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Sulfite Activation of Fe-Mn Bimetallic Oxides for Rapid Oxidative Removal of As(III) in Water: Involvement of Active Mn(III)

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Abstract

The activation of sulfite [S(IV)] by transition metals, a new generation of advanced oxidation processes, has been widely studied for water purification. However, the application of this process to oxidize and remove arsenite [As(III)] from water through Fe-based S(IV) activation and the associated mechanisms are not fully understood. In particular, rapid removal of As(III) and secondary metal contamination have presented challenges. Herein, we develop a novel sea urchin-like magnetic Fe-Mn bimetallic oxides (FeMnO)-activated S(IV) process to address these issues. Under neutral pH, the FeMnO/S(IV) system achieved a 99.2% removal of As(III) within only 10 min with residual arsenic concentration below 10 µg/L, and the removed As(III) was fully oxidized to arsenate [As(V)]. Additionally, FeMnO was recyclable and capable of treating actual arsenic-contaminated water. Furthermore, the oxidation mechanism of non-radical active trivalent manganese [Mn(III)] was discovered during the reaction.
between the FeMnO/S(IV) system and As(III). The FeMnO catalyst activated S(IV) to generate oxy sulfur radicals (i.e., SO$_5^{•–}$, SO$_4^{•–}$ and SO$_3^{•–}$), but they were not the primary oxidizing species for As(III). Instead, As(III) oxidation was mainly attributed to the active Mn(III) generated by the electron transfer between the FeMnO catalyst and SO$_5^{•–}$ radicals. The discovery of active Mn(III) species in this work may provide a new avenue for developing novel Fe-Mn-type adsorbents to purify arsenic-contaminated water.

**Keywords**: As(III), Fe-Mn bimetallic oxides, sulfite, active Mn(III), oxidation

1. Introduction

Arsenic (As), as a toxic metalloid produced by artificial and natural geochemical cycles (such as mining, pesticide use, natural weathering, and volcanic eruptions), has aggravated the harm to global drinking water safety for many years [1, 2]. Over 150 million people worldwide are long-term threatened by drinking As-contaminated water, of which China accounts for about 13% of the population [1]. Thus, more than 70 countries have set the maximum contaminant level (MCL) of As in their drinking water to 10 µg/L according to the World Health Organization (WHO) interim guidelines [3, 4].

Arsenite [As(III)] has received more attention due to its high mobility and toxicity, threatening water safety and aquatic ecosystems [5, 6]. Among existing remediation methods, iron (Fe)-based materials are widely used to remove As(III) in water due to their environmental friendliness and low cost. However, As(III) in an aqueous environment mainly exists in non-ionic H$_3$AsO$_3$, making it difficult to efficiently remove by Fe-based materials without chemical transformation due to its low affinity [7]. Therefore, Fe-based materials coupled with adsorption and chemical oxidation are one of the promising strategies. For example, ferrate and Fenton reactions with oxidizing ability can effectively remove As(III) from water through in situ flocculation of Fe ions [8, 9]. However, disadvantages such as the significant production of iron sludge during the reaction, a narrow working pH range, and the inability to recover Fe-based materials have limited their application prospects. Recently, heterogeneous Fe-based materials synthesized through doping or modification have been found to exhibit Fenton-like catalytic activity and high affinity for As(V) and can be used in combination with H$_2$O$_2$ or light for the removal of As(III) [10, 11]. However, the catalytic efficiency of these metal composite oxides is limited mainly by the Fe(II)/Fe(III) cycling in the solid or liquid phase. Considering the abundance of sources and the simplicity of synthesis, Fe-Mn type adsorption materials are deemed to have more practical application prospects. They typically work through the synergistic removal of As(III) into As(V) via the oxidation of Mn oxides and the high affinity of Fe oxides [12, 13]. However, the release of Mn(II) ions caused by the reduction of Mn oxides has raised concerns about the reusability and safety of Fe-Mn type adsorption materials. In addition, the oxidation rate of As(III) is a critical factor that affects the removal efficiency of Fe-Mn type adsorption materials [12]. Therefore, it is challenging for traditional Fe-Mn type adsorption materials to rapidly reduce As(III) from several
hundred µg/L to below 10 µg/L within a short time (e.g., a few minutes) [14, 15].

Nowadays, advanced oxidation processes (AOPs) based on peroxydisulfate (PDS) or peroxymonosulfate (PMS) have been intensively studied as a viable strategy to replace H₂O₂-AOPs in conventional water treatment [16]. This is because, compared to ‘OH-AOPs, SO₄²⁻−AOPs possess higher oxidation potentials (2.5−3.1 V), free radical formation yields, and wider pH adaptability [17, 18]. However, the main challenges are the high cost and residual toxicity of persulfate species after the reaction [19]. Fortunately, sulfite [S(IV)] as a byproduct of industrial processes has gradually become a viable substitute for persulfate precursors due to its environmentally friendly and relatively stable nature [18, 20]. Various strategies, including light, electricity, and transition metals, have been employed to activate S(IV), with transition metals receiving special attention due to their ability to activate S(IV) without needing special equipment and additional energy input [20-22]. The current research indicates that the primary oxidizing species produced by transition metals (Fe, Mn, Co, and Cu) during the activation of S(IV) are oxysulfur radicals (i.e., SO₅⁻², SO₄⁻² and SO₃⁻²) and ‘OH [22-25]. However, it is not clear yet whether a novel Fe-Mn type catalysts can effectively activate S(IV) and oxidize and remove As(III). Furthermore, it remains unclear which S(IV) activation mechanism dominates in the reaction of the novel Fe-Mn type catalysts with As(III) or whether new oxidative species other than the traditional radical oxidation mechanism would be involved in the oxidation process. These issues warrant further investigation.

