Interfacial Regulation of Iron-Based Materials for Targeted Arsenic Speciation Control , Selective Recognition and Stability in Complex Aquatic Systems

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Abstract. Iron-based materials have been widely recognized as one of the most promising platforms for arsenic remediation owing to their intrinsic affinity for arsenic species, low cost, and compatibility with existing water treatment infrastructures. Nevertheless, their translation from laboratory success to field-scale deployment remains severely limited in complex aquatic environments. This discrepancy arises primarily from three persistent challenges: the inefficient removal of highly toxic and mobile As(III), strong interference from coexisting anions such as phosphate and silicate, and insufficient long-term structural and chemical stability that raises concerns regarding secondary contamination. Accumulating evidence indicates that these limitations do not originate from insufficient adsorption capacity, but rather from inadequate regulation of interfacial microprocesses governing arsenic speciation, selectivity, and environmental fate. In this review, we argue that overcoming the laboratory field performance gap requires a paradigm shift from capacity-oriented material screening toward interface-centered rational design. Recent advances are critically examined from three interrelated perspectives: (i) construction of redox-active heterogeneous interfaces to steer arsenic speciation via in situ As(III) oxidation; (ii) electronic structure and microenvironment engineering to enable arsenic-selective recognition under intense ionic competition; and (iii) stabilization and fate-control strategies to ensure long-term performance and environmental safety. Meanwhile, the influences of natural organic matter, pH fluctuation, ionic strength, and hydrodynamic conditions on interfacial behaviors are systematically analyzed to bridge laboratory research and practical applications. Finally, emerging opportunities enabled by data-driven material discovery and intelligent process coupling are discussed, outlining a roadmap toward efficient, selective, and practically deployable arsenic remediation technologies.

1. Introduction

Arsenic contamination in aquatic environments represents a persistent global challenge, threatening the health of hundreds of millions of people worldwide[2]. Both geogenic processes and anthropogenic activities, including mining, smelting, and agricultural runoff, contribute to elevated arsenic concentrations in groundwater and surface waters[5][24]. Inorganic arsenic species, arsenite [As(III)] and arsenate [As(V)], dominate natural water systems. Among them, As(III) is substantially more toxic, mobile, and difficult to remove than As(V), largely due to its neutral molecular form under circumneutral pH conditions[3][6]. Moreover, arsenic speciation is highly dynamic, continuously regulated by redox conditions, microbial activity, and interfacial reactions at solid–liquid boundaries[3]. Microbial activity and rhizosphere processes further drive arsenic transformation and migration in soil–water systems[7][23][25]. Consequently, effective remediation technologies must not only immobilize arsenic, but also actively regulate its speciation at material interfaces[1].

Arsenic pollution has become a key restrictor for safe drinking water supply in many developing countries and rural regions[4]. Traditional treatment methods including coagulation, precipitation, membrane filtration, and ion exchange often suffer from high cost, secondary waste, or poor adaptability to complex water matrices. Iron-based materials, including iron (hydr)oxides, zero-valent iron, ferrites, and iron-containing composites, have been extensively investigated for arsenic removal[13][14]. Under idealized laboratory conditions, these materials often exhibit exceptionally high adsorption capacities, particularly toward As(V). However, when applied to realistic water matrices containing mixed As(III)/As(V), high concentrations of competing anions, and dissolved organic matter, their performance frequently deteriorates by orders of magnitude. Recent critical analyses demonstrate that adsorption capacity measured under simplified conditions is a poor predictor of field performance. This discrepancy highlights a fundamental limitation of prevailing research strategies that prioritize equilibrium capacity over the regulation of interfacial microprocesses.

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This review argues that overcoming these challenges requires integrated interfacial design to achieve three coupled objectives: (i) active speciation control, (ii) anion-selective recognition, and (iii) long-term stability.

We argue that arsenic remediation is fundamentally an interfacial problem. The fate of arsenic is governed by coupled redox reactions, coordination complexation, competitive adsorption, and solid-phase transformations occurring at the arsenic–iron–water interface. Therefore, deliberate regulation of these interfacial microprocesses through rational material design is essential for achieving targeted, selective, and sustainable arsenic removal in complex aquatic environments.

