Fundamental Research 5 (2025) 612–623

Contents lists available at ScienceDirect

Fundamental Research

journal homepage: http://www.keaipublishing.com/en/journals/fundamental-research/

Review

Confined iron-based nanomaterials for water decontamination: Fundamentals, applications, and challenges

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ARTICLE INFO

Article history:
Received 17 April 2023
Received in revised form 24 June 2023
Accepted 21 July 2023
Available online 10 November 2023

Keywords:
Nanomaterials
Iron
Water treatment
Confinement effects
Adsorbents
Catalysts

ABSTRACT

Nanotechnology-enabled water treatment is the most attractive approach to realizing advanced purification of contaminated waters that challenge the efficacy of traditional water treatment technologies. Confining nanomaterials inside porous scaffolds or substrates is one of the most effective strategies to push nano-enabled water treatment technologies forward from laboratory to field application. As flourishingly reported, confinement effects induce significantly improved decontamination efficiency, such as enhanced adsorption capacity, reaction kinetics, stability, and selectivity. In this review, first we provide an overview of the general fundamentals of nanoconfinement effects and their implications in environmental remediation. Next, we review confined Fe-based nanomaterials, such as different polymorphs of iron-oxides, oxyhydroxides, zero-valent iron, and single-atom iron as representative materials towards their applications in nanoconfinement systems for water decontamination. Finally, we propose future studies based on the missing scientific fundamentals regarding nanoconfinement effects and challenges for translating unique and promising nanoconfinement observations to engineering applications of confined nanomaterials-driven water treatment technologies.

1. Introduction

Clean water supply is a global challenge. The conventional drinking water treatment process, consisting of coagulation, sedimentation, filtration, and disinfection, has been optimized and utilized through the 20th century and is considered as a robust system for decontamination. Although the conventional process enhanced public health and economic development, its efficacy is severely challenged by increasingly stringent water quality standards and emerging contaminants. Carcinogenic pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) bypass traditional treatment processes that are ineffective in removing trace and refractory contaminants, as they are not designed to accommodate this need [1]. Trace amounts of emerging contaminants have been detected in both source waters and drinking water for several decades [2]. To address the current challenges, technological innovations are necessary to upgrade aging drinking water and wastewater treatment facilities.

Towards the end of the 20th century, two prominent advancements in water treatment emerged – membrane filtration and advanced oxidation processes (AOPs). Concurrently, the accompanying advances in nanotechnology offer promising solutions for water supplies contaminated by emerging and trace pollutants [3,4]. Specifically, nanomaterials not only enhance the performance of existing treatment technologies including adsorption, coagulation, disinfection, and AOPs, but also exhibit properties that are not observed on a bulk scale, thus creating novel technologies [5]. Additionally, multifunctional nanomaterials may facilitate the integration of multiple treatment processes to simultaneously target a variety of pollutants that demand a chain of different removal processes [3,6].

Among those multifunctional nanomaterials, iron-based environmental functional materials have been one of the most remarkable categories, primarily owing to their high reactivity, environmental friendliness, and natural abundance on earth [7]. The presence of various valences in iron, such as 0, +2, and +3, leads to the formation of diverse types of iron-based nanomaterials, including iron single atoms, zero-valent iron (ZVI), iron oxides (FeOOH, Fe_2O_3, Fe_3O_4), iron sulfides, iron bimetals, and iron-doped composites. In particular, iron-based nanomaterials have demonstrated outstanding properties for the removal of diverse contaminants in water and wastewater treatment when served as adsorbents, oxidants, reductants, coagulants, catalysts, and disinfectants [7]. Through the Web of Science, we searched 1,063 papers using the keywords “iron”, “nano” and “water treatment”. The literature review shows that the application of iron-based nanomaterials in water and wastewater treatment is the lasting research focus (Fig. 1a).

Although decades of research demonstrated exceptional catalytic, adsorptive, and antimicrobial properties of iron-based nanomaterials, the availability of commercially viable products that can be readily deployed in packed beds for extended operation without metal leach-

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https://doi.org/10.1016/j.fmre.2023.07.011

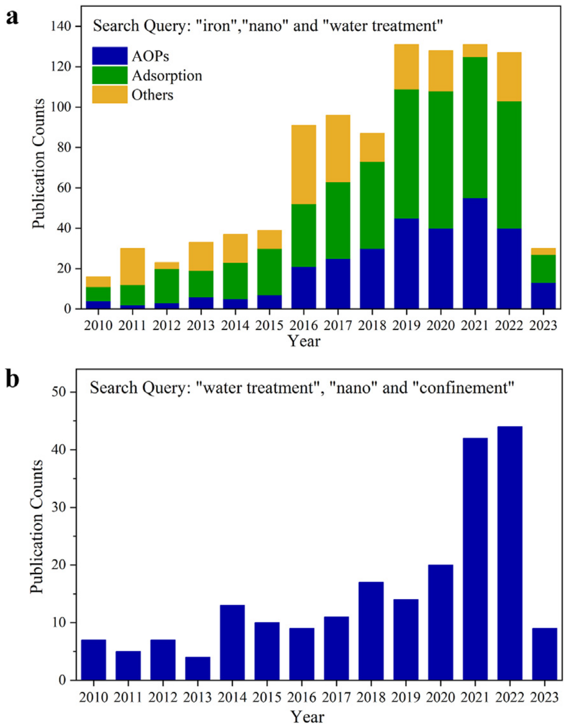

Fig. 1. Publication trends in the field of water and wastewater treatment by using (a) iron-based nanomaterials and (b) nanoconfinement techniques. Source: Web of Science.

ing or excessive head loss remained limited. The practical implementation of nanomaterials in water treatment faces several technical bottlenecks, including ease of agglomeration, difficulty in operation and reuse, risk of leaking to treated wastewater or finished drinking water, and potential hazards imposed on human health and ecosystems. Encapsulating nanoparticles in porous scaffolds or substrates with nanoconfinement structure (“confined nanomaterials” or “nanocomposites”) is one of the most effective strategies for addressing those challenges while maintaining the unique functionality of nanomaterials [8]. Compared to those of free nanomaterials, the performance, stability, and ease-operation of confined nanomaterials are significantly improved. Furthermore, the confinement in macroscopic structure enhances the compatibility of nanomaterials with existing infrastructure, facilitating the translation of nanomaterials from laboratory studies to practical applications [9]. More intriguingly, the nanoconfinement structure renders the confined nanomaterials remarkable properties for water treatment, i.e., confinement effects. This will be elaborated in Section 2.

In recent years, there have been numerous review papers regarding the applications of nanotechnology and nanomaterials in the water treatment [10], while few were focused on iron-based nanomaterials, in particular, with nanoconfined structures. As a model, iron-based nanomaterials are ubiquitously applied across all the stages of water treatment processes, including coagulation, adsorption, disinfection, oxidation, reduction, and AOPs [7]. This review will provide a brief introduction to nanoconfinement configurations and fundamental theories, and then focus on applications of various iron-based nanomaterials featuring nanoconfinement structures, such as confined iron (hydro)oxide, ZVI, iron-doped composites, and iron single atoms used in water decontamination. The characteristics of those nanomaterials will be summarized and their performance and mechanisms of decontamination are particularly elaborated. Finally, this review summarizes the research advances and gives perspectives for future research regarding the missing fundamentals of confinement effects and the barriers to full-scale applications.

2. General fundamentals of nanoconfinement

The phenomena that chemicals confined in a nanoscale space exhibit substantially different properties from their bulk phase counterparts are referred to as “nanoconfinement effect”. The concept was first introduced in 1989, when a change in reaction kinetics was found by the spatial confinement of reactants [11]. Over the years, numerous processes at the nanoscale have been studied in various fields, including spatial confinement, surface confinement, quantum confinement, and electron confinement. Nanoconfinement techniques in water treatment have attracted increasing attention, as evidenced by the increasing number of publications in peer-reviewed journals, especially in the past two years (refer to Fig. 1b).

