (65 °C, 4 h) prior to reaction. The effect of this treatment was evaluated by Mn(II) oxidation tests (Fig. S17). Active BioMnO_x and BioMnO_x@Fh completely removed Mn(II) within 24 h, whereas heat-treated BioMnO_x exhibited no measurable Mn(II) removal capacity. In the heat-treated BioMnO_x@Fh system, only limited Mn(II) removal (~7.7%) was observed, which is consistent with partial Mn(II) adsorption by the Fh-containing phase. These results indicate

that thermal treatment effectively suppressed the biological Mn(II)-oxidizing activity retained in both systems.

XRD patterns and FTIR analyses of BioMnO_x and BioMnO_x@Fh before and after heat treatment revealed no major structural changes (Figs. S18a, b, d, and e), indicating that thermal treatment under these conditions did not cause detectable bulk mineral-phase transformation. However, the semi-quantitative Mn 2p_{3/2} XPS analysis indicated a decrease in Mn AOS after treatment, with ΔAOS values of −0.15 and −0.14 for BioMnO_x and BioMnO_x@Fh, respectively (Figs. S18c, f; Table S10). This decreases may reflect partial reduction of high-valence Mn species during heating, possibly driven by redox interactions between Mn oxides and cell-associated organic matter released or altered during thermal treatment [47]. Therefore, the thermal treatment can be regarded primarily as a means of suppressing retained biological activity, while minor surface-associated changes in the Mn-containing phase cannot be excluded.

As shown in Fig. 5a, heat-treated BioMnO_x exhibited negligible As(III) oxidation. At the same time, continuous Mn release was observed during reaction (Fig. S19), indicating that the Mn oxide phase underwent net reduction rather than sustained oxidative turnover. This

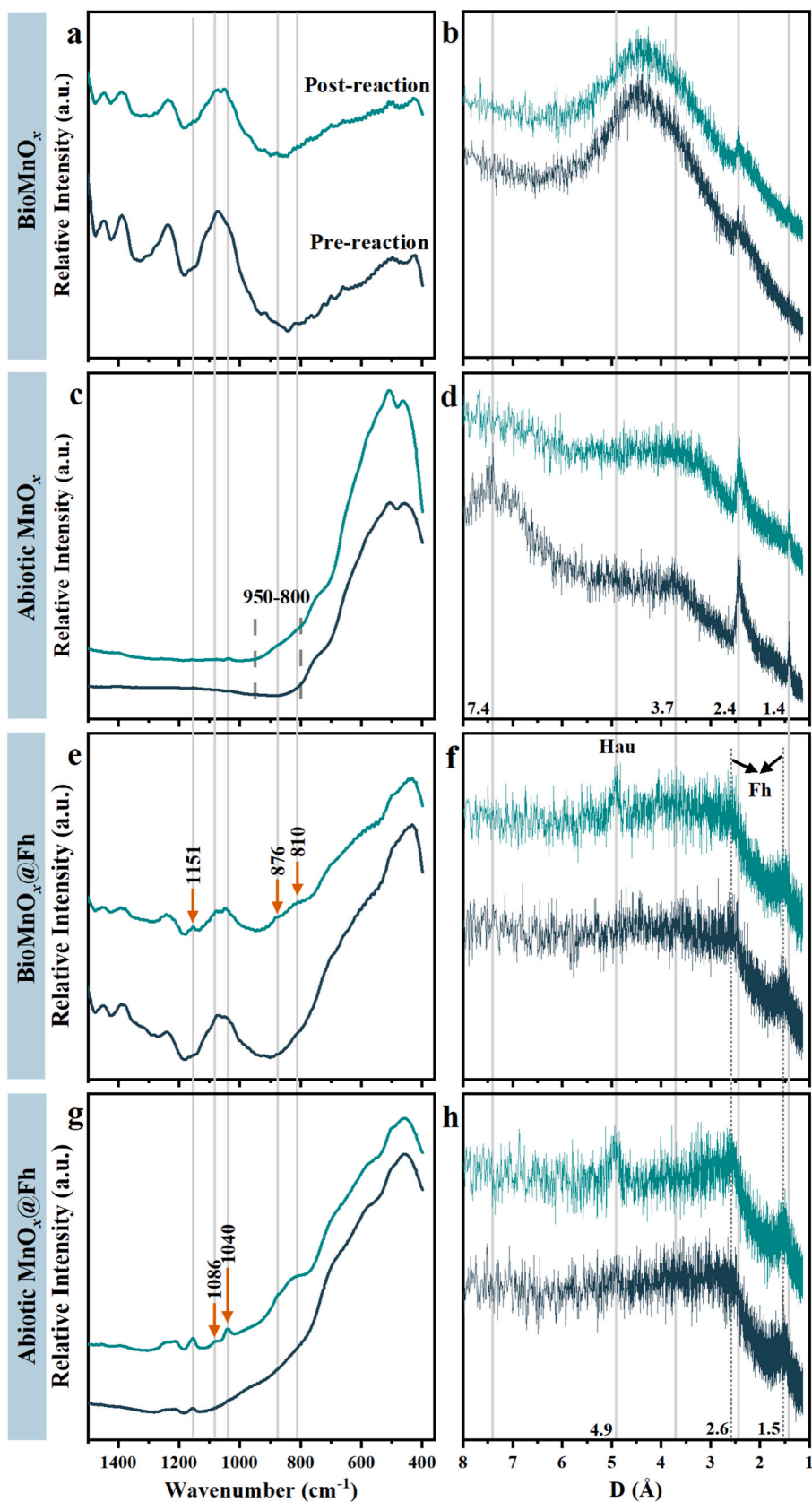


Fig. 4. FTIR spectra (left panels) and XRD patterns (right panels) of solid samples: (a, b) BioMnO_x; (c, d) Abiotic MnO_x; (e, f) BioMnO_x@Fh; (g, h) Abiotic MnO_x@Fh. Black lines: Pre-reaction spectra and diffractograms; Green lines: Post-reaction spectra and diffractograms after As(III) exposure. The O—H bending vibrations of MnO_x were observed around 1000–1150 cm⁻¹. The As—O stretching vibrations were present near 800–950 cm⁻¹. The reflections at 7.4, 3.7, 2.4, and 1.4 Å originate from hexagonal H⁺-bir, the peak at 4.9 Å corresponds to hausmannite (Hau), and the diffraction peaks of Fh are located at 2.6 Å and 1.5 Å, respectively.

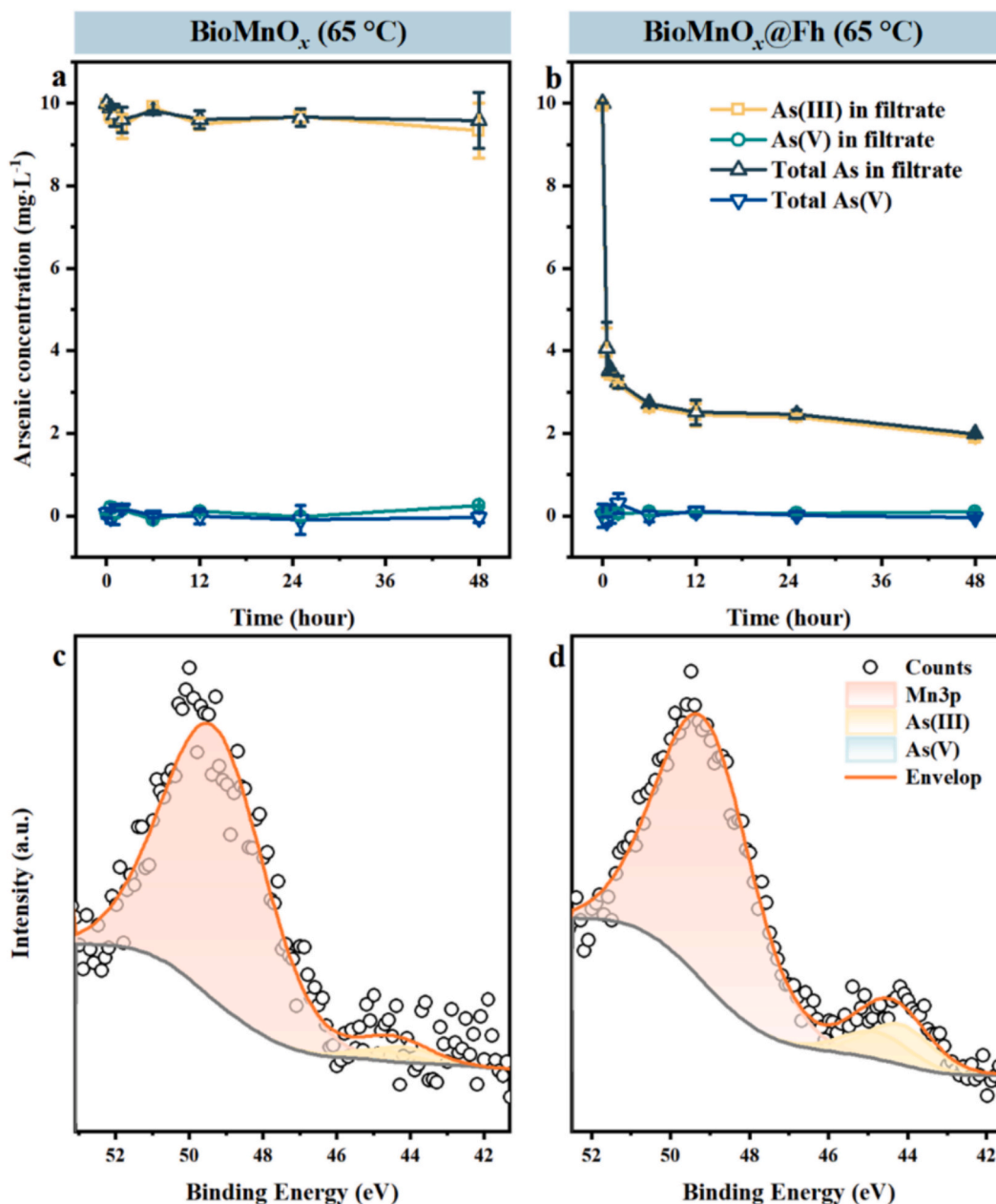


Fig. 5. Arsenic oxidation and removal dynamics and surface speciation analysis of thermally inactivated bio-oxides (65°C , 4 h). Temporal arsenic concentration profiles: (a) BioMnO_x and (b) $\text{BioMnO}_x@\text{Fh}$, showing variations in As(III), As(V), and total arsenic in filtrate, and total As(V) in suspension during removal experiments. Post-reaction surface speciation: Fitted As 3d XPS spectra of (c) BioMnO_x and (d) $\text{BioMnO}_x@\text{Fh}$.

behavior is consistent with continued reductive interactions between cell-associated organic matter and Mn oxides, which would diminish the availability of reactive high-valence Mn species for As(III) oxidation. Because heat-treated BioMnO_x showed negligible arsenic removal (Fig. 5a), the As 3d XPS signal was too weak for reliable XPS fitting (Fig. 5c). Post-reaction XRD and FTIR patterns of heat-treated BioMnO_x showed no obvious structural change relative to pre-reaction material (Fig. S20a, b), suggesting that no major bulk mineral transformation occurred over the reaction period. Correspondingly, the Mn AOS of the post-reaction solid decreased further ($\Delta\text{AOS} = -0.06$; Fig. S20c; Table S10).

In the heat-treated $\text{BioMnO}_x@\text{Fh}$ system, As(III) depletion from solution was dominated by the adsorption capacity of the Fh-containing phase (Fig. 5b). As 3d XPS analysis showed that the retained surface arsenic was primarily present as As(III) (Fig. 5d), while no dissolved As(V) was detected in solution (Fig. 5b). These results indicate that, after

thermal treatment, the Mn oxide component in $\text{BioMnO}_x@\text{Fh}$ no longer sustained effective As(III) oxidation under the tested conditions. Mn release was still observed (Fig. S19), consistent with net reduction of the Mn oxide phase. The lower dissolved Mn concentration relative to the heat-treated BioMnO_x system may reflect partial adsorption of released Mn by the Fh-containing solid phase.

Post-reaction XRD and FTIR analyses of heat-treated $\text{BioMnO}_x@\text{Fh}$ indicated the appearance of additional lower-valence Mn phases, including Hausmannite- and MnOOH -like components (Figs. S20d, e). At the same time, the Mn AOS of the Mn-containing phase decreased slightly after reaction ($\Delta\text{AOS} = -0.03$; Fig. S20f; Table S10). Together, these results suggest that, after suppression of biological Mn regeneration, the remaining organic fraction in the biogenic composite may have acted as a competing reductive sink during As(III) treatment, which would diminish the oxidative contribution of the Mn phase and favor accumulation of lower-valence Mn species.

Overall, the heat-treatment results support the interpretation in Section 3.2, indicating that retained biological activity played an important role in sustaining the Mn redox cycling and maintaining robust As(III) oxidation performance within the biogenic systems.

3.4. Encapsulation of bio-oxides for improved recoverability

3.4.1. As(III) oxidation and removal by encapsulated bio-oxides

To improve material recoverability and examine the application potential of the biogenic oxides, BioMnO_x and BioMnO_x@Fh were encapsulated in alginate capsules using XG- or PEG-based core formulations and tested at a dosage matched to the corresponding suspended systems on an Mn-equivalent basis (Fig. 6). The two capsule matrices differed visibly in internal solid distribution (Fig. S21): the more viscous XG cores maintained a more dispersed distribution of the bio-oxides, whereas the less viscous PEG cores allowed greater settling of the encapsulated solids. These differences are expected to influence solute diffusion, local solid packing, and reaction behavior within the capsules [25].

For encapsulated BioMnO_x, the apparent As(III) oxidation rate constants in the XG and PEG capsules were $0.16 \pm 0.021 \text{ h}^{-1}$ and $0.14 \pm 0.020 \text{ h}^{-1}$, respectively, both higher than that of suspended BioMnO_x ($0.080 \pm 0.013 \text{ h}^{-1}$; Table S9). This increase is consistent with the spatial confinement of BioMnO_x within the capsules, which may increase local contact frequency between dissolved As(III) and the Mn-based oxidizing phase after diffusion into the capsules [25]. The apparent As(III) removal kinetics were also enhanced in the encapsulated BioMnO_x systems, with rate constants of $0.20 \pm 0.038 \text{ h}^{-1}$ for XG capsules and $0.52 \pm 0.15 \text{ h}^{-1}$ for PEG capsules, compared with $0.070 \pm 0.015 \text{ h}^{-1}$ for suspended BioMnO_x (Table S8). However, this faster

depletion of dissolved As(III) should not be attributed solely to the intrinsic reactivity of the encapsulated bio-oxides, because control experiments with bio-oxide-free capsules also showed measurable As(III) uptake (Fig. 7a, S22a). Thus, the enhanced removal behavior of the encapsulated BioMnO_x systems is consistent with the combined effects of BioMnO_x oxidation and matrix-associated uptake of dissolved As(III), particularly during the initial reaction stage. PEG capsules showed greater As(III) uptake than XG capsules, which may reflect differences in internal solid distribution and diffusion resistance between the two capsule matrices.

For encapsulated BioMnO_x@Fh, the PEG capsule system showed faster As(III) removal than the corresponding suspended BioMnO_x@Fh ($1.46 \pm 0.34 \text{ h}^{-1}$ vs. $0.66 \pm 0.096 \text{ h}^{-1}$; Table S8; Fig. 6d), whereas the XG capsule system showed a similar As(III) removal rate ($0.66 \pm 0.096 \text{ h}^{-1}$; Table S8; Fig. 6c). This behavior is consistent with matrix-dependent differences in mass transfer and local retention behavior within the capsules. In particular, the faster removal observed for PEG capsules may reflect a combination of local enrichment of the Fe-containing phase and additional matrix-mediated uptake of dissolved As(III), whereas the more viscous XG matrix may have imposed greater diffusion limitation that offset the potential benefit of spatial confinement. Overall, encapsulation altered the transport and retention behavior of the systems and improved material recoverability, but the superior oxidation-removal performance still depended primarily on the intrinsic reactivity of BioMnO_x@Fh composite itself.

3.4.2. Reuse of bio-oxide capsules

The millimeter-scale size of the capsules allowed direct and efficient separation after reaction using a 2 mm sieve, which facilitated straightforward recovery and transfer between cycles. Their physical

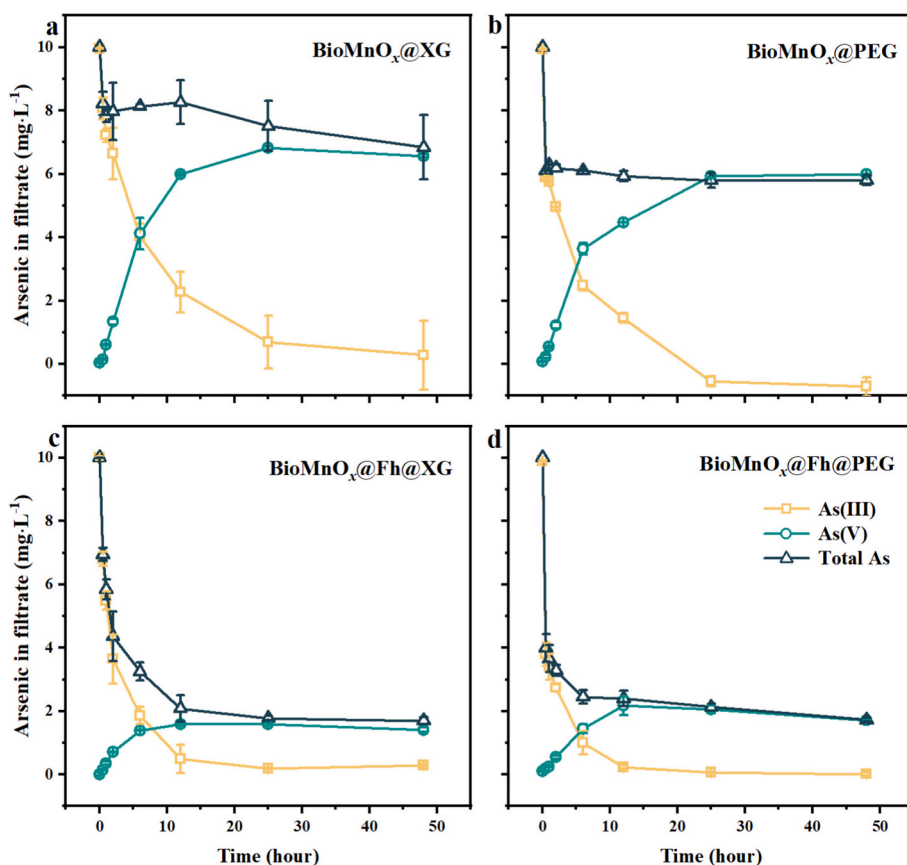


Fig. 6. Temporal variations in As(III), As(V), and total arsenic concentrations during removal experiments with encapsulated systems: (a) BioMnO_x in XG capsules; (b) BioMnO_x in PEG capsules; (c) BioMnO_x@Fh in XG capsules; (d) BioMnO_x@Fh in PEG capsules. Mineral concentrations in encapsulated systems matched those in suspended systems.