In recent years, researchers have gradually realized that interface properties including surface charge, defect density, functional groups, electron transfer ability, and pore structure directly determine the final efficiency of arsenic removal. Therefore, interface engineering has become the core direction of next-generation iron-based arsenic removal materials.

2. Interfacial Redox Engineering for Arsenic Speciation Control

A transformative strategy emerging in recent years involves converting passive adsorption interfaces into redox-active catalytic interfaces capable of in situ As(III) oxidation and synchronous capture of the resulting As(V) . Such interfacial redox regulation fundamentally alters the arsenic–iron–water reaction network, enabling targeted control of arsenic speciation rather than relying on passive adsorption.

Heterogeneous Fenton-like systems based on iron catalysts have demonstrated considerable potential for As(III) oxidation through oxidant activation[11]. Recent studies on Fe–N–C materials derived from metal–organic frameworks reveal that precisely engineered coordination environments favor non-radical oxidation pathways dominated by singlet oxygen and surface-mediated electron transfer[8]. Compared with radical-based pathways, non-radical mechanisms exhibit superior selectivity, broader pH adaptability, and greater resistance to scavenging by background constituents. Non-radical oxidants such as singlet oxygen or direct electron transfer may target As(III) with less interference from background organics that typically scavenge radicals, which links subtly to the next section on selective adsorption. These features make them more suitable for complex aquatic systems. Nevertheless, the reliance on external oxidants increases operational cost and raises concerns regarding residual oxidants[10].

To solve this problem, researchers are developing oxidant-free catalytic systems driven by sustainable energy such as light, electricity, and mechanical force, which can realize continuous and stable As(III) oxidation without additional chemical inputs[9].

Beyond oxidant-driven systems, surface-mediated direct electron transfer provides an oxidant-free route for As(III) activation. Coupling zero-valent iron with conductive carbon materials significantly accelerates interfacial electron transfer, promoting As(III) oxidation while mitigating excessive iron corrosion[12][15]. However, sustaining Fe2+/Fe3+ cycling remains a critical challenge, necessitating rational interface design to balance reactivity, stability, and energy efficiency. Collectively, these studies indicate that fast, localized, and low-energy electron transfer is the most sustainable pathway for interfacial As(III) control.

The construction of heterogeneous interfaces with built-in electric fields can further promote directional electron migration, reduce charge recombination, and improve the efficiency and stability of As(III) oxidation under actual water conditions.

In addition, the redox potential matching between iron-based materials and arsenic species is also crucial. By adjusting the crystal phase, doping ratio, and surface defects of iron-based materials, the redox potential can be precisely regulated to achieve preferential oxidation of As(III) without affecting other components in water, which provides a new idea for highly selective interfacial regulation.

3. Electronic Structure and Microenvironment Engineering for Selective Adsorption

In realistic aquatic environments, intense competition from ubiquitous anions, particularly phosphate, severely suppresses arsenic uptake on conventional iron-based materials. This challenge exposes the intrinsic limitation of non-specific surface complexation. To overcome this bottleneck, recent efforts have shifted toward engineering arsenic-specific recognition sites through electronic structure modulation and microenvironment design.

Heteroatom doping represents an effective strategy to tune the Lewis acidity and electronic configuration of iron sites. Zr-, Ti-, and Al-doped iron oxides consistently exhibit enhanced arsenic selectivity due to localized electron redistribution that stabilizes Fe–O–As configurations relative to Fe–O–P analogues[16]. Density functional theory calculations reveal higher adsorption energies, stronger charge transfer, and more stable binding geometries for arsenate at doped sites. These findings demonstrate that selectivity is fundamentally governed by electronic structure rather than purely electrostatic interactions.

The introduction of high-valence metal dopants can not only adjust the electron cloud distribution of iron sites but also introduce new active sites and lattice defects, which synergistically enhance the binding strength and selectivity for arsenic anions.

Spatial confinement and microenvironment engineering further enhance selectivity. Layered materials and porous frameworks provide confined spaces that discriminate anions based on size, hydration shell, and orientation[17]. Functional group incorporation within these confined domains enables cooperative hydrogen-bonding interactions, which are particularly effective under neutral pH conditions where electrostatic driving forces are weakened. Importantly, no single selectivity mechanism is universally effective, highlighting the need for synergistic coupling of electronic asymmetry and spatial confinement.

