



Application and mechanism of Fenton-like iron-based functional materials for arsenite removal

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Abstract: Between the two major arsenic-containing salts in natural water, arsenite (As(III)) is far more harmful to human and the environment than arsenate (As(V)) due to its high toxicity and transportability. Therefore, preoxidation of As(III) to As(V) is considered to be an effective means to reduce the toxicity of arsenic and to promote the removal efficiency of arsenic. Due to their high catalytic activity and arsenic affinity, iron-based functional materials can quickly oxidize As(III) to As(V) in heterogeneous Fenton-like systems, and then remove As(V) from water through adsorption and surface coprecipitation. In this review, the effects of different iron-based functional materials such as zero-valent iron and iron (hydroxy) oxides on arsenic removal are compared, and the catalytic oxidation mechanism of As(III) in heterogeneous Fenton process is further clarified. Finally, the main challenges and opportunities faced by iron-based As(III) oxidation functional materials are prospected.

Key words: Fenton-like reaction; iron-based functional materials; catalytic oxidation; arsenic removal

1 Introduction

Arsenic (As), a nonmetallic element, is ubiquitous in the atmosphere, lithosphere, hydrosphere, geosphere, and biosphere [1]. Due to natural factors such as volcanic eruptions and rock weathering, and human activities such as mining and nonferrous metal smelting [2,3], the arsenic concentration in local areas has increased, especially in soil and aquatic environments [4,5]. Arsenic poses a huge threat to human health and can cause serious health problems such as skin keratosis and bladder cancer [6,7]. To reduce the environmental risk of arsenic, the World Health Organization (WHO) stipulates that the concentration of arsenic in domestic drinking water should not exceed 10 µg/L [8].

Depending on the pH and redox conditions, arsenic mainly exists in the form of arsenite (As(III)) and arsenate (As(V)) in natural water, and the toxicity and migration ability of As(III) is higher than that of As(V). Therefore, As(III) presents more challenges to treatment than As(V) [9,10]. The oxidation of As(III) to As(V) is the key to effectively reducing the toxicity and mobility of As(III), as well as the treatment difficulty of wastewater containing As(III) [11,12]. The oxidation process of As(III) has been extensively studied to obtain more effective oxidants or catalysts. In natural aquatic environments, oxidation of As(III) is mainly based on dissolved oxygen, microorganisms, ferric iron, nitrate, natural organic matter and manganese (oxyhydr)oxides [13–15]. However, As(III) is hardly oxidized without external light sources, electrochemical means or

catalysts [16]. Common traditional oxidants such as chlorine (Cl_2), sodium hypochlorite (NaClO) and chlorine dioxide (ClO_2) have the problems of low oxidation efficiency and secondary pollution [17–19]. Therefore, efficient and pollution-free advanced oxidation processes (AOPs) have been applied to As(III) oxidation, including photo-chemical oxidation, catalytic wet oxidation, ozone oxidation, electrochemical oxidation, Fenton(-like) oxidation and others [20–24]. Among various AOPs, the Fenton process is widely studied for catalytic oxidation of As(III) because of its excellent oxidation performance [25–27]. However, the conventional homogeneous Fenton reaction has obvious drawbacks, such as a narrow optimal pH range (3–5) and high sludge generation, so its large-scale application is greatly limited [28]. To overcome these drawbacks, various heterogeneous Fenton catalysts, including zero-valent iron (ZVI), iron minerals and other modified iron-based materials, have been explored to facilitate the removal efficiency of As(III) [29–35].

Heterogeneous iron-based functional materials can be employed not only as catalysts for the oxidation of As(III) but also as adsorbents for the in situ removal of As(V). Especially in recent years, research on the modification of iron-based functional materials for the oxidation of As(III) has emerged intensively. To date, numerous studies have reported the adsorption and removal process of arsenic by various synthetic and natural adsorbents [36–40]. However, there are very few comprehensive summaries on the modified methods of iron-based functional materials and their corresponding improvement and catalytic mechanisms for As(III) in Fenton-like systems [41,42]. Creative thinking and accurate directions for the development of new catalysts were provided by a summary of the application, structure-activity

relationship and catalytic mechanism of iron-based arsenic removal catalysts. In this review, the application and reaction mechanisms of iron-based functional materials, including ZVI and iron (oxyhydr)oxides, are discussed in detail. Moreover, the main methods to promote the As(III) removal performance of iron-based functional materials are presented, including carbon doping, metal doping, electrochemistry and magnetization treatment. Importantly, perspectives on the major challenges and opportunities of iron-based functional materials in catalytic oxidation and removal of arsenate are proposed for better development in future research.

2 Zero-valent iron and iron (oxyhydr)oxides for As(III) catalytic oxidation

Benefiting from the advantages of high Fenton activity, low cost, easy availability and negligible toxicity, zero-valent iron (ZVI) and iron (hydroxy)oxides are the two most common iron-based functional materials used for arsenic removal in Fenton-like reactions. In this section, the two main stages of arsenic removal, the catalytic oxidation of As(III) and the absorption of As(V), by zero-valent iron and iron minerals are summarized.

2.1 Zero-valent iron

Iron, a reactive transition metal, is abundant in the Earth's crust [43]. In the past two decades, ZVI has been widely studied for the removal of As(III) because of the effective catalytic activity and adsorption properties of its corrosion products [44–49]. Nanoscale zero-valent iron (nZVI) particles with sizes of 1–100 nm have a higher surface area and reactivity than ZVI and thus have received increasing attention in As(III) removal.

Table 1 shows a representative study using (n)ZVI alone to remove As(III). It can be seen that

Table 1 Oxidation or removal performances of As(III) by ZVI

Iron	Surface area/ ($\text{m}^2 \cdot \text{g}^{-1}$)	[As(III)] _{ini} / ($\text{mg} \cdot \text{L}^{-1}$)	Iron dose/ ($\text{g} \cdot \text{L}^{-1}$)	Optimum pH	Removal efficiency or adsorption capacity	Oxidation rate, $k_{\text{obs}}/\text{s}^{-1}$	Ref.
ZVI filing column	0.1	1	1.57	7.1–8	298 $\mu\text{g/g}$, 30%–40%		[48]
ZVI filing	0.55	100	1	6	82.6%	0.0047	[50]
ZVI filing	2.53	50	1	7.25	99%		[51]
nZVI	37.2	1	1	7	3.5 mg/g , 99.9%		[52]
nZVI/air bubbling	–	1	0.023	4	78%		[53]
nZVI	–	1		3	–	0.3444	[54]

nZVI particles are more effective for As(III) oxidation and adsorption than ZVI filings. The maximum As(III) adsorption capacity of 298 $\mu\text{g/g}$ was obtained in column experiments filled with ZVI filings by LACKOVIC et al [48], whereas 3.5 mg/g was obtained by using nZVI [52]. More effective adsorption is due to a larger specific surface area and higher oxidation efficiency. Comparing the studies of BANG et al [50] and RANA et al [54], the oxidation rate k_{obs} of As(III) by nZVI (0.3444 s^{-1}) was much higher than that of ZVI filing (0.0047 s^{-1}).

