Efficient Removal of Bromate with Core-Shell Fe@Fe₂O₃ Nanowires

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ABSTRACT In this study, we systematically investigated the removal of bromate (BrO_3^-) with core-shell $\text{Fe@Fe}_2\text{O}_3$ nanowires at neutral pH, especially the effects of surface bound ferrous ions and molecular oxygen. In the presence of $\text{Fe@Fe}_2\text{O}_3$ nanowires, bromate was reduced to Br^- efficiently with the generation of HOBr intermediates. Bromide species analyses and nanowires characterizations indicated that surface bound ferrous ions of core-shell $\text{Fe@Fe}_2\text{O}_3$ nanowires could effectively promote the BrO_3^- removal. Meanwhile, molecular oxygen competed electrons from both Fe^{2+} and Fe^0 to generate reactive oxygen species of $\cdot\text{O}_2^-$, H_2O_2 , and $\cdot\text{OH}$ during the bromate removal process. Among the generated reactive oxygen species, $\cdot\text{O}_2^-$ and H_2O_2 favored of bromate removal, but $\cdot\text{OH}$ inhibited. We proposed a bromate removal mechanism with core-shell $\text{Fe@Fe}_2\text{O}_3$ nanowires, which suggested that the effect of surface bound Fe(II) and molecular oxygen be taken into consideration when using nZVI for bromate remediation in waters. This study can not only deepen our understanding on the bromate removal with zero valent iron, and also shed light on the design of high performance bromate removal materials.

Keywords: Bromate; $\text{Fe@Fe}_2\text{O}_3$ nanowires; Molecular oxygen; Surface bound Fe(II) ; Removal Mechanism

1. Introduction

Bromate (BrO_3^-) is a kind of hazardous byproduct frequently detected in natural waters and drinking water from ozonation or chlorination disinfection processes of bromide-containing source waters [1, 2]. It is a stable anion with high solubility and low reactivity and classified as a Group 2B carcinogen by the International Agency for Research on Cancer [3]. BrO_3^- in drinking water could be removed by many technologies including of ion exchange method, TiO_2 photocatalysis, granular activated carbon adsorption, and nanoscale zero valent iron (nZVI) reduction [4-11]. Among them, nZVI has been paid much more attentions for reductive bromate removal because of its environmental benignity and high efficiency. For instance, Wang et al. reported that bromate was removed by nZVI in a few minutes [10]; Xie et al. investigated the effects of operation parameters of iron types, dissolved oxygen concentrations, temperature, and co-existed anions on the bromate removal efficiency with nZVI in aqueous solution. They proposed a bromate removal mechanism which was dependent on the release of Fe (II) during the bromate removal process (Eqs.1-2) [11, 12].

Actually, the released Fe(II) could be adsorbed on the surface of iron to form so-called surface bound ferrous ions ($\text{Fe(II)}_{\text{bound}}$), which has been reported as a more effective reductant than dissolved Fe(II) because of that multiple Fe(II) atoms in close proximity on the surface may promote multiple-electron-transfer reactions [13].

Recently, we demonstrated that $\text{Fe(II)}_{\text{bound}}$ on $\text{Fe@Fe}_2\text{O}_3$ could induce the activation of molecular oxygen through single-electron transfer pathway and thus enhance the oxic 4-chlorophenol degradation [14]. More previously, we reported that $\text{Fe(II)}_{\text{bound}}$ on $\text{Fe@Fe}_2\text{O}_3$ played an indispensable role in aqueous Cr(VI) removal [15]. Inevitably the reaction of bromate and $\text{Fe(II)}_{\text{bound}}$ could happen during the removal process with nZVI, thus to reveal the contribution of $\text{Fe(II)}_{\text{bound}}$ is imperative for deeply understanding the interfacial electron transfer and design more efficient bromate removal technology on the base of nZVI. However, the role of $\text{Fe(II)}_{\text{bound}}$ on bromate removal is unclear yet.

