Efficient conversion of dimethylarsinate into arsenic and its simultaneous adsorption removal over FeC_x/N-doped carbon fiber composite in an electro-Fenton process

Huachun Lan, Jianfei Li, Meng Sun, Xiaoqiang An, Chengzhi Hu, Ruiping Liu, Huijuan Liu, Jiuhui Qu*

Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

ARTICLE INFO

Article history:

Received 21 March 2016
Received in revised form
1 May 2016
Accepted 4 May 2016
Available online 4 May 2016

Keywords:

FeC_x/NCNFs
Dimethylarsinate
Degradation
Adsorption
Electro-Fenton

ABSTRACT

In this study, a FeC_x/N-doped carbon fiber composite (FeC_x/NCNFs) was developed via an electrospinning method. According to the characterization results of XRD, TEM and XPS, FeC_x (a mixture of Fe₇C₃ and Fe₃C) was either embedded in or attached to the NCNFs. It was used for the first time as a catalyst for dimethylarsinate (DMA) degradation and as an adsorbent for inorganic arsenic (As(V)), with degradation and adsorption occurring simultaneously, in an electro-Fenton process. The effects of catalyst dosage, initial DMA concentration, solution pH, and applied current on the treatment efficiency and the corresponding H₂O₂ generation were systematically investigated. The results showed that DMA could be efficiently oxidized into As(V). 96% of DMA was degraded after reaction time of 360 min and the residual As(V) concentration in solution was below the allowable limit of 0.01 mg/L under the optimum treatment conditions. Based on an ESR and radical scavenger experiment, [•]OH was proven to be the sole reactive oxygen species involved in the degradation process of DMA. DMA was oxidized to MMA as the primary oxidation product, which was subsequently oxidized to inorganic arsenic, As(V). TOC was also efficiently removed at the same time. The DMA removal mechanism for simultaneous degradation of dimethylarsinate and adsorption of arsenic over FeC_x/NCNFs in the electro-Fenton process was also proposed based on the experimental results.

© 2016 Published by Elsevier Ltd.

1. Introduction

Arsenic has been proven to be a carcinogenic and highly toxic element for human beings (Han et al., 2016). Organoarsenic compounds, such as monomethylarsinate (MMA) and dimethylarsinate (DMA), are widely reported as problematic pollutants in groundwater at sites with a history of pesticide manufacturing and improper disposal (Zheng et al., 2012; Balázs and Zoltán, 2013; Rivera-Reyna et al., 2013). DMA in the environment mainly comes from the following sources: (1) it is the major urinary metabolite of inorganic arsenic, representing the most abundant arsenic species in the urine of humans and most animals, (2) it has been used as a nonselective herbicide for both agricultural and military purposes (Xu et al., 2008; Lim et al., 2009). Hence, high concentrations of

organic arsenic have been detected in groundwater samples. For example, groundwater at a superfund site in the northeastern U.S. had organic arsenic concentrations as high as 30 mg/L (Xu et al., 2008). Moreover, DMA concentrations as high as 475 ng/g have been found in fish (Velez et al., 1996).

It has been reported that methylated arsenic may cause DNA damage, chromosomal aberrations, and tumor promotion in mice and rats (Xu et al., 2007). Some reports indicated that the pentavalent organoarsenics are genotoxic toward human lung cells, and monomethylarsonic acid (MMA) may act as a promoter of liver carcinogenesis (Yan et al., 2010). The World Health Organization (WHO) has established a guideline of 0.01 mg/L as the maximum allowable level of arsenic in drinking water (Zhang et al., 2007). The removal of organoarsenic compounds before they are converted to highly toxic inorganic compounds is therefore crucial for maintaining the safety of water and soil. A simple, low-cost and effective technology for arsenic removal is thus highly desirable to ensure safe drinking water to the people living in contaminated areas.

* Corresponding author. Tel.: +86 10 62849151; fax: +86 10 62923558.
E-mail address: jhqu@rcees.ac.cn (J. Qu).