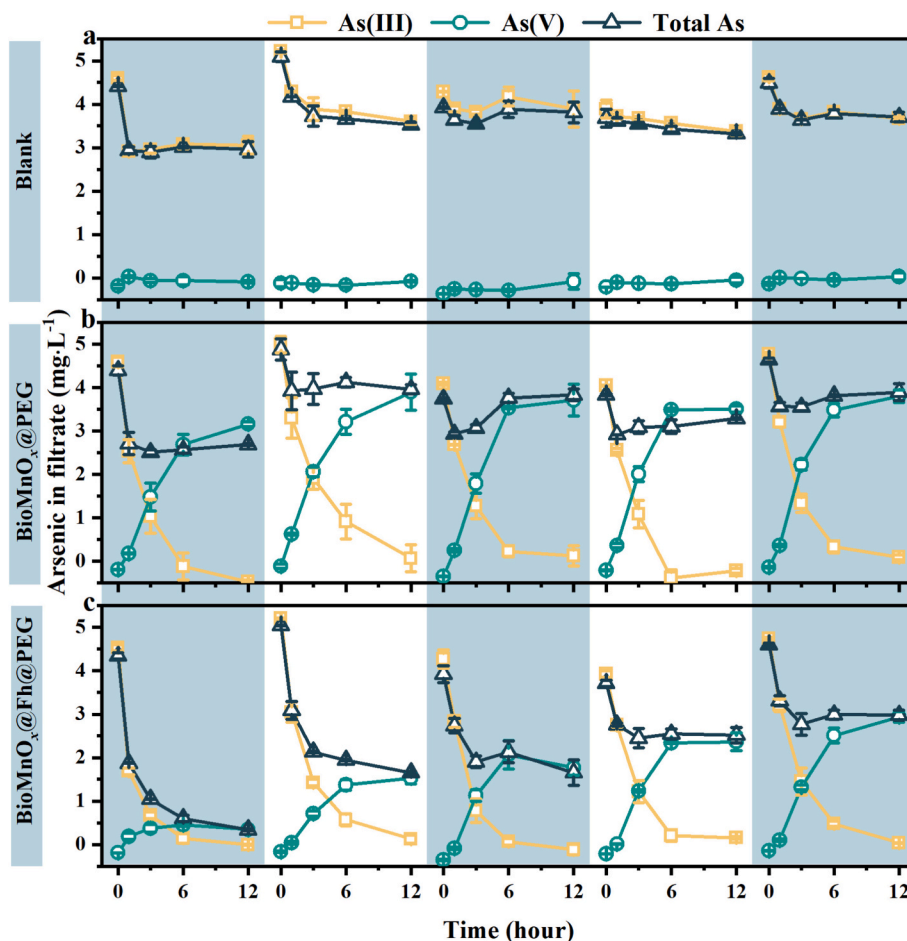


Fig. 7. Repeated oxidation of As(III) by PEG capsules: (a) Blank; (b) encapsulated BioMnO_x ; (c) encapsulated $\text{BioMnO}_x@\text{Fh}$.

integrity and operational stability were first evaluated over five consecutive batch cycles under the main experimental conditions (Figs. 7, S22). Throughout these five cycles, no obvious capsule rupture or deformation was observed, indicating satisfactory short-term mechanical stability of the ionically cross-linked alginate matrices under the tested batch conditions.

The encapsulated BioMnO_x systems maintained As(III) oxidation activity over a five-cycles test (Figs. 7b, S22b). The PEG capsules showed apparent oxidation rate constants in the range of $0.17\text{--}0.25\text{ h}^{-1}$, which were generally higher than those of the XG capsules ($0.08\text{--}0.20\text{ h}^{-1}$; Table S9). These results indicate that encapsulated BioMnO_x retained substantial oxidative reactivity during repeated short-term use.

The encapsulated $\text{BioMnO}_x@\text{Fh}$ systems also maintained relatively high As(III) removal kinetics over a five-cycles test (PEG: $0.39\text{--}0.98\text{ h}^{-1}$; XG: $0.33\text{--}0.40\text{ h}^{-1}$; Figs. 7c, S22c; Table S8), indicating that the composite capsules preserved substantial short-term treatment capacity during reuse. However, the net removal of dissolved arsenic decreased progressively over successive cycles, declining from $92.2 \pm 0.7\%$ to $35.2 \pm 3.1\%$ for PEG capsules and from $91.7 \pm 1.8\%$ to $36.1 \pm 11.2\%$ for XG capsules across five cycles (Figs. 7c, S22c; Table S8). This decline is consistent with progressive occupation of available adsorption sites in the Fh-containing phase, which would limit continued uptake of oxidation products during repeated operation. Despite this decrease in arsenic-adsorption capacity, the encapsulated $\text{BioMnO}_x@\text{Fh}$ systems still outperformed the corresponding BioMnO_x -only capsules in dissolved As(III) removal across all tested cycles, highlighting the combined contribution of Mn-based oxidation and Fh-associated arsenic uptake.

To further assess extended reuse behavior, an additional 15-cycle

batch experiment was conducted with PEG capsules containing $\text{BioMnO}_x@\text{Fh}$ at a lower initial As(III) concentration of $1\text{ mg}\cdot\text{L}^{-1}$ (Fig. S23). Under these conditions, the capsules maintained low residual As(III) concentrations over repeated cycles, indicating sustained oxidative transformation, whereas the concentrations of dissolved As(V) and total As in the filtrate gradually increased with cycle number (Fig. S23a). At the same time, measurable leaching of Ba and Ca was detected (Fig. S23b), indicating that longer-term durability and formulation stability still require further optimization. Overall, alginate encapsulation facilitated separation and supported short-term repeated use of the biogenic Fe–Mn composite, but longer-term stability, regeneration of Fh-promoted retention sites, and elemental leaching remain important constraints for practical implementation.

3.5. Environmental significance and study limitations

The present results highlight the environmental relevance of integrating ferrihydrite with biologically active Mn oxides for arsenic treatment. In this system, ferrihydrite did not function merely as a passive adsorptive phase, but was associated with improved maintenance of Mn redox reactivity while also contributing to arsenic uptake. This coupling is environmentally meaningful because it enables oxidative transformation of As(III) and retention of dissolved arsenic to occur within a single material system, thereby helping to mitigate the common trade-off between oxidative transformation and removal efficiency. In addition, alginate encapsulation facilitated solid-liquid separation and material recovery, which improves the short-term operational relevance of the system in application-oriented batch treatment settings.

Despite these advantages, several limitations should be recognized.

First, the current results were obtained under controlled laboratory batch conditions. Although the material showed effective performance across the tested pH range and tolerance to several common inorganic ions, its performance was inhibited by silicate, phosphate, natural organic matter, and more complex simulated water matrices. Accordingly, the behavior of the system in authentic waters and under continuous-flow operation still requires verification. Second, the evidence for Fh-associated enhancement of biologically mediated Mn regeneration remains supportive rather than definitive. The observed changes in Mn valence composition, Mn(II) re-oxidation behavior, heat-treatment response, transcriptomic response, and overall reaction behavior are consistent with improved Mn redox maintenance, but the underlying biochemical pathway has not yet been directly resolved. Third, the capsule experiments demonstrated only short-term reuse. Although the capsules facilitated recovery and retained substantial treatment capacity over repeated short-term cycles, longer-term durability, microbial activity retention, regeneration of Fh-associated retention sites, mechanical stability, and elemental leaching still require further evaluation before practical implementation can be fully assessed. Future work should therefore focus on validation in authentic waters, continuous-flow testing, longer-term cycling, direct mechanistic verification, and further optimization of capsule formulation and operating conditions.

4. Conclusions

This study shows that incorporating ferrihydrite into a biogenic Mn oxide system was associated with improved As(III) treatment performance under the tested conditions. Compared with BioMnO_x alone, $\text{BioMnO}_x\text{@Fh}$ showed a higher Mn(IV) fraction, faster As(III) oxidation, and much greater dissolved arsenic removal under the tested conditions. Relative to abiotic $\text{MnO}_x\text{@Fh}$, the biogenic composite exhibited lower Mn(II) accumulation and more sustained redox reactivity, indicating that ferrihydrite was associated not only with arsenic retention, but also with improved maintenance of reactive high-valence Mn species in the biogenic system. Together, the kinetic results and post-reaction solid-phase characterization support a coupled treatment mechanism in which the Fh-containing phase promotes arsenic retention, whereas the biogenic Mn oxide phase sustains oxidative transformation of As(III). Alginate encapsulation further improved material recoverability and supported repeated short-term use, although dissolved arsenic removal declined over successive cycles. Overall, $\text{BioMnO}_x\text{@Fh}$ represents a promising biologically mediated Fe–Mn composite for As(III) treatment. However, the mechanism by which Fh promotes biologically mediated Mn redox maintenance still requires direct verification, and further evaluation in authentic waters, continuous-flow systems, and longer-term reuse scenarios is needed.

CRedit authorship contribution statement

Feng Zhang: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Huilin Yin:** Formal analysis, Data curation. **Stanislav Jelavić:** Writing – review & editing, Validation. **Bruno Lanson:** Writing – review & editing, Validation. **Xiaoming Wang:** Writing – review & editing, Validation. **Hui Yin:** Writing – review & editing, Validation. **Wenfeng Tan:** Writing – review & editing, Validation. **Xionghan Feng:** Writing – review & editing, Validation, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 42030709, 42377303, and W2521004).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.176560>.

Data availability

Data will be made available on request.

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Efficient As(III) oxidation and removal by encapsulated BioMnO_x@Fh with ferrihydrite-promoted Mn regeneration

Text S1. Synthesis of ferrihydrite (Fh)

Ferrihydrite (Fh) was synthesized according to the method described by Wang et al. After synthesis, the solid was thoroughly washed with deionized water to remove residual ions, freeze-dried, ground, passed through a 100-mesh sieve, and stored at 4 °C until use. XRD analysis confirmed that the obtained product was a single-phase ferrihydrite. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2460 instrument (Version 3.01).

Text S2. Preparation of Abiotic MnO_x and MnO_x@Fh and Their As(III) Treatment

To prepare abiotic MnO_x, 0.1187 g of MnCl₂·4H₂O was dissolved in 900 mL of 11.1 mM HEPES-NaOH buffer solution (pH 7.0). The pH was adjusted to 7.0 using 1 M NaOH. Under continuous stirring, 100 mL of 4 mM NaMnO₄ solution was added dropwise while maintaining the pH near neutral. The resulting suspension was stirred overnight to ensure complete precipitation of dissolved Mn species. The final Mn concentration in the abiotic MnO_x suspension was 1 mM.

For the preparation of abiotic MnO_x@Fh, 1 g of ferrihydrite was first dispersed in 10 mM HEPES-NaOH buffer (pH 7.0) and hydrated for 12 h. Mn²⁺ and MnO₄⁻ were then sequentially added according to the procedure described above for abiotic MnO_x synthesis. The total reaction volume was adjusted to 1 L, resulting in a final Mn concentration of 1 mM and an Fe/Mn molar ratio of 10.6.

As(III) treatment by the abiotic oxides was evaluated using mineral suspensions dosed at 0.2 mM Mn-equivalent. The Mn/Fe loading ratio was matched to that of the corresponding bio-oxide materials, and the suspensions were reacted with 10 mg·L⁻¹ As(III) for 2 d under identical operating conditions. The reaction pH was maintained at 7.0 ± 0.05 using 10 mM HEPES-NaOH buffer.

Text S3. Effects of pH on As(III) Oxidation and Removal by BioMnO_x@Fh

To evaluate the effects of pH on As(III) treatment by suspended BioMnO_x@Fh, batch experiments were conducted using 0.2 mM bio-oxides, expressed on an Mn-equivalent basis, and 10 mg·L⁻¹ As(III) at pH 5.0, 6.0, 7.0, and 8.0. The pH was maintained using appropriate buffer systems selected according to their effective buffering ranges and adjusted with NaOH. Specifically, MES was used for pH 5.0–6.0, whereas HEPES was used for pH 7.0–8.0.

BioMnO_x@Fh showed effective dissolved As(III) removal over the tested pH range of 5–8 (Figs. S12a-d). The apparent As(III) removal rate constants at pH 5, 6, 7, and 8 were $0.52 \pm 0.083 \text{ h}^{-1}$, $0.68 \pm 0.09 \text{ h}^{-1}$, $0.66 \pm 0.096 \text{ h}^{-1}$, and $0.44 \pm 0.053 \text{ h}^{-1}$, respectively (Table S8). These results indicate that dissolved As(III) removal was relatively stable under mildly acidic to neutral conditions, but declined at pH 8. The corresponding endpoint dissolved total As removal values are summarized in Table S8. In parallel, As(III) oxidation was also influenced by pH. The generation of As(V) increased from acidic to circumneutral and slightly alkaline conditions, whereas oxidation was clearly suppressed at pH 5 (Fig. S12a, Table S9).

The lower oxidation performance at pH 5 is consistent with less favorable maintenance of the biological Mn redox cycle and reduced stability of the Mn-containing phase[1]. At pH 5, dissolved Mn(II) accumulated more strongly in solution (Fig. S13), indicating that reduced Mn species were less efficiently re-oxidized under acidic conditions. Acidic conditions may also promote partial dissolution of Mn-containing phases and alter the local interfacial environment, which would weaken the overall oxidation capacity. In other words, the Mn-rich phase became less effective as an oxidizing component under acidic conditions, and this directly reduced As(III) oxidation.

The concentration of dissolved As(V) in the filtrate increased with increasing pH (Figs. S12a-d). This trend is consistent with the pH-dependent adsorption behavior of the Fe-containing phase. At higher pH, Fh surfaces become less favorable for retaining anionic As(V), because the surface charge becomes more negative and the affinity for

arsenate decreases[2]. As a result, a larger fraction of the generated As(V) remained in solution at pH 8. Thus, pH affected the system in two different ways: acidic conditions mainly suppressed Mn-mediated oxidation, whereas alkaline conditions mainly weakened As(V) retention by the Fe-containing phase.

Text S4. Effects of Fe/Mn composition on As(III) Oxidation and Removal by BioMnO_x@Fh

To evaluate the effect of Fe/Mn composition on As(III) treatment by BioMnO_x@Fh, a series of BioMnO_x@Fh materials was synthesized by keeping the Fh concentration constant during preparation while varying the initial Mn(II) precursor concentration. The resulting materials therefore differed in their intrinsic Fe/Mn balance. These BioMnO_x@Fh materials were subsequently subjected to As(III) treatment experiments under otherwise identical conditions. For comparison among treatments, the oxide suspensions were normalized on an Mn-equivalent basis where appropriate, whereas the primary experimental variable in this series was the Fe/Mn composition established during synthesis rather than a simple change in reaction-stage dosage. Batch reactions were carried out at relative Mn loading of 0.05, 0.1, 0.2 and 0.4 mM under otherwise identical conditions (Figs. S14a-d). Increasing the loading markedly accelerated As(III) oxidation, as the apparent pseudo-first-order rate constant (k_{ox}) for As(V) generation increased from $0.023 \pm 0.0073 \text{ h}^{-1}$ at 0.05 mM to $0.074 \pm 0.015 \text{ h}^{-1}$ at 0.1 mM, $0.18 \pm 0.04 \text{ h}^{-1}$ at 0.2 mM, and $0.23 \pm 0.04 \text{ h}^{-1}$ at 0.4 mM (Table S9). These results indicate that a higher proportion of Mn-associated reactive sites favored oxidative transformation of As(III).

In contrast, the apparent As(III) removal kinetics did not improve proportionally with increasing Mn loading. The k_{rm} values were 0.73 ± 0.080 , 0.71 ± 0.11 , 0.66 ± 0.096 , and $0.59 \pm 0.039 \text{ h}^{-1}$ at 0.05, 0.1, 0.2, and 0.4 mM, respectively (Table S8). The corresponding endpoint dissolved total As removal efficiencies were $96.45 \pm 0.48\%$, $95.97 \pm 0.38\%$, $90.31 \pm 2.11\%$, and $79.75 \pm 0.55\%$, respectively (Table S8). Although a higher Mn loading accelerated As(III) oxidation, it did not proportionally improve

total As removal. A plausible explanation is that, at high Mn loading, the BioMnO_x phase may partially cover the As adsorption sites on the Fh surface, thereby weakening the interfacial retention of oxidized arsenic species (Figs. S14a-d). As a result, although As(III) oxidation was enhanced, the adsorption-driven removal of total dissolved As was compromised. Therefore, 0.2 mM Mn loading was selected for the subsequent experiments to balance oxidation and adsorption performance.