Porous structures with suitable pore size can exclude large interfering molecules and selectively capture arsenic species through size screening effect, which significantly improves the anti-interference ability in actual water containing humic acid, silicate, and carbonate.

Moreover, the wettability and surface hydrophilicity of iron-based materials also affect selective adsorption. Properly hydrophilic surfaces can accelerate the mass transfer of arsenic species while reducing the non-specific adsorption of organic pollutants, thus improving the overall utilization efficiency of active sites.

4. Stability and Environmental Fate Control

Long-term stability is a critical prerequisite for the practical deployment of iron-based remediation materials. Iron dissolution and structural degradation not only diminish removal efficiency but also introduce secondary contamination risks[20]. Structural reinforcement strategies, including carbon encapsulation and core–shell architectures, have proven effective in suppressing iron leaching while preserving interfacial reactivity[18].

Carbon coating can not only inhibit the corrosion and dissolution of iron components but also improve the dispersion and recyclability of materials, which is especially suitable for continuous flow water treatment systems.

Beyond material stability, increasing attention has been directed toward controlling the environmental fate of immobilized arsenic. Accumulating evidence suggests that adsorption is often a transient state, with long-term immobilization governed by solid-phase transformations during aging[19]. The conversion of amorphous ferric arsenate into crystalline minerals such as scorodite significantly reduces arsenic mobility and bioavailability. These observations highlight the importance of coupling adsorption with thermodynamically stable end states when designing remediation materials.

Controlling the mineralization process of arsenic-loaded iron-based materials can convert arsenic from adsorbed state to lattice-doped or mineral-bound state, which fundamentally reduces the risk of arsenic re-release under pH mutation, redox fluctuation, and microbial action.

A strategic choice must be made between regenerable adsorbents and materials intended for permanent immobilization. This decision dictates material composition, structural features, and lifecycle management strategies, underscoring the need for application-specific design.

For drinking water treatment, regenerable materials with high stability and easy desorption are preferred; for groundwater remediation, permanent immobilization materials with long-term stability and low leakage risk are more suitable, which requires targeted interface design and structural optimization.

Long-term field simulation experiments show that well-designed iron-based materials can maintain stable arsenic fixation capacity for more than several years, which provides an important basis for large-scale engineering applications.

5. Future Perspectives

The increasing complexity of interfacial design necessitates data-driven approaches that integrate experimental databases, theoretical descriptors, and machine learning models to accelerate material discovery[21]. Intelligent process coupling, including electrochemically assisted adsorption and self-indicating materials, offers promising routes to enhance efficiency, controllability, and sustainability. From a broader perspective, arsenic remediation should be viewed not only as a treatment challenge but also as a materials management problem, aligning with the principles of circular economy.

Machine learning can quickly screen the optimal composition, structure, and preparation parameters of iron-based materials, greatly shortening the research and development cycle; intelligent monitoring systems can realize real-time feedback of arsenic concentration and material status, realizing automatic and precise control of the remediation process.

Future research will also focus on green synthesis, low-cost preparation, and large-scale manufacturing of iron-based materials to reduce energy consumption and environmental impact in the production process[22]. At the same time, the safety assessment and life-cycle evaluation of arsenic-loaded waste materials need to be further improved to ensure the environmental friendliness of the whole technology chain.

6. Conclusions

This review demonstrates that the persistent gap between laboratory performance and field effectiveness of iron-based arsenic remediation materials originates from insufficient control of interfacial microprocesses. By shifting the design paradigm from adsorption capacity toward deliberate regulation of arsenic speciation, selectivity, and environmental fate, substantial progress has been achieved. Future breakthroughs will rely on the deep integration of materials science, environmental chemistry, and engineering design, ultimately enabling iron-based materials to transition from promising laboratory concepts to reliable solutions for global arsenic contamination.

Interface-centered design will continue to be the core driving force for the development of high-performance arsenic removal materials, providing solid technical support for solving global aquatic arsenic pollution and ensuring drinking water safety.

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