At present, numerous studies have covered the remediation of inorganic arsenic using conventional technologies such as adsorption (Cao et al., 2012), precipitation (Tresintsi et al., 2012) and coagulation (Hu et al., 2012). Due to the inadequate removal efficiency for As (III), various oxidation processes such as chemical oxidants (chlorine dioxide, hypochlorite, potassium permanganate and monochloramine) (Sorlini and Gialdini, 2010), ozonation and Fenton reagent have been used to improve the removal efficiency by converting As (III) to As (V) (Hug and Leupin, 2003). However, there have been few studies of the removal of organoarsenic compounds, in contrast to the case for the removal of inorganic arsenic compounds. For example, DMA was very difficult to remove by traditional oxidants and coagulation aids (Hu et al., 2015a). Adsorption has demonstrated to be a promising technology for methylated arsenic removal because it is simple, has a low operating temperature and pressure, and does not need expensive reagents and catalysts. Different materials have been investigated for the adsorptive removal of methylated arsenic from water, including titanium dioxide, iron- or aluminum-based materials, carbon nanotubes and nanoporous functional materials (Chen and Huang, 2012; Jung et al., 2015). The removal of methylated arsenic by these sorbents is less efficient than that of inorganic arsenic. The photocatalytic degradation of MMA and DMA using Degussa P25 and nanocrystalline TiO_2 has been investigated. TiO_2 materials have been recognized as excellent choices for photocatalysis due to their photoactivity, modest cost, nontoxic nature, and large band gap (Xu et al., 2007, 2008). During the reaction process, the methyl groups in MMA and DMA were transformed to organic carbon and the converted inorganic arsenate was subsequently removed by adsorption onto the titanium dioxide. Reactive oxygen species ($\cdot\text{OH}$, $\text{O}_2\cdot^-/\text{HO}_2\cdot$, H_2O_2 et al.) were proven to be involved in the degradation process of organoarsenic compounds.

Oxidation of organoarsenic compounds to As (V) would greatly improve the overall removal of arsenic species from solution through adsorption. Only recently, the Fenton process ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) alone or assisted by plasma has started to be used to treat organoarsenic compounds (*p*-arsanilic acid and roxarsone) by fast oxidation of organoarsenic and efficient immobilization of inorganic arsenic at the same time (Hu et al., 2015b; Xie et al., 2016). Although the target arsenic species could be removed with high efficiency (oxidation and then adsorption by iron precipitate), Fe (III) directly added into the reaction solution is hard to recover and may cause secondary pollution (by arsenate-bearing ferric oxyhydroxides). Besides, the need for addition of H_2O_2 would also increase the treatment cost in the decontamination processes. Thus, it remains crucial to explore methods for iron immobilization and in situ H_2O_2 generation that can provide an alternative to disposal of this kind of wastewater.

The Electro-Fenton (EF) process, the most common indirect electro-oxidation method, can generate H_2O_2 continuously by two-electron reduction of oxygen on a catalytic cathode. In addition, another drawback of Fenton reagents (difficulty in recovery) could be solved by immobilizing Fe (III) onto supporting matrices, including inorganic and organic compounds. To the best of our knowledge, no previous study has investigated the treatment of organoarsenic-containing wastewater through an Electro-Fenton (EF) process. Hence, the objective of this study was to dispose of DMA by combining the advantages of electrogenerated H_2O_2 and a heterogeneous Fenton catalyst in a three-dimensional electrochemical reactor. A novel Fenton catalyst, Fe_3C -loaded carbon nanofiber, was prepared and used as particle catalyst in the electrochemical reactor. The influence of different parameters on the DMA removal efficiency was further investigated in detail including initial DMA concentration, catalyst dosage, solution pH and applied current. In addition, the reactive oxygen species involved and the

fate of DMA during the reaction process were also determined.