Herein, our study aimed to synthesize a novel sea urchin-like magnetic Fe-Mn bimetallic oxide (FeMnO) via a one-pot method and couple it with S(IV) for the first time for rapid oxidative removal of As(III) from water. It is simple to synthesize and operate, possesses a high specific surface area, and exhibits excellent catalytic performance. With the FeMnO/S(IV) system, the effects of different reaction conditions (including S(IV) dosage, solution pH, reaction temperature, etc.) on the removal of As(III) were studied. Besides, the oxidation mechanism of ROS-mediated non-radical active Mn(III) was explored. To our knowledge, As(III) oxidation through active Mn(III) is rarely reported. Note that the active Mn(III) generated in the FeMnO/S(IV) system is a strong one-electron oxidant, which is not complex with ligands other than −OH and H₂O [26]. The activation pathway of S(IV) in the FeMnO/S(IV) system was also proposed. Moreover, the stability, recyclability, and regeneration ability of the FeMnO catalyst were evaluated. Finally, the potential application of the novel FeMnO catalyst was demonstrated by assessing its As(III) removal performance in different actual water samples using the FeMnO/S(IV) system.

2. Experimental section

2.1 Reagents and Chemicals

All the reagents and chemicals utilized in the experiments were of analytical grade and were used without further purification. Fresh S(IV) working solution was prepared
using sodium sulfite (Na$_2$SO$_3$) before use. Disodium hydrogen arsenate heptahydrate (Na$_2$HAsO$_4$·7H$_2$O) and sodium arsenite (NaAsO$_2$) purchased from Sigma Aldrich were used to prepare As(V) and As(III) working solutions. Other reagents were purchased from China Aladdin Chemical Reagent Co. Ltd. Deionized (DI) water obtained from a water purification system was used in all experiments unless otherwise specified.

### 2.2 Synthesis of FeMnO

The synthesis of FeMnO was via a facile one-pot method. In brief, KMnO$_4$ (0.0075 mol) and FeSO$_4$·7H$_2$O (0.0375 mol) were first dissolved respectively in 0.1 L of DI water. Heated the KMnO$_4$ solution to 100 °C in an oil bath. Then, the FeSO$_4$·7H$_2$O solution was added to the boiling KMnO$_4$ solution under vigorous stirring. After that, 0.022 L of NaOH solution (5 M) was added dropwise to the mixture (pH about 13.5), followed by a continuous reaction at 100 °C for 1 h. The obtained precipitate was recovered by a magnet and washed 5 times with DI water to remove impurities. Finally, the precipitate was dried in an oven at 80 °C for 24 h.

### 2.3 Batch experiments

Unless otherwise stated, all removal experiments were carried out at room temperature (20 ± 2 °C) in 1.5 L beakers containing 1 L of As(V) or As(III) solution. Typically, the working pH of the reaction solution was adjusted to 7.0 using 0.1 M H$_2$SO$_4$ or NaOH after adding 0.2 mM of freshly prepared S(IV) solution to the beaker above. Then, 0.2 g of adsorbent was added to the beaker, and the reaction was initiated at a stirring speed of 400 rpm after ultrasonic dispersion for 30 s. Next, a series of 4 mL of the reaction solution was removed at predetermined time intervals and filtered through a 0.22 µm aqueous filter membrane for addition to a 10 mL container containing 1 mL of HCl (6 M). Finally, the residual arsenic concentration in the filtrate was detected by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 8300, PerkinElmer, USA. limit of detection of 2 µg/L) or inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7700X, CA, USA). To understand the non-homogeneous catalytic oxidative adsorption process, a pseudo-first-order kinetic model and a pseudo-second-order kinetic model (Supplementary Information Text S1) were used to fit the above experimental data. It is worth noting that the adsorption isotherm studies were conducted in a 0.1 L single-necked conical flask, with FeMnO dosage of 0.2 g/L, solution volume of 50 mL, initial arsenic concentration of 0-20 mg/L, S(IV)/As molar ratio of 15, temperature at 20 °C, pH value of 7.0, and shaking time of 24 h. The Freundlich and Langmuir isotherm models (Supplementary Information Text S2) were used to fit the above adsorption equilibrium data for As(III) or As(V), respectively. The effects of sodium pyrophosphate (pp), coexisting ions, quencher or humic acid (HA) on the As(III) removal were observed by adding a specific amount of PP, Na$_2$SiO$_3$·9H$_2$O, Na$_3$PO$_4$, NaCl, Na$_2$SO$_4$, Na$_2$CO$_3$, ethanol (EtOH), methanol (MeOH), aniline (AN), tert-butanol (TBA) or HA to the solution.