Nanoconfinement structure refers to the units fabricated by confining nanomaterials inside nanospaces of hosts. The structural configuration and material composition are the most important factors impacting the nanoconfinement effect. In confinement studies, hosts are generally categorized in terms of dimensions, including macro- and microscopic nanocomposites (i.e., porous membranes, resins), spatial confinement with 1D (i.e., nanotube), 2D (i.e., hexagonal boron nitride, graphene oxide nanosheet) and 3D nanomaterials (i.e., core-shell-like structure), and interfacial confinement of metal single atoms (i.e., iron single atom) [8]. Some of them are designed for exploring the scientific nature of the nanoconfinement effect rather than to promote practical applications. Specifically, carbonaceous materials, natural minerals, mesoporous materials, polymers, and metal oxides have been commonly employed as hosts.

Nanoconfined materials are typically achieved by immobilizing nanomaterials inside the natural or fabricated porous scaffolds, or by dispersing pre-synthesized nanomaterials into the precursors of the hosts. Various preparation strategies have been reported, such as hydrothermal methods, impregnation, precipitation, deposition, and “two-solvents” method. Several reviews are available regarding the construction of nanoconfined systems and materials, including the procedures and materials [8,12–14]. For example, our group conducted a review that comprehensively discusses various methods used to establish nanoconfinement structures through physical, physicochemical, and chemical routes. The review also presents the advantages, features, and mechanisms of confined synthesis strategies and outlines examples of their applications in the water decontamination [8].

In recent years, the study of nanoconfinement effects has emerged in the environmental field, with unique phenomena related to water treatment being reported such as adsorption, catalytic oxidation, and membrane filtration [15–17]. Those phenomena offer additional features that are beneficial to the objectives of water treatment. In this section, we provide a concise overview of the fundamental theories behind the confinement effects (Fig. 2), including their impacts on the crystallization of nanomaterials, water structures and properties, solution chemistry, chemical reactions (e.g., adsorption and AOPs), and their interplays.

Crystallization under nanoconfinement. Confined nanomaterials exhibit unique properties that have not been found in the bulk phase, such as emerging phase structures or crystalline forms, prolonged stability of metastable polymorphs, and preferential crystal facets. Those properties improve the reactivity and lifespan of confined nanoparticles (NPs) when used in adsorption and AOPs. Nanoconfinement manipulates the growth of nanoparticles, governs the morphology of nanoparticles, and results in an exposure of specific crystal facets [18]. Thus, nanoconfinement is expected to be an effective method to synthesize nanomaterials with desirable structures and properties for water treatment. Specifically, nanoconfinement is a potential strategy of facet engineering for the nanocatalysts or adsorbents with an anisotropic affinity towards oxidants or target pollutants.

Solution chemistry under nanoconfinement. Nanoconfined water exhibits abnormal properties and behaviors (e.g., anomalously low dielectric constant, water diffusion coefficient, and viscosity), which further affect the processes including the distribution, diffusion, and dynamics

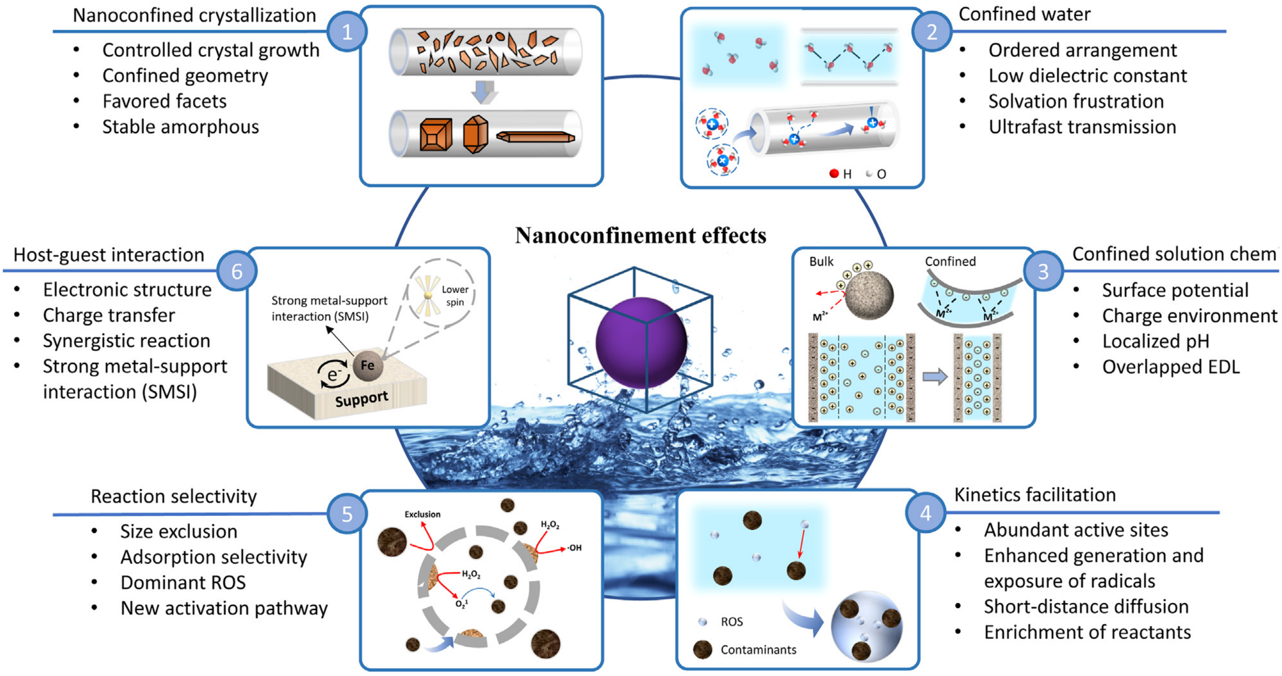

Fig. 2. Overview of fundamentals of confinement effects in the field of water decontamination. (1) Crystallization under nanoconfinement, (2) abnormal properties of confined water, (3) localized solution chemistry, (4) facilitated reaction kinetics, (5) improved selectivity via different activation pathways and size exclusion, and (6) host-guest interactions.

of ions, hydration and dehydration, adsorption and desorption, as well as thermodynamics of chemical reactions [15,17]. Nevertheless, such changes in the properties of confined water inevitably affect the performance of decontamination processes. For example, overlapped electric double layers would be formed at the interface of confined spaces that can substantially change the charge environment and potential, affecting the selectivity and kinetics of chemical reactions [19]. However, sparse studies examine the relationships between the properties of nanoconfined solutions and pollutant removal, necessitating more research to shed light on the research gap.

Chemical reactions under nanoconfinement. The nanoconfinement effect can alter the thermodynamics and kinetics of numerous chemical reactions, such as the acceleration of reaction rate, enhancement of reaction selectivity, and even development of new reaction pathways. First, the electronic structures of nanomaterials could be modified under nanoconfinement, and thus the reactivity is changed. For instance, the geometric and electronic structures of host materials can alter the intrinsic catalytic activity of confined NPs, which in turn affects the catalytic performance of the host [14]. Second, the nanoconfinement could concentrate reactants to accelerate reaction kinetics, improve the selectivity via specific adsorption, enhance the radical utilization efficiency via shortened diffusion distances, and prevent radical quenching via the exclusion of competing substances. Researchers have put forward the concept of “nanoreactor” which refers to the configurations that host chemical reactions and alter reactivity under nanoconfinement. Finally, the energy diagram, transition states, and pathways of chemical reactions can be impacted by interactions between nanoconfinement and either reactants, intermediates, or products. Thus, the rational design of confinement structure for water treatment processes can efficiently improve decontamination efficacy and minimize energy and chemical consumption.