2. Materials and methods

2.1. Chemicals and reagents

Sodium arsenate ($\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$), dimethylarsinate (DMA, $\text{C}_2\text{H}_6\text{AsO}_2\cdot 3\text{H}_2\text{O}$), monomethylarsonate ($\text{CH}_3\text{AsO}_3\cdot 1.5\text{H}_2\text{O}$, MMA) and polyacrylonitrile (PAN) were obtained from Sigma. N, N-dimethylformamide (DMF), Iron (III) acetylacetonate, sodium sulfate, H_2SO_4 , NaOH, KI, ethanol and ammonium molybdate tetrahydrate were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. All chemicals were of analytical grade and used as received without further purification. All solutions were prepared with ultra-pure water obtained from a Millipore AutoPure WT101UV system (Millipore S. A. S., Molsheim, France) with a resistivity of $18.2\text{ M}\Omega\text{ cm}$ at $25\text{ }^\circ\text{C}$. Pressurized oxygen gas (99.9%) was used to saturate the solutions.

2.2. Preparation and characterization of $\text{FeC}_x/\text{NCNFs}$

To synthesize the $\text{FeC}_x/\text{NCNFs}$ material, the $\text{Fe}_2\text{O}_3/\text{C}$ composite was first prepared by electrospinning. Briefly, 1.0 g of iron (III) acetylacetonate was dissolved into 10 mL of N, N-dimethylformamide with a concentration of 0.4 M. Then, 1.0 g of PAN was added into the solution with vigorous stirring at room temperature overnight. The obtained solution was electrospun into fibers. The distance between the needle tip and rotating drum fiber collector was 15 cm and a high voltage of 15 kV was used during the electrospinning process. The collected polymer fibers were first stabilized in air at $280\text{ }^\circ\text{C}$ for 2 h with a heating rate of $2\text{ }^\circ\text{C}/\text{min}$, followed by a carbonization process in a tube furnace at $850\text{ }^\circ\text{C}$ for 1 h under an N_2 atmosphere with a heating rate of $5\text{ }^\circ\text{C}/\text{min}$. After the carbonization process, the glass tube was naturally cooled to room temperature, and the $\text{FeC}_x/\text{NCNFs}$ composite was obtained.

The crystal structure of the as-prepared materials was characterized by using powder X-ray diffraction on a Scintag-XDS-2000 diffractometer with a $\text{Cu K}\alpha$ radiation source ($\lambda = 1.54059\text{ \AA}$) operated at 40 kV and 40 mA in the 2θ range of $20\text{--}70^\circ$. The morphology of samples was characterized by a scanning electron microscope (S-3000N, Hitachi) and a Hitachi H-7500 transmission electron microscope. The BET surface area was determined by N_2 adsorption/desorption experiments using a surface area and porosity analyzer (ASAP2020 HD88). The X-ray photoelectron spectroscopy (XPS) data were taken on an AXIS-Ultra instrument from Kratos using monochromatic Al K α radiation (225 W, 15 mA, 15 kV) with low-energy electron flooding for charge compensation. To compensate for surface charge effects, the binding energies were calibrated using the C 1s hydrocarbon peak at 284.80 eV.

2.3. Experimental setup

Experiments were conducted at room temperature in an undivided, two-electrode quartz cell containing a 125-mL solution stirred with a magnetic stir bar, as shown in Fig. S1. The anode was a $4\text{ cm} \times 5\text{ cm}$ RuO_2/Ti mesh while the cathode was a 20 cm^2 ACF felt coated on RuO_2/Ti mesh. Pure O_2 was fed into the solution at 50 mL/min, and prior to the electrolysis, O_2 was bubbled through the aqueous solutions for 30 min. The current passing through the solution was measured and displayed continuously throughout electrolysis using a regulated digital DC power supply (DH1718E-4, Beijing Dahua Radio Instrument Factory, China). Unless otherwise specified, 100 mL of 5.0 mg/L DMA solution was added into the reactor and the pH of the initial solutions was adjusted by 0.2 mol/L H_2SO_4 or NaOH solution. The ionic strength was maintained at a

constant value of 0.05 mol/L by the addition of Na_2SO_4 . After the addition of the desired amount of $\text{FeC}_x/\text{NCNFs}$, the reaction was started. The current was maintained at a constant 0.015 A. At given time intervals, part of the suspension sample was withdrawn and filtered to remove catalyst powders for analysis.