2.2 Iron (oxyhydr) oxides

Iron oxides composed of iron and oxygen are the most common substances in nature, mainly magnetite, maghemite and hematite. Compared with iron oxides, the composition and structure of iron oxyhydroxides are more complex. Ferrihydrite, goethite, akageneite, lepidocrocite, ferroxhyte, and limonite are well-known iron oxyhydroxide derivatives, among which ferrihydrite, goethite, and lepidocrocite have been applied to the catalytic oxidation and removal of As(III).

2.2.1 Iron oxides (magnetite, maghemite and hematite)

Magnetite (Fe_3O_4) is an important iron oxide mineral. It is the most widely studied iron oxide in heterogeneous catalytic oxidation of As(III) because it contains divalent iron (Fe^{2+}) and trivalent iron (Fe^{3+}). Fe(II) can initiate the Fenton reaction in the presence of oxygen or hydrogen peroxide, and magnetite will transform into maghemite ($\gamma\text{-Fe}_2\text{O}_3$) under suitable conditions. As an oxidation product

of magnetite in soils, maghemite could further transform into hematite ($\alpha\text{-Fe}_2\text{O}_3$) at temperatures above $300 \text{ }^\circ\text{C}$ [55].

The surface area and adsorption removal performance of various magnetite samples for As(III) were tested. Table 2 shows that the magnetite sample with the smallest specific surface area has the lowest oxidation and removal efficiency of As(III), which indicates that the specific surface area of magnetite is an important factor affecting the arsenic removal performance. The redox state of arsenic adsorbed on magnetite surface #1 was analyzed by X-ray photoelectron spectrometry, and it was found that 8% of As(III) was transformed into As(V) [56]. The catalytic oxidation efficiencies for As(III) by biogenic magnetite and #2 magnetite synthesized by the coprecipitation method were 43% and 73%, respectively, as analyzed by arsenic K-edge X-ray absorption near-edge structure spectroscopy (XANES) [57].

Few studies have been reported on the removal of arsenic by pure maghemite, especially the catalytic oxidation and adsorption of As(III). Mixed magnetite–maghemite particles were used to remove As(III) by CHOWDHURY et al [58]. The maximum adsorption capacity and oxidation efficiency of As(III) were 4.75 mg/g and 29%, respectively. In fact, magnetite–maghemite particles will not only lead to the oxidation of As(III) but also the reduction of As(V) to As(III) during the transformation from magnetite to maghemite. As a result, the arsenic that has been adsorbed was released into the environment. Therefore, it is

Table 2 Oxidation or removal performances of As(III) by iron (oxyhydr) oxides

Iron (oxyhydr) oxide	Condition	Surface area/ ($\text{m}^2\cdot\text{g}^{-1}$)	Removal or oxidation efficiency/%	Ref.
1# magnetite	$[\text{As(III)}]_{\text{ini}}=2 \text{ mg/L}$	11.2	91	[56]
Biogenic magnetite	pH 6–8, 24 h	83	73 (Oxi)	[57]
2# magnetite		28	43 (Oxi.)	[57]
Magnetite/maghemite			29 (Oxi.)	[58]
Ferrihydrite	$[\text{As(III)}]_{\text{ini}}=2 \text{ mg/L}$, 8 d, pH 7		31 (Oxi.)	[59]
Ferrihydrite/light	$[\text{As(III)}]_{\text{ini}}=2 \text{ mg/L}$, 8 h, pH 7		75–80 (Oxi.)	[60]
Goethite	20 d		20 (Oxi.)	[61]
Goethite/light	$[\text{As(III)}]_{\text{ini}}=18.75 \text{ mg/L}$, 8 h, pH 7		45 (Oxi.)	[62]

Oxi.: Oxidation efficiency

discouraged to use magnetite–maghemite particles as a catalyst and adsorbent for As(III) oxidation.

The catalytic oxidation of As(III) by hematite was observed using XANES analysis. Under anoxic conditions, 16% of As(III) adsorbed on the surface of hematite was oxidized. The authors inferred that As(III) was oxidized during the beam exposure rather than the adsorption experiment.

2.2.2 Iron oxyhydroxides (ferrihydrite, goethite, and lepidocrocite)

Ferrihydrite, a naturally occurring iron hydroxide, is common in near-surface environments. Its chemical formula is in dispute, formerly ascribed with the formula $\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$, latter with the formula $\text{Fe}_5\text{O}_7\text{OH} \cdot 4\text{H}_2\text{O}$, and MICHEL et al [63] gave the formula $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$. In terms of the structure of ferrihydrite, a core-shell structure consisting of Fe-13 Keggin center surrounded by Fe-depleted shell is widely accepted [64,65]. In the laboratory, ferrihydrite with a surface area in the range of 200–600 m^2/g is generally synthesized by neutralizing $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or FeCl_3 solution with KOH or NaOH at a pH of 8 [59,66,67]. Because of the extremely high surface area and reactivity [66], ferrihydrite plays a substantial role in wastewater treatment through catalytic oxidation [31], adsorption [66], and coprecipitation [68].

Ferrihydrite has been used as a catalyst for the oxidation of As(III) in the presence of light radiation [60] and dissolved oxygen [59]. Without light, ferrihydrite played the role of catalyst, and the dissolved oxygen functioned as the oxidant for the As(III)/As(V) reaction. However, the efficiency of this catalytic reaction was extremely low, with only 31% of As(V) produced after 192 h [59]. In contrast, ferrihydrite could oxidize 75%–80% of As(III) to As(V) within 8 h under UV light [60]. Under natural light conditions, the oxidation of As(III) can be observed immediately by in situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) when hydrogen peroxide is added to the reaction system [67]. Therefore, hydrogen peroxide and UV illumination play an important role in the catalytic activity of Fe(III) on the surface of ferrihydrite to As(III).