Several review papers have thoroughly outlined the current understanding of nanoconfinement effects and technological innovation in the field of nanoconfined materials for water decontamination [15,17]. Readers are referred to those reviews for details regarding the connections between the nanoconfinement effect and its implication in environmental processes. This review particularly covered the topic of nanoconfined Fe-based nanomaterials for water treatment in the subsequent section.

3. Confined iron-based nanomaterials for water treatment

Iron-based nanomaterials have been widely applied in environmental remediation. Previous reviews have provided a comprehensive summary of the synthesis and applications of the iron-based nanomaterials [20,21]. This review will focus on confined iron-based nanomaterials and their functions in water decontamination.

3.1. *Confined iron (hydro)oxide*

Iron (hydro)oxides have various forms in the natural environment, including hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), iron oxy-hydroxide (FeOOH), and hydrous ferric oxide (HFO), which have received considerable attention regarding scientific, technological, and industrial applications [20]. Table 1 summarizes the typical applications of confined iron (hydro)oxide in water treatment.

3.1.1. *Fe_2O_3*

Hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) are the most known and stable forms of iron(III) oxides and they are eco-friendly, biocompatible, and economically competitive. Fe_2O_3 has received great attention as an earth-abundant adsorbent, photocatalyst, and electrocatalyst. Despite that iron-based nanomaterials possess a high adsorption capacity, their use as magnetic adsorbents is limited due to their tendency to aggregate and low selectivity. Consequently, for use as an adsorbent, encapsulation is important during water decontamination. For instance, the inner lumen of halloysite nanotubes (HNTs) was used as a nanoconfined reactor for the synthesis of α-Fe_2O_3 nanomaterials via a chelating ligand to direct adsorption and calcination [22]. The produced α-Fe_2O_3/HNTs nanocomposites exhibited solar light-induced enhanced photocatalytic activity and achieved 88% removal of methylene blue from simulated wastewater in 2 h under sunlight irradiation, following the pseudo-first-order kinetic model. In another finding, Fe_2O_3

Table 1
Applicationsof confined iron (hydro)oxide in water treatment.

Iron phase	Host materials	Synthesis method	NPs size (nm)	Iron content	SSA^a (m^2/g)	Target contaminants	Removal capacity	Environmental application	Oxidants	Refs.
Fe_2O_3	CNT	Wet solvothermal	1.9	1.93%	206	Methylene blue	>98%	Electro-Fenton	H_2O_2	[24]
Fe_2O_3	g-C_3N_4	Impregnation-coprecipitation	3–4	2.8 wt.%	81.7	Diclofenac	98.7% in 20 min	Photocatalysis	/	[23]
α-Fe_2O_3	Halloysite nanotubes	Adsorption-calcination	N.A.	~2.4 wt.%	53.14	Methylene blue	88% in 120 min	Photocatalysis	O_2	[22]
γ-Fe_2O_3	CNT	Wet solvothermal	N.A.	1~4 wt.%	152.1	Tetracycline	98.40%	Electro-Fenton	H_2O_2	[25]
Fe_3O_4	AAO	Solvothermal	N.A.	0.78 wt.%	18.816	*P*cba	>90%	Fenton	H_2O_2	[27]
Fe_3O_4	Anatase TiO_2 shell	Sol-gel, calcination, etching treatment	100	N.A.	101	Tetracycline	~100% in 10 min	Photo-Fenton-like reaction	H_2O_2	[28]
Fe_3O_4	Graphite	One-pot solvothermal	~10	N.A.	256	Pararosaniline	198.23 mg/g	Adsorption	/	[26]
Fe_3O_4	3D reduced graphene oxide	In situ crystal growth	25	58.07%	61.9	Roxarsone	454.48 mg/g	Adsorption	/	[18]
α-FeOOH	Mesoporous polystyrene	Coprecipitation	2.0 ± 0.6	5.99 wt.%	149	As(III), As(V)	>180.0 mg/g	Adsorption	/	[32]
HFO	Cross-linked anion exchangers	Solvothermal	11.6	7.4 wt.%	214	As(III), As(V)	24.2–31.6 mg/g	Adsorption	/	[35]
HFO	Hyper-cross-linked resin	Ion-exchange + coprecipitation	N.A.	5.0 wt.%	589	Phosphonates	15.0 mg P/g	Adsorption	/	[36]

nanoparticles confined in g-C_3N_4 were prepared via an impregnation-coprecipitation method and applied to remove diclofenac from a simulated wastewater [23]. Results showed that confined Fe_2O_3 possessed low-spin Fe^{III}, which boosted the generation of hydroxyl radicals and superoxide ions under solar light and promoted the degradation of diclofenac. The confined Fe_2O_3 in g-C_3N_4 also possessed a large surface area, adaptability to a wide range of pH, and ~5 times higher kinetic constant than bulk g-C_3N_4.

Yang et al. reported a singlet oxygen ($^1O_2$) mediated Fenton-like process catalyzed by Fe_2O_3 confined within a carbon nanotube (CNT) [24], which demonstrated adsorption-dependent selectivity, wide working pH range, and fast degradation of methylene blue, compared with those in unconfined Fe_2O_3/CNT (Fig. 3a). Using the similar strategy, Guo et al. incorporated a CNT filter loaded with Fe_2O_3 nanoparticles as the cathode material and designed an enhanced flow-through electro-Fenton system for selective degradation of antibiotic tetracycline [25]. The Fe_2O_3-in-CNT filter showed 1.65 times higher kinetics toward tetracycline degradation than the surface-coated Fe_2O_3 on the CNT filter. More importantly, the efficacy of tetracycline removal was maintained at >85% during a 3-day continuous experiment, and the co-existing inorganic anions and natural organic matters had negligible negative impacts on tetracycline degradation kinetics.

3.1.2. Fe_3O_4

Fe_3O_4 nanomaterials have been widely used as adsorbents, Fenton catalysts, and photocatalysts in water treatment processes due to their high stability, outstanding Fenton-like catalytic activity, and reusability. The decrease in the size of nanoparticles results in magnetic Fe_3O_4 becoming superparamagnetic and easy separation for recovery.

As shown in Table 1, a superparamagnetic graphene- Fe_3O_4 nanocomposite synthesized by a one-pot solvothermal method was used as an adsorbent to remove organic dye pararosaniline from wastewater with a maximum adsorption capacity of 198 mg/g [26]. The adsorption equilibrium was achieved within 20 min and the kinetic data followed a pseudo-second-order model. Furthermore, the graphene-Fe_3O_4 nanocomposite could be regenerated and used repeatedly. For the adsorption of roxarsone [18], the nanoconfinement provided by 3D graphene modulated Fe_3O_4 NPs (20–50 nm) with dominant (400) planes and showed enhanced removal efficiency than unconfined Fe_3O_4 NPs with commonly exposed (111) planes. The enhanced adsorption of roxarsone from real wastewater was attributed to a synergetic interaction of As–Fe coordination, strong hydrogen bonding between roxarsone and confined Fe_3O_4, and π–π interaction between roxarsone and the graphene.

As Fenton-like catalysts, a series of Fe_3O_4-loaded anode aluminum oxide (AAO) nanoreactors with different pore diameters were synthesized to degrade *para*-chlorobenzoic acid (*p*CBA). It was found that the pore diameter below 25 nm is critical to avoid the limited diffusion of short-lived HO· (Fig. 3b), and the degradation kinetics of *p*CBA were increased by 820 times that of bulk reaction [27]. Du et al. prepared the yolk-shell structured Fe_3O_4@void@TiO_2 sphere through a sol-gel process and an ultrasound etching method, and used it as a heterogeneous catalyst for the photocatalytic degradation of tetracycline (TC) [28]. Almost total removal of TC was achieved within 6 min at pH = 3 due to the enrichment of TC and HO· under the confinement of the yolk-shell structure (Fig. 3c), as well as the efficient reduction of Fe^{3+} to Fe^{2+} by the photo-generated electrons from the TiO_2 shell.