2.4. Analysis method

Quantitative analysis of arsenic species was conducted on a 7700x Inductively Coupled Plasma Mass Spectrometer (ICP-MS) combined with a 1200 High Performance Liquid Chromatograph (HPLC) (Agilent, Santa Clara, USA). DMA, MMA and As (V) were separated on a PRP-X100 anion exchange chromatographic column (5 μm , 4.6×250 mm) (Hamilton, Reno, USA) by isocratic elution with 20% H_2O and 80% 50 mmol/L $(\text{NH}_4)_2\text{HPO}_4$ (pH 6, acidified by acetic acid) at 1.0 mL/min. The quadrupole mass analyzer was operated in single-ion monitoring mode ($m/z = 75$), and the signals were monitored in time-resolved analysis mode. The concentrations of arsenic species were calculated based on the corresponding chromatogram peak areas and calibration curves established with the respective standards using the MassHunter Workstation. The adsorbed MMA and As (V) on $\text{FeC}_x/\text{NCNFs}$ were measured after the catalyst containing arsenic was dissolved in hydrochloric acid assisted by ultrasonication. All of the above experiments were repeated in triplicate and the data are presented as the average of the triplicate measurements, with standard deviation less than 5%.

Electron spin resonance (ESR) spectra for $\cdot\text{OH}$ measurement were obtained with a Bruker A300-10/12 ESR spectrometer using DMPO as a spin trap agent at room temperature (center field: 3512.00 G; microwave frequency: 9.857 GHz; and power: 2.3 mW). The quantitation of $\cdot\text{OH}$ generated under different conditions was determined by the reaction of $\cdot\text{OH}$ with DMSO (Babbs and Gale, 1987). The H_2O_2 concentration was determined using a DPD method described in the literature (Bader et al., 1988).

3. Results and discussion

3.1. Characterization of $\text{FeC}_x/\text{NCNFs}$

Fig. 1A shows the XRD patterns of different samples during the preparation process of $\text{FeC}_x/\text{NCNFs}$ and the relevant electrochemical activity in DMA degradation. When the prepared polymer fibers were stabilized in air at 280°C for 2 h, all peaks could be assigned to the phase pure rhombohedral Fe_2O_3 (JCPDS Card No.33-0664) (Chen et al., 2015), while in the carbonization process, the

three most probable phases (Fe_7C_3 , Fe_3C and $\alpha\text{-Fe}$) were considered, which have positions around $2\theta \sim 45^\circ$ for the most intense maxima. The Fe_7C_3 phase with 00-017-0333 JCPDS code has distinct peaks at $2\theta = 50.5^\circ$ and 53.2° attributed to (202) and (220) crystallographic planes. Fe_3C (00-035-0772 JCPDS code) has a distinct peak at $2\theta = 58.1^\circ$ with Miller Index (301). The presence of $\alpha\text{-Fe}$ crystalline phase (00-006-0696 JCPDS code) is not certain due to the fact that the diffraction absolute maximum placed at $2\theta = 44.7^\circ$ is obscured by the convoluted peak centered at 45° . Moreover, the $\alpha\text{-Fe}$ second peak located at $2\theta = 65.1^\circ$ for (200) Miller Index was not clearly observed (Huminic et al., 2015). This indicated that iron in the fibers was likely in the state of Fe_7C_3 and Fe_3C after calcination at 850°C , and the sample was then abbreviated as $\text{FeC}_x/\text{NCNFs}$. As shown in Fig. 1B, the catalytic activity of the as-prepared sample was also different in terms of DMA removal efficiency. In comparison with Fe/PAN and $\text{Fe}_2\text{O}_3/\text{C}$, $\text{FeC}_x/\text{NCNFs}$ exhibited the highest efficiency in catalytic degradation of DMA, with 96% DMA removal under the conditions used. Hence the following characterization was mainly focused on the $\text{FeC}_x/\text{NCNFs}$ sample. The analysis of the Raman spectrum of the $\text{FeC}_x/\text{NCNFs}$ sample (Fig. S2) revealed a dominant presence of D (1317 cm^{-1}) and G (1591 cm^{-1}) bands attributed to amorphous carbon phases (Huminic et al., 2015), but there were no peaks ascribed to the iron oxide phases. This absence can be explained by the good passivation provided by the amorphous carbon shell for the iron-based core, preventing oxidation.