Goethite, $\alpha\text{-FeOOH}$, is a widely distributed iron oxide. Goethite is thermodynamically stable at room temperature. However, it transforms to hematite at temperatures above 200–400 °C. The

synthetic method of goethite was similar to that of ferrihydrite, except that the suspension produced by neutralization needs to be aged above 70 °C for 60 h.

SUN et al [61] studied the oxidation of As(III) on the goethite surface for the first time and found that approximately 20% of As(III) adsorbed on goethite was oxidized to As(V) after 20 d under air-dried conditions. Similar to other iron minerals, the catalytic oxidation of As(III) by goethite under natural conditions is a long-term process. Therefore, photocatalytic oxidation of As(III) by an external light source was proposed to accelerate the rate of As(III) oxidation due to its high reaction efficiency [62]. A significant amount of ferrous iron was released under anoxic conditions, in sharp contrast to the situation in the presence of dissolved oxygen. JEON et al [69] evaluated the effect of pH and humus on the arsenite photocatalytic oxidation process. The results showed that neutral pH was more conducive to the oxidation of As(III), while humus reduced the oxidation reaction rate of As(III) due to its competition with active oxygen species.

Lepidocrocite, $\gamma\text{-FeO}(\text{OH})$, is a metastable iron mineral that can be transformed into goethite by dissolution and recrystallization. The oxidation of As(III) on lepidocrocite was examined by WANG and GIAMMAR [70]. Under both aerobic and anoxic conditions, As(III) could be oxidized to As(V) when containing $\text{Fe}(\text{II})_{\text{aq}}$. However, the difference in the oxidation mechanism of As(III) under aerobic or anoxic conditions is that the Fenton reaction only occurs in the presence of oxygen.

Table 2 shows that the crystal structure of iron oxyhydroxides has a certain influence on the oxidation and removal efficiency of As(III). The change in the crystal structure of FeOOH will cause a change in the surface active adsorption sites. In the heterogeneous catalytic oxidation process, adsorption of target pollutants is the first step of catalytic oxidation, so the change in crystal structure will affect its catalytic performance.

In addition, the catalytic oxidation of arsenic on iron (oxyhydr) oxides is deeply affected by factors such as the Fe/As ratio, oxygen, pH value, coexisting ions and light radiation. Therefore, it is a prerequisite for the efficient application of this technology when the complex effects of these

factors on the process of arsenic oxidation by iron-containing minerals are revealed. It was apparent that the scavenged As(III) on ferrihydrite increased with the applied Fe/As ratio [64]. Fe(II) and Fe(III) solids are beneficial for arsenic removal because Fe(II) can induce As(III) oxidation to As(V) and thus alter arsenic adsorption behavior [70]. This is consistent with Fe(II) adsorption shifting the surface potential to a more positive value, which reduces the As(V) surface complex electrostatic activity coefficient and thus increases the adsorbed concentration. Light and oxygen are also important factors affecting arsenic oxidation. The comparison showed that after 2 h of light exposure, the instantaneous rate of aqueous-phase As(V) formation in the presence of goethite ($12.4 \times 10^{-5} \text{ M s}^{-1} \text{ m}^{-2}$) was significantly faster than that in the presence of ferrihydrite ($6.73 \times 10^{-6} \text{ M s}^{-1} \text{ m}^{-2}$). It was proposed that this increased rate of ferrous iron oxidation in the presence of goethite and dissolved oxygen was the primary reason for the higher As(III) oxidation rate when compared to the As(III)/ferrihydrite system [62].

At acidic and neutral pH, the oxidation degree of As(III) increased due to heterogeneous oxidation on ferrihydrite. It was also observed that more As(III) was oxidized on goethite at acidic pH [61]. Arsenate and low pH values favor the slow growth of dense-structured Fe(hydr)oxides such as spherical ferric arsenate. Generally, an acidic environment with pH of 4–7 is more conducive to the oxidation of arsenic on Fe(hydr)oxides, including ferrihydrite, goethite and lepidocrocite [59,62,70]. Furthermore, some negative ions compete with arsenic for adsorption sites on minerals and thus can inhibit the catalytic oxidation of arsenic. ZHAO et al [59] proved that coexisting inorganic ions with the same concentration,

including NaCl, CaCl₂ and Na₂SO₄, affect the oxidation of arsenic in the following order: Na₂SO₄ > CaCl₂ > NaCl. However, some metal cations, such as manganese, can promote the oxidation of arsenic. As(III) oxidation was enhanced upon increasing the molar ratio of Mn(II) to As(III), and the presence of Mn(II) significantly promoted As(III) oxidation in the ferrihydrite suspension.

In general, light radiation, oxygen, and iron ions have a positive effect on the oxidation of arsenic, while competing anions provide a negative effect. Iron (oxyhydr) oxides are more capable of catalyzing oxidation under acidic conditions.

3 Design of iron-based functional materials

Although natural iron minerals can efficiently catalyze the oxidation of As(III) without producing byproducts, there are still some disadvantages in their application, such as low efficiency and rate of both oxidation and removal [71,72]. In addition, some iron-based functional materials, such as nZVI, become more easily agglomerated after adsorption of As, which decreases the removal efficiency of As(III). Therefore, to solve these problems, many studies have modified iron-based functional materials. The modification of the iron source can increase the oxidation of As(III) and promote its removal (Table 3). The specific modification methods reported in the literature will be introduced in detail in the following sections.

In summary, the combination of carbon-based materials with zero-valent iron or iron minerals greatly improves the arsenic removal performance of materials, which broadens the scope of applicable conditions and improves the efficiency of As(III) oxidation and removal.

Table 3 Oxidation or removal performances of As(III) by modified iron-based functional materials

Material	Oxidant	Condition	As(III) oxidation efficiency/%	Removal efficiency/%	Adsorption capacity/(mg·g ⁻¹)	Ref.
Ferrihydrite/biochar	O ₂	[As(III)] _{ini} =112 mg/L, 1 h, pH 7		99.53	98.49	[73]
Magnetite/cerium oxides	H ₂ O ₂	[As(III)] _{ini} =1.0 mg/L, pH 3, 3 h	>99.9	99.66		[74]
ZVI/copper sulfate	O ₂	[As(III)] _{ini} =525 mg/L, pH 2.4, 0.5 h		99.8		[75]
Fe ⁰ -Cu ⁰	O ₂	[As(III)] _{ini} =25 mg/L, pH 7, 2 h		98	453	[76]

3.1 Carbon materials support iron-based functional materials

Carbon-based materials are widely used as supports and adsorbents due to their hydrophobicity, chemical inertness, and low cost [77]. Moreover, recent studies have demonstrated that biochar has the potential to act as a persistent environmental free radical, electron donor, and electron shuttler [73], which shows the great potential of biochar to promote the Fenton reaction and further oxidize As(III).