Besides reduction of bromate, both Fe^0 and Fe(II) could donor electrons to oxidation agents co-existed in aquatic environment. For example, dissolved molecular oxygen accepts electrons from either Fe(II) or Fe^0 to generate reactive oxygen species (ROS) including hydroxyl radical ($\bullet\text{OH}$), superoxide ($\bullet\text{O}_2^-$), and hydrogen peroxide (H_2O_2) [16]. Usually dissolved oxygen concentration increases significantly after ozone distiction process of bromate-contaminated drinking water [11]. When Fe^0 was applied to remove bromate, the activation of molecular oxygen by Fe^0 or Fe(II) must be taken into consideration because ROS could react with bromine species with low oxidation states [1, 17], thus affect the efficiency of bromate removal. To the best of our knowledge, there was no studies reported the effect of ROS or mediated the species of ROS in bromate removal with nZVI.

Core-shell $\text{Fe@Fe}_2\text{O}_3$ nanowires is a kind of special nZVI with air stable core-shell structure [18-20]. In this study we systematically investigated the removal of bromate

and provided mechanistic insight into the bromate removal with nZVI.

2. Experimental section

2.1 Chemicals and materials. KBrO₃, FeCl₃•6H₂O, NaBH₄, commercial zero-valent iron powder (Fe⁰), 1,10-phenanthroline (C₁₂H₈N₂•H₂O), FeSO₄•7H₂O, Fe₂O₃, NaClO, KBr, HClO₄, NaOH, H₂SO₄, ethanol (C₂H₆O), and hydroxylamine hydrochloride (NH₂OH•HCl) were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. Catalase (CAT) and superoxide dismutase (SOD) were purchased from Shanghai Kayon Biological Technology CO., Ltd. Terephthalic acid (TPA, analytical reagent) and Horseradish peroxidase (POD, analytical reagent) were bought from Aladdin Chemistry CO., Ltd. 2, 2'-azino-bis (3-ethylbenzothiazoline) -6-sulfonic acid- diammonium salt (ABTS) was purchased from J & K Chemical CO., Ltd. ABTS stock solution (1 g•L⁻¹) stored at 4 °C was used for the determination of hypobromous acid [21]. NaHCO₃, Na₂CO₃ were obtained from Aladdin Chemistry CO., Ltd. All of the chemicals were used without further purification. High purity argon gas (Ar ≥ 99.9%) was provided by Hubei Minghui gas company, China. The oxygen free DI water was obtained through bubbling Ar gas into deionized water for 30 min. Hypobromous acid (HOBr) standard solution was prepared with sodium hypochlorite (NaClO) and potassium bromide (KBr) according to literature reports [22, 23].

2.2 Preparation of core-shell Fe@Fe₂O₃ nanowires. Fe@Fe₂O₃ was prepared with FeCl₃•6H₂O and NaBH₄ according to our previous report [18]. In a typical synthesis

procedure, 3 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 6 g NaBH_4 was dissolved in 1 L and 0.4 L of deionized water, respectively, and then the NaBH_4 solution was added dropwise to FeCl_3 solution in 10 min. The reaction time was 2 h unless special instruction, and the black solid produced during the reaction time was obtained by filtration. Subsequently, the black solid was dried under the infrared lamp with the protection of inert gas.

2.3 Bromate removal experiments. All experiments were conducted in duplicate in 50 mL conical flasks containing 40 mL of potassium bromate ($1 \text{ mg} \cdot \text{L}^{-1}$), followed by adding 4 mg of $\text{Fe}@\text{Fe}_2\text{O}_3$ under anoxic and/or oxic conditions at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$). Anoxic bromate removal experiments were performed in oxygen free deionized water (or solutions), the oxic experiments were carried out in deionized water (solutions) exposed in air. The samples were collected at regular intervals by a 2 mL syringe and filtered immediately through a $0.22 \text{ }\mu\text{m}$ nylon syringe filter for the measurement of bromine species concentration. To unravel the influence of ferrous ions on the bromate removal, high concentration of bromate aqueous solution was added to 1, 10-phenanthroline ($2 \text{ g} \cdot \text{L}^{-1}$) solution after the addition of $\text{Fe}@\text{Fe}_2\text{O}_3$ nanowires, as 1, 10-phenanthroline could form a reddish orange Fe(II) complex and prevent the reaction between Fe^{2+} and bromate [24]. After the anoxic/oxic removal process, the suspension was transferred to a centrifuge tube from the three-neck flask bottle and then centrifuged (8000 rpm for 5 minutes using an Eppendorf 5840R Centrifuge) to remove the $\text{Fe}@\text{Fe}_2\text{O}_3$ particles from the supernatant. The used $\text{Fe}@\text{Fe}_2\text{O}_3$ were dried under Ar gas flow for further characterizations. In

order to investigate the bromate removal mechanism more easily, the initial concentration of bromate was 1 ppm which was higher than that in real environment.