Fig. 2 shows the SEM, TEM, STEM images and EDS elemental mapping of commercial ACF (A) and $\text{FeC}_x/\text{NCNFs}$ (B–G). The commercial ACF (Fig. 2A) had a smooth surface with few impurities, while the morphology of $\text{FeC}_x/\text{NCNFs}$ (Fig. 2B) changed significantly and the surface became uneven and rough. This indicated that FeC_x were fixed securely and dispersed within the NCNFs, which was consistent with the TEM and STEM images (Fig. 2C,D and F). All FeC_x particles were obviously dispersed in and encapsulated by the fibers. The TEM EDS elemental mapping (Fig. 2E for C and Fig. 2G for Fe) further demonstrated that the nanoparticles were composed of iron and carbon elements, manifesting that the nanoparticles were FeC_x . The metallic state of iron and the composition of the iron-based active component were characterized by XPS analysis, and the results are shown in Fig. 3. From the $\text{Fe}2p$ XPS spectra, the $\text{Fe}2p_{1/2}$ and $\text{Fe}2p_{3/2}$ peaks centered at 709.9 and 723.2 eV could be assigned to Fe (II), and the bands centered at 712.4 and 725.6 eV corresponded to the characteristic values for Fe (III) (Nie et al., 2015); in particular, a satellite peak around 718.0 eV confirmed the presence of Fe (III) species in $\text{FeC}_x/\text{NCNFs}$. However, no signal was detected for Fe^0 at 707 eV (Nie et al., 2007). This indicated that

Fig. 1. XRD patterns and catalytic activity in DMA removal of different samples during the preparation of $\text{FeC}_x/\text{NCNFs}$. ($[\text{DMA}]_0 = 5\text{ mg/L}$, $[\text{Catalyst}] = 500\text{ mg/L}$, pH 3.0, $I = 0.15\text{ A}$, $O_2 = 50\text{ ml/min}$).

Fig. 2. SEM images of (A) ACF, (B) $\text{FeC}_x/\text{NCNFs}$; TEM images of $\text{FeC}_x/\text{NCNFs}$ (C) and (D); STEM image of $\text{FeC}_x/\text{NCNFs}$ (F); EDS elemental mapping of C (E) and Fe (G).

Fig. 3. XPS spectrum of $\text{FeC}_x/\text{NCNFs}$ for C1s and Fe2p.

both divalent and trivalent states of Fe existed in FeC_x . A C1s survey scan was further conducted to characterize the surface carbon

functional groups. As shown in Fig. 3, a broad band centered at 289 eV was due to surface contamination and oxidation products

that were not removed prior to analysis (Lewin et al., 2008), while the typical $\text{sp}^2\text{C}-\text{C}$ peak at 284.4 eV along with a $\text{sp}^3\text{C}=\text{C}$ peak at 285.8 eV was attributed to the carbon layers in NCNFs. The appearance of $\text{C}-\text{Fe}$ bonding at 283.7 eV could be attributed to the formation of FeC_x in $\text{FeC}_x/\text{NCNFs}$ (Li et al., 2015).