Real water samples collected from Harbin, Heilongjiang Province, China, were
utilized to assess the capacity of the FeMnO/S(IV) system to remove arsenic from contaminated water. The water quality parameters are listed in Table S1 in the Supplementary Information. The entire experimental procedure was the same as above. In an experiment to evaluate the regeneration capacity of FeMnO, the arsenic-adsorbed FeMnO was placed in a 0.5 M NaOH solution and stirred for 4 h. After desorption is completed, the FeMnO was recovered with a magnet and washed 5 times with DI water, dried and used for the next adsorption-desorption cycle.

2.4 Characterization and analysis

The crystal structure and morphology of the FeMnO were characterized by X-ray powder diffraction (XRD, Ultima IV, Rigaku Co., Japan) equipped with Cu Kα radiation (λ = 1.5418 Å), scanning electron microscopy (SEM, ZEISS Gemini 300, Germany) and transmission electron microscopy (TEM, TalosF200x, ThermoFisher Scientific, Netherlands) equipped with an energy dispersive X-ray spectrometer (EDS, Super-X EDS, Netherlands). The zeta potentials of the FeMnO were determined using a potentiometer (Malvern Zetasizer Nano ZS90, UK). The UV-Vis diffuse reflectance spectrum of FeMnO was acquired using a UV-Vis spectrophotometer (Shimadzu UV-3600i Plus, Japan). The FeMnO's specific surface area was determined using the Brunauer-Emmett-Teller (BET) N₂ adsorption-desorption technique on a Micromeritics ASAP 2460 instrument. The functional groups on the FeMnO surface were identified with Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet iS20, USA). The phases of the synthesized Fe-Mn bimetallic oxides were identified by Raman spectroscopy (Horiba LabRAM HR Evolution, Japan). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA) was employed to investigate the changes in the surface chemistry of FeMnO before and after the adsorption process. The presence and type of radicals during the reaction were determined on an electron paramagnetic resonance spectrometer (EPR, Bruker EMXplus-6/1, Germany) by using DMPO as an indicator. The magnetometer type 7404, manufactured by LakeShore in the USA, was used to measure the magnetic properties of FeMnO. Hydride generation-atomic fluorescence spectrometry (BAF-2000, Baode Instrument Co., Ltd., Beijing) was utilized to quantify the concentration of As(III) and As(V) in the solution.

3. Results and discussion

3.1 Physicochemical properties of FeMnO

The SEM images clearly showed the FeMnO morphology as consisting of urchin-like particles averaging approximately 600 nm in size (Fig. 1a). EDS analysis showed that FeMnO was mainly composed of three elements, Mn, Fe and O, with a Fe/Mn atomic ratio of approximately 5:1, consistent with the initial dosing ratio (Fig. 1b). The XRD pattern in Fig. 1c matched JCPDS card numbers 10-0319 and 29-0713, identifying the product as having a spinel crystal structure and mixed crystal features (MnFe₂O₄ and α-FeOOH). Raman analysis revealed that the bands at 219, 282, 395 and 609 cm⁻¹
belong to goethite, further proving the existence of α-FeOOH (Fig. S1) [27]. High-resolution TEM images revealed that the FeMnO particles were composed of a spherical core and many nanorods grown radially from the core (Fig. 1d, e). The diameter of the spherical core was about 300 nm, while the length of the nanorods was about 150 nm and the width of about 10 nm. The lattice fringes spacing of 0.39 nm and 0.25 nm were observed in Fig. 1f, corresponding to the (110) and (111) planes of α-FeOOH, respectively. The lattice fringes spacing of 0.17 nm and 0.25 nm were observed in Fig. 1g, corresponding to the (422) and (311) planes of MnFe₂O₄, respectively. The above results were consistent with the analysis of the XRD data. On the other hand, the corresponding elemental mapping of the individual FeMnO structures indicated (Fig. 1h-k) that the three elements Fe, Mn and O were uniformly distributed in the catalyst, facilitating the synergistic effect between the components and possibly improving the As(III) removal performance. Notably, Fe and O were present throughout the urchin-like structure of FeMnO, while Mn was present almost exclusively in the core. Thus, the nanorods grown on the surface of FeMnO might be α-FeOOH. Compounds based on iron oxyhydroxide (FeOOH) have been extensively studied as effective adsorbents for controlling the fate of heavy metals [10, 28, 29]. Thus, the emergence of α-FeOOH might endow FeMnO with an abundance of active functional groups (–OH₂ and –OH) and a strong arsenic affinity. Moreover, the BET surface area (186.3 m²/g) and average pore size (7.6 nm) of FeMnO were obtained according to Fig. S2 and Table S2, indicating its slit-shaped mesoporous structure [30]. FeMnO had a higher BET surface area compared to other reported 3D nanomaterials (Table S3), which suggested the presence of more active sites. The synthesized FeMnO revealed ferromagnetism by vibrating sample magnetometer (VSM), and the maximum saturation magnetization intensity was 23.3 emu/g (Fig. S3). Thus, the rapid separation of FeMnO from water could be achieved through external magnets.
3.2 Kinetics and isotherms studies

