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Emerging hybrid approaches combining bioremediation and nanostructured materials for arsenic removal from water

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Abstract
Arsenic contamination of drinking water and groundwater remains a major global public health and environmental concern because of the high toxicity of inorganic Arsenic species and their widespread occurrence from both natural and anthropogenic sources. Conventional physicochemical treatment methods often face limitations of high cost, secondary waste generation, incomplete removal of arsenite, and operational complexity. Hybrid systems that combine bioremediation with nanostructured materials provide synergistic advantages by integrating the high surface area, reactivity, and separability of nanomaterials with the cost-effectiveness, selectivity, and biotransformation potential of microorganisms or biosorbents. This review synthesises recent advances in hybrid technologies for the removal of aqueous Arsenic. Four representative categories are examined: live-cell magnetic nanoparticle systems, graphene oxide–iron nanohybrids integrated with microbial activity, biochar-supported magnetic nanocomposites, and nZVI-influenced microbial or bio-nanocomposite systems. Hybrid approaches consistently show higher adsorption capacities, faster kinetics, improved stability, and easier recovery than standalone biological or nanostructured methods. Remaining challenges include long-term performance in complex real-water matrices, potential nanomaterial ecotoxicity, regeneration efficiency, and scale-up. Future research should prioritise green synthesis, multifunctional materials capable of simultaneous oxidation and adsorption, pilot-scale validation, and life-cycle assessment to support sustainable implementation.

Keywords: Arsenic removal, hybrid bioremediation, nanostructured materials, bio-nanocomposites, water treatment

Introduction
Arsenic (As) is a toxic metalloid that contaminates groundwater and surface water in numerous regions worldwide. Natural processes such as weathering of Arsenic-bearing minerals and reductive dissolution under anaerobic conditions, together with anthropogenic activities including mining, smelting, and historical use of Arsenical pesticides, release both arsenite [As(III)] and arsenate [As(V)] into aquatic systems (Irshad *et al*., 2021; Alidokht *et al*., 2021; Siddiqui *et al*., 2019) [1, 10, 17]. As(III) is generally more mobile and toxic than As(V). Chronic exposure through drinking water is associated with skin lesions, cancers of the skin, lung and bladder, cardiovascular disease, and other adverse health outcomes.

Conventional removal technologies include coagulation–flocculation, adsorption on activated alumina or iron oxides, ion exchange, membrane filtration, and chemical oxidation followed by precipitation. Although these methods can achieve substantial removal under controlled conditions, they commonly suffer from incomplete As(III) removal without a pre-oxidation step, generation of toxic sludge, interference by competing anions (particularly phosphate and silicate), high chemical or energy demand, and costs that limit application in resource-constrained settings (Siddiqui & Chaudhry, 2017; Alka *et al*., 2021; Lata & Samadder, 2016) [2, 12, 16].

Bioremediation employs Arsenic-resistant microorganisms or plants capable of biosorption, bioaccumulation, oxidation, reduction, or methylation. It is environmentally compatible and potentially low-cost, yet kinetics are often slow, and performance can be sensitive to environmental conditions (Irshad *et al*., 2021; Andreasen *et al*., 2018; Altowayti *et al*., 2020) [3, 4, 10]. Nanostructured materials, especially iron-based nanoparticles, graphene oxide composites, and magnetic nanocomposites, offer high specific surface area, tunable surface chemistry, and strong affinity for Arsenic species (Das *et al*., 2020; Alidokht *et al*., 2021; Siddiqui *et al*., 2019) [1, 8, 17]. Aggregation, difficult recovery, and possible environmental release remain practical concerns.

Hybrid approaches that deliberately combine bioremediation with nanostructured materials address many of these individual limitations. Biological components can stabilise nanoparticles, contribute additional binding sites, or perform redox transformations, while nanomaterials increase capacity and kinetics and enable magnetic separation. Literature demonstrates clear performance gains and supports the need for systematic evaluation of these integrated systems (Alidokht *et al*., 2021; Irshad *et al*., 2021; Kim *et al*., 2019; Wen *et al*., 2021; Das & Bezbaruah, 2021) [1, 7, 10, 11, 20].

Hybrid Bioremediation-Nanotechnology Approaches

1. Live-Cell Fabricated Magnetic Nanoparticles

Immobilisation of magnetic iron nanoparticles on living Arsenic-tolerant microorganisms creates a hybrid biocatalyst–adsorbent. Kim *et al*. (2019) [11] developed magnetic iron nanoparticles immobilised on the extremophile *Deinococcus radiodurans* R1 (DR-FeNPs). The bacterial cells served as a biocompatible scaffold that limited nanoparticle aggregation while contributing cell-wall functional groups for biosorption.

Under optimised conditions, the hybrid removed more than 98 % of As(V) within 1 h and maintained high efficiency for at least 32 h. Magnetic recovery enabled straightforward solid–liquid separation. Mechanisms involved surface complexation on the iron oxide phase and interactions with bacterial surface moieties. Advantages include rapid kinetics, high stability, and reusability. Limitations include the need to maintain cell viability under varying pH conditions or in the presence of competing ions, as well as potential scale-up constraints associated with living cells (Kim *et al*., 2019; Irshad *et al*., 2021) [10, 11]. Related studies using other tolerant strains or biofilms have demonstrated enhanced biosorption (Andreasen *et al*., 2018; Altowayti *et al*., 2020) [3, 4].