3.2. Efficient removal of DMA over $\text{FeC}_x/\text{NCNFs}$ in EF process

As shown in Fig. 4, the catalytic activity of $\text{FeC}_x/\text{NCNFs}$ in the EF process was evaluated by the DMA removal efficiency under different conditions, and the arsenic mass balance during the DMA degradation process was also calculated (inset of Fig. 4). As can be seen, there was almost no DMA adsorption on either NCNFs or $\text{FeC}_x/\text{NCNFs}$, indicating that the contribution of adsorption to DMA removal could be neglected. In contrast, DMA could be completely removed in the EF process catalyzed by $\text{FeC}_x/\text{NCNFs}$ after reaction for 360 min. According to the results of arsenic mass balance, DMA was entirely converted into MMA and As (V) since the total arsenic concentration was maintained at 5.0 mg/L during the DMA degradation process. It was necessary to explain the fact that the amount of produced MMA and As (V) was the sum of adsorbed arsenic species on $\text{FeC}_x/\text{NCNFs}$ and the arsenic in solution. Hence, Fig. 5 further depicts the ratios of various arsenic species during the DMA degradation process. The DMA concentration clearly decreased with the reaction time, while the ratios of the adsorbed MMA and As (V) on $\text{FeC}_x/\text{NCNFs}$ increased significantly at the same time. In addition, there was almost no As (V) detected in solution, and the MMA concentration in solution increased and then decreased with reaction time. The results indicated that MMA, as the main product of DMA degradation, could be further converted into As (V), and most of the degradation intermediates, such as MMA and As (V), should also be efficiently adsorbed on the catalyst. This was later confirmed by the results shown in Fig. 6. When DMA, MMA and As (V) were present in solution, they could not be adsorbed by NCNFs and the maximum adsorption efficiency was below 10%. DMA also could not be efficiently adsorbed by $\text{FeC}_x/\text{NCNFs}$; however, MMA and As (V) could be quickly and completely removed over $\text{FeC}_x/\text{NCNFs}$, and adsorption equilibrium was achieved at only 20 min (inset of Fig. 6). Hence, $\text{FeC}_x/\text{NCNFs}$ has been proven to be an ideal alternative for the catalytic degradation of DMA and adsorption of arsenic species at the same time.

It was necessary to investigate the influence of different parameters on the efficiency of the $\text{FeC}_x/\text{NCNFs}$ -based EF process. As shown in Fig. 7A, in the tested concentration range from 1 to 10 mg/L, all the DMA in solution could be degraded, with removal efficiency above 90% at 360 min of electrolysis. According to Fig. 7B, the DMA removal rate increased with the dosage of $\text{FeC}_x/\text{NCNFs}$

Fig. 4. DMA removal under different processes and the inset showed the As mass balance during the DMA degradation process over $\text{FeC}_x/\text{NCNFs}$. ($[\text{DMA}]_0 = 5 \text{ mg/L}$, $[\text{Catalyst}] = 500 \text{ mg/L}$, $\text{pH } 3.0$, $I = 0.15 \text{ A}$, $\text{O}_2 = 50 \text{ ml/min}$).

Fig. 5. The ratios changes of various arsenic species during the DMA degradation process. ($[\text{DMA}]_0 = 5 \text{ mg/L}$, $[\text{Catalyst}] = 500 \text{ mg/L}$, $\text{pH } 3.0$, $I = 0.15 \text{ A}$, $\text{O}_2 = 50 \text{ ml/min}$).

Fig. 6. The adsorption of DMA, MMA and As (V) on NCNFs and $\text{FeC}_x/\text{NCNFs}$ (inset). ($[\text{DMA}]_0 = 5 \text{ mg/L}$, $[\text{Catalyst}] = 500 \text{ mg/L}$, $\text{pH } 3.0$, $I = 0.15 \text{ A}$, $\text{O}_2 = 50 \text{ ml/min}$).