The FeMnO alone failed to reduce the initial concentration of 1054 µg/L As(III) to less than 10 µg/L (the As content in standard drinking water) within 30 min, with a removal efficiency of only 80.5% (Fig. 2a). In contrast, at an S(IV) dose of 200 µM, the removal efficiency of As(III) was significantly improved, achieving 99.2% in only 10 min with a residual arsenic concentration below 10 µg/L. Two kinetic models were employed to fit the experimental data (Fig. 2b), and the obtained kinetic constants were summarized in Table S4. We found that the pseudo-second-order kinetic model fitted the data better, suggesting that As(III) removal may be a chemisorption process [31]. In addition, the participation of S(IV) increased the value of the adsorption rate constant $k_2$ significantly from 0.14 to 0.21 g/mg/min, indicating that S(IV) does accelerate the adsorption of As(III). The conversion of As(III) to As(V) may be responsible for the enhanced removal of As(III) from the FeMnO/S(IV) system. To test this hypothesis, we tested the adsorption kinetics of As(V) removal from the FeMnO/S(IV) system and fitted them using pseudo-first- and pseudo-second-order kinetic models (Fig. 2b). The...
results indicated that the presence of S(IV) not only did not affect the $k_2$ value of FeMnO for the removal of As(V) but also had a similar $k_2$ value to the FeMnO/S(IV) system for the removal of As(III) (0.23 vs 0.21 g/mg/min). Therefore, the FeMnO/S(IV) system with integrated oxidation and adsorption has an advantage over FeMnO alone in removing As(III). Considering the relatively low concentration of arsenic in natural groundwater, the effect of the initial As(III) concentration (0–1000 µg/L) on As(III) removal in the FeMnO/S(IV) system was investigated (Fig. 2c). The results demonstrated that all As(III) concentrations were reduced to below the standard drinking water level of arsenic within 10 min. Exceptionally, As(III) with an initial concentration of 600 µg/L was almost completely removed in 4 min. Thus, this exciting removal speed could apply to most arsenic-contaminated groundwater.

To further investigate the effect of S(IV) in promoting As(III) removal by FeMnO, the adsorption isotherms were analyzed using Freundlich and Langmuir models (Fig. 2d). The adsorption constants obtained from the models are presented in Table S5. We found that under different conditions, the Freundlich model had a higher correlation coefficient ($R^2$) than the Langmuir model, indicating that As removal by FeMnO follows an irreversible multilayer adsorption mechanism on heterogeneous adsorption sites [32]. For chemisorption through complex formation via shared oxygen, As(III) can only offer three potential edge sites, whereas As(V) can offer four potential edge sites to form inner-sphere arsenic complexes with FeMnO [33]. Besides, when the solution pH was in the range of 3.5–8, the mean O–As(V) distance of arsenate species was smaller than the mean O–As(III) distance of arsenite species (1.69 vs 1.78 Å) [34, 35]. Therefore, As(III) was more difficult to be adsorbed by FeMnO than As(V). Interestingly, the maximum adsorption capacities of FeMnO/S(IV) for As(III) and As(V) (40.5 and 44.6 mg/g, respectively) were higher than that of direct adsorption by FeMnO alone (25.8 and 28.9 mg/g, respectively). This indirectly proves that the As(V) transformation occurred in the FeMnO/S(IV)/As(III) system. On the other hand, the XRD pattern showed no change in the crystal structure of FeMnO after S(IV) treatment (Fig. S4). Instead, the solid UV spectrum of FeMnO after S(IV) treatment was significantly red-shifted compared with virgin FeMnO, which indicated that the surface properties of FeMnO changed after the reaction (Fig. S5). This change may be caused by the oxidation of S(IV) adsorbed on the FeMnO surface to generate some active radicals (SO$_x$•$^-$). Correspondingly, the changes in surface chemistry may eventually expose more fresh adsorption sites on FeMnO, thereby enhancing arsenic adsorption. Compared to many previously reported Fe-Mn-based adsorbents, the FeMnO/S(IV) system exhibits faster As(III) removal speed and higher adsorption capacity (Table S6).
Fig. 2. (a) Effect of S(IV) dosage in the reaction system on As(III) removal; (b) As(III,V) removal kinetic curves; (c) Effect of initial As(III) concentration; (d) As(III,V) removal isotherms. Reaction conditions: S(IV) = 200 µM, FeMnO = 0.2 g/L, As(III, V) = 1054 µg/L, S(IV)/As molar ratio = 15, pH = 7, t = 24 h and T = 20 °C.