Text S5. Effects of coexisting ions and simulated water matrices on As(III) oxidation and removal by BioMnO_x@Fh

To evaluate the influence of background water chemistry on the performance of BioMnO_x@Fh, batch experiments were conducted in the presence of representative coexisting ions, natural organic matter (NOM), and simulated groundwater (GW), surface water (SW), and challenge water (CW) matrices (Fig. S15; Table S2). Under the tested conditions, Ca²⁺ and Mg²⁺ caused little change in either total As removal or As(V) generation (Figs. S15a, d), indicating that common alkaline earth cations did not strongly interfere with As(III) treatment by BioMnO_x@Fh. Similarly, Cl⁻, SO₄²⁻, and HCO₃⁻ had only minor effects on system performance (Figs. S15b, e). In contrast, SiO₂ and phosphate more clearly decreased both total As removal and generated As(V), suggesting stronger interference with the coupled oxidation-retention process, likely through competition for surface-associated reactive sites.

In addition, NOM also inhibited BioMnO_x@Fh performance, with stronger suppression observed at the higher NOM level (Figs. S15c, f). Among the simulated water matrices, GW and SW caused moderate decreases in total As removal and As(V) generation, whereas CW produced the strongest inhibition. These results indicate that BioMnO_x@Fh is relatively tolerant to several common inorganic background ions, but its performance can be constrained by coexisting constituents that strongly compete for Fe-oxide-associated retention sites and may also interfere with interfacial arsenic redox reactions in Mn-containing systems[3-6].

Text S6. Determination of As(III) and Total As in the Desorption Supernatant

The concentrations of As(III) and total As in the desorption supernatant were determined by atomic fluorescence spectrometry (AFS; Kylin S12) according to the Chinese National Standard method (GB/T 5009.11-2003). After desorption and centrifugation, the supernatant was divided into two aliquots for parallel analysis. Each aliquot was diluted as required to bring the arsenic concentration within the calibrated working range of the instrument. For As(III)-specific determination, the sample was adjusted to 1% (v/v) HCl. For total As determination, the sample was adjusted to 5% (v/v) HCl. Samples were analyzed within the validated holding time established by the preservation test described below.

For total As determination, a pre-reducing solution containing 5% (w/v) ascorbic acid and 5% (w/v) thiourea was added to convert As(V) to As(III) prior to measurement. For As(III)-specific analysis, the carrier solution was 1% (v/v) HCl, and the reductant was 1% (w/v) potassium borohydride (KBH_4) prepared in 0.5% (w/v) NaOH. For total As analysis, the carrier solution was 5% (v/v) HCl, and the reductant was 2% (w/v) KBH_4 in 0.5% (w/v) NaOH. The concentration of desorbed As(V) was calculated as the difference between total As and As(III).

To ensure the reliability of this difference-based speciation approach, explicit quality-control procedures were implemented. External calibration was performed using at least 5 arsenic standards covering the working range of 5–100 $\mu\text{g}\cdot\text{L}^{-1}$, and calibration was accepted only when the coefficient of determination (R^2) was ≥ 0.99 . A calibration blank and an independently prepared check standard (50 $\mu\text{g}\cdot\text{L}^{-1}$) were analyzed every 30 samples to verify instrumental stability. Method precision and recovery were evaluated using matrix-spike experiments. The method detection limit (LOD) and limit of quantification (LOQ) were calculated as 3σ and 10σ , respectively, based on repeated analyses ($n = 6$) of 5 $\mu\text{g}\cdot\text{L}^{-1}$ standards processed through the same dilution and acidification steps as the samples (Table S12).

Method precision and recovery were evaluated using matrix-spike experiments. Known amounts of arsenic standards (5–80 $\mu\text{g}\cdot\text{L}^{-1}$) were added to the NaOH desorption

matrix, and analyzed using the same procedure as for the samples. The relative standard deviation (RSD) for replicate measurements was 1.02–1.49%, and the spike recovery was 91.62–96.99%. Matrix effects were further assessed by comparing the slopes of solvent-based and matrix-matched calibration curves. Because arsenic speciation may be altered during storage and pretreatment, a short-term preservation/stability test was performed to validate the adopted sample-handling procedure. Mixed As(III)/As(V) standard solution was stored under the same conditions used for analytical samples and reanalyzed after 0, 6, 24, and 48 h. The stability test (Fig. S25) confirmed that no significant interconversion between As(III) and As(V) occurred within 48 h under the adopted preservation conditions.

Text S7. Characterization Methods

Scanning electron microscopy (SEM) was used to examine the morphology of MnB1 cells associated with the bio-oxides. Briefly, the bio-oxide samples were collected by centrifugation ($5000 \times g$, 5 min, 4 °C) and washed three times with HEPES-buffered saline (137 mM NaCl, 2.7 mM KCl, and 10 mM HEPES, pH 7.2). The recovered solids were fixed in 2.5% (v/v) glutaraldehyde for 4 h, followed by three additional washes with the same buffer. The samples were then dehydrated through a graded ethanol series, mounted on silicon wafers, and sputter-coated with a thin Pt layer prior to imaging using a ZEISS field-emission SEM.

The morphology and elemental composition of the bio-oxides were further analyzed by field-emission scanning electron microscopy equipped with energy-dispersive spectroscopy (FESEM–EDS; TESCAN MIRA LMS with an Oxford Xplore 30 EDS detector). Powdered samples were mounted on conductive substrates using conductive adhesive and coated with a thin conductive layer before observation at an accelerating voltage of 15 kV.

Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were acquired using a FEI Tecnai F20 transmission electron microscope (FEI, USA) operated at an accelerating voltage of 200 kV. For

TEM analysis, the samples were ultrasonically dispersed in deionized water, and a drop of the suspension was deposited onto a carbon-coated copper grid, followed by air drying at room temperature before observation.

The crystalline structures of the samples were characterized by X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer equipped with a LynxEye detector and Ni-filtered Cu K α radiation ($\lambda = 0.15418$ nm). The instrument was operated at 40 kV and 40 mA. Diffraction patterns were collected over a 2θ range of 5–85° with a step size of 0.02° and a scanning rate of 10° min⁻¹.

Surface functional groups were identified by Fourier transform infrared spectroscopy (FTIR) using a Bruker VERTEX 70 spectrometer. Samples were mixed with dried KBr at a mass ratio of 1:80, finely ground, and pressed into transparent pellets. Spectra were recorded over the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹ and 64 scans.

The valence states of key elements, including Mn and As, were determined by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic Al K α X-ray source (1486.7 eV, 15 kV, 10 mA). High-resolution spectra were acquired with a step size of 0.1 eV and pass energies of 20–40 eV. All XPS spectra were processed and analyzed using Thermo Scientific Advantage software. The spectra were energy-calibrated against adventitious carbon (C 1s = 284.8 eV). The Mn 2p_{3/2} spectra were fitted semi-quantitatively by including Mn(II), Mn(III), and Mn(IV) multiplet components. Initial peak positions, relative intensities, and multiplet splitting parameters (Table S11) were constrained according to reported reference spectra[7]. Unless otherwise stated, the multiplet splitting pattern, relative intensity ratios, and peak-shape settings were shared across samples, while only limited energy shifts (± 0.1 eV) were allowed to vary during fitting. Fit quality was evaluated using the normalized χ^2 value, and the corresponding fitting settings are summarized in Table S10. The As 3d spectra were fitted using spin-orbit doublets with a fixed splitting energy of 0.69 eV and a fixed 2:3 area ratio for the 3d_{3/2} and 3d_{5/2} components. Accordingly, the XPS-derived Mn valence fractions and Mn AOS reported in this study should be interpreted as semi-quantitative.

Text S8. Preparation of BioMnO_x and BioMnO_x@Fh Capsules

Alginate capsules containing BioMnO_x or BioMnO_x@Fh were prepared by inverse gelation with minor modifications based on the method of Zvulunov and Radian[8]. Briefly, the core phase was prepared by mixing the bio-oxide suspension with a thickening agent, glycerol, and divalent cross-linking cations at predefined ratios. Two core formulations were used to provide suitable viscosity for capsule formation: (1) 0.2% (w/v) xanthan gum (XG) with 20% (v/v) glycerol, and (2) 10% (w/v) PEG 8000 with 20% (v/v) glycerol. In both formulations, the cross-linking cations in the core phase consisted of a mixed Ba²⁺/Ca²⁺ system containing 50 mM Ba²⁺ and 50 mM Ca²⁺ (100 mM total divalent-cation concentration). The amount of bio-oxides added to the core phase was adjusted so that the final capsule dosage in subsequent batch experiments corresponded to 0.2 mM Mn on an Mn-equivalent basis.

A 5 mL aliquot of the core solution was loaded into a 10 mL syringe fitted with a 24G needle. The syringe tip was positioned 10–15 cm above the surface of a stirred alginate bath containing 1% (w/v) sodium alginate and 0.1% (w/v) Tween® 80, and the core solution was introduced dropwise at a constant rate of 1.3 mL·min⁻¹. Tween® 80 was included in the alginate bath to improve droplet formation and capsule sphericity[8]. Upon contact with the alginate bath, an ionically cross-linked shell formed at the liquid–liquid interface. After completion of droplet addition, the resulting capsules were stirred in the alginate bath for an additional 10 min to allow sufficient shell formation.

The capsules were then collected, thoroughly rinsed with deionized water, and transferred to a salt solution matching the ionic composition of the core solution for a further 10 min of cross-linking. After this step, the capsules were rinsed again and gently stirred overnight in excess deionized water to extract glycerol from the capsule interior. The capsules were then rinsed once more and stored in deionized water at 4 °C until use. To maintain consistent hydrodynamic conditions during preparation, all capsules were produced in a 500 mL low-form beaker containing 250 mL of alginate solution and stirred with a 50 mm magnetic stir bar. The stirring speed was adjusted to generate a vortex of approximately 1.5 cm depth. Capsule morphology and size were

examined using an optical microscope. The capsules prepared with XG or PEG as core-phase additives are shown in Fig. S21.

Text S9. Transcriptomic response of strain MnB1 to Fh treatment

Transcriptome sequencing and differential expression analysis

Strain MnB1 was cultivated under the same experimental conditions as those used for the comparison between the control (CK) and Fh treatment. For transcriptomic analysis, cells were collected from CK and Fh-treated cultures after 24 h of incubation, with 3 independent biological replicates for each group. The concentration of Fh used in the transcriptomic experiment was $1 \text{ g} \cdot \text{L}^{-1}$, consistent with the conditions used during BioMnO_x@Fh preparation. After sampling, the cell suspensions were immediately centrifuged at 10000 rpm for 10 min at 4 °C. The bacterial pellets were frozen in liquid nitrogen for transcriptomics analyses.

Total RNA was extracted using the TRIzol® Reagent following the manufacturer's instructions (Invitrogen, USA). Libraries were prepared using the TruSeq™ Stranded Total RNA Library Prep Kit and sequenced on an Illumina HiSeq×TEN system (2 × 150 bp) (Illumina, USA). All bioinformatics analyses were performed using the Majorbio Cloud Platform (www.majorbio.com) of Shanghai Majorbio Bio-pharm Technology Co., Ltd.[9]. Raw reads were processed to remove adapter sequences, low-quality reads, and reads containing excessive ambiguous bases using Sickle 1.33. Clean reads were then mapped to the reference genome of *Pseudomonas putida* NBRC 14164, which was used as the annotation reference for transcriptomic analysis, using Bowtie2 2.5.4. Gene expression levels were quantified as TPM using RSEM 1.3.3. Differential expression analysis between the Fh and CK groups was performed using edgeR 4.0.2. Genes with an adjusted P value (P_{adjust}) < 0.05 and $|\log_2 \text{ fold change}| > 2$ were considered differentially expressed. KEGG pathway enrichment analysis of the differentially expressed genes (DEGs) was performed using clusterProfiler, and pathways with $P_{\text{adjust}} < 0.05$ were regarded as significantly enriched.

Transcriptomic response of strain MnB1 to Fh treatment

Transcriptomic analysis showed that Fh treatment induced a distinct yet selective transcriptional response in strain MnB1. The transcript sets under CK and Fh conditions largely overlapped, with 3,577 shared genes, whereas 179 and 45 genes were uniquely detected under CK and Fh, respectively (Fig. S5a). Differential expression analysis further identified 631 genes responsive to Fh, including 107 up-regulated and 524 down-regulated genes (Fig. S5b).

KEGG enrichment analysis of the up-regulated genes showed that the most relevant pathways included bacterial secretion system, flagellar assembly, oxidative phosphorylation, and protein export (Fig. S6; Table S7). In the bacterial secretion/protein export category, genes encoding a T2SS/T4P/T4SS-family ATPase, XcpP, GspG, and the TatA/TatB/TatC translocation system were significantly up-regulated (Table S6), suggesting an increased capacity for protein translocation and extracellular export. In parallel, several genes involved in flagellar assembly, including *fliE*, *flgB*, *flgC*, *flgF*, *fliL*, and *fliJ*, were also significantly induced, indicating enhanced flagellar biogenesis and potentially altered cell-surface responsiveness. In addition, genes assigned to oxidative phosphorylation, including those encoding cbb3-type cytochrome c oxidase subunits I and II and cytochrome o ubiquinol oxidase subunits III and IV, were up-regulated under Fh treatment. Together, these results suggest that Fh upregulated genes involved in secretion-related processes, flagellar/surface-response functions, and respiration-associated electron-transfer pathways in MnB1, changes that may have favored Mn(II) oxidation.

In contrast, the down-regulated genes were enriched in mineral absorption and several additional KEGG categories (Fig. S7). Among them, two genes involved in mineral absorption, encoding a heavy metal-translocating P-type ATPase and a cation transporter, were significantly down-regulated (Table S6), suggesting that Fh also affected metal transport and ion homeostasis in MnB1.

Notably, genes encoding putative multicopper oxidases and peroxidases previously implicated in Mn oxidation were not broadly induced by Fh treatment (Table S5). The MnxG-like multicopper oxidase gene *PP4_RS12010* showed slight down-regulation, *PP4_RS18180* was significantly down-regulated, and most peroxidase-related genes

showed either no clear change or inconsistent responses. These data suggest that the promoting effect of Fh on Mn(II) oxidation was unlikely to result from direct transcriptional activation of Mn-oxidizing enzymes alone. Instead, Fh appeared to favor Mn(II) oxidation primarily through broader physiological remodeling, particularly by enhancing secretion-related pathways, flagellar/surface-associated functions, and respiratory electron-transfer components.

Text S10. Characterization of Abiotic MnO_x and MnO_x@Fh

SEM images showed that abiotic MnO_x occurred as aggregated particles without well-defined crystal habits, consistent with a nanoscale, poorly ordered morphology (Fig. S8a). The XRD pattern (Fig. S8d) displayed two reflections at 11.9° and 23.8° (2 θ), corresponding to *d*-spacings of 7.40 and 3.70 Å, which can be assigned to the (001) and (002) planes of a layered Mn oxide, respectively. These reflections indicate periodic stacking of MnO₆ octahedral sheets with an interlayer spacing of 7.40 Å, whereas their low intensities and broad widths suggest limited long-range stacking order. Broad *hk* bands with *d*-spacings of 2.42 Å and 1.41 Å were observed in both abiotic MnO_x (Fig. S8d) and BioMnO_x (Fig. 1f). The ratio of these two *d*-spacings (1.72) is close to $\sqrt{3}$, consistent with the theoretical *b/a* axial ratio of a hexagonal structure[10]. In the FTIR spectrum of abiotic MnO_x, the band at 1614 cm⁻¹ was assigned to the O-H bending mode of water, while the broad bands at approximately 3196 and 3337 cm⁻¹ were attributed to O-H stretching vibrations. The bands at 456 and 500 cm⁻¹ were assigned to Mn-O lattice vibrations and showed slight shifts relative to those of reference hexagonal birnessite (reference peaks: 432 cm⁻¹ and 496 cm⁻¹; Table S3)[11]. These shifts may reflect variations in local Mn–O bonding environments that are more sensitively captured by FTIR than by XRD. Semi-quantitative deconvolution of the Mn 2p_{3/2} XPS spectrum (Fig. S8c) gave Mn(II), Mn(III), and Mn(IV) fractions of 8.7%, 45.3%, and 46.1%, respectively, corresponding to an Mn AOS of 3.38, which was higher than that of BioMnO_x.

For abiotic MnO_x@Fh, SEM imaging showed that the Mn-containing phase formed

in the presence of Fh had a morphology generally similar to that of the Fh-free abiotic MnO_x system (Fig. S8b). EDS mapping (Fig. S9) showed that Mn was distributed around Fe-rich domains; within the selected Fe-Mn region, the atomic fractions of Fe and Mn were 80.95% and 19.05%, respectively, consistent with deposition of Mn-containing phases on the Fh surface. The XRD pattern of abiotic $\text{MnO}_x@\text{Fh}$ showed only two broad Fh-related diffraction bands near 35° and 62° (2θ), with no clearly resolved MnO_x reflections (Fig. S8d), indicating lower apparent crystallinity of the Mn-containing phase than in the Fh-free abiotic MnO_x system. FTIR analysis (Fig. S8e) showed Mn-O lattice vibration bands at 459 and 506 cm^{-1} , consistent with a birnessite-like Mn oxide environment, whereas the broader band profiles further supported reduced structural order. Semi-quantitative deconvolution of the Mn $2p_{3/2}$ XPS spectrum (Fig. S8c) gave Mn(II), Mn(III), and Mn(IV) fractions of 14.2%, 60.2%, and 25.7%, respectively, corresponding to an Mn AOS of 3.12. Relative to abiotic MnO_x (Mn AOS = 3.38), this lower Mn AOS and higher Mn(III) fraction suggest that the Fe-containing abiotic system favored formation of a more reduced Mn oxide phase under the tested synthesis conditions, although the mechanism responsible for this shift cannot be resolved from the present dataset alone. Notably, this trend contrasted with the biogenic system, in which the presence of Fh slightly increased the Mn oxidation state of BioMnO_x (Fig. 1h), further underscoring the distinct role of MnB1-mediated mineralization in determining the structure and redox properties of the composite Mn phases.