NZVI supported onto activated carbon for As(III) catalytic oxidation and removal was studied by ZHU et al [78]. The results showed that the maximum adsorption capacity (15 mg/g) was more than 4 times that of pure nZVI, which was studied by SUSHIL et al [52]. ZVI nanoparticles assembled on porous covalent organic frameworks were selected to adsorb and remove As(III), with a maximum adsorption capacity of 135.78 mg/g and removal efficiency of approximately 100%, while pure ZVI was only 50% [79]. LIU et al [34] developed a novel graphene-like biochar (GB)-supported nZVI, which had a high removal capacity of 363 mg/g for As(III) at pH 4, approximately 1.4 times that for nZVI alone. GB promotes nZVI oxidation to form a Fenton-like system, causing 35% of As(III) to convert As(V).

CHUN et al [80] investigated the arsenic removal ability of Fe₃O₄-loaded mesocellular carbonaceous material, which was synthesized by a wet impregnation method. Magnetite particles were distributed in mesopores of as-prepared catalysts. In the presence of Fe₃O₄-loaded mesocellular carbonaceous material and H₂O₂, arsenic could be completely removed in two steps: arsenic(III) was oxidized to As(V) and then adsorbed As(V) on the catalyst surface. In the research of HUANG et al [81], ferrihydrite-loaded biochar was obtained by freeze-drying. The maximum adsorption capacities of ferrihydrite-loaded biochar for As(III) and As(V) were 1.315 and 1.325 mmol/g, respectively. Ferrihydrite-loaded biochar works well under both natural water and laboratory conditions.

3.2 Metal-doped iron-based functional materials

Compared with the classical homogeneous Fenton reaction, the heterogeneous Fenton-like reaction over Fe-containing catalysts has the advantages of low Fe dissolution, less iron sludge

production, and recycling of iron promoters. However, it usually requires ultrasonic and ultraviolet light irradiation assistance due to its weak catalytic activity, which increases energy demand and wastewater treatment costs [82–84]. To overcome the above drawbacks, researchers [85,86] introduced a second suitable metal into Fe-containing materials to form magnetic bimetal oxide nanoparticles. They have enhanced performance compared to their single metal nanoparticle counterparts because they combine the respective advantages of each component. The metals used for the doping of Fe-containing materials include common transition metals (Mn, Cu) and some rare and precious metals.

Fe-containing materials are usually doped by manganese to form bimetallic oxides. The application of Fe–Mn binary oxides in the oxidation removal of As(III) has attracted the attention of many scholars [82–93]. Fe–Mn binary oxide was prepared by SHAN and TONG [94] to remove As(III) from water. The results showed that the removal rate reached 95% under the condition of pH 7.0 and dosage of 0.1 g/L Mag–Fe–Mn particles within 20 min. As(III) could be effectively removed by Mag–Fe–Mn particles at an initial pH range from 4 to 8, and the residual arsenic was completely oxidized to less toxic arsenate As(V). YU et al [85] synthesized bimetallic oxide-encapsulated magnetic nanoparticles with the main components of Fe₂O₃, FeOOH, Fe₃O₄, and Mn₃O₄. It exhibits a competitive As(III) capture capacity (56.1 mg/g), contributing to the combination of As(III) oxidation and simultaneous adsorption.

The doping of Cu- and Fe-containing materials has been the most widely studied in the field of arsenic removal. FENG et al [95] prepared Cu-doped Fe@Fe₂O₃ core-shell nanoparticles containing Fe, Cu, CuO, Cu₂O and Fe₂O₃ by dropping NaBH₄ reduced iron and copper into CuSO₄ and FeSO₄ solutions. The As(III) removal efficiency was as high as 97.8% within 30 min at pH 7. Based on this work, XU et al [96] synthesized a similar catalyst, Cu nanoshell-decorated nZVI (CFNs), with varying copper content. When the copper content was 10%, the arsenic removal efficiency was more than 98% after reaction for 2 h at pH 7, and the adsorption capacity of CFNs was twice as high as that of conventional nZVI (i.e., 453 and 263 mg/g). ZHANG et al [97] obtained Fe–Cu

binary oxide via a facile coprecipitation method. The results indicated that the Fe–Cu binary oxide with a Cu:Fe molar ratio of 1:2 had excellent performance in the removal of both As(V) and As(III) from water. The maximum adsorption capacities for As(V) and As(III) were 82.7 and 122.3 mg/g at pH 7.0, respectively. However, in the research of BABAE et al [98], with the same pH, the maximum sorption capacities for As(III) and As(V) were 19.68 and 21.32 mg/g, respectively. Furthermore, LI et al [99] prepared Fe–Cu–Y trimetal oxide nanoparticles by doping with rare earth element Y. The investigation of the mechanism revealed that As(III) could be oxidized to As(V) by $O_2^{\cdot-}$ and $\cdot OH$ free radicals. The maximum removal capability for As(III) reached 202.0 mg/g at pH 7.0. To improve the oxidation of As(III), the TiO_2 nanoparticles were positioned onto the shell of Fe_2O_3 –CuO. Almost all As(III) was oxidized and removed under ultraviolet irradiation, which was 30% higher than that of the catalysts without TiO_2 modification [100]. WU et al [101] assembled magnetic $Fe_3O_4@CuO$ nanocomposites on graphene oxide sheets (GO) for the enhanced removal of arsenic(III/V), and the maximum amounts of adsorbed As(III) and As(V) were determined to be 70.36 and 62.60 mg/g, respectively.

WEN et al [74] synthesized magnetic mesoporous Fe–Ce bimetallic oxide by cerium hybridization as an effective heterogeneous Fenton catalyst for arsenite oxidation. The Fe–Ce bimetallic oxide presented excellent catalytic activity for the oxidation of As(III), which almost oxidized 1 mg/L As(III) after 60 min and removed arsenic species after 180 min completely under the reaction conditions of 0.4 g/L catalysts, pH 3.0, and 0.4 mmol/L H_2O_2 .