3.3 Factors affecting the removal of As(III)

Fig. 3a shows the pH as a function of As(III) removal by the FeMnO/S(IV) system. According to the pK_a value of sulfite, the distribution of sulfite species will gradually shift from HSO_3^- to SO_3^{2-} in the pH range from 1.9 to 7.2 (Fig. S6). The redox potential of HSO_3^- is higher compared to SO_3^{2-} [E(SO_3^{2-}/HSO_3^-) = 0.84 V vs E(SO_3^{2-}/SO_3^{4-}) = 0.63V] [36]. Accordingly, when the solution pH increases from 3 to 7, SO_3^{2-} was more easily activated by transition metals to generate SO_x^{2-} active components, thereby enhancing the ability of FeMnO to remove As(III). Furthermore, As(III) in the pH range 3 to 7, mainly in the non-ionic form H_3AsO_3, leads to its adsorption onto FeMnO via a surface complexation mechanism rather than electrostatic interactions (Fig. S7a) [37]. Thus, an increase in pH favored the deprotonation of Fe(III) in the FeMnO surface to form more >Fe(III)-OH complexes, which were the most active Fe(III) species for Fe-based adsorbents to capture As(III) [7, 13, 38]. However, when the pH of the solution was increased to 10, the distribution of As(III) and the oxidized As(V) mainly existed as H_2AsO_5^- and HAsO_4^{2-} anions according to the distribution of arsenic species at
294 different pHs (Fig. S7). The point of zero charges of FeMnO is about 6.6 (Fig. S8). Consequently, the electrostatic repulsion between arsenic and FeMnO gradually strengthened, and the removal of As(III) was inhibited. Fig. S9 shows that the ionic strength did not affect the reaction system. The results indicated that the adsorbed arsenic ions on the FeMnO surface followed the chemical adsorption mechanism of inner-sphere complexes, as the ionic strength would significantly affect the outer-sphere complexation between the adsorbent surface and the solute [39]. Furthermore, Fig. 3b showed that except for PO$_4^{3-}$, which significantly inhibited As(III) removal due to its similar chemical properties to As(III), the FeMnO/S(IV) system was almost unaffected by other common anions [40]. The widespread presence of HA in natural water slightly affected As(III) removal by the FeMnO/S(IV) system (Fig. 3c). Interestingly, increasing temperature enhanced As(III) removal kinetics in the reaction system (Fig. 3d). The adsorption rate constant $k_2$ increased significantly from 0.13 to 0.91 g/mg/min at 10 to 40 °C (inset in Fig. 3d). Therefore, it was suitable for practical application to consider adding thermal activation to As(III) removal in the FeMnO/S(IV) system in the future.

![Fig. 3](image_url)

Fig. 3. Effects of (a) solution pH, (b) common anions, (c) HA and (d) reaction temperature on As(III) removal in FeMnO/S(IV) system. Inset: adsorption rate constant $k_2$. Reaction conditions: S(IV) = 200 µM, FeMnO = 0.2 g/L, As(III) = 1054 µg/L, pH = 7 and $T = 20$ °C.
3.4 Mechanism investigation

3.4.1 Arsenic removal mechanism

FTIR spectra were used to investigate the interaction between FeMnO and As(III) or As(V) (Fig. S10). The characteristic peak at 591 cm$^{-1}$ was attributed to metal–O stretching vibrations in the ferromanganese oxides [41]. Correspondingly, the distinct peaks located at 1631 and 3375 cm$^{-1}$ were related to the vibration and stretching of H–O–H groups and H–O groups in water molecules, respectively [42]. The bands related to the Fe–OH bending vibration at 1342, 1044, 893 and 801 cm$^{-1}$ after the adsorption of arsenic gradually weakened or even disappeared, which directly proved that the –OH group on the FeMnO surface participated in the adsorption of arsenic [43].

To further study the mechanism of As(III) adsorption in the FeMnO/S(IV) system, the surface chemical properties of FeMnO were analyzed by XPS. As shown in Fig. 4a, the spectra of As 3d consist of deconvoluted two overlapping peaks assigned to As(V) at 45.2 eV and As(III) at 44.1 eV, respectively [38]. The peak area ratio calculation showed that when FeMnO alone removed As(III), it failed to oxidize 82.2% of As(III) to As(V), while the As adsorbed by other reaction systems existed in the form of As(V) (Table S7). Part of the oxidation of As(III) (17.8%) might be associated with hydroxyl groups adsorbed on the FeMnO surface, which was demonstrated in Section 3.4.2. The above results provided conclusive evidence that the adsorbed As(III) in the reaction system had been completely oxidized to As(V).

In general, the interaction of arsenic with –OH in metal oxides can generate three different inner-sphere As complexes (i.e., bidentate binuclear, bidentate mononuclear, and monodentate mononuclear) [44]. Hence, according to the possible configurations of As complexes, the stoichiometric ratios of surface –OH before and after FeMnO saturated adsorption of arsenic was 2:1 for bidentate complexes and 1:2 for monodentate complexes, respectively. When As forms bidentate or monodentate complexes on the FeMnO surface, the surface–OH content should decrease or increase.