Text S11. Kinetic Interpretation of As(III) Treatment by $\text{BioMnO}_x@\text{Fh}$

The uptake behavior of As(III) by the Fh-CM control can be described using the intraparticle diffusion model[12]:

$$C_t = k_p \times t^{0.5} + C \quad (1)$$

Where k_p is the intraparticle diffusion rate constant ($\text{mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1/2}$), and C ($\text{mg}\cdot\text{L}^{-1}$) was a constant related to the thickness of the boundary layer.

Application of this model to the Fh-CM composite showed an apparent two-stage

kinetics behavior (Fig. S24b): an initial rapid stage (0–2 h), with an apparent rate constant of $5.27 \pm 0.31 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1/2}$, followed by a slower stage after 2 h, with an apparent rate constant of $0.26 \pm 0.029 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1/2}$. The initial stage was therefore approximately 20 times faster than the later stage. This result indicates that As(III) uptake by the Fh-containing control was initially dominated by rapid surface-associated transfer, followed by a slower diffusion-limited process.

Based on this kinetic contrast, the behavior of $\text{BioMnO}_x@\text{Fh}$ can be interpreted as involving two temporally distinct but coupled stages. During the initial period (approximately the first 2 h), the decrease in dissolved As(III) is consistent with rapid uptake by the Fh-containing phase, which contributed substantially to the early dissolved As(III) removal observed in Fig. 2g. As the reaction proceeds and the fast initial uptake stage weakens, the Mn-containing phase likely contributes increasingly to continued As(III) conversion through oxidation. Under this interpretation, the Fe-containing phase primarily promotes early depletion of dissolved As(III), whereas the BioMnO_x phase supports continued oxidative transformation at later times.

Therefore, the overall performance of $\text{BioMnO}_x@\text{Fh}$ is consistent with a coupled adsorption-oxidation process, in which the Fe-containing and Mn-containing components make complementary contributions to As(III) treatment. However, this description should be regarded as a kinetic interpretation based on the available data rather than as direct proof of a fully resolved stepwise reaction pathway.

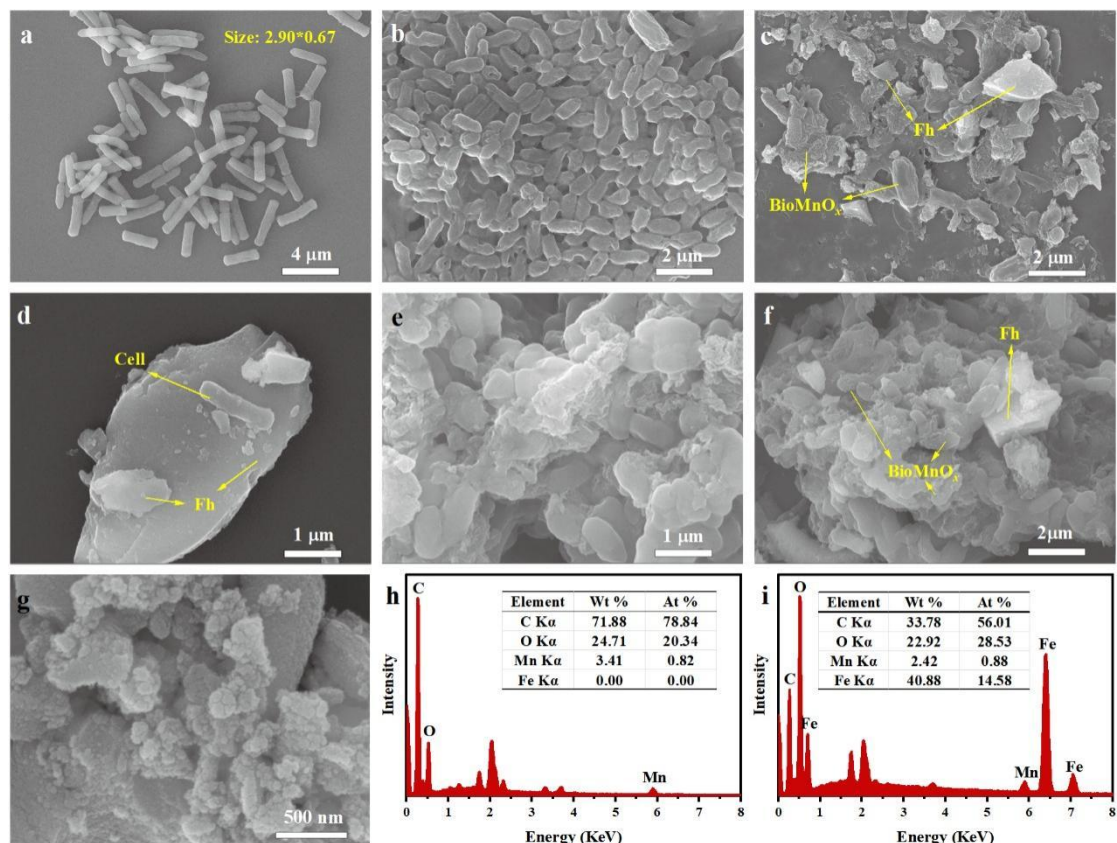


Fig. S1. FESEM micrographs of (a) *Pseudomonas* sp. MnB1, (b, e) BioMnO_x, (c, f) BioMnO_x@Fh, (d) *Pseudomonas* sp. MnB1 associated with ferrihydrite after 12 h of incubation, and (g) Fh; EDS spectra of (h) BioMnO_x and (i) BioMnO_x@Fh. Samples in panels (a-d) were fixed with glutaraldehyde prior to imaging.

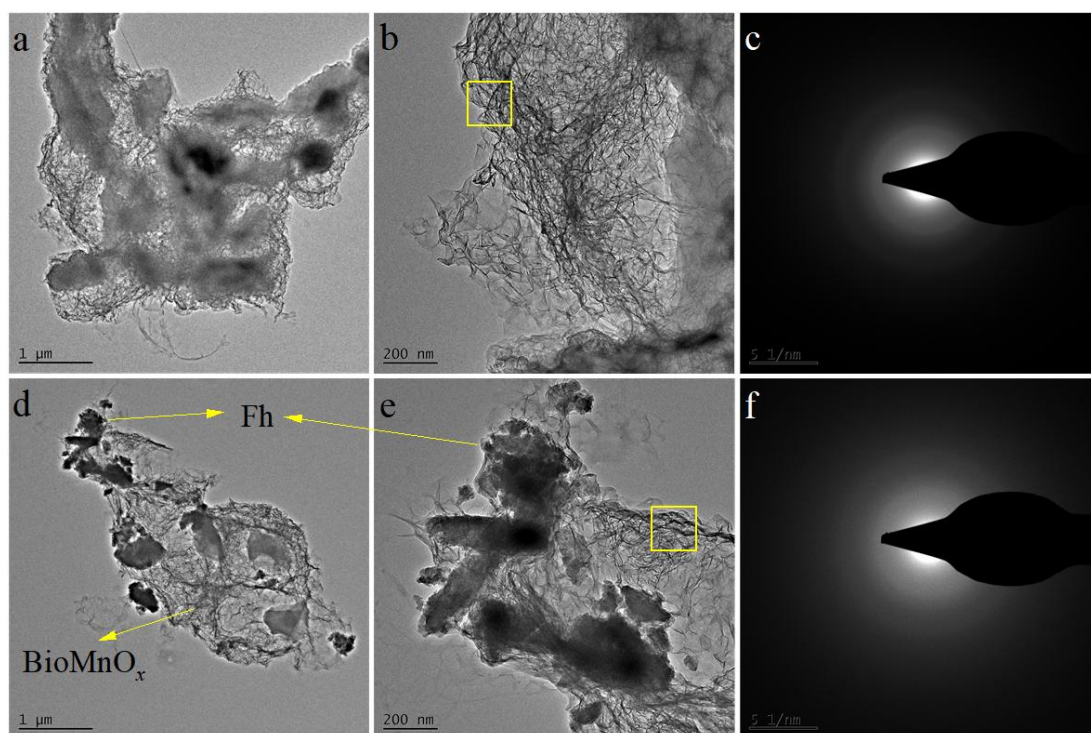


Fig. S2. TEM micrographs of (a, b) BioMnO_x and (d, e) BioMnO_x@Fh. Selected area electron diffraction (SAED) patterns corresponding to the boxed regions.

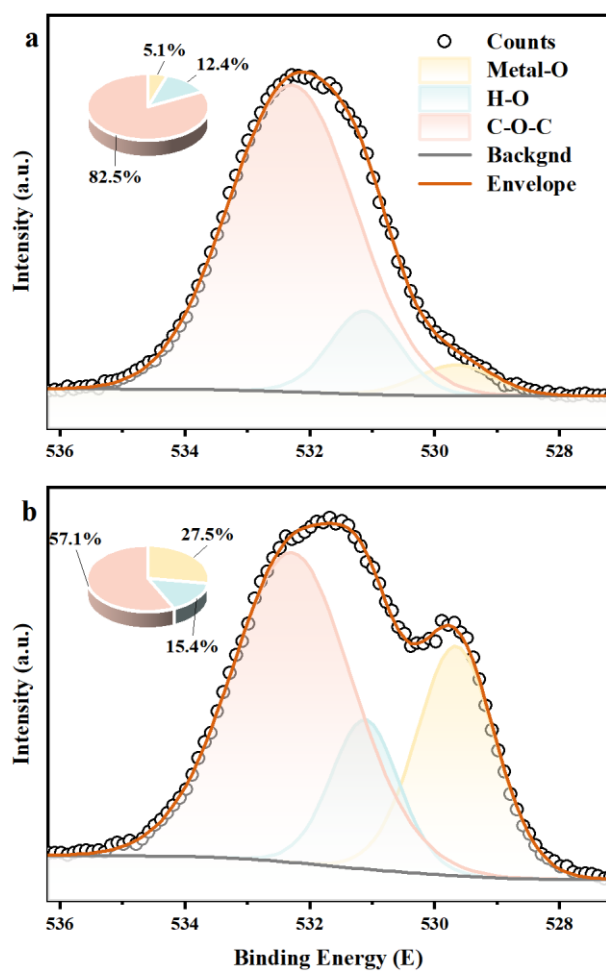


Fig. S3. Semi-quantitative fitted O1s XPS spectra of (a) BioMnO_x and (b) BioMnO_x@Fh. The components centered at 529.66 eV, 531.12 eV, and 532.29 eV are assigned to metal-O, H-O, and C-O-C bonds, respectively[13].

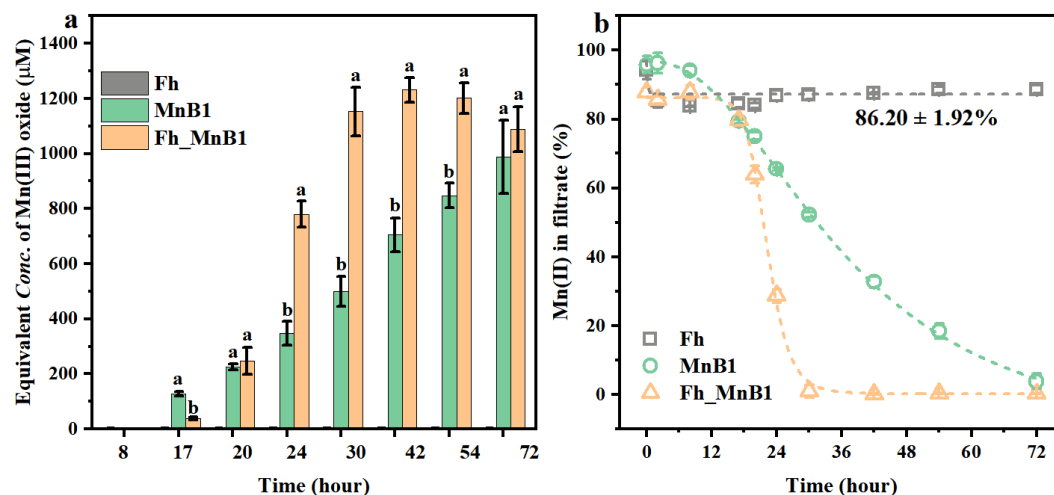


Fig. S4. Influence of Fh on Mn(II) oxidation by strain MnB1. (a) Changes in the equivalent concentration of Mn(III) oxides determined by the leucoberbelin blue (LBB) method[14]. (b) Changes in dissolved Mn(II) concentration in the supernatant. Different letters indicate statistically significant differences ($p < 0.05$). Experimental conditions were otherwise consistent with those used for BioMnO_x@Fh synthesis.

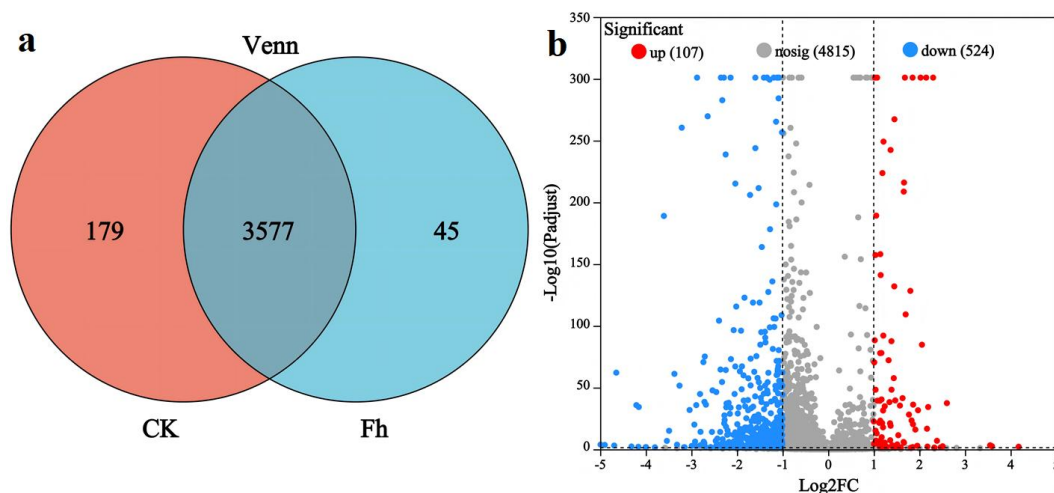


Fig. S5. (a) Venn diagram showing the overlap of DEGs between CK and ferrihydrite (Fh) treatment. (b) Volcano plot of DEGs in strain MnB1 under Fh treatment relative to CK, with log₂ fold change (log₂FC) and -log₁₀(Padjust) shown on the x- and y-axes, respectively.

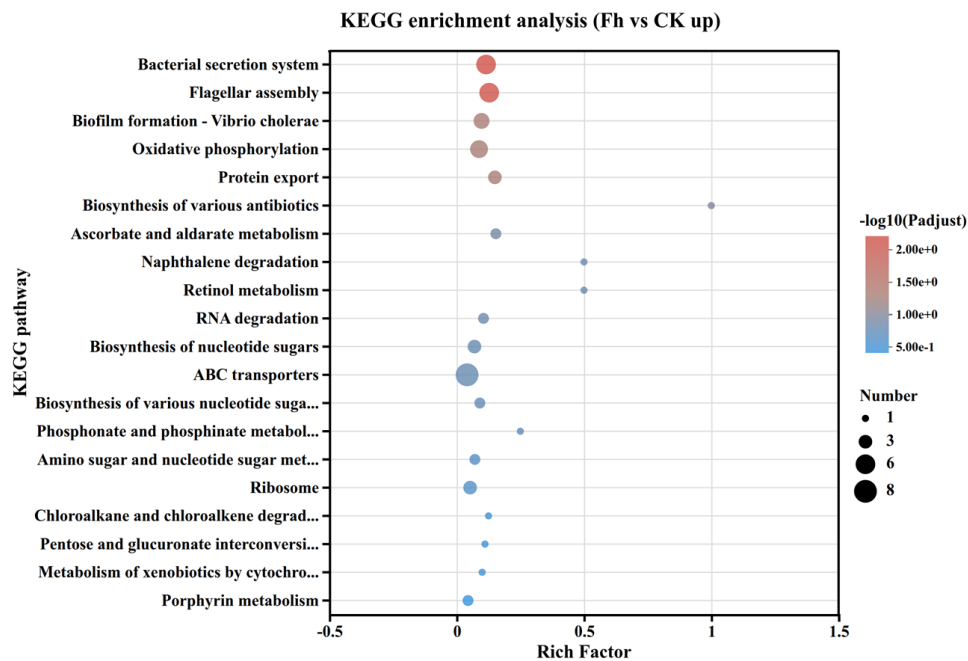


Fig. S6. KEGG pathway enrichment bubble plot of up-regulated DEGs in strain MnB1 under Fh treatment relative to CK. The x-axis represents the rich factor, and the y-axis shows KEGG pathways. Bubble size indicates the number of DEGs, and color represents $-\log_{10}(\text{Padj})$.