In general, the Fe-containing materials formed by multimetal doping were conducive to the occurrence of Fenton-like reactions for As(III) oxidation. Fe–Mn and Fe–Cu binary oxides were more suitable for removing As(III) with a neutral pH, while that of Ce was acidic.

3.3 Electrochemistry and magnetization of iron-based functional materials

As(III) is generally removed by adsorption or coprecipitation after being oxidized to As(V). Recently, electrochemical technologies have been

extensively developed and applied in arsenic removal due to the advantages of high efficiency [102]. In the electrocoagulation removal process of As, the Fe anode was sacrificially oxidized to Fe^{2+} and released into the solution. Subsequently, dissolved oxygen oxidized Fe^{2+} to amorphous iron (hydroxide) oxides, which fixes and removes arsenic [103].

LIU et al [104] explored the removal efficiency of As(III) in a three-electrode system, in which a mixture of coated hematite was used as a working electrode, while blank carbon fiber and saturated calomel electrode acted as the counter electrode and reference electrode, respectively. The removal efficiency of As(III) reached 98.6% at an initial pH of 7.0 with 15 mg hematite after 600 charge–discharge cycles. Apart from hematite, rod-shaped iron [105], carbon steel plates [106], mild steel plates [107], iron cylinders [108], were also selected as working electrodes for the removal of arsenic from water.

Premagnetization was employed to enhance the reactivity of ZVI toward As(III) sequestration [109]. Compared to pristine ZVI, premagnetized ZVI showed a 3 times higher As(III) oxidation rate over the pH_{ini} range of 4.0–9.0. Furthermore, the removal efficiency increased progressively with the increasing intensity of the magnetic field for premagnetization. The durations necessary to achieve 99% total As removal were 120.0, 113.5, 84.8, 82.4, and 52.2 min for MagZVI-50, Mag-ZVI-100, Mag-ZVI-200, Mag-ZVI-300, and MagZVI-500, respectively.

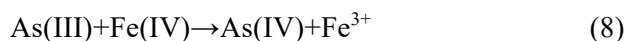
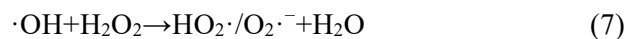
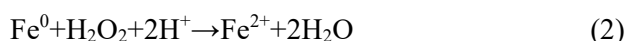
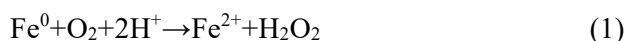
4 Catalytic mechanisms of heterogeneous Fenton-like systems

The mechanisms of catalytic oxidation include a homogeneous Fenton mechanism induced by surface-leached catalytic ions and a heterogeneous surface catalysis mechanism. Hydroxyl radicals ($\cdot OH$), hydroperoxyl radicals/superoxide anions ($HO_2^{\cdot}/O_2^{\cdot-}$), and high valent iron (Fe(IV)) are the main reactive oxygen species (ROS) [110,111]. In this section, the heterogeneous surface catalytic oxidation mechanism for arsenic is discussed.

4.1 Role of ROS in As(III) oxidation

Hydroxyl radicals ($\cdot OH$), hydroperoxyl radicals/superoxide anions ($HO_2^{\cdot}/O_2^{\cdot-}$), and high

valent iron (Fe(IV)) are common ROS in heterogeneous Fenton-like systems. The transfer of two electrons from ZVI to O_2 produces H_2O_2 (Eq. (1)). Moreover, H_2O_2 received two electrons from ZVI to convert to H_2O (Eq. (2)). Then, the combination of H_2O_2 and Fe(II) (known as the Fenton reaction) could produce hydroxyl radicals (Eq. (3)) [43]. It is more difficult to cause Fenton's reaction in the iron oxyhydroxide system. The H_2O_2 (Eq. (4)) or light radiation was necessary to reduce Fe(III). For magnetite, these conditions were not necessary because of the Fe(II) contained in itself. The Fe(II) produced can react with O_2 to generate H_2O_2 (Eq. (5)), and then the Fenton reaction occurs further. Hydroperoxyl radical ($HO_2\cdot$) and its conjugated base, superoxide anion ($O_2^{\cdot-}$) (Reaction (6) are generated from Reactions (5) and (7) [112]. Their function is to reduce Fe(III) to Fe(II) so that the Fenton reaction can be recycled.



As(III) could be oxidized by multiple sources of $\cdot OH$ radicals, such as the surface-bound $\cdot OH_{ads}$ generated on the catalyst surface and free $\cdot OH_{free}$ generation by soluble iron ions. CHAI et al [113] investigated the molecular mechanism of H_3AsO_3 oxidation to H_3AsO_4 by density functional theory calculations. The reaction pathways of $\cdot OH_{free}$ with H_3AsO_3 in the solution were $H_3AsO_3 \rightarrow H_2AsO_3\cdot \rightarrow H_3AsO_4$ and $H_3AsO_3 \rightarrow H_4AsO_4\cdot \rightarrow H_3AsO_4$. Ferryl iron (Fe(IV)) was produced in heterogeneous Fenton systems, especially at neutral or basic pH. Fe(IV) has been identified as the Fenton intermediate [114] and the main oxidant for As(III) at neutral pH (Eq. 8) [115,116].

$\cdot OH$ has a high redox potential, which has an absolute advantage for the oxidation of As(III) under acidic conditions. Under alkaline conditions, Fe(IV) is the main active oxygen species for As(III) oxidation. The redox potential of $O_2^{\cdot-}$ is relatively low, and its contribution to the oxidation of As(III)

is relatively limited.

4.2 Catalytic oxidation mechanism of modified catalysts

Loading the basic catalyst with substrate materials, doping with multiple metals, electrochemistry and magnetization can greatly improve the catalytic oxidation performance and the removal efficiency for As(III). This section will explain the improvement mechanism of these three methods.

4.2.1 Carbon materials loading improvement mechanism

Adding substrates to immobilize nanoparticles can improve the catalytic oxidation performance to promote the removal of As(III) through two paths: one is to avoid particle aggregation to retain the reaction site, and the other is that the substrate material participates in the catalytic reaction and accelerates the rate of the catalytic reaction. Generally, the two mechanisms exist simultaneously.