The spectra of O1s were deconvoluted into three overlapping peaks at 529.7, 531.0, and 532.5 eV, which correspond to lattice oxygen (O$^{2-}$), a hydroxyl group (OH$^-$), and adsorbed moisture (H$_2$O), respectively (Fig. 4b) [45]. Based on the fitting data, we found that the OH$^-$/O$^{2-}$ ratio after FeMnO reacted with As(III) or As(V) in the presence or absence of S(IV) increased from 0.82 to 1.05, 1.27, 1.04, and 1.07 (Table S8). The results indicated that arsenic was mainly adsorbed on the FeMnO surface in the form of monodentate mononuclear complexes, and this form helps arsenic to utilize more adsorption sites [46]. The involvement of S(IV) resulted in the most significant increase in OH$^-$/O$^{2-}$ ratios for As(III), which is what we would expect.
Fig. 4. The As 3d (a) and O 1s (b) XPS spectra of FeMnO under different reaction conditions.

3.4.2 As(III) oxidation mechanism

To confirm that As(III) was oxidized in the FeMnO/S(IV) system, the form of arsenic in the solution was monitored during the reaction. As shown in Fig. S11, As(V) appeared at the early stage of the reaction and reached a peak within 2 min, which indicated that As(III) was indeed oxidized. Furthermore, within the first 2 min, the As(III) concentration decreased much faster than the As(V) concentration increased, which indicated that As(III) adsorption was faster than the oxidation in the early stage. Thus, most As(III) might be heterogeneously oxidized on the FeMnO surface.

Activation of S(IV) using transition metal oxides may generate ROS to oxidise As(III). Therefore, we used the EPR test to identify the ROS species generated during the reaction. Fig. 5a shows obvious characteristic signals of DMPO–SO₃⁻ adducts observed in the FeMnO/S(IV) system. Interestingly, we also observed that the characteristic signal of DMPO–•OH adduct was detected in FeMnO alone, which is the free radical adsorbed on the FeMnO surface (Fig. 5b). Because the EPR spectra of FeMnO added with MeOH or TBA still observed obvious DMPO–•OH signals, consistent with previous studies showing that surface-adsorbed radicals are difficult to be scavenged by highly hydrophilic alcohols [47, 48]. The above results suggested that the surface-adsorbed •OH and SO₃⁻ radicals may play an important role during the oxidation of As(III). However, the SO₃⁻ radical, the most important in the oxysulfur radical chain reaction, had a very weak oxidation ability and could not oxidize As(III) (Fig. 5c). Thus, SO₃⁻ often combined rapidly with oxygen and further evolved into SO₅⁻, SO₄⁻ and •OH via eqs. 1–3 [18]. The contribution of ROS (SO₅⁻, SO₄⁻ and •OH) to As(III) removal by the FeMnO/S(IV) system was evaluated using free radical quenchers. Herein, EtOH, which effectively quenches SO₄⁻ ($k = 5.6 \times 10^7$ M⁻¹s⁻¹) [49] and •OH ($k = 1.9 \times 10^9$ M⁻¹s⁻¹) [50], and TBA, which quenches •OH ($k = 7.6 \times 10^8$ M⁻¹s⁻¹),
were considered among the quencher candidates. It was observed that neither of them significantly inhibited the removal of As(III) (Fig. 5d). Subsequently, AN, which can effectively quench SO₅⁻ (k = 5.8 × 10⁶ M⁻¹ s⁻¹), SO₄⁻ (k = 7.7 × 10⁹ M⁻¹ s⁻¹) and 'OH (k = 8.6 × 10⁹ M⁻¹ s⁻¹) simultaneously, was selected as the quencher [52]. It was found that the final removal efficiency of As(III) was also not affected. On the other hand, S(IV) acted as an effective scavenger for SO₄⁻ and •OH (eqs. 4–5) [20]. If they were the main cause of As(III) oxidation, excess S(IV) would inhibit As(III) removal. Results Fig. S12 showed that as the addition of S(IV) increased from 200 to 500 µm, the final As(III) removal efficiency hardly changed, except that the removal efficiency decreased by 6.5% in the first 10 min. Combined with the little change of k₂ value under different quencher conditions, we concluded that the ROS generated in the FeMnO/S(IV) system participated in As(III) oxidation, but the contribution of the oxidation was minimal. Furthermore, the As 3d XPS spectra showed that the •OH adsorbed on the FeMnO surface might only contribute 17.8% to the As(III) oxidation efficiency (Fig. 4a). This surface-adsorbed •OH might come from α-FeOOH in FeMnO [53]. However, the •OH adsorbed on the FeMnO surface was not related to the presence of S(IV). Therefore, we did not consider its influence on the oxidation of As(III).