Table 1: Comparative performance of live-cell magnetic nanoparticle hybrids and related systems

System	As species	Removal efficiency / capacity	Contact time	Key advantages	Reference
DR-FeNPs (*D. radiodurans*)	As(V)	>98 %	1 h	Magnetic recovery, high stability	Kim *et al*. (2019) [11]
Bare Fe nanoparticles	As(V)	Lower	Longer	Simple synthesis	Kim *et al*. (2019) [11]
Free bacterial biomass	As(V)	Moderate	Hours–days	Low cost	Irshad *et al*. (2021) [10]
Magnetic biochar composites	As(III)/As(V)	High capacity	Variable	Easy separation	Wen *et al*. (2021) [20]
Chitosan–magnetic systems	As(III)/As(V)	Moderate–high	Variable	Biocompatible	Nisticò *et al*. (2018) [13]

2. Graphene Oxide–Iron Nanohybrids Combined with Microbial Processes

Graphene oxide (GO) supported iron or zero-valent iron nanoparticles exhibit exceptionally high Arsenic adsorption capacities. Das *et al*. (2020) [8] reported a graphene oxide–iron nanohybrid (GFeN) with Langmuir capacities of 306 mg g^{-1} for As(III) and 431 mg g^{-1} for As(V). Rapid kinetics (>99 % removal in <10 min at environmentally relevant concentrations) and good performance across a wide pH range were observed. Comparative studies confirmed that GO-supported nanoscale zero-valent iron (GNZVI) outperformed magnetite-based counterparts and bare nanoparticles over pH 3–9 (Das & Bezbaruah, 2021) [7].

Integration with microbial communities adds further functionality. Application of nZVI can lower redox potential, increase Fe(II), and shift bacterial community structure toward sulfate-reducing or Arsenic-transforming populations that contribute to sequestration (Castaño *et al*., 2021) [6]. Mechanisms include surface complexation, electrostatic attraction, and electron transfer mediated by the GO sheets that help rejuvenate the iron surface (Das *et al*., 2020; Siddiqui & Chaudhry, 2019) [8, 17]. Advantages are ultra-high capacity and fast kinetics; limitations include the relatively high cost of GO synthesis and the need to control long-term nanoparticle release (Alidokht *et al*., 2021; Wang *et al*., 2019) [1, 14].

Table 2: Performance comparison of graphene- and carbon-supported iron nanohybrids

Material	As(III) capacity (mg g^{-1})	As(V) capacity (mg g^{-1})	Optimal pH range	Notes	Reference
GFeN	306	431	Broad	Ultra-high capacity, rapid kinetics	Das *et al*. (2020) [8]
GNZVI	High	High	3–9	Superior to magnetite hybrids	Das & Bezbaruah (2021) [7]
NZVI/GS composite	~45.6	~45.1	Variable	Silica-stabilised	Zhu *et al*. (2019) [22]
Biochar–$MnFe_2O_4$	High for mixed species	~90 at low eq. conc.	3–7	Simultaneous organic/inorganic As	Wen *et al*. (2021) [20]
GO–magnetite	Moderate–high	High at low pH	pH-dependent	Good dispersibility	Das & Bezbaruah (2021) [7]

3. Biochar-Supported Magnetic Nanocomposites with Biosorptive Enhancement

Porous biochar derived from agricultural residues provides a low-cost, sustainable support for magnetic nanoparticles. Wen *et al*. (2021) [20] prepared a biochar-supported $MnFe_2O_4$ nanocomposite (BC-MF) that simultaneously removed inorganic As(V) and the organic Arsenic species p-arsanilic acid with capacities of approximately 90 mg g^{-1} and 105 mg g^{-1}, respectively, at low equilibrium concentrations.

Biochar contributes abundant oxygen-containing functional groups and a hierarchical pore structure that disperses the magnetic nanoparticles and supplies additional biosorptive sites. Mechanisms include electrostatic

interaction, inner-sphere complexation, hydrogen bonding, and π–π interactions for organic Arsenic (Wen *et al*., 2021; Shaheen *et al*., 2019) [14, 20]. Magnetic recovery is straightforward. Advantages are low cost, dual organic/inorganic capability, and good performance in complex matrices. Limitations include variability in biochar feedstock and potential competition from natural organic matter (Alidokht *et al*., 2021; Bakshi *et al*., 2018) [1, 5]. Related systems using black cumin seed or other biomass supports have also shown effective removal of Arsenic and dyes, as well as antibacterial activity (Siddiqui *et al*., 2019) [17].