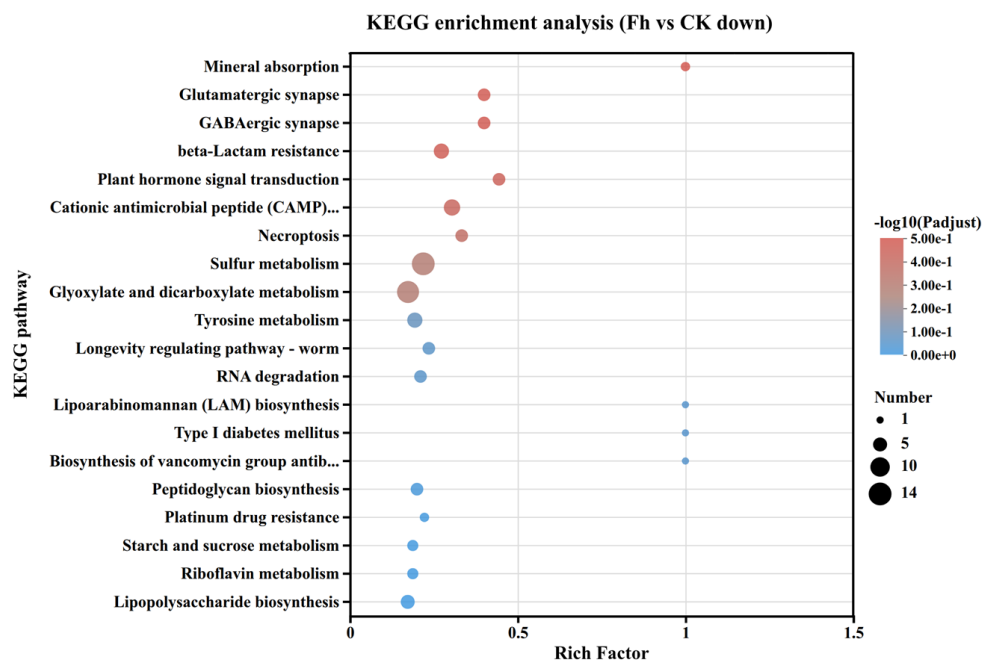


Fig. S7. KEGG pathway enrichment bubble plot of down-regulated DEGs in strain MnB1 under Fh treatment relative to CK. The x-axis represents the rich factor, and the y-axis shows KEGG pathways.

Bubble size indicates the number of DEGs, and color represents $-\log_{10}(\text{P}_{\text{adjust}})$.

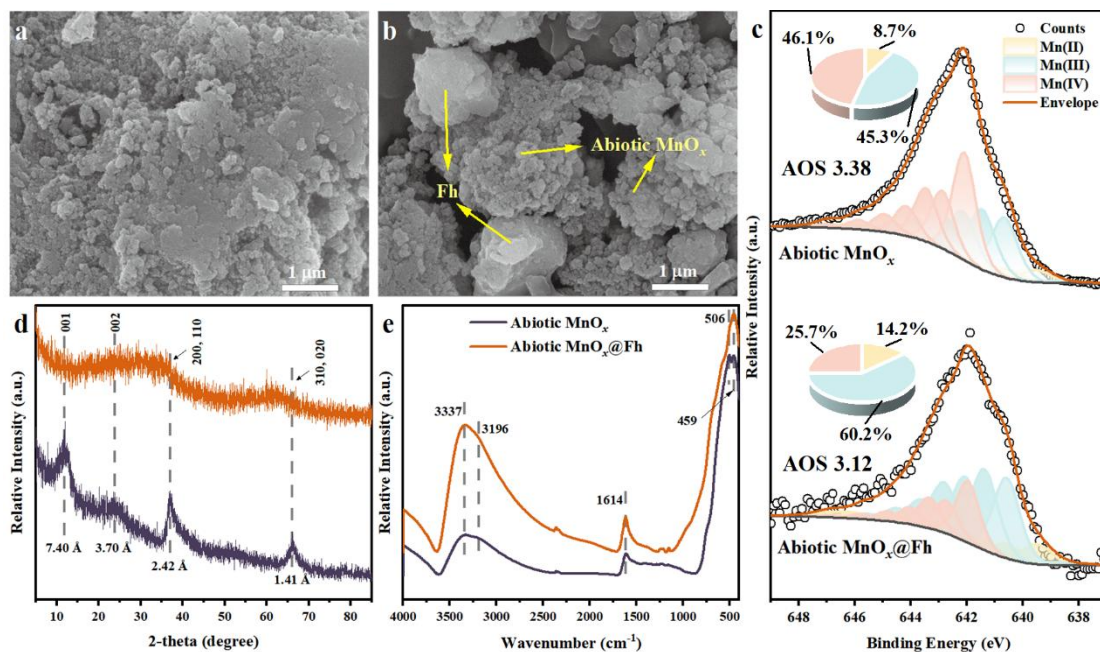


Fig. S8. Characterization of abiotic Mn-based materials: FESEM micrographs of (a) abiotic MnO_x and (b) abiotic $\text{MnO}_x@\text{Fh}$; semi-quantitative fitted Mn $2p_{3/2}$ XPS spectra (c); XRD patterns (d); and FTIR spectra (e).

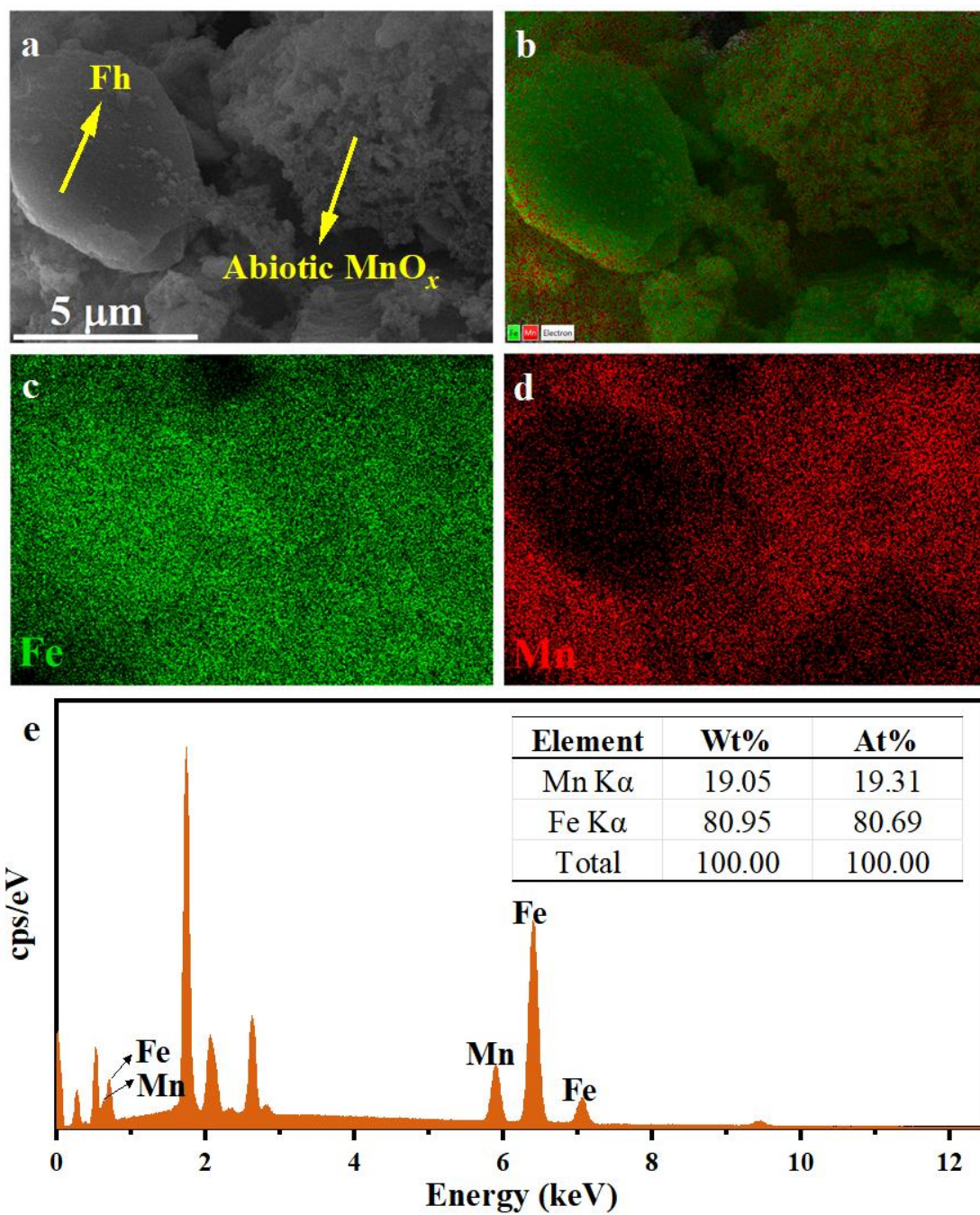


Fig. S9. EDS analysis of abiotic $\text{MnO}_x@\text{Fh}$: (a) analyzed area, (b–d) EDS mapping images, and (e) the corresponding EDS spectrum.

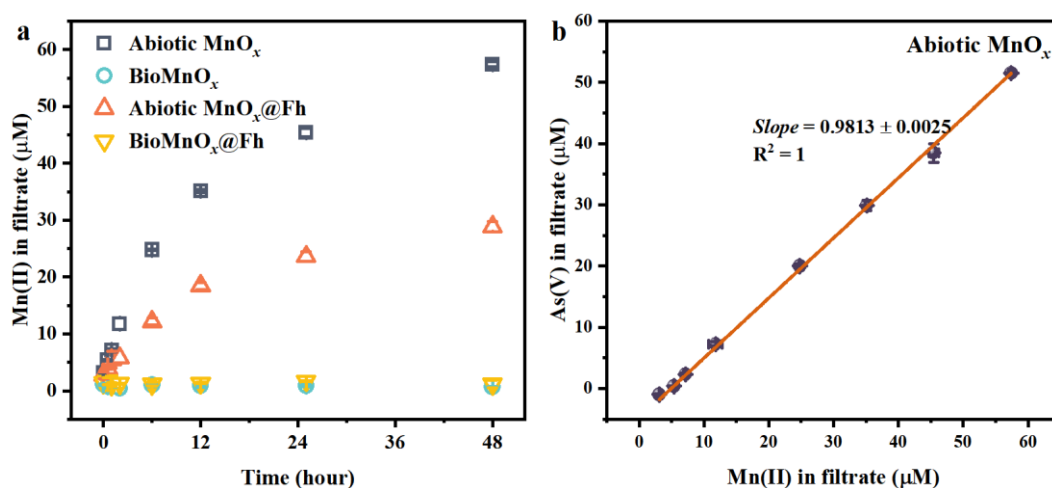


Fig. S10. Dissolved Mn(II) release during As(III) treatment by biotic and abiotic oxides (a), and the relationship between dissolved Mn(II) and generated As(V) in the abiotic MnO_x system (b). The red line indicates the linear regression fit.

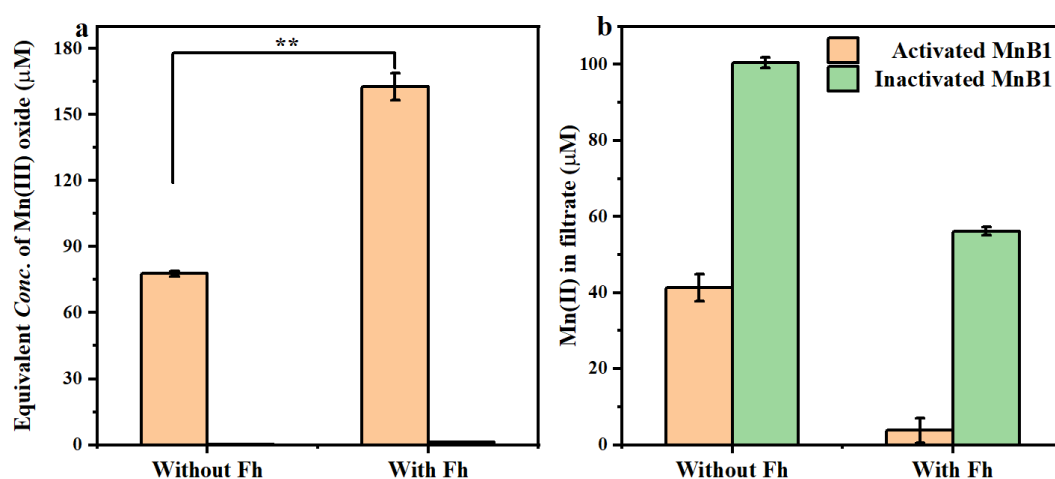


Fig. S11. Effect of Fh on Mn(II) re-oxidation by MnB1 cells released from BioMnO_x after ascorbic-acid dissolution. Cells released from BioMnO_x after ascorbic-acid dissolution were washed with 10 mM HEPES buffer (pH 7.0) to remove residual ascorbic acid, resuspended in the same buffer, adjusted to OD₆₀₀ = 2.0, and incubated with 100 μM Mn(II) in the presence or absence of 1 g/L Fh at 26 °C and 200 rpm for 12 h. Activated and inactivated MnB1 cells (65 °C, 4 h) were included for comparison, and all measurements were conducted at the same time point. (a) The equivalent concentration of Mn(III) oxide produced by activated MnB1 cells was significantly higher in the presence of Fh than in its absence, whereas negligible Mn(III) oxide was detected in the inactivated controls, indicating that Fh promoted MnB1-associated Mn(II) re-oxidation. (b) The residual Mn(II) concentration in the filtrate decreased in the presence of Fh for both activated and inactivated

treatments. However, the lower Mn(II) concentration in the activated treatment, together with the greater production of Mn(III) oxide in panel (a), suggests that Fh enhanced cell-associated Mn(II) re-oxidation while also contributing to abiotic Mn(II) retention. Error bars represent standard deviations of three biological replicates ($n = 3$), and ** indicates a significant difference at $p < 0.01$.

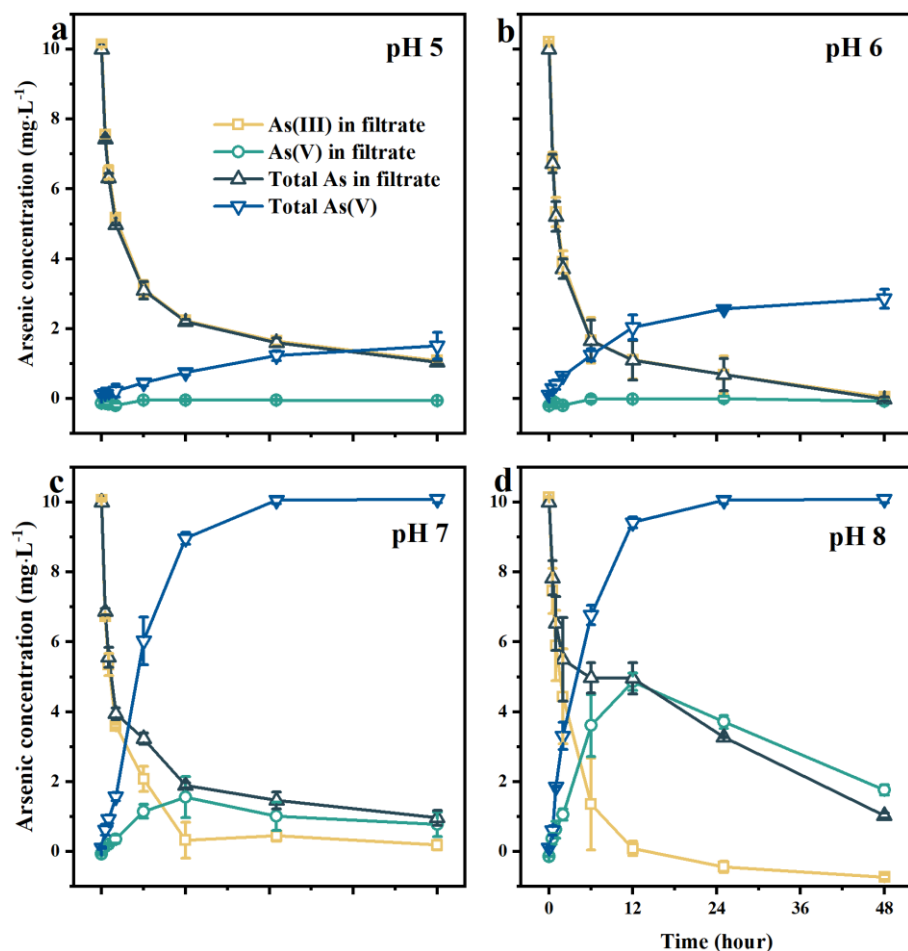


Fig. S12. Temporal profiles of dissolved As(III), dissolved As(V), dissolved total As in the filtrate, and generated As(V) during batch reaction with BioMnO_x@Fh at different pH values.

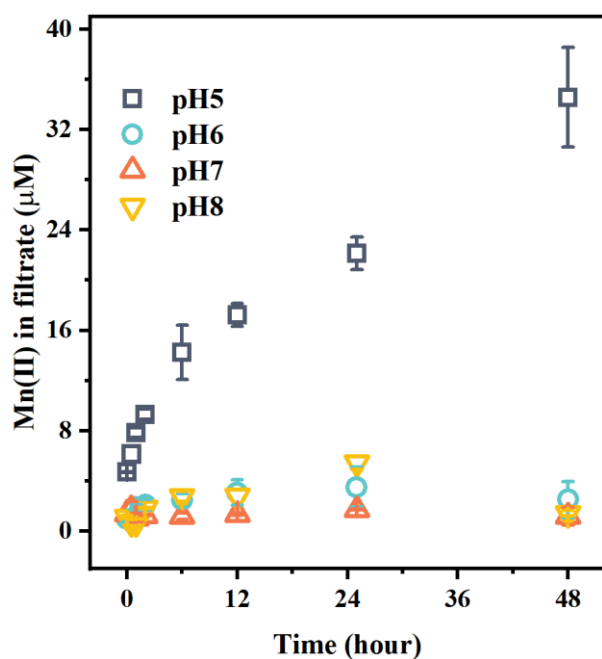


Fig. S13. Dissolved Mn(II) release during As(III) treatment by BioMnO_x@Fh at different pH values.