3.1.3. Iron oxy-hydroxides

Iron oxy-hydroxide (FeOOH) is an environmentally friendly, economical, and stable material with abundant hydroxyl groups on the surface. Its tunnel structure offers extra active sites to form complexes with various ions, such as phosphorus and arsenic oxyanions, and F^-. Zhang et al. prepared FeOOH/anion exchanger nanocomposites via a glycol-solvothermal synthesis method for the phosphate adsorption [29]. The nanocomposites exhibited a high adsorption capacity of 19.05 mg P/g,

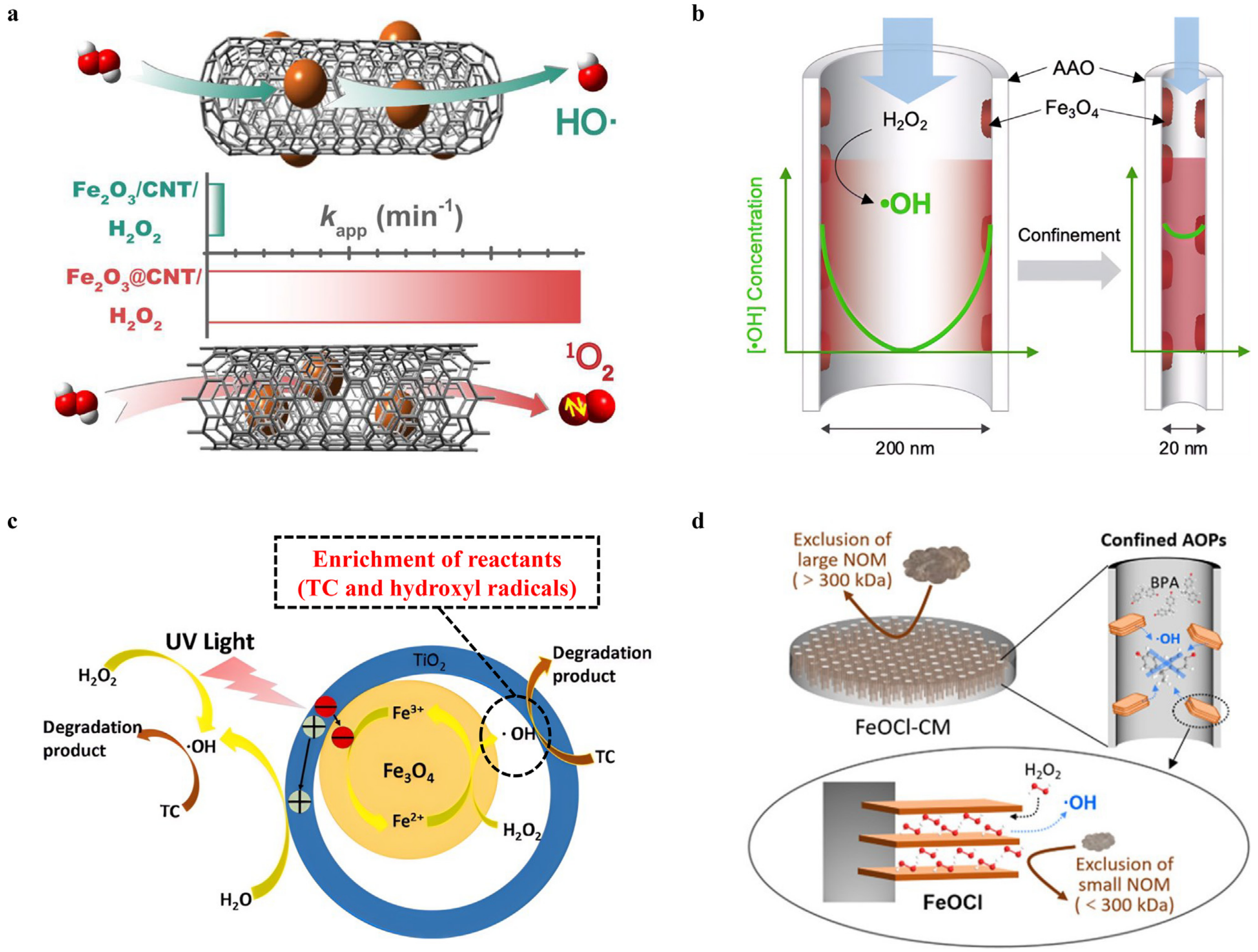

Fig. 3. The enhancement mechanisms under nanoconfinement. (a) Nanoconfinement of CNT results in unprecedented singlet oxygen mediated Fenton-like reactions. Reproduced with permission from [19]. Copyright 2019 National Academy of Sciences of the United States of America. (b) Short-distance diffusion of radicals. Reproduced with permission from [22]. Copyright 2020, American Chemical Society. (c) Confinement of Fe_3O_4 NPs inside TiO_2 hollow space enables enrichment of reactants, facilitating the degradation of TC. Reproduced with permission from [23]. Copyright 2016 Elsevier. (d) Size exclusion of interferencing substances. Reproduced with permission from [54]. Copyright 2021, American Chemical Society.

high selectivity, along with improved utilization of Fe sites and largely reduced metal leakage. Fe(III)-OH is the dominant efficient species for phosphate adsorption. However, the synthesis reaction time is excessively long. In another work, a FeOOH/BF composite that loads porous basalt fiber (BF) with β-FeOOH was utilized to remove phosphate from an aqueous solution [30]. The FeOOH/BF adsorbent revealed a high selectivity for phosphate despite the presence of coexisting anions (e.g., Cl^-, SO_4^{2-}, and NO_3^-) in water. FeOOH/BF primarily relied on inner-sphere complexation, electrostatic attraction, and ligand exchange mechanisms for phosphate removal.

With respect to As removal, α-FeOOH was incorporated into graphene oxide (GO)-carbon nanotubes (CNTs) aerogel via a facile self-assembly method of GO-CNTs induced by in-situ Fe^{2+} reduction. This nanocomposite evinced exceptional As(V) adsorption capacity at 56.43 mg/g, which was higher than the pristine α-FeOOH adsorption capacity of 25.71 mg/g [31]. The incorporation of α-FeOOH inside GO-CNTs prevented nanomaterial aggregation and enabled wide-ranging pH applicability for As species adsorption, high adsorption kinetics, and outstanding reusability. To further promote the direct use of FeOOH NPs in scaled-up water purification, Zhang et al. prepared millimeter-sized polymer-based FeOOH with NPs sizes in a range of 2.0 to 7.3 nm via a flash freezing method [32]. Compared to unconfined α-FeOOH NPs, the resulting nanocomposites exhibited a 14.8-fold enhancement in adsorption capacity, which can be attributed to the higher density of surface hydroxyl groups and stronger affinity of the embedded NPs towards As.

FeOOH is also used as a peroxymonosulfate (PMS) activator to degrade organic pollutants. However, the severe aggregation and difficult reusability of FeOOH suspensions hinder practical applications. To address this issue, Zhang et al. developed a catalytic membrane by confining β-FeOOH within a polyvinylidene fluoride (PVDF) membrane matrix via an in-situ mineralization method [33]. The resulting PVDF/β-FeOOH showed excellent separation capacity and catalytic oxidation performance via activating PMS, resulting in over 98% fast degradation of recalcitrant pollutants in approximately 1 s and up to 99.1% rejections of oil under low operating pressure. This favorable catalytic degradation performance was attributed to the confinement effect that induced enhanced mass transfer and enrichment of radicals and pollutants within membrane pores.