(0–0.5 g/L) and then maintained a steady level when the amount of $\text{FeC}_x/\text{NCNFs}$ in solution was further increased to 0.7–1.0 g/L. Hence, the 0.5 g/L dosage of $\text{FeC}_x/\text{NCNFs}$ was used in the subsequent experiments. A notable pH effect was found for the electro-Fenton process, in which 100% of DMA was degraded after reaction for 360 min at pH 3.0, while the DMA removal efficiency was 50% and 24.8% at solution pH of 2.0 and 4.0 respectively (Fig. 7C). H_2O_2 generation under different pH values was also monitored, and its concentration generally increased with reaction time. However, the amount of H_2O_2 at pH 3 and 4 was almost the same, and much higher than that at pH 2 (Fig. 7D). Therefore, the lower DMA degradation efficiency at pH 2 could be attributed to the lower H_2O_2 generation, while the decrease of $\cdot\text{OH}$ oxidation potential and dissolved fraction of iron species should be responsible for the low DMA decomposition rate at pH 4. The influence of applied current on the EF efficiency was also examined at 0–0.2 A. As shown in Fig. 7E, the EF efficiency markedly increased with the applied current (0–0.15 A) and the DMA removal was 6%, 54%, 75.8% and 96% respectively. If the applied current was further increased to 0.2 A, the DMA removal efficiency then decreased to 78%. The above results were consistent with the production rate of H_2O_2 generated at the NCNFs cathode, with the maximum H_2O_2 at 0.15 A and the minimum H_2O_2 at 0.2 A (Fig. 7F), which resulted in the enhancement of $\cdot\text{OH}$ generation since the production of $\cdot\text{OH}$ in the medium is proportional to the H_2O_2 concentration. Based on the above results, the optimum reaction conditions for the $\text{FeC}_x/\text{NCNFs}$ -based EF process were as follows: pH 3.0, $[\text{catalyst}] = 0.5 \text{ mg/L}$, $I = 0.15 \text{ A}$ and inlet $\text{O}_2 = 50 \text{ mL/min}$.

The iron leaching from $\text{FeC}_x/\text{NCNFs}$, including Fe^{3+} and Fe^{2+} ,

Fig. 7. Influence of different parameters on the oxidation efficiency of $\text{FeC}_x/\text{NCNFs}$ based electro-Fenton process: initial DMA concentration (A) catalyst dosage (B) effect on DMA removal; solution pH effect on DMA removal (C) and H_2O_2 production; applied current effect on DMA removal (E) and H_2O_2 production (F).

during the EF process under the optimum conditions was measured, and the results are shown in Fig. 8. The total iron concentration decreased quickly from 2.05 mg/L to 0.3 mg/L with

reaction time, while the DMA was still removed efficiently over $\text{FeC}_x/\text{NCNFs}$. This indicated that the dissolved iron ion could be re-immobilized on the surface of the catalyst during the reaction process. To assess the stability of $\text{FeC}_x/\text{NCNFs}$ during the EF process, the catalysts were separated from the reaction mixture by

Fig. 8. The changes of Fe^{3+} and Fe^{2+} concentration leaching from $\text{FeC}_x/\text{NCNFs}$ during the EF process and the inset showed the DMA removal efficiency of $\text{FeC}_x/\text{NCNFs}$ in cycle experiment.

Fig. 9. TOC changes in DMA solution and $\cdot\text{OH}$ formation in $\text{FeC}_x/\text{NCNFs}$ based electro-Fenton process. The inset showed the DMPO spin trapping ESR spectra of $\cdot\text{OH}$.

Fig. 10. Effect of *tert*-Butyl with different concentration on the DMA removal efficiency over $\text{FeC}_x/\text{NCNFs}$.

centrifugation and rinsed twice with ammonium oxalate solution before reuse. As shown in the inset of Fig. 8, the catalyst did not exhibit significant loss of activity and could be reused for at least six cycles. This suggested that the catalyst had excellent long-term stability.