2.4 Analytical method. Bromate and bromide species in aqueous solutions were determined by ion chromatograph (IC, Dionex ICS-900, Thermo) equipped with an AS23 analytical column. Ferrous ions (Fe(II)) and ferric ions (Fe(III)) in solutions were removed by cation exchange resin before samples injected into IC. A mixture of sodium carbonate (Na_2CO_3 , $4.5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) and sodium bicarbonate (NaHCO_3 , $8.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$) was used as the mobile phase at a flow rate of $1.0 \text{ mL}\cdot\text{min}^{-1}$, a 100 μL injection loop was used. The concentration of dissolved Fe(II) was analyzed with the 1, 10-phenanthroline method by using UV-vis spectrophotometer (UV-2550, Shimadzu, Japan) at 510 nm. The standard solutions of Fe(II) were prepared from the stock ferrous sulfate solution ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, 99.9%). All the samples were kept in dark for 30 min prior to analysis. Total dissolved iron was determined with the 1, 10-phenanthroline method after reduction of Fe(III) to Fe(II) using hydroxylamine hydrochloride as the reducing reagent [24]. Terephthalic acid (TA) was employed as the fluorescent probe for the detection of hydroxyl radicals. 2-hydroxyterephthalic acid (TAOH), which is the fluorescent product of the reaction of TA with $\cdot\text{OH}$, has a strong fluorescent emission at around 426 nm when excited at 312 nm [25]. Hydrogen peroxide (H_2O_2) was measured by using the horseradish peroxidase-mediated dimerization and 4-hydroxyphenylacetic acid (POHPAA) [26].

2.5 Characterizations. X-ray diffraction (XRD) patterns were collected with a Bruker D8 Advance X-ray diffractometer at 40 kV and 40 mA using Cu K α radiation

($\lambda = 1.54178 \text{ \AA}$). Scanning electron microscopy (SEM) analysis was performed on a LEO 1450VP scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was recorded with a Kratos ASIS-HS X-ray photoelectron spectroscope equipped with a standard and monochromatic source operated at 150 W (15 kV, 10 mA). The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s line at 284.8 eV.

3. Results and discussion

3.1 Characterization of the as-prepared Fe@Fe₂O₃. The composite and morphology of the fresh prepared Fe@Fe₂O₃ was investigated by XRD, SEM and EFTEM. The XRD patterns of the Fe@Fe₂O₃ showed main diffraction peaks at $2\theta = 44.7^\circ$ can be indexed to the cubic Fe (JPCDS file NO. 3-1050) (fig. 1a). The morphology of Fe@Fe₂O₃ was of spherical shape in the size of about 100 nm and formed chain-like clusters via magnetic and electrostatic interactions (fig. 1b). Moreover, the EFTEM analysis indicated that Fe and O elements co-existed and dispersed in Fe@Fe₂O₃ samples (fig. 1c-e). These results were in good agreement with our previous reports [14, 18].

3.2 Bromate removal and bromine mass balance. It is well-known that ROS is formed via reduction of molecular oxygen by nZVI in an oxidic nZVI/Air process. In order to rule out the influence of ROS, argon gas was used to purge oxygen out to keep an anoxic nZVI/Ar condition. Firstly, the anoxic bromate removal with the Fe@Fe₂O₃ and the commercial Fe⁰ were compared, it can be observed that 100% of

bromate removal was achieved with the Fe@Fe₂O₃ in 90 minutes, in contrast, bromate could not decay with the commercial Fe⁰ at neutral pH (pH = 6-7)(fig. 2a). Electrons could spontaneously transfer from core iron to the nanoscale iron oxide shell (4-6 nm in thickness [14]), however, the thicker iron oxide layer around the commercial Fe⁰ was too compact and thick for electron transfer or arrive to the shell surface. The anoxic bromate removal process was in good agreement with a pseudo-first-order kinetics, the apparent rate constant (*k*) for the BrO₃⁻ removal with Fe@Fe₂O₃ was calculated to be 0.0423 min⁻¹ (fig. 2b). This result suggested that Fe@Fe₂O₃ could effectively remove bromate at neutral pH.