3.1.4. *Hydrous ferric oxide*

Fe(III) has a high affinity for As species and selectively adsorbs As from aqueous solution via inner-sphere surface complexation. HFO is particularly efficient in removing both As(III) and As(V) owing to its high specific surface area and point of zero charge. Anion-exchanger-supported HFO nanoparticles have been shown to offer high arsenic removal capacity, with less than 10% of influent arsenic broke through after 10,000 bed vol. [34]. Li et al. confined HFO NPs inside three kinds of cross-linked anion exchangers with different pore size distributions to investigate the confinement effect on the adsorption kinetics of As(V) [35]. The decrease in the pore size of the anion exchangers led to a decrease in the mean diameter of confined HFO NPs and an increase in the number of active sites. Furthermore, the nanocomposites demonstrated enhanced adsorption of As(V) over a wide pH range from 3 to 10, with negligible interferences from competing anions.

Moreover, Yan et al. confined HFO inside hyper-cross-linked resins (NDA88) for selective adsorption of phosphonates [36]. The resultant nanocomposite (HFO@NDA88) exhibits an adsorption capacity of 15.0 mg P/g towards a model phosphonate, higher than that of the NDA88 host (7.9 mg P/g) and the bare HFO (7.4 mg P/g). HFO@NDA88 demonstrates excellent resistance to various coexisting interference substances, particularly the organic analogue nitrilotriacetic acid and phosphate. Such superior selectivity is attributed to the synergetic effect of various interactions, including the formation of Fe-O-P inner-sphere complexation, electrostatic interaction between positively charged HFO@NDA88 and phosphonate anions, hydrophobic interaction between the organic skeleton of phosphonates and the polymeric matrix of NDA88, etc.

The above works proved that nanocomposite adsorbents with confined HFO are promising for highly selective removal of As and phosphorus from the complex water matrix. It is well known that the poorly crystalline HFO undergoes a transformation into more crystalline iron polymorphs (e.g., hematite, goethite) over time, a process which substantially diminishes its superior reactivity with As [37]. As mentioned above, the nanoconfinement structure might enable the stabilization of metastable polymorphs and nanoconfined HFO is expected to be more stable than free HFO NPs to maintain its high efficiency for As removal. This ongoing study has been carried out in our research group.

3.2. *Confined zero valence iron*

Investigations on the synthesis of ZVI and its application in the decontamination of groundwater and wastewater polluted with various contaminants have received considerable attention from researchers [38]. Zero-valent iron NPs (nZVI) were usually applied for the removal of nitrates, phosphates, heavy metals, and dyes from aqueous solutions through various mechanisms, such as adsorption, reduction, and photocatalytic degradation [39]. However, the release of soluble iron ions is a technical drawback of nZVI, which can be addressed through the encapsulation of nZVI in porous support to suppress iron leaching through coordination formation and maintain activity. Table 2 summarizes the applications of confined nZVI in water treatment.

Back to two decades ago, nZVI embedded inside resin was shown to enhance the removal rates of Cr(VI) and Pb(II) from water by 5- and 18-fold, respectively [40]. Liu et al. confined nZVI in anion exchange resin by in situ reduction and deposition [41]. The phosphate adsorption capacity of the composite adsorbents was found to be high over a wide pH range (3.0–11.0), with a maximum adsorption capacity of 56.27 mg P/g at pH 7.2. More importantly, the confinement of nZVI in anion exchange resins realized selective adsorption of phosphate through electrostatic interaction and surface complexation, reducing the negative effects from interfering humic acid, sulfate and nitrate anions present in simulated and real wastewater. Furthermore, supported nZVI on natural minerals, such as kaolinite [42], kaolin [43], rectorite [44] and bentonite [45] have been used to reduce the extent of aggregation of nZVI and enhance its reactivity toward Cr(VI), Pb(II) and dyes via adsorption and reduction. Zhang et al. confined nZVI in the channels of mesoporous silica materials with different pore lengths via “two solvents” impregnation followed by the H_2 reduction process [46]. The confined nZVI in short channels exhibited enhanced reduction ability for nitrobenzene compared to that in long channels, favoring diffusion of reactants and products with less pore blockage.

Table 2
Applications of confined nZVI in water treatment.

Support	Synthesis method	nZVI size (nm)	Fe content	SSA[a] (m^2/g)	Target contaminants	Removal capacity	Removal mechanisms	Oxidants	Refs.
Anion exchange resin	In situ reduction and deposition	N.A.	6.18%	N.A.[b]	Phosphorus	56.27 mg P/g	Adsorption	/	[41]
Clay (bentonite)	Chemical reduction	30	50 ± 3%	40	Azo dyes	92.70%	Catalytic degradation	H_2O_2	[53]
Kaolin	In-situ reduction	44	20 wt.%	26.11	Pb(II), Cr	98.8% for Pb(II), 99.8% for Cr	Adsorption and reduction	/	[78]
Mesoporous silica	“Two solvents” impregnation and H_2 reduction	5.8	15 at.%	0.56	Nitrobenzene	94%	Reduction	/	[46]
Natural rectorite	Ion-exchange and $NaBH_4$ reduction	10.3	9.94 wt.%	58.1	Orange II	100%	Adsorption and reduction	/	[44]
Activated carbon	Chemical reduction	5	7 wt.%	826.54	Antibiotics	100%	Catalytic degradation	Persulfate	[51]
Graphene	Reduction of ferrous salts	100	N.A.	139.82	Methylene Blue	98%	Fenton-like reaction	H_2O_2	[52]
3D graphene network	Chemical reduction	120–200	N.A.	20.1	Sulfadiazine	98%	Fenton-like reaction	O_2	[49]
Biochar	Bio-assembly and in-situ reduction	50–100	N.A.	N.A.	Uranium (VI)	720.8 mg/g	Chemical adsorption	/	[79]

Note: a. SSA: specific surface area; b. N.A.: Not available.

With a standard redox potential of −0.44 V, nZVI can effectively remove pollutants via the interfacial electron transfer [47]. The direct electron transfer from the ZVI surface to pollutants could attack the latter via a reductive removal [48]. nZVI could also transfer electrons to H_2O, dissolved oxygen, and dosed oxidants (PMS, H_2O_2) to produce highly reactive species (e.g., HO·, $SO_4^{\cdot -}$) that would oxidatively remove contaminants [39,49–52]. Kerkez et al. synthesized clay-supported nZVI for oxidative degradation of industrial azo dye [53]. The clays not only dispersed and stabilized nZVI but also improved the adsorption and degradation of dyes through enhanced heterogeneous Fenton oxidation, which was superior to reductive degradation.

In general, nZVI mediated-decontamination processes are reduction/oxidation hybrid processes with uncontrolled interfacial electron transfer. Thus, it is crucial to control the pattern of interfacial electron transfer when designing nZVI catalysts to achieve optimal performance. Su et al. confined nZVI in CNTs with an inner diameter of 3–30 nm and studied the spatial effect on phenolics degradation by heterogeneous Fenton process [54]. The findings suggested that spatial confinement had a crucial impact on reducing iron leaching, enriched generation, and enhanced utilization of HO· radicals, leading to up to a 2.13-fold improvement in the degradation of contaminants compared with the homogeneous Fenton process. The enhancement was particularly significant in the range of 3–7 nm of the CNTs cavity, evincing the importance of spatial confinement in electron transfer between Fe and CNTs via an internal-micro-electrolysis pathway.

Recently, Chi et al. prepared a magnetic mesoporous SiO_2 shell on the nZVI surface to manipulate the electron transfer kinetics and reaction pathway of nZVI via the magnetic spatial confinement effect and selectively cleave the carbon-halogen (C-X) bond of halogenated phenols without forming highly toxic intermediates [55]. Therein, under the magnetic confinement effects, Fe atoms orderly release electrons to surface adsorbed H_2O molecule to generate H^* as the reactive species for selective cleavage of the C-X bond and switch the reaction pathway from reduction/oxidation reaction to hydrohalogenation. Meanwhile, Fe atoms were transformed to penetrable γ-FeOOH instead of a dense FeO_x layer, allowing continuous inward diffusion of H_2O and outward diffusion of H^*.