There was a synergistic effect between GB and nZVI on the removal of As(III) by GB/nZVI materials. Because of the relatively higher production rate of Fe(II) by GB/nZVI than nZVI, more reactive oxygen species were generated, which enhanced the As(III) oxidation rate. The generation of secondary iron oxyhydroxides may have further favored As(III) removal. The removal mechanism of As(III) by GB/nZVI can be described by two pathways (Fig. 1): 1) during the rapid oxidation of nZVI and the formation of iron oxyhydroxide within the first 5 min, some As(III) species can directly adsorb on nZVI through inner-sphere bidentate mononuclear complexes; 2) the partial oxidation of As(III) to As(V) by reactive oxygen species takes place. More importantly, the presence of highly graphitized GBs with a strong electron transfer capability can further enhance the electron transfer from ZVI, thereby accelerating the above reaction process.

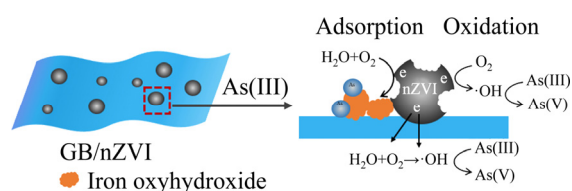


Fig. 1 Schematic representation of oxidation and removal of arsenic using GB/nZVI as catalyst [34]

CHUN et al [80] investigated the arsenic removability of Fe₃O₄-loaded mesocellular carbonaceous material, which was synthesized by a wet aging method. Compared with simple magnetite, it was found that the decomposition rate of H₂O₂ had no obvious change, but the oxidation rate of As(III) was obviously increased. Therefore, the introduction of mesocellular carbonaceous material improves the utilization efficiency of hydrogen peroxide, which appears to be attributable to the affinity of As(III) for the mesoporous carbon support. The molecules of As(III) adsorbed on the mesoporous carbon foam are retained in close proximity to the active site of iron, at which ·OH is generated, increasing the chance for As(III) to be exposed to ·OH.

The mechanism of oxidation and adsorption of As(III) in water using ferrihydrite-loaded biochar is shown in Fig. 2. Biochar in ferrihydrite-loaded biochar materials plays multiple roles in adsorption and oxidation processes. In addition to having self-active groups for adsorption and immobilization arsenate anions, biochar can serve as a persistent free radical to produce superoxide radicals. Furthermore, biochar can donate or shuttle electrons from Fe(III) to Fe(II), which accelerates the generation rate of free radicals and the circulating rate of Fe(III)/Fe(II) and thus improves the oxidation rate of As(III).

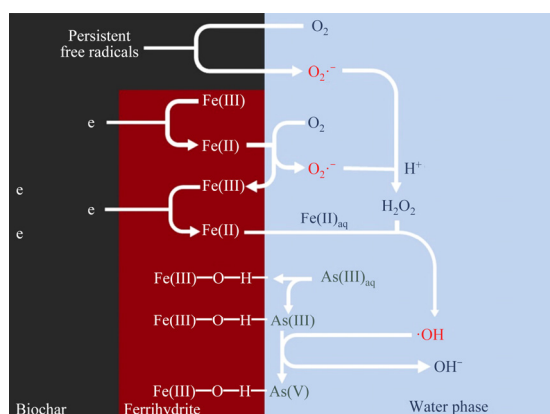


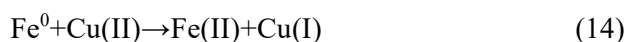
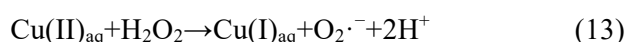
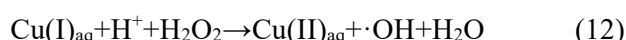
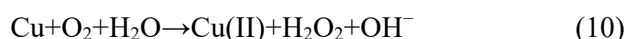
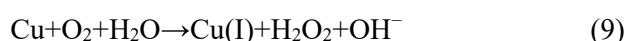
Fig. 2 Mechanism of oxidation and adsorption of As(III) in water using ferrihydrite-loaded biochar [82]

4.2.2 Multi-metal doping improvement mechanism

Compounding specific metals (Cu, Ce, Mn) with ZVI or iron minerals was an effective means to improve the oxidation and removal efficiency of As(III), which may be due to metal doping changing the structure and surface properties of the

iron catalyst and increasing the path of the catalytic reaction.

The iron–copper (Fe⁰/Cu⁰) bimetallic particles act as catalysts for the oxidation of As(III). The Fenton reaction was initiated by oxygen corrosion of iron and copper, in which the synergistic effect between Fe and Cu promoted the reaction. First, the formation of the Fe–Cu galvanic cell system will accelerate the corrosion of ZVI and then accelerate the production of free radicals. Second, Cu, as a transition metal, has the properties of activating oxygen and catalyzing the decomposition of hydrogen peroxide (Reactions (9)–(13)), which increases the amount of active oxygen and improves the oxidation efficiency of As(III). In addition, Cu(II) produced by Cu oxidation will be reduced by Fe⁰ to produce Cu(I) (Reaction (14)), and Cu(I) can activate dissolved oxygen through single electron transfer (Reactions (11) and (13)) more easily than Fe(II) because of the much higher $E^0[\text{Fe(III)/Fe(II)}]$ than $E^0[\text{Cu(II)/Cu(I)}]$ to O₂ to generate O₂^{·-} and H₂O₂. Moreover, after the reaction, Fe⁰ disappears, and Cu⁰ still exists, which indicates that the existence of Cu⁰ can inhibit the corrosion passivation of iron and improve the catalytic efficiency. The following scheme (Fig. 3) describes the mechanism of catalytic oxidation and removal of As(III) by Fe–Cu bimetallic particles.