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\begin{align*}
SO³⁻ + O₂ & \rightarrow SO₂⁻ \\
SO₅⁻ + SO₂⁻ (HSO₃⁻) & \rightarrow SO₄²⁻ + SO₄⁻ (+ H⁺) \\
SO₄⁻ + HO⁻ (H₂O) & \rightarrow •OH + SO₄²⁻ (+ H⁺) \\
SO₄⁻ + SO₂⁻ (HSO₃⁻) & \rightarrow SO₄²⁻ (HSO₄⁻) + SO₃⁻ \\
•OH + SO₂⁻ (HSO₃⁻) & \rightarrow OH⁻ (H₂O) + SO₃⁻
\end{align*}
\]

The above results together indicated that As(III) oxidation in the FeMnO/S(IV) system was not based on FeMnO activation of S(IV) to generate ROS (‘OH, SO₅⁻ and SO₄⁻) as the main oxidation pathway. Hence, we speculated that the Mn species in this system might play a leading role in As(III) oxidation. Previously, Sun et al. [26, 54] established a permanganate/bisulfite (PM/BS) system and found that the generation of high oxidation activity Mn(III) can rapidly degrade organic pollutants, which has received extensive attention. Thus, it was necessary to use the Mn(III) efficient complexing agent pp to detect the presence of active Mn(III) in the FeMnO/S(IV) system. As shown in Fig. 5e, the FeMnO/S(IV) system with pp added had a characteristic absorption peak at 275 nm in the presence or absence of As(III), which was a typical characteristic signal of pp-Mn(III) complexes [54]. As expected, Fig. 5f showed that adding pp significantly inhibited As(III) oxidation in the reaction system. Note that the addition of pp did not inhibit the generation of active Mn(III) between FeMnO and S(IV) (Fig. 5e). Besides, the addition of pp simultaneously suppressed the total As removal due to the property of pp being condensed phosphate. The above results indicated that the oxidized species of As(III) in the FeMnO/S(IV) system was mainly active Mn(III).
Fig. 5. (a) EPR spectra of FeMnO/S(IV) system with DMPO as spin trapping agent; (b) EPR spectra of FeMnO after addition of quencher; (c) EPR spectra of FeMnO/S(IV) system after adding As(III); (d) Effect of different quenchers on As(III) removal; (e) UV-Vis spectra of various reaction systems; (f) Influence of pp on total As removal and As(III) oxidation. Reaction conditions: S(IV) = 200 µM, FeMnO = 0.2 g/L, As(III) = 1054 µg/L, pH = 7 and T = 20 °C.

3.4.3 Oxidation pathways of As(III)

As mentioned above, in addition to the ROS-mediated reaction pathway in the heterogeneous FeMnO/S(IV) system, there was also a FeMnO-mediated electron transfer process, which would lead to a change in the valence state of the metal sites on the FeMnO surface. Thus, to confirm the active sites in the FeMnO/S(IV) system, the XPS spectra of FeMnO before and after As(III) removal were analyzed. As illustrated in Fig. 6a, the two spin-orbit peaks at 653.9 eV (Mn 2p\textsubscript{1/2}) and 642.1 eV (Mn 2p\textsubscript{3/2}) were attributed to Mn(III), while the peaks at 652.2 eV (Mn 2p\textsubscript{1/2}) and 640.7 eV (Mn 2p\textsubscript{3/2}) belonged to Mn(II) [55]. Also, the peak located at 645.8 eV was marked as a satellite peak (Sat.). Similarly, the Fe 2p spectrum in Fig. 6b had two spin-orbit peaks at 723.5 eV and 710.3 eV corresponding to Fe(II), while the peaks at 725.7 eV and 711.9 eV corresponded to Fe(III) [55]. Moreover, the 714.9 eV and 719.2 eV represent the satellite peaks of Fe 2p\textsubscript{3/2}. The ratios of Mn(II)/Mn(III) to Mn species and Fe(II)/Fe(III) to Fe species were calculated according to the peak area ratio (Table S9, S10). We concluded that the chemical valence content of Fe and Mn hardly changed after reaction of the independent FeMnO with As(III). Conversely, after the reaction of FeMnO with As(III) in the presence of S(IV), the content of Fe(III) and Mn(III) decreased by 6.1% and increased by 4.3%, respectively. These results not only indicated a significant electron transfer process between FeMnO and S(IV) during As(III) oxidation but also involved two redox pairs to generate active Mn(III) [Fe(II, III) and Mn(II, III)].
Fig. 6. Mn 2p (a) and Fe 2p (b) XPS spectra of FeMnO under different reaction conditions.