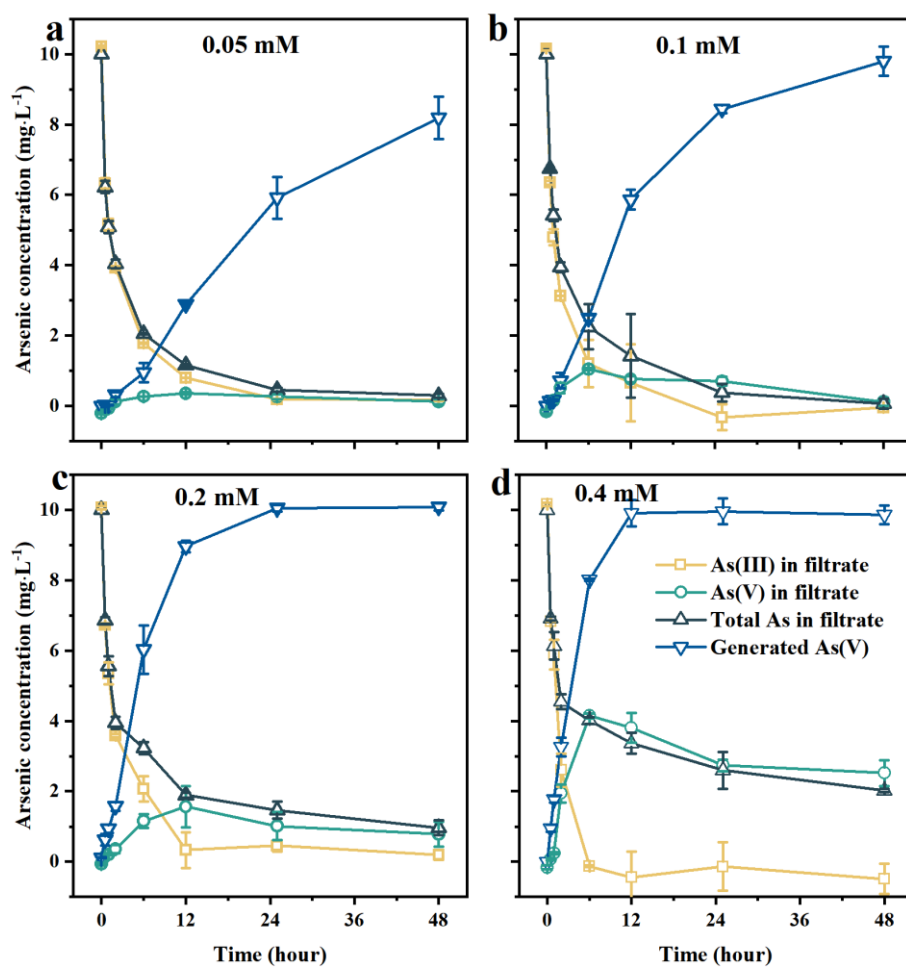


Fig. S14. Temporal profiles of dissolved As(III), dissolved As(V), dissolved total As in the filtrate, and generated As(V) during batch reaction with BioMnO_x@Fh at different Mn loading.

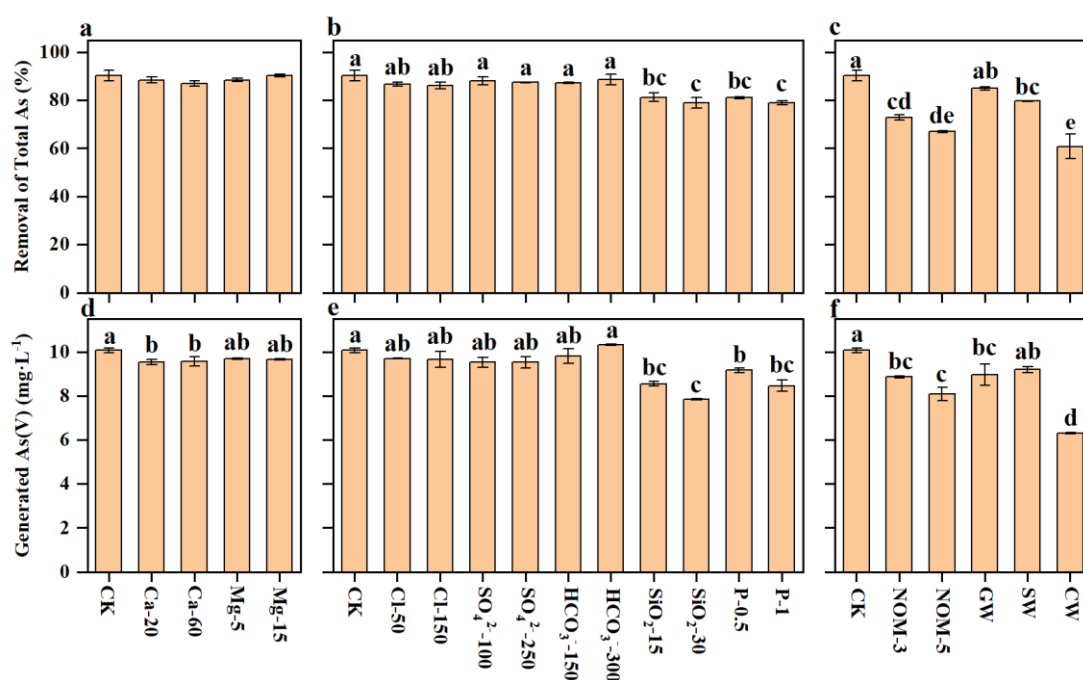


Fig. S15. Effects of coexisting ions, simulated groundwater (GW), surface water (SW), and challenge water (CW) on the removal of total arsenic (a–c) and the generation of As(V) (d–f) by BioMnO_x@Fh in aqueous solution. CK, control without added ions. Ca-20 and Ca-60 denote Ca²⁺ concentrations of 20 and 60 mg·L⁻¹, respectively; other labels indicate the corresponding ion types and concentrations. Different letters indicate statistically significant differences (p < 0.05). The compositions of GW, SW, and CW are provided in Table S2.

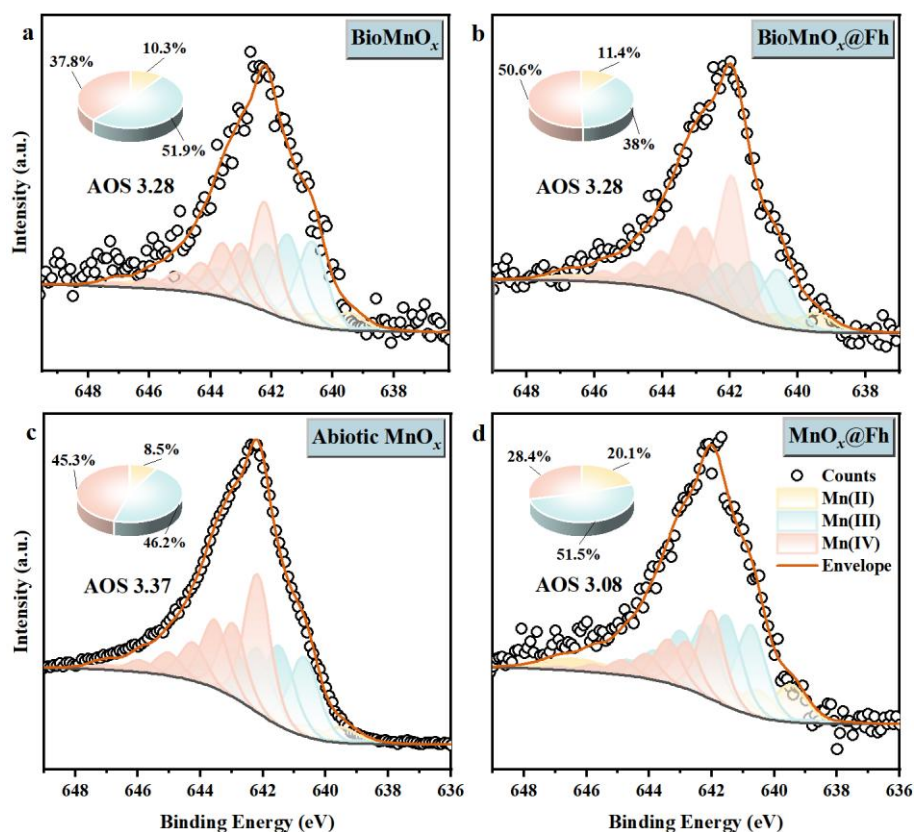


Fig. S16. Semi-quantitative fitted Mn 2p_{3/2} XPS spectra of post-reaction solids after As(III) treatment: (a) BioMnO_x; (b) BioMnO_x@Fh; (c) abiotic MnO_x; (d) abiotic MnO_x@Fh.

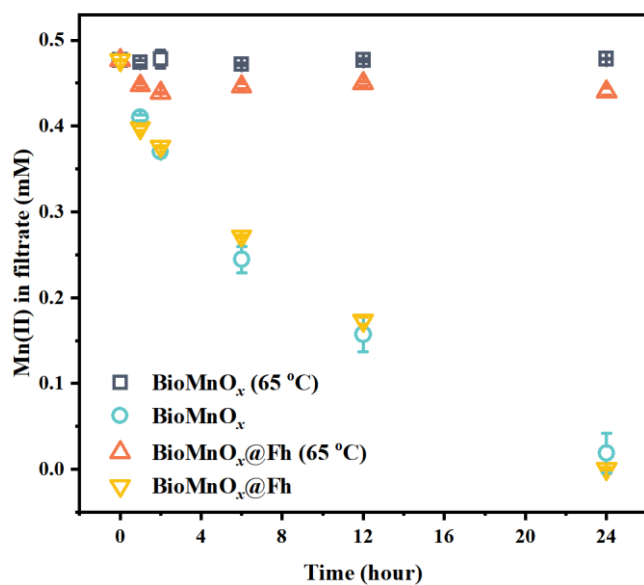


Fig. S17. Mn(II) oxidation kinetics of active and heat-treated bio-oxides (0.2 mM on an Mn-equivalent basis) at pH 7.0 ± 0.05 in 10 mM HEPES buffer.

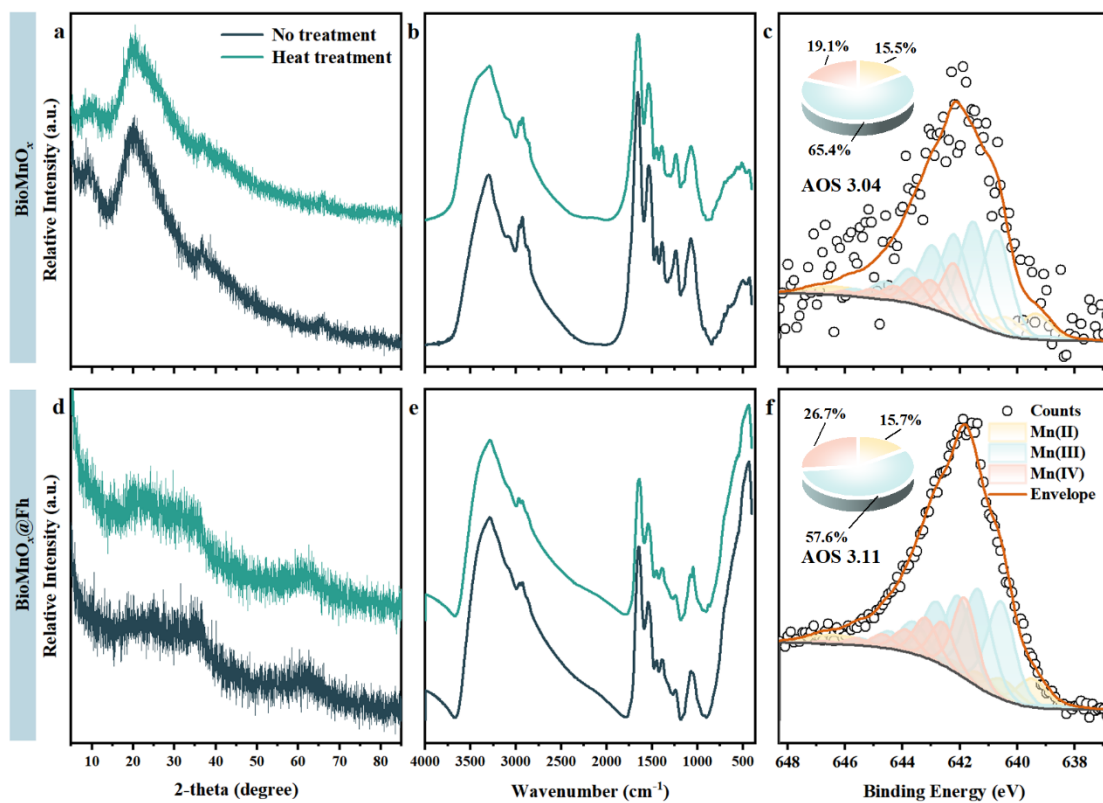


Fig. S18. XRD patterns, FTIR spectra, and semi-quantitative fitted Mn 2p_{3/2} XPS spectra of heat-treated BioMnO_x (a–c) and heat-treated BioMnO_x@Fh (d–f). Untreated bio-oxides are shown as controls (black lines).

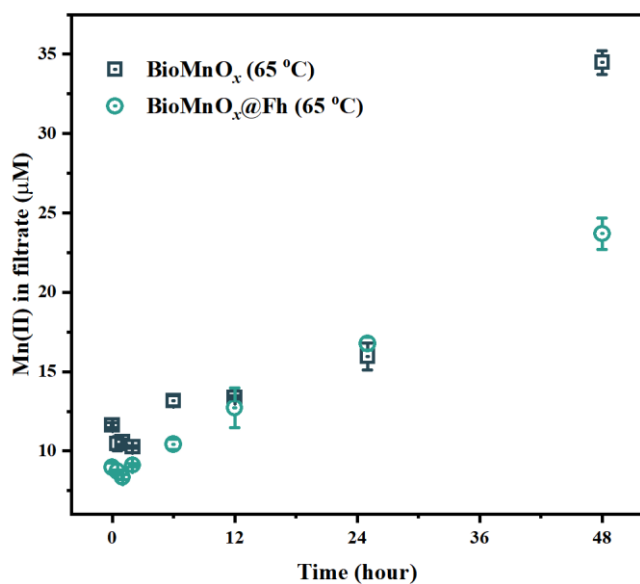


Fig. S19. Dissolved Mn(II) release during As(III) treatment by heat-treated bio-oxides.

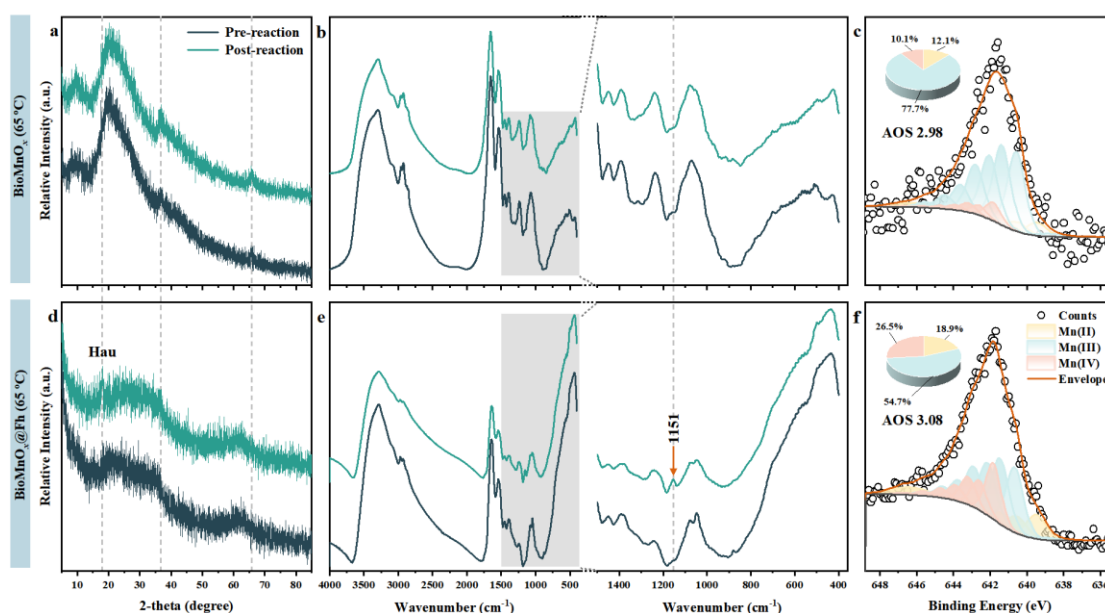


Fig. S20. XRD patterns, FTIR spectra, and semi-quantitative fitted Mn 2p_{3/2} XPS spectra of heat-treated BioMnO_x (a–c) and heat-treated BioMnO_x@Fh (d–f) after As(III) treatment. The corresponding pre-reaction solids are shown as controls (black lines). The reflection at 18° (2θ) is assigned to hausmannite (Hau), and the band at 1151 cm^{−1} is assigned to an O–H-related vibration in manganite (Man).