The catalytic oxidation mechanism of As(III) by Fe–Ce bimetallic particles is different from the Fenton reaction mechanism, which is initiated by other catalysts. In addition to Fe(II) and Ce(III) catalyzing H₂O₂ to generate active oxygen radicals to oxidize As(III) (Reactions (15) and (16)), there is also a nonfree radical pathway, and Ce-hydroperoxo surface complexes ($\equiv\text{Ce}^{\text{IV}}\text{—OOH}$) are responsible for the oxidation of As(III) adsorbed on the catalyst surface (Reaction (17)) (Fig. 4). This was proposed by SHAN [117] based on comprehensive studies, including scavenging, enzymatic, and other experiments. The surface free radical oxidation of cerium oxide (Reactions (18) and (19)) has only a

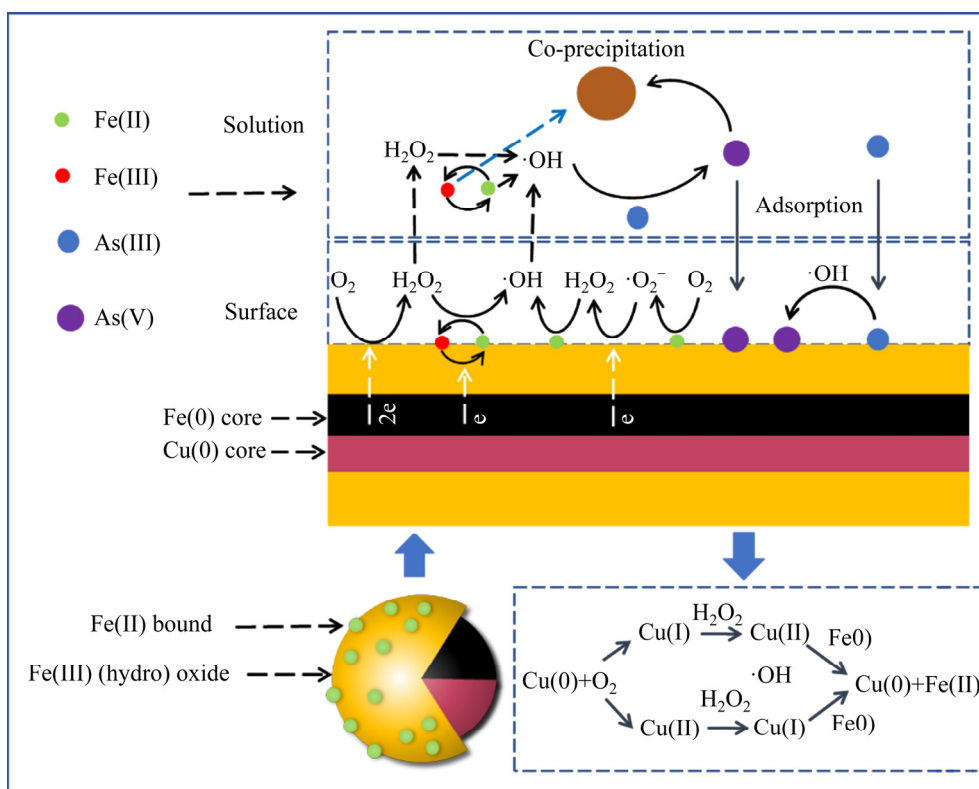


Fig. 3 Mechanism of catalytic oxidation and removal of As(III) by Fe–Cu bimetallic particles [96]

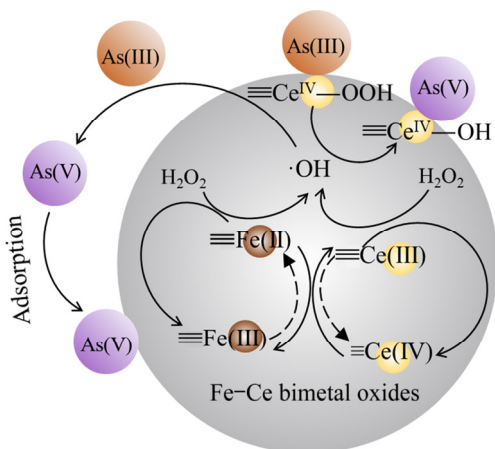
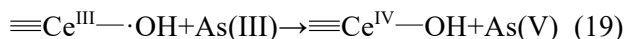
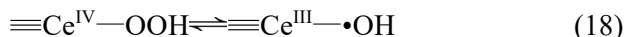
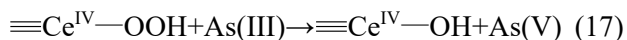
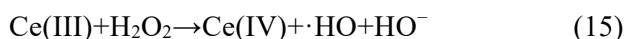


Fig. 4 Mechanism of catalytic oxidation and removal of As(III) by Fe–Ce bimetallic particles [117]

very minor contribution.



4.2.3 Electrochemistry and magnetization modification mechanism

The basic principle of improving arsenic

removal by the electrochemical Fenton-like method is to control the reaction rate of Fe(II) with dissolved oxygen or H₂O₂ [118,119]. In addition, the pH and ionic environment near the electrode are important factors that govern the electrochemical Fenton-like reaction. Electrochemical systems used in arsenic removal are divided into single anode systems and double anode systems. In this section, the mechanism of the generation of reactive oxygen species and the oxidation and removal of As(III) will be introduced in detail in these two systems.

In the single anode system, the removal of As(III) using a hematite electrode was performed by multicycle galvanostatic charge–discharge (Fig. 5) [104]. The hematite electrode obtained electrons, and thus, the Fe(III) and dissolved oxygen adsorbed on the electrode surface was reduced to Fe(II) and H₂O₂ released into the solution. As(III) could be directly oxidized to As(V) on the carbon electrode surface. In the discharge process, Fe(II) was oxidized to Fe(III) by H₂O₂, leading to the generation of ·OH for As(III) oxidation. The hematite electrode undergoes a periodic oxidation–reduction reaction in every charge and discharge process, which effectively avoids passivation of the electrode. In addition, it is

worth noting that NaCl was used as the electrolyte, and Cl^- would be oxidized to ClO^- during the charging process, which also contributes to the oxidation of As(III).

In the study of TONG et al [120], a double anode system was used to remove As(III). One iron anode was used to generate Fe(II) under the condition of iron deficiency, and the other inert anode (IrO_2 and Ta_2O_5 coated on titanium diamond mesh) generated O_2 by electrolyzing water for the oxidation precipitation of Fe(II). The As(III) near the anode was oxidized directly. In addition, most of the As(III) oxidation was caused by the reaction of Fe(II) and O_2 , but the main oxidation was the intermediate active product Fe(IV) instead of hydroxyl radicals. Cl^- did not play an oxidation role in this system because the author chose IR instead of Ru oxide coatings, with a low overpotential for oxygen evolution of Ir.

The excellent performance of the double anode due to the double anode can not only control the amount of Fe(II) in the solution but also control the content of dissolved oxygen in the solution and provide a continuous supply of OH^- through the reduction of H^+ on the inert cathode.