In order to investigate the reaction between bromate and Fe@Fe₂O₃, bromine species of bromate, hypobromous acid/hypobromite, and bromide were analyzed. The overall bromine balance in the anoxic Fe@Fe₂O₃/Ar process was depicted (fig. 2c), it was found that the concentration of bromate decreased rapidly in the presence of Fe@Fe₂O₃, bromide, on the contrary, increased sharply with reaction time in the initial 30 min of the anoxic removal. After 30 minutes, the bromate decayed and the bromide formation were found to be more gently. Moreover, free hypobromous acid/hypobromite was also detected. As the *pK_a* of hypobromous acid is approximately 8.8 [23], the majority of the free bromine exists in the form of HOBr at neutral pH during the bromate removal process. The concentration of HOBr increased in the initial stage and diminished after 30 min, a maximum of 0.56 μM HOBr was observed in 5 min, indicating that HOBr was an inevitable intermediate during the bromate removal process. Actually, HOBr can disproportionate to bromate and

bromide, in which HOBr reacts to a reduced Br^- species and to oxidized BrO_2^- , BrO_3^- species (Eqs. 3-5). Moreover, the bromine mass balance was evaluated during the removal, we found that the sum of bromate, hypobromous acid, and bromide ions were of 98-101 percent in mass balance of bromine corresponding to the initial bromate concentration, indicating that BrO_3^- was reduced to Br^- completely via the HOBr intermediates. That means BrO_3^- , HOBr, and Br^- are three main species during the removal process. The perfect bromine recovery also suggested that little adsorption of bromate happened on the surface of Fe_2O_3 . Therefore, we concluded that the bromate removal with $\text{Fe@Fe}_2\text{O}_3$ was mainly ascribed to the reductive reaction between bromate and $\text{Fe@Fe}_2\text{O}_3$ (Eq.1) ($\text{Fe@Fe}_2\text{O}_3$ was expressed as Fe^0 , as the effective composite of $\text{Fe@Fe}_2\text{O}_3$ during the bromate removal process was Fe^0).

3.3 Iron species determination and the role of surface bound Fe(II).

Furthermore, the concentrations of dissolved iron species were measured during the anoxic bromate removal process (fig. 3). Fe(II) was generated immediately after $\text{Fe@Fe}_2\text{O}_3$ was added into the bromate solution in the $\text{Fe@Fe}_2\text{O}_3/\text{Ar}$ system (fig. 3a). The concentration of dissolved Fe(II) increased to a maximum value of $11 \mu\text{mol}\cdot\text{L}^{-1}$ in the first 15 min and then kept constant. In the anoxic process, Fe^0 was readily oxidized to ferrous ion via electrochemical corrosion process. The available electron acceptors were associated to H^+ and H_2O in anoxic $\text{Fe}^0/\text{H}_2\text{O}$ system (Eqs. 6-7). In

addition, the low concentration of dissolved ferric ions suggested that ferric ions could be reduced to ferrous ions by Fe^0 core and a ferric/ferrous ions cycle exist in this system (Eq. 8). This result was in good agreement with the previous publication [27].