Table 3: Comparison of biochar- and biomass-supported magnetic hybrids

Hybrid system	Target As forms	Approximate capacity	Reusability	Cost aspect	Reference
BC-MF ($MnFe_2O_4$/biochar)	Inorganic + organic	90–105 mg g^{-1}	Good	Low (waste-derived)	Wen *et al*. (2021) [20]
Fe_2O_3-ZrO_2 / black cumin seed	As + dyes	Moderate for As	Not fully specified	Very low	Siddiqui *et al*. (2019) [17]
Chitosan–bio-based magnetic NPs	Inorganic As	Effective	Magnetic recovery	Moderate	Nisticò *et al*. (2018) [13]
nZVI–biochar	As(III)/As(V)	Variable, often high	Good	Low–moderate	Bakshi *et al*. (2018); Shaheen *et al*. (2019) [5, 14]
Free biochar	Mainly As(V)	Lower	Limited	Lowest	Alidokht *et al*. (2021) [1]

4. nZVI-Influenced Microbial Communities and Bio-Nanocomposites

In situ application of nanoscale zero-valent iron modifies groundwater chemistry (elevated Fe(II) and lowered oxidation–reduction potential) and bacterial community composition, frequently favouring sulfate-reducing bacteria that can promote Arsenic sequestration via sulfide precipitation or further biotransformation (Castaño *et al*., 2021) [6]. Deliberate construction of bio-nanocomposites that combine nZVI or iron oxides with selected microbial consortia, extracellular polymeric substances, or biopolymers further enhances performance (Andreasen *et al*., 2018; Altowayti *et al*., 2020) [3, 4].

Mechanisms encompass reductive transformation, adsorption onto iron (oxyhydr)oxides formed during nZVI corrosion, and microbial methylation or oxidation (Irshad *et al*., 2021; Glodowska *et al*., 2020) [9, 10]. Advantages include suitability for in situ groundwater treatment and potential for long-term immobilisation. Limitations include transient fluctuations in dissolved Arsenic concentrations, a possible reduction in microbial diversity, and the need for careful dosing to avoid excessive nanoparticle toxicity (Castaño *et al*., 2021; Alidokht *et al*., 2021) [1, 6]. Chitosan–magnetic graphene oxide and related biopolymer nanocomposites also fall within this broader category and offer additional biocompatibility and magnetic recoverability (Sherlala *et al*., 2019; Yoon *et al*., 2017) [15, 21].

Table 4: Overview of hybrid systems involving nZVI and microbial or biopolymer components

Approach	Primary mechanism	Removal performance	Scale suitability	Key limitation	Reference
nZVI + indigenous bacteria	Redox change + adsorption/biosorption	Substantial initial decrease; later fluctuations	In-situ groundwater	Community shifts	Castaño *et al*. (2021) [6]
Live-cell FeNPs	Biosorption + complexation	>98 % As(V)	Batch / semi-continuous	Cell viability	Kim *et al*. (2019) [11]
GO–iron nanohybrid	Complexation + electron transfer	Ultra-high capacity	Advanced treatment	Synthesis cost	Das *et al*. (2020) [8]
Biochar–magnetic oxide	Adsorption + surface complexation	High for mixed As species	Decentralized	Feedstock variability	Wen *et al*. (2021) [20]
Chitosan–magnetic Graphene Oxide	Complexation + biosorption	Moderate–high	Batch / fixed-bed	Competition by phosphate	Sherlala *et al*. (2019) [15]

Comparative analysis

Across the four hybrid categories, clear synergistic benefits emerge. Live-cell magnetic systems provide rapid kinetics and convenient recovery. Graphene iron nanohybrids deliver the highest reported adsorption capacities. Biochar-supported composites offer the most favourable cost–performance balance and dual-species capability. nZVI–microbial systems enable in situ treatment but require careful management of ecological side effects. In virtually all direct comparisons, hybrid materials outperform pure biological biomass or bare nanoparticles in capacity, kinetics, or separability (Alidokht *et al*., 2021; Das & Bezbaruah, 2021; Irshad *et al*., 2021; Wen *et al*., 2021; Kim *et al*., 2019; Siddiqui *et al*., 2019) [1, 7, 10, 11, 17, 20]. Competing ions, particularly phosphate, remain a common challenge that must be addressed through asurface engineering or process design.

Conclusion

Hybrid approaches that integrate bioremediation with nanostructured materials represent a significant advance for Arsenic removal from water. They achieve higher removal efficiencies, faster kinetics, improved selectivity, and easier recovery than either biological or nanostructured methods alone, while retaining important sustainability attributes.

Nevertheless, several challenges persist. Long-term stability and performance in complex real-water matrices containing competing ions and natural organic matter require further validation. The potential ecotoxicity of released nanomaterials, regeneration efficiency over multiple cycles, and cost-effective large-scale production require additional research. Scalability from laboratory to field and seamless integration with existing treatment infrastructure remain limited.

Future efforts should prioritise green synthesis routes that utilise waste biomass, development of multifunctional hybrids capable of simultaneous As(III) oxidation and adsorption of both species, rigorous pilot- and full-scale demonstrations, and comprehensive life-cycle and risk assessments. With continued interdisciplinary collaboration, these emerging hybrid technologies can make meaningful contributions to safe, affordable, and sustainable solutions for Arsenic-contaminated water worldwide.

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