3.3. Other confined iron-based nanomaterials

3.3.1. Iron oxychlorides

In recent years, iron oxychlorides (FeOCl) have proven to be a highly effective and pH-intensive Fenton catalyst for environment remediation [56,57]. In particular, FeOCl is composed of self-stacked iron layers and a linear configuration of [O-Fe-Cl], which contributes to a high yield of hydroxyl radicals [57]. To improve the stability and reusability of FeOCl, some researchers combined FeOCl with porous supports [56,58,59]. Sun et al. fabricated PVDF/FeOCl ultrafiltration membranes via a thermal-treatment method [58], and the PVDF/FeOCl possessed long-term antifouling properties attributed to the in-situ generation of hydroxyl radicals and excellent regeneration ability. Kim's research group further designed a ceramic membrane reactor with confined FeOCl nanocatalysts and investigated the confined Fenton reactions in the membrane pores (~20 nm) [59]. It was found the degradation rate of *p*CBA confined within the membrane reactors was increased by 3 orders of magnitude compared with the batch suspension reaction. The enhanced AOP kinetics is due to the nanoconfinement effect that augmented HO· radicals exposure to target emerging organic contaminants and excluded natural organic matters (NOM) to avoid the competitive quenching of radicals (Fig. 3d).

3.3.2. Iron-doped nanomaterials

Solid iron-based catalysts are limited by the low production rate of Fe^{2+} and high oxidant consumption. Researchers have explored doping them with other metals or incorporating reducing agents to enhance the redox cycle of Fe^{3+}/Fe^{2+} and promote catalytic efficiency. For example, confined $CuFe_2O_4$ in carbon hollow spheres was prepared by a hard-templating method to achieve the excellent performance of $CuFe_2O_4$-mediated heterogeneous Fenton reaction, as the confinement structure facilitates the redox cycle of M^{n+1}/M^{n+} [60]. Due to article length limitation, the survey of this part is omitted in this review.

3.4. Single-atom Fe

Recently, single-atoms (SAs), with the anchored NPs downsized to an atomic level to form isolated single-atom (SA) metal sites in supporting materials, have attracted increasing attention. In particular, SAs are promising catalysts in AOPs for environmental remediation due to the ultra-low metal loading, maximum utilization of metal atoms, and unique electronic features of the SA metal sites [61]. As shown in Table 3, various SA Fe catalysts have been reported with excellent catalytic performances in activating different peroxides, such as H_2O_2, PMS, and peroxodisulfate (PDS). The support served as an anchoring site that can effectively anchor and confine Fe atoms at the atomic level, making single-atom Fe a type of interfacially confined Fe-based nanomaterials.

Currently, the nitrogen-coordinated Fe single atoms on carbon-based supports (Fe-N-C) have been extensively studied in the Fenton-like reactions [62–64]. Ma et al. fabricated the SA Fe-based carbon composites using $g\text{-}C_3N_4$ as the chelating agent [63]. The SA Fe sites anchored onto the graphitized mesoporous carbon composite (GMC) in the Fe-N coordination form, which facilitated the redox cycle of Fe(II)/Fe(III) and the generation of HO· through the Fe(III)-initiated chain reactions. Thus, carbon-based SA Fe catalysts demonstrated high activities for H_2O_2 decomposition across a wide pH range (4–10), overcoming the universal challenge of narrow working pH for most iron-based Fenton catalysts. Li et al. deposited SA Fe catalysts on biochar for PMS-based degradation of phenol [64]. Owing to its higher surface area and improved electrical conductivity, SA Fe catalyst facilitated a non-radical electron-transfer pathway, resulting in a rate constant for phenol degradation that was ~33 times higher than that of Fe NPs catalysts.

Additionally, metal-organic framework (MOF) and covalent organic framework (COF) were used to confine SA Fe in porous carbon with in situ coordinated Fe-N_x sites [65,66]. As shown in Fig. 4, the SA Fe catalyst confined in COF (Fe@COF) was prepared via the pyrolysis of a mixture of Fe^{3+} ions and porous COFs under a N_2 flow at 700 °C [66]. Fe@COF showed prominent catalytic properties for PMS activation and $^1O_2$ was identified as the primary ROS responsible for the decomposition of Orange II in the Fe@COF/PMS system, rather than HO· and $SO_4^{-}\cdot$. In another work, Li et al. prepared SA Fe-based catalyst via one-step pyrolysis derived from a Fe-doped zeolite imidazole framework (ZIF) [61]. Atomically dispersed Fe-N-C structure was formed in the carbon frameworks with modified electronic structures, exhibiting remarkably higher catalytic PMS activation for bisphenol A (BPA) degradation than that of Fe NPs loaded N-doped carbon. Significantly, high-valent iron-oxo species (e.g., Fe(V)=O and Fe(IV)=O) were determined as the dominant ROS instead of HO·, $SO_4^{-}\cdot$, or $^1O_2$, for the BPA degradation.

In addition to the construction of Fe-N_x sites, as-made mesoporous silica (SBA-15) was used as a support to accommodate SA Fe [67]. An iron precursor of $Fe(NO_3)_3$ was mixed with SBA-15 through grinding and then the mixture was calcinated at 500 °C to anchor SA Fe in the nanopores, wherein the confined space with substantial Si–OH groups facilitated the dispersion of Fe at an atomic level and improved the activity of Fe sites for H_2O_2 decomposition to produce abundant hydroxyl radicals for phenol degradation.

Despite various strategies have been developed to achieve the atomic distribution of Fe sites, large-scale synthesis of commercial SA Fe catalysts remains a major challenge. The current synthesis of SA Fe catalysts still relies on a trial-and-error process, which is time, chemical, and energy consuming. There is a need for universal design principles to precisely control the structural configurations and catalytic performance of SA Fe catalysts.

Table 3
Various single-atom Fe for AOP applications.

Support		Synthesis method	Metal amount	Target contaminants	Reaction time	Removal capacity	AOP oxidants	Refs.
Carbon-based	g-C_3N_4	Hydrothermal	0.5–1.57 at.%	Acid Red 73	40 min	99.4%	H_2O_2	[63]
	Biochar	Pyrolysis	2.4 wt.%	Phenol	6 min	100%	PMS	[64]
	g-C_3N_4	Pyrolysis	3.46 wt.%	*P*-chlorophenol	20 min	100%	PMS	[80]
	g-C_3N_4	Pyrolysis	18.2 wt.%	Methylene blue	11 min	98.9%	H_2O_2	[81]
MOFs and COFs	ZIF-8	Pyrolysis	0.24–0.57 wt.%	Phenol	10 min	97%	PDS	[82]
	ZIF-8	Hydrothermal	0.93–2.09 mg/kg	Bisphenol A	30 min	>99%	PMS	[61]
	COF	Chemical reduction	2.14 wt.%	Orange II	90 min	100%	PMS	[66]
Others	SBA-15	Calcination	/	Phenol	120 min	100%	H_2O_2	[67]
	MoS_2	Hydrothermal method	/	Propranolol	30 min	~90%	Sulfite	[83]