As discussed above, the anoxic bromate removal with $\text{Fe}@\text{Fe}_2\text{O}_3$ was mainly related to the reduction process where both Fe in the $\text{Fe}@\text{Fe}_2\text{O}_3$ core and Fe(II) could react with bromate inevitably (Eqs. 1-2). Fe(II) existed on the surface of $\text{Fe}@\text{Fe}_2\text{O}_3$ during the preparation and Fe(II) released as the corrosion product absorbed on the iron oxide shell of $\text{Fe}@\text{Fe}_2\text{O}_3$ are surface-bound Fe(II) ($\text{Fe(II)}_{\text{bound}}$) with enhanced reductive performance. For example, Liu demonstrated that $\text{Fe(II)}_{\text{bound}}$ could improve the electron transfer from the Fe^0 core to the solid-liquid interface [28]. The enhanced reactivity of $\text{Fe(II)}_{\text{bound}}$ on the mineral surface was attributed to the increase of electron density at the iron center and the decrease of $\text{Fe(III)}-\text{Fe(II)}$ redox potential [13]. To investigate the significance of $\text{Fe(II)}_{\text{bound}}$ on the anoxic bromate removal with $\text{Fe}@\text{Fe}_2\text{O}_3$, control experiments of bromate removal using $\text{Fe}@\text{Fe}_2\text{O}_3$, ferrous ions, Fe_2O_3 powders, ferrous ions and Fe_2O_3 were performed respectively (fig. 3b). It was found that Fe_2O_3 could not absorb any bromate, this result is consistent with the result of perfect 100% bromine recovery. On contrast, Fe(II) showed reductive activity for bromate removal, interestingly, the combination of Fe_2O_3 and Fe(II) displayed an

enhanced bromate removal efficiency. The combination of Fe(II) and Fe₂O₃ accelerated the bromate removal rate by 1.5-fold over Fe(II) alone (fig. 3c). This result confirmed that the adsorbed Fe(II) on the surface of iron oxide (as Fe(II)_{bound}) owned higher reductive performance. Furthermore, we employed 1, 10-phenanthroline to complex the Fe(II)_{bound} and the *in situ* released Fe(II) from the Fe@Fe₂O₃ in the anoxic bromate removal process (fig. 3d). It was observed that the addition of 1, 10-phenanthroline totally suppressed the bromate removal in the Fe(II)/Ar and Fe(II)/Fe₂O₃/Ar systems according to the complex of Fe(II). The inhibition of bromate removal with Fe@Fe₂O₃ was 33%, suggesting that Fe(II) species contributed to 33% in reductive removal of bromate over Fe@Fe₂O₃ besides the contribution of Fe⁰ core in Fe@Fe₂O₃/Ar system (Eqs. 1-2).

3.4 Effect of molecular oxygen on bromate removal. Dissolved molecular oxygen in bromate-contaminated water could compete electron with bromate to generate reactive oxygen species (ROS) as shown in Eqs. 9-12 [29]. The effect of molecular oxygen on bromate reduction by Fe@Fe₂O₃ was investigated by conducting experiments under argon purging (anoxic) and atmosphere (oxic) conditions (fig. 4a), a dramatic decline was observed in bromate removal when the reaction was exposed to air. The *k* value was found to be 0.0165 min⁻¹ in the oxic process, decrease by 61% as compared to (0.0423 min⁻¹) in the anoxic process. As O₂ competes with BrO₃⁻ for the electrons of Fe@Fe₂O₃, it was reasonable that more BrO₃⁻ was reduced in the air-free system.

Additionally, ROS like $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and H_2O_2 are able to oxidize or reduce bromate or bromine intermediates in the oxic Fe@Fe₂O₃ process. To clarify the influence of ROS on the removal of bromate and the reaction between ROS and bromine species, we measured the concentrations of $\bullet\text{OH}$ and H_2O_2 during the entire Fe@Fe₂O₃/air system. It was found the $\bullet\text{OH}$ and H_2O_2 concentration in the solution increased gradually with time (fig. 4b). ROS scavengers (SOD for $\bullet\text{O}_2^-$, CAT for H_2O_2 , isopropanol for total $\bullet\text{OH}$) were further added into the Fe@Fe₂O₃/air system to explore the role of each ROS to the bromate removal (fig. 4c). It was observed the oxic bromate reduction was largely depressed by the addition of SOD and CAT, the removal rate constant decreased from 0.0165 min⁻¹ to 0.0029 and 0.0113 min⁻¹ in the presence of SOD and CAT respectively, demonstrating that both $\bullet\text{O}_2^-$ and H_2O_2 species could contribute to the bromate reduction, suggesting that $\bullet\text{O}_2^-$ and H_2O_2 competed with bromate for electrons to a certain extent and then gradually transferred the electrons to reduce bromate. These results were further conformed by reduction of bromate with H_2O_2 (fig. 4d). Apart from reduction ability, H_2O_2 is also able to produce $\bullet\text{OH}$ via Fenton reaction (Eq. 12). We found the adding of isopropanol accelerated the bromate removal as the rate constant increased to 0.0196 min⁻¹, suggesting that $\bullet\text{OH}$ inhibited the bromate removal. This is because that hypobromous acid could be oxidized by $\bullet\text{OH}$, bromate might be formed in this way