Based on the above discussion and results, an overall mechanism for oxidative removal of As(III) was proposed in the FeMnO/S(IV) system (Scheme 1). First, S(IV) adsorbed on the FeMnO surface generated SO$_3$$^\cdot$$^-$ according to eqs. 6–7, which was the decisive step for activating S(IV). During this process, O$_2$ rapidly induced SO$_3$$^\cdot$$^-$ to produce secondary radical SO$_5$$^\cdot$$^-$ (eq. 1). Fig. S13 showed that the dissolved oxygen (DO) in the solution first decreased and then increased as the reaction proceeded, confirming the participation of O$_2$. Subsequently, Mn(II) was oxidized to active Mn(III) by SO$_5$$^\cdot$$^-$ via eq. 8 [22]. Note that the failure of the three quenchers to significantly inhibit As(III) removal might be related to the higher reaction rate between Mn(II) and SO$_5$$^\cdot$$^-$ that is, equations $2\ (k = 1.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1})$ and $3\ [k = (10^3 - 10^4) \text{ M}^{-1}\text{s}^{-1}]$, which produce SO$_4$$^\cdot$$^-$ and ‘OH, might be inhibited by the reaction according to eq. 8 ($k = 2.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) [18, 56]. This was evidenced by the failure of the quencher AN to significantly inhibit the removal of As(III). Active Mn(III), as the main oxidative species of As(III), not only accelerated the cycle of oxysulfur radicals but also was the driving force behind the redox pairs of Fe(II, III) and Mn(II, III) (eqs. 9–11) [20, 22]. Meanwhile, the adsorbed ‘OH on the surface oxidized part of As(III) to As(V). Finally, the –OH group on the surface of FeMnO removed the As(V) formed by oxidation through a monodentate mononuclear complex.
Mn(III) + SO$_3^{2–}$ (HSO$_3^{–}$) $\rightarrow$ Mn(II) + SO$_3^{–}$ (+ H$^+$) \hspace{1cm} (11)

**Scheme 1.** The reaction mechanism of oxidation and removal of As(III) in FeMnO/S(IV) system.

### 3.5 Regeneration and practical application

Reusability was a key factor in evaluating FeMnO for further applications. Therefore, five adsorption-desorption cycles were carried out using 0.5 M NaOH as the eluent. The catalytic and adsorption performance of FeMnO did not decrease significantly (only 2.1%) during the five cycles, as shown in Fig. 7a. In addition, the elution efficiency of FeMnO was consistently above 93.6% during the regeneration process. Notably, no Fe and Mn ions leaching was observed during the cycle (Fig. S14). These results implied the superior regenerative ability and stability of FeMnO. Although the oxidative removal of As(III) was closely related to the redox process of Fe(II, III) and Mn(II, III) in FeMnO. However, this satisfactory stability might be attributed to the rapid return of Mn(II) and Fe(II) in water to the FeMnO surface and the formation of new mineral phases mediated by S(IV) and Mn/Fe oxides, thereby significantly reducing the release of Mn(II) and Fe(II). Fig. S15 showed that the release concentration of Mn and Fe ions in the solution increases first and then decreases as the reaction progresses. A new diffraction peak appeared at $\sim$59° in the XRD pattern of FeMnO after use (Fig. S16), which proved this. Meanwhile, we tested the ability of the FeMnO/S(IV) system to remediate arsenic contamination in natural water bodies (Fig. 7b). The results indicated that the FeMnO/S(IV) system could reduce initial arsenic concentration in different water matrices from 524 µg/L to below MCL within 10 min. Thus, the FeMnO/S(IV) system had broad application prospects in As(III) oxidation and removal.
Fig. 7. (a) Reusability and desorption efficiency of FeMnO with 0.5 M NaOH as eluent. (b) FeMnO/S(IV) system for removal of As in different aqueous matrices. Reaction conditions: S(IV) = 200 µM, As(III) = 1054 µg/L (a), As [As(V) + As(III)] = 229 + 295 = 524 µg/L (b), pH = 7, FeMnO = 0.2 g/L and T = 20 °C.

4. Conclusions

This study synthesized sea urchin-like FeMnO nanomaterials using a facile one-pot method and coupled it with S(IV) to oxidize and remove As(III) in water. The S(IV) activation pathway in the FeMnO/S(IV) system was revealed by quencher experiments, EPR and XPS. It was determined that the oxidation of As(III) was not based on FeMnO activation of S(IV) to generate ROS (SO$_5^{•−}$, SO$_4^{•−}$ and ‘OH) as the main oxidation pathway. The active Mn(III) produced by the SO$_5^{•−}$ oxidation of Mn(II) was responsible for the major oxidation of As(III). The –OH groups on the FeMnO surface effectively adsorb the As(V) generated by oxidation as monodentate mononuclear complexes. Furthermore, the reacted FeMnO could be quickly recovered by the magnet and eluted with an alkaline solution to regenerate, and it showed satisfactory stability and regeneration ability. In particular, the FeMnO/S(IV) system has good As treatment ability in different real water bodies. Nowadays, the excessive discharge of various acid wastewater or the formation of acid rain leads to the ubiquity of S(IV) in the natural environment. Therefore, the FeMnO/S(IV) system provides a promising strategy for effectively reducing As pollution in water bodies. This study may also shed light on transforming and transferring inorganic arsenic in groundwater environments containing Fe-Mn minerals.

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Declaration of competing interest

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

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

Highlights:

- Coupling of FeMnO with S(IV) improves the removal speed of As(III).
- The FeMnO/S(IV) system integrates adsorption and oxidation functions.
- Active Mn(III) is mainly responsible for the oxidation of As(III).
- The possible activation pathway of S(IV) in the FeMnO/S(IV) system is proposed.
- FeMnO has excellent stability and regeneration/recovery ability.