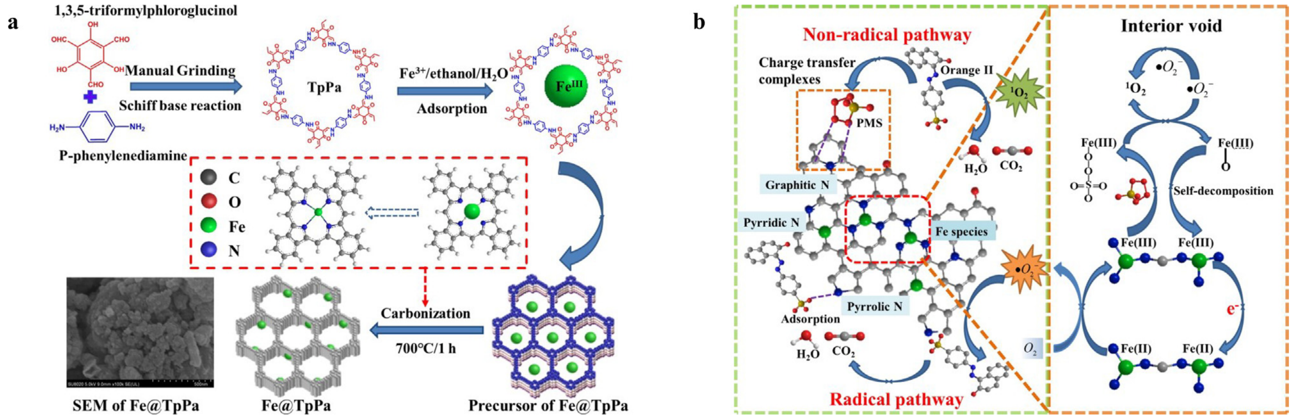

Fig. 4. Schematic illustration of (a) the fabrication procedure of Fe@COF catalysts and (b) activation and reaction mechanisms in Fe@COF/PMS system. Reproduced with permission from [61]. Copyright 2019 Elsevier.

4. Challenges and opportunities

The increasing stringency of water quality standards, accompanied by the emergence of refractory and trace organic contaminants, has brought new scrutiny to the conventional water treatment and supply systems widely implemented in developing and developed countries. Nanomaterials have emerged as the most promising candidates for the development of the next-generation water treatment technology, given their high capacity, fast kinetics, preferable selectivity, and enhanced catalytic activity towards target contaminants. Iron-based nanomaterials have been proven to be highly efficient functional materials for decontamination as adsorbents, catalysts, reductants, and disinfectants [20]. Confined nanomaterials tackled the challenges and improved the stability, operation, and recycling of nanomaterials while leveraging both the host and the confined functional nanoparticles. Plenty of examples described in previous sections have evidenced the exciting accomplishment of confined Fe-based nanomaterials in water decontamination. However, considerable challenges and opportunities remain in research related to confined nanomaterials from both fundamental and engineering aspects.

4.1. Understanding of nanoconfinement effects

With the development of characterization methods and simulation calculations, new theories and mechanistic hypotheses have emerged in recent years, but the fundamental processes under nanoconfinement are still far from being well understood. Some future challenges are proposed for the mechanistic recognition of nanoconfinement effects on water decontamination.

(1) Complexity of confined reaction systems. The design of nanomaterials with tunable activity and selectivity presents a significant challenge, and it is a top priority to understand how the functional properties of nanomaterials are affected by their physicochemical characteristics. The confined reaction system is complex, involving multiple elements/variables that collectively impact the reactions thermodynamically and kinetically, including active species, active sites, confined structures, reactants, and products. These variables interact and contribute to the final decontamination performance, making it difficult to identify their precise contributions. In particular, active Fe species involved in the heterogeneous AOPs are extremely complex, consisting of free Fe^{2+} ions, Fe(III)/Fe(II), high-valent iron-oxo species, and redox transformation among them. Consequently, it is critical yet challenging to enable precise control of the reaction process through rational design of materials simply from a structural aspect. Researchers need to make efforts to strictly control the variables and establish a structure-performance relationship based on systematic decontamination performance enhancement. In addition, kinetic experiments and theoretical simulations can be applied to quantify nanoconfinement effects on the adsorptive and degradative removal of contaminants.

(2) Gap between the model and functional materials. Currently, understanding how structural changes of nanomaterials affect their functional properties under nanoconfinement is still a case-by-case endeavor. The complexity and heterogeneity of constructed nanomaterials, especially those for practical water treatment applications, make them unsuitable for fundamental research on nanoconfinement effects. Meanwhile, model materials with uniform structures fail to simulate exact confinement effects that occur in practical nanocomposites usually with random nanoconfined structures. More importantly, the unique structures and properties of confined water differ from those of bulk water, posing pro-

found effects on the adsorption and catalytic reactions occurring in confined spaces. Despite this, current studies of confined water are limited to ideal systems that exclude interferences from other molecules. Making a direct connection between abnormal properties of nanoconfined water and decontamination performances in water treatment remains a challenge due to the complexity of reaction systems. Nevertheless, the unique properties of confined water might subtly affect the decontamination process, including proton transfer, charge distribution, diffusion coefficient, and hydration process, especially for the adsorption of ions that are strongly hydrated, such as F^- ions.

(3) Lack of in-situ characterization tools. Early studies attributed the confinement effect to changes in surface properties and electronic structures of confined NPs, such as density of active sites, surface area ratio, and unsaturated coordination of atomic species, which could be well characterized now. The developments of real-time detection techniques and state-of-the-art platforms facilitate increasing documentation of nanoconfinement effects. Advanced characterization techniques, such as environmental transmission electron microscope, tip-enhanced Raman spectroscopy, and density-functional theory (DFT) modeling, provide crucial tools for real-time observation of nanoscale reaction systems [68,69]. However, signal interferences from the host make it challenging to observe details of metal-host interfacial interaction, transition state, active species, and real-time reactions inside nanospaces. A better understanding of chemical reactions from thermodynamic and dynamic perspectives would enable us to manipulate the structure and properties of nanoparticles through nanoconfinement for water decontamination. Further development in characterization science is required for advancement in this area.

4.2. Rational and controllable design of confined Fe-based nanomaterials

Though the synthesis of high-performance nanomaterials is the objective of researchers, the rational and controllable design of nanoconfined systems remains a challenge.

(1) Controllable configuration of host and confined NPs. The encapsulation of NPs is not always beneficial for performance improvement as it might hinder chemical reactions. It is important to develop effective methods to secure NPs into porous scaffolds to reduce the loss and facilitate recycling without compromising their functions. Meanwhile, those scaffolds mentioned above feature a wide pore size distribution from < 1 to > 100 nm [70], leading to a broad range of particle sizes ranging from several to dozens of nanometers for embedded iron-based NPs. Thus, it is challenging to obtain confined NPs with uniform size and shape. Additionally, the configuration of both the host and confined nanomaterials affects performances, with the former one affecting local enrichment, mass transfer, and selective sieving. There is a need to optimally modulate the configurations of the host and confined NPs to maximize confinement effects.

(2) Interactions between host and NPs. The electronic and geometric structures of nanomaterials primarily determine their decontamination performance, yet the interactions between the host and NPs have not been fully elucidated. Specifically, there is a need to investigate the effects on nucleation, crystal growth, and electronic structure of nanoparticles and further on the decontamination performances. For example, it is crucial to investigate the confined crystallization of iron-based nanocrystals, including the crystal structure and exposed facets that directly affect catalytic activities and adsorption performances. Our current understanding of the relationship between the preferred growth behavior of NPs and the physicochemical properties of scaffolds, such as dimension and surface chemistry remains unclear. For another example, the rational design of SA catalysts depends on a solid understanding of the atomic structure of the metal atoms and the strong metal–support interaction (SMSI) in SA catalysts. Tremendous efforts have been devoted to exploring SMSI in SA catalysts and identifying the atomic structure via advanced characterization techniques [62]. However, the influence of support/host on electronic properties/structure of metal clusters and exact correlationships between the structural configurations of SA sites with the catalytic reactivity are far from being well understood.