(Eqs. 13-18) [17].

3.5 The role of ROS in bromate removal by mediating ROS in the Fe@Fe₂O₃/air system. In order to further identify the individual effect of each ROS discussed above, we tried to mediate the species of ROS in the Fe@Fe₂O₃/air system. Our previous study revealed a core-shell structure dependent reactivity of Fe@Fe₂O₃ nanowire for molecular oxygen activation, where more Fe(II)_{bound} favored the single-electron molecular oxygen activation to produce more $\bullet\text{O}_2^-$ radicals [18]. Therefore, we used Fe@Fe₂O₃ obtained through tuning the aging time from 0, 2, 4, to 6 h (named as AT-0, AT-2, AT-4, and AT-6 respectively) to remove bromate (fig. 5a). It was found that the bromate removal decreased from AT-0 to AT-2, and then increased from AT-4 to AT-6. This trend is in good agreement with the generation of $\bullet\text{OH}$ with Fe@Fe₂O₃ nanowires prepared by water aging time of 0 to 6 h [29], suggesting that the existence of hydroxyl radical could inhibit the bromate removal with Fe@Fe₂O₃. Moreover, as tetrakisphosphate could complexation with ferrous ions and produced more $\bullet\text{OH}$ via single-electron molecular oxygen reduction pathway [29], TPP was applied in Fe@Fe₂O₃/air system to mediate species of ROS during the bromate removal process. The rate of bromate removal decreased sharply after the addition of TPP, while the reduction rate in the Fe@Fe₂O₃/TPP/isopropanol/air is much faster than that

in the Fe@Fe₂O₃/TPP/air system (fig. 5b). This results further confirmed the •OH radicals with strong oxidative ability could inhibit the reduction of bromate.

3.6 Structure and composition of the Fe@Fe₂O₃ nanowires before and after the bromate removal. Compared to the nanowires' morphology of fresh Fe@Fe₂O₃, the nanowires were broken to uneven nanoparticles after the oxic bromate removal process (fig. 6a), in contrast, the morphology of nanowires was kept even after the anoxic bromate removal process (fig. 6b). The XRD pattern of the solid sample after reaction was showed in fig. 7a, and an obvious diffraction peak arisen from the corrosion product in the anoxic bromate removal system was iron oxide maghemite (Fe₂O₃, JPCDS file NO. 39-1402), while the appearance of new diffraction peaks, which were ascribed to Fe₃O₄ (magnetite, JPCDS file NO. 75-1609), indicating the corrosion product was iron oxide magnetite (Fe₃O₄) in the oxic removal system. This result confirmed the surface redox reactions between bromate and Fe@Fe₂O₃ during the anoxic and oxic bromate removal with Fe@Fe₂O₃. Meanwhile, the diffraction peak intensities showed that more Fe⁰ was consumed in the oxic Fe@Fe₂O₃/air system in comparison with the anoxic Fe@Fe₂O₃/Ar system, because molecular oxygen could additionally react with Fe⁰. The composition of Fe@Fe₂O₃ before and after reaction was further compared by using X-ray photoemission spectroscopy technique. The survey XPS spectra showed that iron and oxygen elements co-existed on the surface of the Fe@Fe₂O₃ besides adventitious carbon with the peak at 284.8 eV (fig. 7b). High resolution XPS of Br 3d indicated bromine species could not chemisorbed on the surface of Fe@Fe₂O₃ (fig. 7c), which was consist with the