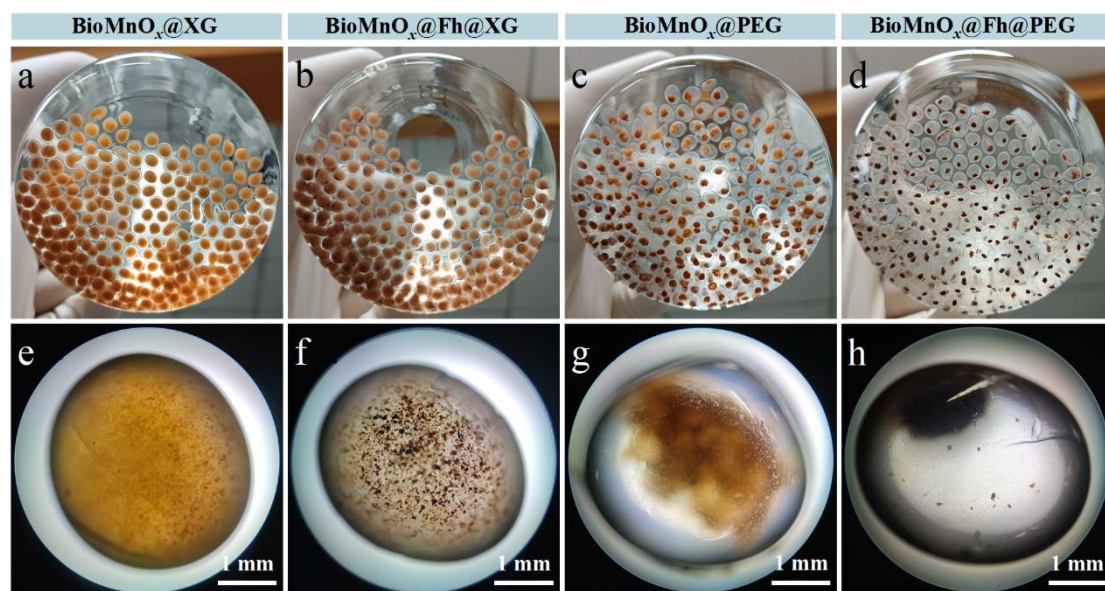


Fig. S21. Images of alginate capsules prepared with 20% glycerol and either 0.2% XG or 10% PEG as core-phase additives: (a, e) BioMnO_x in XG cores; (b, f) BioMnO_x@Fh in XG cores; (c, g) BioMnO_x in PEG cores; and (d, h) BioMnO_x@Fh in PEG cores. The more viscous XG cores maintained a more dispersed distribution of bio-oxides, whereas the less viscous PEG cores allowed greater settling of the encapsulated solids.

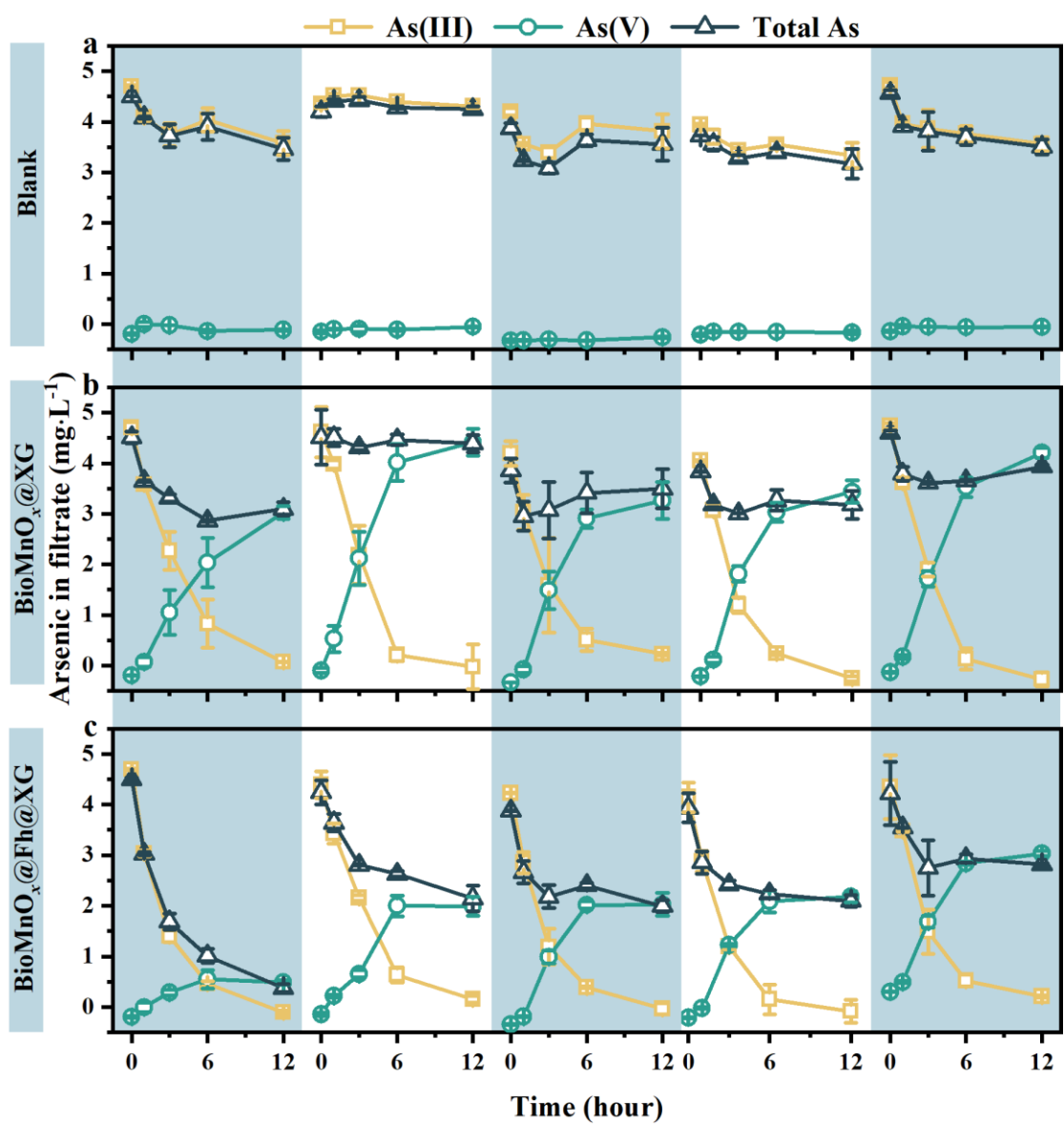


Fig. S22. Reuse performance of XG-based capsules over five batch cycles: (a) blank capsules without bio-oxides; (b) capsules containing BioMnO_x; and (c) capsules containing BioMnO_x@Fh.

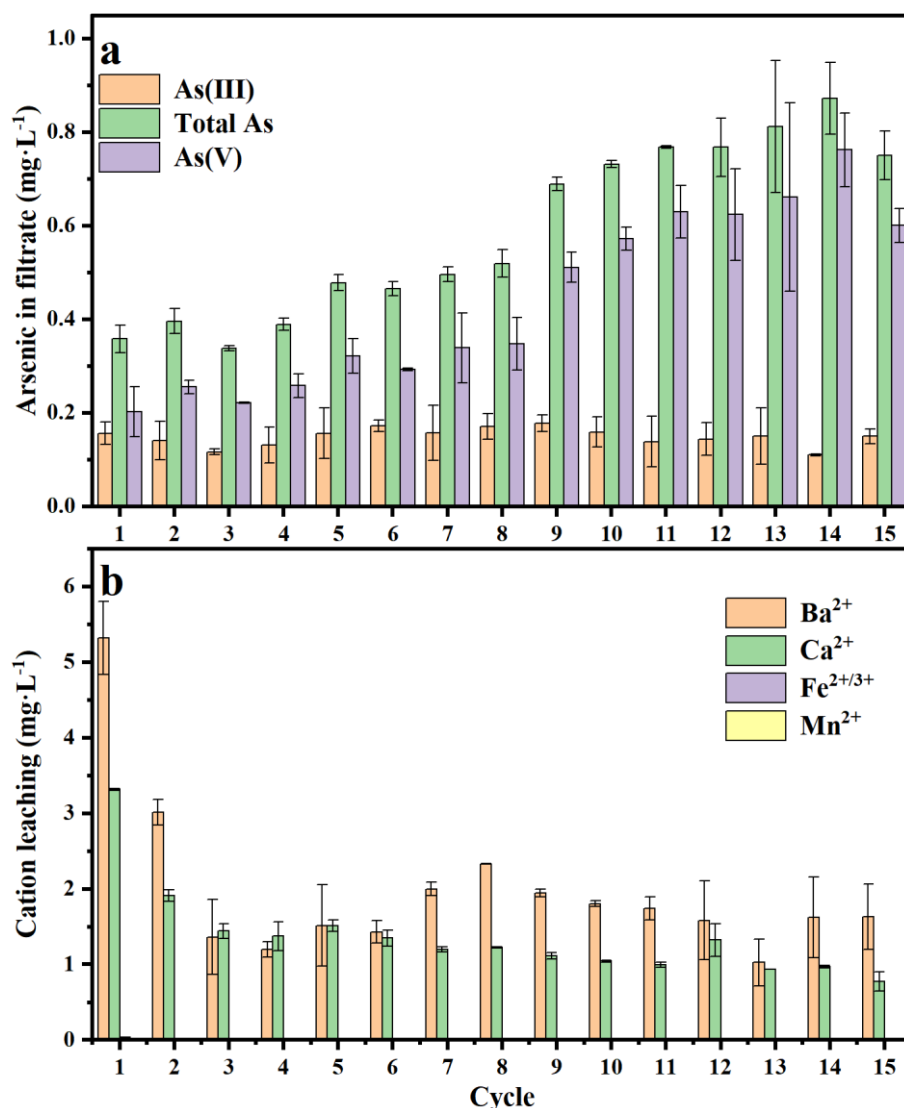


Fig. S23. Long-term reuse performance of PEG capsules containing BioMnO_x@Fh over 15 consecutive batch cycles at an initial As(III) concentration of 1 mg·L⁻¹. (a) Concentrations of As(III), As(V), and total As in the filtrate. (b) Leaching of cations (Ba²⁺, Ca²⁺, Fe^{2+/3+}, and Mn²⁺) during repeated cycles. The capsules maintained low residual As(III) concentrations over repeated cycles, indicating sustained oxidative transformation, whereas the concentrations of dissolved As(V) and total As in the filtrate gradually increased with cycle number. Fe and Mn release remained negligible throughout the repeated cycles, indicating good stability of the Fe- and Mn-containing functional phases. In comparison, Ba²⁺ and Ca²⁺ concentrations in the supernatant were relatively high in the first two cycles, likely due to the release of loosely associated surface-bound cross-linking cations, and then stabilized at approximately 1–2 mg·L⁻¹ in subsequent cycles. Despite this cation release, no visible capsule rupture was observed during the 15-cycle experiment, further supporting the structural robustness of the capsules during prolonged reuse. Nevertheless, Ba²⁺ leaching may still

pose a potential risk of secondary contamination. Future studies should therefore seek to minimize the use of cross-linking cations with unfavorable environmental profiles and develop capsule formulations with lower environmental release risks.

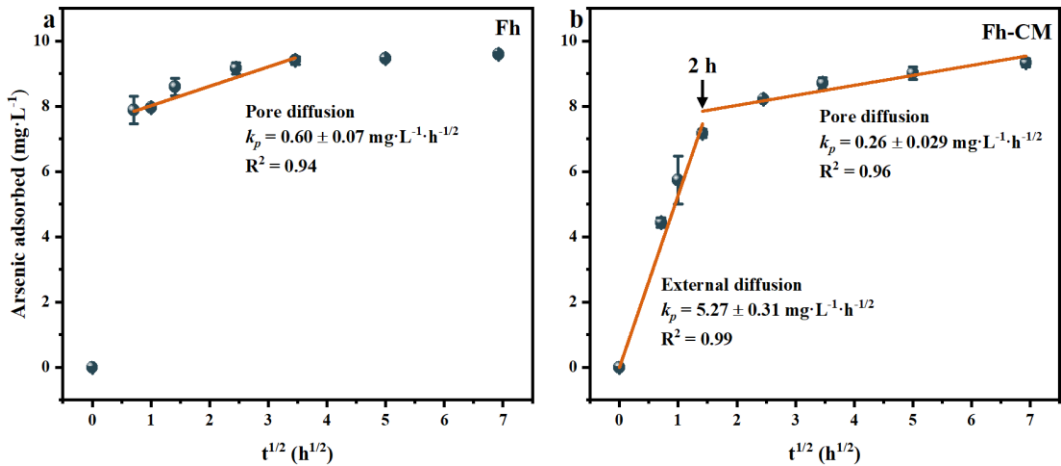


Fig. S24. Intraparticle-diffusion fitting of As(III) uptake by (a) Fh and (b) Fh-CM. The external diffusion stage for Fh could not be reliably fitted because of insufficient data points.

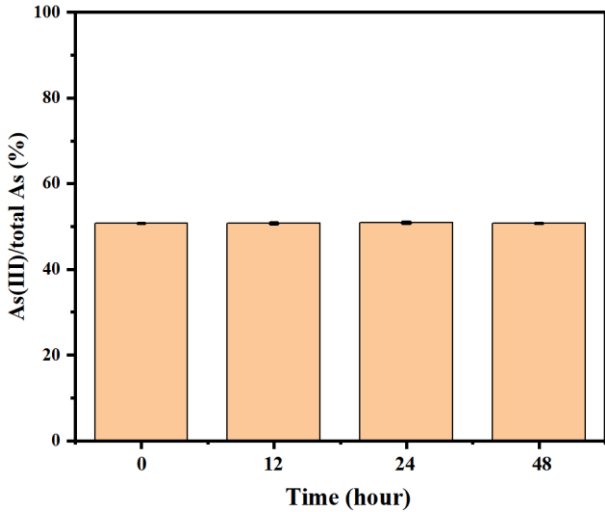


Fig. S25. Short-term stability test for As(III) determination in the NaOH desorption matrix.

Table S1. Composition of the liquid growth medium used for BioMnO_x synthesis[15].

Component	Concentration in deionized H ₂ O (g·L ⁻¹)
Yeast extract	0.5
Casamino acids	0.5

Glucose	1
HEPES buffer	2.38
CaCl ₂	0.222
MgSO ₄ ·7H ₂ O	0.8118
FeCl ₃ ·6H ₂ O	0.001
^a Trace element solution	1 mL·L ⁻¹

^a Trace element solution (mg·L⁻¹ in deionized water) include 10 CuSO₄·5H₂O, 44 ZnSO₄·7H₂O, 20 CoCl₂·6H₂O and Na₂MoO₄·2H₂O.

Table S2. Chemical composition of simulated groundwater (GW), surface water (SW), and challenge water (CW) used in this study.

Component	Unit	GW (Groundwater-like)	SW (Surface-water-like)	CW (Challenge water)
HCO ₃ ⁻	mg·L ⁻¹	150	80	300
Ca ²⁺	mg·L ⁻¹	40	20	60
Mg ²⁺	mg·L ⁻¹	10	5	/
Cl ⁻	mg·L ⁻¹	30	15	/
SO ₄ ²⁻	mg·L ⁻¹	50	25	/
SiO ₂	mg·L ⁻¹	10	5	20
PO ₄ -P	mg·P·L ⁻¹	/	0.2	1.0
NOM	mg·C·L ⁻¹	0.5	2	5

Table S3. Principal FTIR band assignments of the bio-oxides and related phases.

Wavenumber (cm ⁻¹)	Assignment	Component
2965	$\nu_{as}(\text{CH}_3)$	Lipids in cell material[16]
2933	$\nu_{as}(\text{CH}_2)$	
2872	$\nu_s(\text{CH}_3)$	
2852	$\nu_s(\text{CH}_2)$	
1655	Amide I	Protein in cell material[16]
1637	Amide II	
1447	$\delta_s(\text{CH}_2)$	
1400	$\nu_s(\text{COO}^-)$	

1310-1240	Amide III		
1250-1220	$\nu_{as}(P=O)$	Nucleic acid in cell material[16]	
1200-900	C-O-C, C-O ring vibration	Carbohydrate in cell material[16]	
1151	$\delta(Mn\cdots O-H)$		
1086	$\gamma(Mn\cdots O-H)$		
1040	Mn $\cdots$ O-H bending vibrations	MnOOH[17, 18]	
876	$\nu(As-O-Fe)$		
810	uncomplexed As-O band	As(V) adsorbed on Fh[19, 20]	
659	Mn-O band vibration		
496/500	Mn-O band vibration		
432/456	Mn-O band vibration	Hexagonal H ⁺ -birnessite[11, 21]	

Note. ESD's are ± 2 cm⁻¹. ν , stretching; ν_s , symmetric stretching; ν_{as} , asymmetric stretching; δ , in-plane bending; δ_s , symmetric in-plane bending; γ , out-of-plane bending.

Table S4. BET surface area and pore characteristics of ferrihydrite (Fh), BioMnO_x, and BioMnO_x@Fh.

Sample	BET Surface area (m ² /g)	t-Plot Micropore Area (m ² /g)	Total Pore Volume $\times 10^{-3}$ (cc/g)	Average pore Diameter (nm)
Fh	314.54	88.26	0.14	2.32
BioMnO _x	0.94	2.74	0.0084	35.57
BioMnO _x @Fh	136.29	126.10	0.050	2.51

Table S5. DEGs encoding multicopper oxidases and peroxidases putatively involved in manganese oxidation in strain MnB1 under Fh treatment relative to CK.