(3) Manipulation of microenvironment for decontamination enhancement. The microenvironment is increasingly recognized as a key variable affecting the adsorption and catalysis performances, as critical as active sites in the heterogenous catalysis [71]. Interactions among the microenvironments, active sites, and reactants are weak individually but strong collectively, initiating significant confinement effects on chemical reactions [72]. However, the synthesis of catalysts featuring desired microenvironments presents a significant challenge. Future research needs to explore the pathways for microenvironment modulation, following a comprehensive acknowledgement of its role in performance enhancement.

4.3. Key considerations regarding novel nanoconfinement systems

The development of heterogeneous Fenton/Fenton-like catalysts is gaining interest as a means of overcoming the limitations of conventional Fenton catalysis. Recent research has reported highly efficient Fenton-like heterogeneous catalysts, along with newly synthesized catalysts, newly-found active species, activation and degradation pathways, and proposed mechanisms.

(1) Newly-found active species and reaction pathways. It is exciting and desirable to explore new treatment processes that improve reaction selectivity towards priority pollutants. For example, in the nanoconfinement system of Fe_2O_3-filled CNTs, singlet oxygen instead of hydroxyl radical was found to be the reactive species during Fenton-like oxidation, which also regulated the reaction selectivity towards various reactants [24]. Confined Fenton-like reactions with newly-found active species have also led to new treatment technologies, such as the selective cleavage of phenol via generated H^* by the confined nZVI in magnetic mesoporous SiO_2 shell [55]. However, the potential environmental risk of newly-formed byproducts when promoting novel heterogeneous Fenton processes has not been fully considered.

(2) Novel decontamination strategy based on oxidative polymerization. The degradation and transformation of toxic organic compounds into nontoxic species remain challenging in wastewater treatment. The intensive use of chemicals and mineralization with unknown safety risks of by-products limit the wide application of oxidative degradation processes. The use of nanomaterials offers a promising strategy for enhancing the efficiency of treatment processes, reducing costs, and enabling the design of novel treatment processes. Rather than mineralization, polymerization under nanoconfinement is another strategy for removing pollutants in an effective and economical way [73], Nanoconfinement facilitates the polymerization process under real wastewater scenarios via enriching target pollutants and regulating the reactivities of iron-centered active species through host-guest interaction. This study has been an ongoing work in our research group.

(3) Subnano-confinement configurations. An attractive direction for future research is exploring the nanoconfinement effects induced by confined dimensions further reduced to the angstrom scale. Layered nanomaterials with sub-nm interlayer spaces (e.g., MoS_2 and Co-Ti oxide nanosheets) have been used as specific adsorbents or catalytic filters [74,75]. Intriguingly, angstrom-scale confined space promoted the spontaneous dissociation of PMS via S-O bond cleavage to produce more $^1O_2$ [74]. However, the significantly improved catalytic performance resulting from angstrom-scale confinement has been elucidated similarly to nanoscale configuration, including the enhanced ROS yield, short-distance diffusion of ROS, facilitated reaction kinetics, and reduced matrix effect. It remains to be explored whether the angstrom-scale confinement effects are the same as nanoscale confinement.

4.4. Barriers to full-scale applications

Nano-enabled technologies hold great potential in minimizing energy input, chemical consumption, and waste disposal in water decontamination. Though the above-mentioned technologies have demonstrated proof of concept, few have been scaled up and applied in the field. To push forward practical applications of confined nanomaterials, it is essential to realize the following goals.

(1) Risk assessment of confined nanomaterials. It is crucial to pay to the newly-formed byproducts and evaluate their toxicity, especially those unknown byproducts generated by the application of confined nanomaterials in actual environments. Current studies in the laboratory primarily focus on the impact of individual ions or organics on the performance of iron-based adsorption or catalytic oxidation, whereas the synergistic interplay of organic matters and inorganic ionic species in real water and wastewater is much more complicated but scarcely studied. Though extensive studies on nanomaterial toxicity have been implemented, risks associated with the release of nanomaterials into the environment during the applications as a composite are nuanced. Hence there is a need to establish evaluation protocols to quantify the release of nanomaterials during infrastructure application.

(2) Development of green and cost-effective synthesis methods of nanomaterials. Some studies propose that the fabrication of engineered nanomaterials has a higher environmental burden due to the use of resources and energy required for synthesis, outweighing the direct impacts of their exposure by several orders of magnitude [76]. While iron-based nanomaterials are generally more cost-effective than other metal-based ones, most iron-based nanomaterials are still somewhat expensive, and it is difficult to verify their techno-economic feasibility in real scenarios. Constructing nanoconfined materials usually requires synthesis processes (e.g., chemical vapor deposition) that are relatively costly and difficult to scale up. For instance, carbon-based materials, such as CNTs and GO, are commonly used as host/substrate for nanoconfinement, but the challenge of overcoming cost barriers to technology adoption persists. Alternatively, natural minerals should be further explored as host alternatives in practical applications. Similarly, many synthesis methods have been proposed to realize the atomic distribution of Fe sites, but commercialization of SA Fe catalysts remains the bottleneck in engineering applications. Therefore, developing green synthesis methods for functional nanomaterials is crucial to scaling up the production and weakening or even diminishing the environmental impact. Given the complexity and high cost associated with nanomaterials, there is a growing demand for designing multifunctional nanomaterials that are compatible with the existing water treatment infrastructure. Fortunately, Fe-based nanomaterials show promise in fulfilling diverse demands with multifunctionality and enhancing the performance of existing treatment technologies, prompting further exploration in future studies.

(3) The need for pilot-scale studies in real scenarios. The demonstration of promising technologies on a larger scale is necessary to make a real impact. Particularly, drinking water, municipal wastewater, and industrial wastewater at centralized treatment plants are usually of large scale, and nanotechnologies need to be both scalable and affordable. Pilot-scale operation is a critical step to evaluate the structural and reactivity stability, mechanical strength, hydraulic properties, and economic efficiency of target nanomaterials for practical applications. Furthermore, cost-effective protocols are needed to regenerate passivated nanomaterials. For instance, functional nanocomposites encapsulated in millimeter-sized resin are designed to advance the practical applications of confined nanomaterials. In this regard, our research group conducted scaled-up manufacturing and long-term field assays of various nanocomposites for real wastewater and river water. Notably, the HZO@D201 nanocomposite showed promising efficacy in the groundwater defluoridation [77], while the La@201 nanocomposite effectively removed phosphorous from river water and real wastewater with high stability during long-term operation [9]. The demonstrated robustness of these pilot-scale adsorption systems over extended operation periods highlights their potential for practical applications. More importantly but always neglected, academia's work should be geared towards practical application, rather than merely developing new technology or materials and subsequently finding applications. To achieve practical applications, process-specific conditions and compatibility with the existing infrastructure must be considered much more heavily when designing new nanomaterials. It would be beneficial to design nanomaterials for decontamination that function with high stability in complex real-world water environments, rather than under optimized conditions.

5. Summary

The flourishing research on confined nanomaterials in recent years has provided a mechanistic understanding of nanoconfinement effects, ultimately leading to revolutionary upgrades to traditional water treatment technologies. This review briefly introduces the general fundamentals of nanoconfinement effects and methods for constructing confined systems. With a particular focus on confined iron species, this review provides inspiring perspectives on the connection of nanoconfinement and high-performance water treatment processes. However, there is a long way to integrating nanoconfinement effects into water treatment processes in a cost-efficient and scalable approach. Thus, we propose some challenges and opportunities for nanoconfinement research and applications in terms of mechanistic recognition, rational design, environmental impacts, and economic issues. The insights afforded by this review are expected to stimulate future interest and breakthroughs for rational design and practical applications of confined nanomaterials in water decontamination, making the best use of nanoconfinement effects.

Declaration of competing interest

The authors declare that they have no conflicts of interest in this work.

Acknowledgments

This study was supported by National Key R&D Program (2022YFA1205601 and 2022YFA1205602) and National Natural Science Foundation of China (21925602 and 22236003)

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