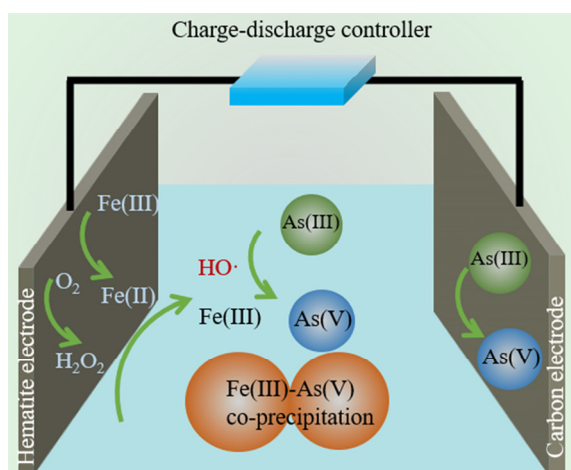


Fig. 5 Mechanism of catalytic oxidation and removal of As(III) using hematite electrode by multi-cycle galvanostatic charge–discharge [104]

5 Effect of coexisting ions on oxidation and removal of As(III) by Fenton-like method

Whether it is industrial wastewater or natural water, arsenic often coexists with other substances, such as common anions (SO_4^{2-} , PO_4^{3-} , SiO_4^{2-} , Cl^- ,

NO_3^- , CO_3^{2-}) and natural organic substances (humus), which may affect arsenic removal. This section discusses the common pairs of coexisting substances mentioned above.

5.1 Inorganic oxyanion

It has been reported that PO_4^{3-} is the most powerful competing anion because it has aqueous behavior similar to that of arsenic. Hence, PO_4^{3-} can decrease the adsorption capacity by competing for similar chemical binding sites. Because adsorption is an important step in Fenton-like heterogeneous catalytic oxidation, the reduction of adsorption capacity of catalysts for As(III) will lead to the reduction of oxidation and removal efficiency of As(III). HUANG et al [81] showed that in the catalytic oxidation of As(III) with ferrihydrite-loaded biochar as the catalyst, with the addition of PO_4^{3-} , the maximum adsorption capacity of ferrihydrite-loaded biochar for As(III) decreased from 1.30 (without added PO_4^{3-}) to 1.24 mmol/g and that for As(V) decreased from 1.32 (without added PO_4^{3-}) to 1.27 mmol/g. The results are consistent with the research conclusion of WU et al [102]. Other anions (such as SO_4^{2-} , Cl^- and CO_3^{2-}) can hardly affect the adsorption capacity of a catalyst [98]. KANEL et al [52] found that H_4SiO_4 could reduce the uptake of As(III) from 99.9%.

5.2 Natural organic matter

Humic acid is a common organic matter in natural water, and its influence on the oxidation and removal of As(III) by Fenton-like iron-based functional materials has been reported. It was found that NZVI was markedly passivated for the treatment of arsenic-containing water in the presence of 20 mmol/L HA, and thus humic acid reduced the removal effect of As(III) [79]. This result is consistent with the research results of LIU et al [34].

In summary, the influence of coexisting ions in water on the oxidation and removal of As(III) by the Fenton-like process is as follows: SO_4^{2-} , CO_3^{2-} and NO_3^- have no significant effect on the removal of As(III); PO_4^{3-} , SiO_4^{2-} and humic acid could obviously inhibit the oxidation and removal of As(III). There are two influencing mechanisms: adsorption competition and oxidation competition. PO_4^{3-} and SiO_4^{2-} combined with iron-based materials occupy a large number of active adsorption sites,

which reduces the removal efficiency of As(III). Humic acid is a kind of organic matter that consumes free radicals in the system, reduces the oxidation efficiency of As(III), and then reduces its removal efficiency. In addition, humic acid has a good affinity for iron-based materials, which will reduce arsenic removal efficiency by the principle of adsorption competition.

6 Conclusions and prospectives

The Fenton-like method has a wide range of reaction pH values and iron sources, including iron minerals, ZVI and other modified iron-based materials, and can reduce the quenching of free radicals by controlling the reaction rate through the design of materials. The improved methods include synthesizing iron/carbon composites, doping metals, magnetizing catalysts, and electrochemical methods. The catalytic oxidation and removal performance of modified iron-based materials for arsenic are greatly improved, especially in low-concentration arsenic-containing wastewater. The oxidation efficiency increased from 8%–30% to 33%–99.9%, and the removal efficiency was improved from below 70% to above 98%. In conclusion, the Fenton-like method is very attractive in the catalytic oxidation and removal of arsenic. Iron-based materials are not only good catalysts but also have a high affinity for arsenic. In this review, progress in the study of various iron-based functional materials for arsenic removal and their catalytic adsorption synergistic arsenic removal mechanisms are summarized, which provides guidance for the development of efficient and stable iron-based functional materials.

However, although some progress has been made in the removal of arsenic by iron-based functional materials, there are still some key problems, such as insufficient arsenic removal capacity and nonrecyclability of materials, which deserve further research. First, enhancing the synergy effect among the elements of the catalyst to improve the oxidation rate of arsenic, for example, by loading multimetal doped particles on carbon-based materials. Second, combining element doping and nanostructure fabrication with specific morphologies, including nanosheets, mesostructures, nanorods, nanotubes, and nanofibers, could increase the specific surface area and adsorption active sites,

which could be conducive to the adsorption of arsenic by iron-based functional materials. Finally, the reusability of iron-based materials should be further improved to reduce the treatment cost of arsenic-containing wastewater. Therefore, the targeted development of an iron-based functional material with stable cycling performance for arsenic removal is of great importance.

Acknowledgments

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类芬顿铁基功能材料除砷的应用与机制

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摘要: 亚砷酸盐(As(III))和砷酸盐(As(V))是天然水中砷的主要存在形态, 其中 As(III)由于其高毒性和高迁移率, 对人类和环境的危害远大于 As(V)。因此, 将 As(III)预氧化为 As(V)被认为是降低砷毒性、提高砷去除率的有效手段。由于铁基功能材料具有较高的催化活性和砷亲和力, 在非均相类芬顿体系中可以快速将 As(III)氧化为 As(V), 然后通过吸附和表面共沉淀将 As(V)从水中去除。本文综述零价铁和铁(羟基)氧化物等不同铁基功能材料对砷去除的影响, 以进一步阐明非均相芬顿法中 As(III)的催化氧化及去除机理。最后, 本文还展望了应用于 As(III)氧化的铁基功能材料目前面临的主要挑战和机遇。

关键词: 类芬顿反应; 铁基功能材料; 催化氧化; 砷去除

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