Gene ID	Log ₂ FC	P value	P adjust	Significant	Regulate	NR description
PP4_RS12010	-0.4216	1.83E-03	5.84E-03	No	Down	manganese-oxidizing multicopper oxidase MnxG [<i>Pseudomonas</i>]
PP4_RS21565	-0.9394	4.37E-04	1.52E-03	No	Down	MULTISPECIES: multicopper oxidase family protein [<i>Pseudomonas</i>]
PP4_RS18180	-1.4069	1.58E-05	6.45E-05	Yes	Down	MULTISPECIES: copper resistance system multicopper oxidase [<i>Pseudomonas</i>]
PP4_RS09825	0	1	1	No	No change	MULTISPECIES: multicopper oxidase domain-containing protein [<i>Pseudomonas</i>]
PP4_RS10790	-0.8022	6.05E-114	3.14E-112	No	Down	MULTISPECIES: catalase/peroxidase HPI [<i>Pseudomonas</i>]
PP4_RS13040	0.008103	9.89E-01	1	No	Up	MULTISPECIES: Dyp-type peroxidase [<i>Pseudomonas</i>]
PP4_RS14775	0	1	1	No	No change	MULTISPECIES: catalase family peroxidase [<i>Pseudomonas</i>]
PP4_RS22670	0.6436	5.46E-12	3.68E-11	No	Up	MULTISPECIES: glutathione peroxidase [<i>Pseudomonas</i>]
PP4_RS20600	-0.4004	4.78E-04	1.65E-03	No	Down	MULTISPECIES: glutathione peroxidase [<i>Pseudomonas</i>]
PP4_RS19705	2.8155	2.48E-02	6.28E-02	No	Up	MULTISPECIES: glutathione peroxidase [<i>Pseudomonas</i>]
PP4_RS11370	-0.07174	1.76E-01	3.49E-01	No	Down	MULTISPECIES: thiol peroxidase [<i>Pseudomonas</i>]

Table S6. DEGs involved in KEGG pathways of bacterial secretion system, flagellar assembly, oxidative phosphorylation, and mineral absorption in strain MnB1 under Fh treatment relative to CK.

Gene ID	Log ₂ FC	P value	P adjust	Significant	Regulate	NR description
Bacterial secretion system						
PP4_RS21500	1.4369	1.14E-03	3.77E-03	yes	up	MULTISPECIES: ATPase, T2SS/T4P/T4SS family [<i>Pseudomonas</i>]
PP4_RS21510	4.1780	2.86E-03	8.88E-03	yes	up	MULTISPECIES: type II secretion system protein XcpP [<i>Pseudomonas</i>]
PP4_RS21530	1.1012	1.21E-05	4.99E-05	yes	up	MULTISPECIES: twin-arginine translocase TatA/TatE family subunit [<i>Pseudomonas</i>]
PP4_RS21535	3.5931	1.05E-03	3.48E-03	yes	up	MULTISPECIES: Sec-independent protein translocase protein TatB [<i>Pseudomonas</i>]
PP4_RS21540	1.1601	3.37E-07	1.61E-06	yes	up	MULTISPECIES: twin-arginine translocase subunit TatC [<i>Pseudomonas</i>]
PP4_RS21490	1.5151	2.64E-05	1.05E-04	yes	up	MULTISPECIES: type II secretion system major pseudopilin GspG [<i>Pseudomonas</i>]
Flagellar assembly						
PP4_RS07185	2.1494	0.00E+00	0.00E+00	yes	up	MULTISPECIES: flagellar hook-basal body complex protein FliE [<i>Pseudomonas</i>]
PP4_RS07020	1.3260	2.31E-74	7.75E-73	yes	up	MULTISPECIES: flagellar basal body rod protein FlgC [<i>Pseudomonas</i>]
PP4_RS07040	1.1902	2.43E-226	2.49E-224	yes	up	MULTISPECIES: flagellar basal body rod protein FlgF [<i>Pseudomonas</i>]
PP4_RS07235	1.8027	9.41E-131	5.69E-129	yes	up	MULTISPECIES: flagellar basal body-associated protein FliL [<i>Pseudomonas</i>]
PP4_RS07015	2.1680	2.34E-18	2.12E-17	yes	up	MULTISPECIES: flagellar basal body rod protein FlgB [<i>Pseudomonas</i>]
PP4_RS07210	1.4231	7.49E-03	2.15E-02	yes	up	MULTISPECIES: flagellar export protein FliJ [<i>Pseudomonas</i>]
Oxidative phosphorylation						
PP4_RS07755	1.4391	9.17E-60	2.37E-58	yes	up	MULTISPECIES: cytochrome-c oxidase, cbb3-type subunit II [<i>Pseudomonas</i>]
PP4_RS01580	1.1704	2.25E-42	4.15E-41	yes	up	MULTISPECIES: polyphosphate kinase 2 [<i>Pseudomonas</i>]
PP4_RS22485	1.9128	1.21E-17	1.07E-16	yes	up	MULTISPECIES: cytochrome o ubiquinol oxidase subunit IV [<i>Pseudomonas</i>]
PP4_RS22490	1.4719	1.46E-41	2.63E-40	yes	up	MULTISPECIES: cytochrome o ubiquinol oxidase subunit III [<i>Pseudomonas</i>]
PP4_RS07760	1.2140	7.42E-252	8.78E-250	yes	up	MULTISPECIES: cytochrome-c oxidase, cbb3-type subunit I [<i>Pseudomonas</i>]
Mineral absorption						

PP4_RS03365	-1.7501	1.23E-59	3.17E-58	yes	down	MULTISPECIES: heavy metal translocating P-type ATPase [<i>Pseudomonas</i>]
PP4_RS03375	-1.7941	6.04E-27	7.34E-26	yes	down	MULTISPECIES: cation transporter [<i>Pseudomonas</i>]

Table S7. KEGG pathway enrichment analysis of up-regulated DEGs in strain MnB1 under Fh treatment relative to CK, including pathway ID, pathway description, gene number, P value, and gene list.

Pathway ID	Pathway Description	No. of genes	P value	Gene list
map02040	Flagellar assembly	6	0.0003	PP4_RS07185, PP4_RS07020, PP4_RS07040, PP4_RS07040, PP4_RS07015, PP4_RS07210
map03070	Bacterial secretion system	6	0.0005	PP4_RS21500, PP4_RS21510, PP4_RS21530, PP4_RS21535, PP4_RS21540, PP4_RS21490
map00190	Oxidative phosphorylation	5	0.005	PP4_RS07755, PP4_RS01580, PP4_RS22485, PP4_RS22490, PP4_RS07760
map03060	Protein export	3	0.0067	PP4_RS21530, PP4_RS21535, PP4_RS21540
map05111	Biofilm formation - <i>Vibrio cholerae</i>	4	0.0083	PP4_RS21500, PP4_RS21510, PP4_RS07175, PP4_RS21490
map00998	Biosynthesis of various antibiotics	1	0.0199	PP4_RS19500
map00053	Ascorbate and aldarate metabolism	2	0.0264	PP4_RS14545, PP4_RS14540
map02010	ABC transporters	8	0.0385	PP4_RS16005, PP4_RS16000, PP4_RS26200, PP4_RS15995, PP4_RS26195, PP4_RS27135, PP4_RS27140, PP4_RS16400
map00626	Naphthalene degradation	1	0.0394	PP4_RS09365
map00830	Retinol metabolism	1	0.0394	PP4_RS09365

Table S8. Apparent pseudo-first-order rate constants (k_{rm}) for dissolved As(III) removal, defined as the decrease in dissolved As(III) concentration in the filtrate, under different experimental conditions. Endpoint dissolved total As removal values are also listed where applicable. “N.A.” indicates that the corresponding endpoint value was not reliably determined or not applicable to that dataset.

Samples		k_{rm} (h ⁻¹)	R ²	Dissolved total As removal (%)
Blank		N.A.	N.A.	N.A.
Cellular material		N.A.	N.A.	N.A.
Fh		1.84 ± 0.14	0.99	96.19 ± 0.61
Fh-CM		0.85 ± 0.092	0.98	93.54 ± 1.43
BioMnO _x		0.080 ± 0.013	0.98	N.A
Abiotic MnO _x		0.20 ± 0.053	0.91	8.09 ± 0.17
BioMnO _x @Fh		0.66 ± 0.096	0.97	90.31 ± 2.11
Abiotic MnO _x @Fh		1.90 ± 0.35	0.95	95.24 ± 0.85
BioMnO _x (65 °C)		N.A.	N.A.	N.A.
BioMnO _x @Fh (65 °C)		1.71 ± 0.21	0.98	80.20 ± 0.27
pH 5		0.52 ± 0.083	0.96	89.58 ± 0.56
pH 6		0.68 ± 0.090	0.97	93.14 ± 4.68
pH 8		0.44 ± 0.053	0.98	89.66 ± 0.74
0.05 mM		0.73 ± 0.080	0.98	96.45 ± 0.48
0.1 mM		0.71 ± 0.11	0.96	95.97 ± 0.38
0.4 mM		0.59 ± 0.039	0.99	79.75 ± 0.55
BioMnO _x @XG		0.20 ± 0.038	0.96	0.96
BioMnO _x @PEG		0.52 ± 0.15	0.88	0.88
BioMnO _x @Fh @XG		0.63 ± 0.079	0.97	0.97
BioMnO _x @Fh@PEG		1.46 ± 0.34	0.91	0.91
BioMnO _x @XG	Cycle 1	0.24 ± 0.017	1.00	31.21 ± 4.63
	Cycle 2	0.27 ± 0.054	0.98	9.64 ± 4.55
	Cycle 3	0.35 ± 0.020	1.00	14.70 ± 7.62
	Cycle 4	0.32 ± 0.034	0.99	17.10 ± 7.24
	Cycle 5	0.27 ± 0.039	0.99	14.50 ± 1.62
BioMnO _x @Fh@XG	Cycle 1	0.40 ± 0.022	1.00	91.72 ± 1.84
	Cycle 2	0.30 ± 0.033	1.00	49.51 ± 3.27
	Cycle 3	0.40 ± 0.013	1.00	48.65 ± 3.04
	Cycle 4	0.38 ± 0.024	1.00	46.51 ± 6.98
	Cycle 5	0.33 ± 0.055	0.98	36.10 ± 11.22
BioMnO _x @PEG	Cycle 1	0.45 ± 0.045	1.00	38.81 ± 2.00
	Cycle 2	0.34 ± 0.043	0.99	18.70 ± 6.20
	Cycle 3	0.42 ± 0.031	1.00	N.A.
	Cycle 4	0.40 ± 0.067	0.98	14.27 ± 0.089
	Cycle 5	0.42 ± 0.016	1.00	16.08 ± 5.05

<i>BioMnO_x@Fh@PEG</i>	<i>Cycle 1</i>	0.98 ± 0.13	0.99	92.17 ± 0.68
	<i>Cycle 2</i>	0.51 ± 0.045	0.99	67.22 ± 0.77
	<i>Cycle 3</i>	0.46 ± 0.045	0.99	57.63 ± 9.58
	<i>Cycle 4</i>	0.40 ± 0.039	0.99	36.38 ± 6.08
	<i>Cycle 5</i>	0.39 ± 0.0041	1.00	35.24 ± 3.09

Table S9. Apparent pseudo-first-order rate constants (k_{ox}) for As(III) oxidation, expressed as generated As(V), under different experimental conditions. “N.A.” indicates that the corresponding oxidation fit was not reliably obtained because the generated As(V) profile did not support stable fitting under that condition.

Samples		k_{ox} (h ⁻¹)	R ²
<i>BioMnO_x</i>		0.080 ± 0.013	0.98
<i>BioMnO_x@Fh</i>		0.18 ± 0.04	0.99
<i>Abiotic MnO_x</i>		0.074 ± 0.012	0.98
<i>Abiotic MnO_x@Fh</i>		0.078 ± 0.015	0.97
<i>pH 5</i>		N.A.	N.A.
<i>pH 6</i>		0.14 ± 0.0091	0.98
<i>pH 8</i>		0.20 ± 0.0083	1.00
<i>0.05 mM</i>		0.023 ± 0.0073	0.98
<i>0.1 mM</i>		0.074 ± 0.015	0.97
<i>0.4 mM</i>		0.23 ± 0.04	0.99
<i>BioMnO_x@XG</i>		0.16 ± 0.021	0.98
<i>BioMnO_x@PEG</i>		0.14 ± 0.020	0.98
<i>BioMnO_x@XG</i>	<i>Cycle 1</i>	0.080 ± 0.046	0.97
	<i>Cycle 2</i>	0.20 ± 0.064	0.96
	<i>Cycle 3</i>	0.16 ± 0.10	0.91
	<i>Cycle 4</i>	0.20 ± 0.085	0.94
	<i>Cycle 5</i>	0.15 ± 0.067	0.95
<i>BioMnO_x@PEG</i>	<i>Cycle 1</i>	0.17 ± 0.069	0.95
	<i>Cycle 2</i>	0.22 ± 0.031	0.99
	<i>Cycle 3</i>	0.20 ± 0.096	0.93

<i>Cycle 4</i>	0.25 ± 0.097	0.94
<i>Cycle 5</i>	0.24 ± 0.077	0.96

Table S10. Semi-quantitative Mn valence composition and Mn average oxidation state (Mn AOS) derived from Mn 2p_{3/2} XPS fitting for pre- and post-reaction samples.

Samples	Mn(II) (At. %)	Mn(III) (At. %)	Mn(IV) (At. %)	Mn AOS	Goodness of fit (normalized χ^2)
¹ BioMnO _x	8.71	63.4	27.89	3.19	0.3120
² BioMnO _x	10.32	51.86	37.82	3.28	0.3954
¹ BioMnO _x @Fh	14.89	45.56	39.55	3.25	0.3239
² BioMnO _x @Fh	11.41	37.98	50.61	3.39	0.3629
¹ Abiotic MnO _x	8.69	45.25	46.06	3.37	1.2829
² Abiotic MnO _x	8.54	46.20	45.26	3.37	2.0392
¹ MnO _x @Fh	14.20	60.15	25.65	3.11	0.4282
² MnO _x @Fh	20.08	51.53	28.39	3.08	0.4887
¹ BioMnO _x ⁶⁵ °C	15.53	65.36	19.11	3.04	0.3664
² BioMnO _x ⁶⁵ °C	12.10	77.70	10.10	2.98	0.5023
¹ BioMnO _x @Fh ⁶⁵ °C	15.71	57.59	26.76	3.11	0.5142
² BioMnO _x @Fh ⁶⁵ °C	18.85	54.66	26.49	3.08	0.5434

¹Pre-reaction samples; ²Post-reaction sample

Table S11. Constraint scheme and fitting settings used for semi-quantitative fitting of Mn 2p_{3/2} XPS spectra.

Valence component	Anchor peak position (eV)	Position Treatment	Multiplet splitting pattern	Relative intensity pattern	Background	G/L	FWHM treatment	Energy shift allowed during fitting	Shared across samples	Reference basis
Mn(II)	639.28	Narrowly constrained	Fixed to literature	Fixed to literature	Shirley	30	Fixed to literature	±0.1 eV	Yes	Ilton et al. (2016)
Mn(III)	640.78	Narrowly constrained	Fixed to literature	Fixed to literature	Shirley	50	Fixed to literature	±0.1 eV	Yes	Ilton et al. (2016)
Mn(IV)	642.03	Narrowly constrained	Fixed to literature	Fixed to literature	Shirley	50	Fixed to literature	±0.1 eV	Yes	Ilton et al. (2016)

Note: Table S11 summarizes the constraint scheme applied uniformly to all Mn 2p_{3/2} spectra. The corresponding sample-specific Mn valence fractions, Mn AOS values, and normalized χ^2 values are listed in Table S10, and the full fitting procedure is described in Text S7.

Table S12. Analytical validation parameters for the determination of As(III) and total As in deionized water and NaOH desorption matrices.

Analyte	Matrix	Calibration range ($\mu\text{g}\cdot\text{L}^{-1}$) ¹⁾	Regression equation	R ²	LOD ($\mu\text{g}\cdot\text{L}^{-1}$)	LOQ ($\mu\text{g}\cdot\text{L}^{-1}$)	Precision (RSD, %, n=6)	Spike recovery (%)	Matrix-effect slope ratio (matrix/solvent)
As(III)	Deionized water	5–80	$y = 0.9634x - 0.0205$	0.996	0.04217	0.1406	1.49	96.99	/
As(III)	NaOH desorption	5–80	$y = 0.9492x - 0.2708$	0.990	0.2819	0.9397	2.44	92.20	98.5%
Total As	Deionized water	5–80	$y = 0.9624x - 0.2268$	0.995	0.04567	0.1522	1.02	94.15	/
Total As	NaOH desorption	5–80	$y = 0.9307x - 0.5084$	0.991	0.2254	0.7514	1.02	91.62	96.7%

Table S13. Endpoint arsenic mass balance at 48 h under the main batch conditions.

Sample	Initial total As (0 h)	Dissolved total As at 48 h	Dissolved As(III) at 48 h	Dissolved As(V) at 48 h	Retained total As	solid-associated As(V)	Total generated As(V)
Blank	10.05 ± 0.14	9.80 ± 0.54	9.80 ± 0.54	NA	NA	NA	NA
Cellular material	10.10 ± 0.36	10.32 ± 0.47	10.32 ± 0.47	NA	NA	NA	NA
Fh	10.03 ± 0.12	0.44 ± 0.057	0.44 ± 0.057	NA	9.59 ± 0.061	NA	NA
Fh-CM	10.01 ± 0.22	0.65 ± 0.14	0.65 ± 0.14	NA	9.37 ± 0.075	NA	NA
BioMnO _x	10.02 ± 0.052	10.49 ± 0.22	NA	10.49 ± 0.22	NA	NA	NA
Abiotic MnO _x	10.05 ± 0.30	9.19 ± 0.017	5.20 ± 0.21	4.09 ± 0.051	0.85 ± 0.28	0.34 ± 0.17	4.44 ± 0.12
BioMnO _x @Fh	10.08 ± 0.097	0.97 ± 0.21	0.19 ± 0.14	0.78 ± 0.35	9.11 ± 0.11	9.30 ± 0.26	10.08 ± 0.099
Abiotic MnO _x @Fh	9.96 ± 0.099	0.48 ± 0.085	0.48 ± 0.085	NA	9.48 ± 0.014	4.46 ± 0.21	4.46 ± 0.21

Note: Small deviations around 100% recovery, including slight over-recovery in some treatments, should be interpreted as analytical uncertainty associated with independent determination of dissolved species and difference-based speciation.

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