bromine recovery result, confirming that the reduction reaction happened on the surface of Fe@Fe₂O₃ was the dominant pathway of bromate removal. High resolution XPS of Fe 2p suggested that Fe⁰, Fe(II), and Fe(III) species coexisted in the Fe@Fe₂O₃ before and after the bromate removal (fig. 7d). A peak at a low binding energy of 706.9 eV was ascribed to Fe⁰, the strong peaks at 710.5 and 723.5 eV were related to Fe(II), while the peaks at 712.5 and 725 eV were assigned to Fe (III) [30]. The calculation of the peak in Fe 2p core level spectra gave ratios of ferrous ion to total iron (Fe(II)/Fe_{total}) and ferric ion to total iron (Fe(III)/Fe_{total}) (Table 1). The value of Fe(II)/Fe_{total} was found to decrease from 64.37% to 55.30% and 56.73% in the Fe@Fe₂O₃/air and Fe@Fe₂O₃/Ar systems respectively, confirming that surface bound Fe(II) species contributed to the reduction of bromate and more Fe(II)_{bound} were consumed in the presence of oxygen.

3.7 Mechanism for the bromate removal with Fe@Fe₂O₃. On the basis of above results and discussion, we proposed a possible mechanism for the efficient bromate removal in anoxic and oxic Fe@Fe₂O₃ systems (Scheme 1). In the anoxic system, the adsorption of bromate on the surface of Fe@Fe₂O₃ was negligible at neutral pH, while the reduction of bromate is a predominant process which was dependent on both Fe⁰ core and Fe(II)_{bound}. In the initial stage of the reaction, bromate was reduced by Fe⁰ core with the formation of Fe(II) subsequently (Eqs. 1-2). As time elapsed, the released Fe(II) could be adsorbed on the surface of iron oxide and form Fe(II)_{bound} which could accelerate the reduction of bromate significantly (Eq. 19). Here the Fe⁰ was the major electron source, Fe(II) seemed to be electron mediators. In the presence

of oxygen during the oxic Fe@Fe₂O₃ process, ROS including of •O₂⁻, H₂O₂, and •OH were generated by the reaction of oxygen and Fe(II) and Fe⁰ through one-electron or two-electron pathways. Among the ROS, •O₂⁻ and H₂O₂ contributed to reductive bromate removal, but •OH inhibited the reduction of bromate due to its strong oxidation ability.

3.8 Environmental implications. The results obtained here suggest that the adsorptive removal of bromate does not occur on the surface of nZVI, while the reductive generation of bromide anions by both Fe and Fe(II) is the major contribution for the bromate removal with nZVI, accompanying the Fe(II) release. The released Fe(II) could be adsorbed on the surface of iron oxide and form Fe(II)_{bound} which could accelerate the reduction of bromate due to its higher reductive ability. Meanwhile, ROS is generated by activation of oxygen with Fe⁰ and/or Fe(II) because molecular oxygen is always rich in bromate-contaminated water. Although •O₂⁻ and H₂O₂ contribute to reductive bromate removal, •OH inhibits the reduction of bromate, resulting in decreasing of bromate removal under air atmosphere. It is expected that a higher and quicker bromate removal by nZVI is obtained in the anoxic condition. Therefore, if nZVI technologies were applied to drinking water treatment for reduction of bromate in the long term operation, the supersaturated dissolved oxygen after ozonation must be taken into consideration to achieve high efficiency. These methods require almost complete removal of dissolved oxygen from water, leading to the significant increase of treatment costs.

4. Conclusion

In summary, core-shell Fe@Fe₂O₃ nanowires showed effective bromate removal performance at neutral pH. During the removal process, the adsorptive removal of bromate does not occur on the surface of nZVI, while the reductive generation of bromide anions by both Fe and Fe(II) is the major contribution for the bromate removal with nZVI, accompanying the Fe(II) release. The released Fe(II) could be adsorbed on the surface of iron oxide and form Fe(II)_{bound} which could accelerate the reduction of bromate due to its higher reductive ability. Meanwhile, ROS is generated by activation of oxygen with Fe⁰ and/or Fe(II) because molecular oxygen is always rich in bromate-contaminated water. Although •O₂⁻ and H₂O₂ contribute to reductive bromate removal, •OH inhibits the reduction of bromate, resulting in decreasing of bromate removal under air atmosphere. It is expected that a higher and quicker bromate removal by nZVI is obtained in the anoxic condition. Therefore, if nZVI technologies were applied to drinking water treatment for reduction of bromate in the long term operation, the supersaturated dissolved oxygen after ozonation must be taken into consideration to achieve high efficiency. These methods require almost complete removal of dissolved oxygen from water, leading to the significant increase of treatment costs.

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Figure Captions

Fig. 1. (a) Characteration of as-prepared Fe@Fe₂O₃ (a) XRD pattern, (b) SEM image, (c) EFTEM image, (d, e) EFTEM element mapping images of the prepared nZVI.

Fig. 2. (a) The anoxic removal of bromate with Fe@Fe₂O₃ and commercial iron. (b) Plots of $\ln(C/C_0)$ versus time for the anoxic bromate removal. (c) Concentration profiles of the three bromine species and the corresponding total bromine balance. ($[\text{BrO}_3^-]_0 = 1 \text{ mg}\cdot\text{L}^{-1}$, $[\text{Fe@Fe}_2\text{O}_3]_0 = 100 \text{ mg}\cdot\text{L}^{-1}$, $[\text{commercial iron}]_0 = 100 \text{ mg}\cdot\text{L}^{-1}$).

Fig. 3. (a) The concentrations of ferrous ions, ferric ions and total iron determined by 1, 10-phenanthroline method in the Fe@Fe₂O₃/Ar system. (b) Comparison of bromate removal with ferrous ions, and iron oxide under anoxic condition. (c) Plots of $\ln(C/C_0)$ versus time for the anoxic bromate removal in different systems. (d) Capture of ferrous irons with 1,10-phenanthroline in the absence of oxygen.

Fig. 4. (a) The rate of bromate removal under air and argon condition with Fe@Fe₂O₃. (b) Generation of H₂O₂ and •OH by Fe@Fe₂O₃. (c) The rate constant of bromate removal in the Fe@Fe₂O₃/air system with adding different scavengers (isopropanol for •OH, CAT for H₂O₂, SOD for •O₂⁻). (d) Removal of bromate with H₂O₂.

Fig. 5. (a) Removal of bromate by Fe@Fe₂O₃ with different aging time under air. (b) Removal of bromate with Fe@Fe₂O₃/air, Fe@Fe₂O₃/TPP/air and Fe@Fe₂O₃/isopropanol/air systems.

Fig. 6. SEM images of the Fe@Fe₂O₃ after the bromate removal process: (a) 90 min of the reaction in the Fe@Fe₂O₃/air system, and (b) 90 min of the reaction in the Fe@Fe₂O₃/Ar system.

Table 1. The ratio of ferrous iron to total iron ($\text{Fe(II)}/\text{Fe}_{\text{total}}$) and ferric ion to total iron ($\text{Fe(III)}/\text{Fe}_{\text{total}}$) in Fe 2p core level spectra, and ratio of oxygen in oxides to total oxygen ($\text{O}_{(\text{O}_2^-)}/\text{O}_{\text{total}}$) and surface absorbed oxygen species to total oxygen ($\text{O}_{(-\text{OH})}/\text{O}_{\text{total}}$, $\text{O}_{(\text{H}_2\text{O})}/\text{O}_{\text{total}}$) in O 1s core level spectra of the Fe@Fe₂O₃.

	$\text{Fe(II)}/\text{Fe}_{\text{total}}$	$\text{Fe(III)}/\text{Fe}_{\text{total}}$	$\text{O}_{(\text{O}_2^-)}/\text{O}_{\text{total}}$	$\text{O}_{(-\text{OH})}/\text{O}_{\text{total}}$	$\text{O}_{(\text{H}_2\text{O})}/\text{O}_{\text{total}}$
0 min	64.37%	24.98%	56.18%	41.01%	2.81%
90 min / air	55.30%	44.70%	51.28%	44.62%	4.1%
90 min / Ar	56.73%	39.16%	62.89%	35.85%	1.26%

Graphical Abstract