The TOC removal during the catalytic degradation of DMA in EF

process was also measured, and the results are provided in Fig. 9. All of the TOC came from the methyl groups of DMA, and its removal could then provide direct proof of DMA degradation. The TOC concentration decreased with reaction time, with a removal efficiency of 86% at 360 min, which also indicated that DMA had been efficiently degraded into MMA and As (V) and MMA was further converted into As (V). DMPO spin-trap ESR was used to detect the reactive oxygen species (ROS) involved in the DMA degradation process. As shown in the inset of Fig. 9, the measured ESR spectra exhibited the 4-fold characteristic peak of DMPO- $\cdot\text{OH}$ adducts with an intensity ratio of 1:2:2:1 (Nie et al., 2008). Moreover, the $\cdot\text{OH}$ amount also increased with reaction time and reached a steady state at 180 min. This indicated that $\cdot\text{OH}$ radicals were generated, resulting in higher DMA removal efficiency. *Tert*-Butyl alcohol has a reaction rate constant of $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ with hydroxyl radicals, and it is hence adopted as the indicator of $\cdot\text{OH}$ for radical-type reactions (Yang et al., 2009). Based on the results in Fig. 10, the DMA degradation was significantly inhibited in the presence of *tert*-Butyl alcohol, and the removal efficiency also decreased with the *tert*-Butyl alcohol concentration. Moreover, the DMA degradation was completely depressed when the *tert*-Butyl alcohol concentration was 100 mmol/L. These results confirmed that $\cdot\text{OH}$ is the sole reactive oxygen species responsible for the DMA degradation.

Fig. 11. The proposed reaction mechanism of DMA abatement in $\text{FeC}_x/\text{NCNFs}$ based EF process.

The degradation pathway for DMA and the electro-Fenton reaction mechanism over $\text{FeC}_x/\text{NCNFs}$ were proposed according to the above experimental results (Fig. 11). First, oxygen was activated on the ACF surface and H_2O_2 was then efficiently generated through the reduction of oxygen on the cathode. Meanwhile, the added $\text{FeC}_x/\text{NCNFs}$ catalyzed H_2O_2 decomposition into $\cdot\text{OH}$, presumably through a Haber-Weiss mechanism, and DMA in solution was attacked by $\cdot\text{OH}$, leading the formation of MMA and the release of a methyl group. At the same time, as the reaction proceeded, $\text{FeC}_x/\text{NCNFs}$ were slowly deposited on ACF. The MMA was then quickly adsorbed onto the $\text{FeC}_x/\text{NCNFs}$ and further converted to As (V) due to oxidation by $\cdot\text{OH}$, while the released methyl group (together with that from DMA degradation) could be eventually mineralized to CO_2 and H_2O . Finally, the produced As (V) was immobilized on the surface of the catalyst, and the inorganic arsenic concentration in solution was hence below the allowable limit of 0.01 mg/L. During the reaction process, iron species could be recycled on the surface of $\text{FeC}_x/\text{NCNFs}$, which resulted from the excellent stability of the highly efficient $\text{FeC}_x/\text{NCNFs}$.

4. Conclusions

$\text{FeC}_x/\text{NCNFs}$, prepared using an electrospinning method, was proven to be both an efficient catalyst in oxidation of DMA and an adsorbent in the adsorption of MMA and As (V) in the electro-Fenton process. $\cdot\text{OH}$ was proven to be the sole reactive oxygen species involved in the degradation process of DMA. DMA was oxidized to MMA as the primary oxidation product, which was subsequently oxidized to inorganic arsenic As (V). The optimum treatment conditions were further determined as followed: pH 3.0, [catalyst] = 0.5 mg/L, $I = 0.15$ A and inlet $\text{O}_2 = 50$ mL/min. The results showed that DMA could be efficiently oxidized into inorganic arsenic. 96% of DMA was degraded after reaction for 360 min and the residual inorganic arsenic concentration in solution was also below the allowable limit of 0.01 mg/L under the optimum treatment conditions. The results demonstrated that the $\text{FeC}_x/\text{NCNFs}$ -based EF process provided a new alternative for efficient decontamination of water containing organoarsenic pollutants.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (Nos. 51478455, 51438011, 51422813).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.05.018>.

References

- Babbs, C.F., Gale, M.J., 1987. Colorimetric assay for methanesulfinic acid in biological samples. *Anal. Biochem.* 163 (1), 67–73.
- Bader, H., Sturzenegger, V., Hoigne, J., 1988. Photometric-method for the determination of low concentrations of hydrogen-peroxide by the peroxidase catalyzed oxidation of N,N-diethyl-P-phenylenediamine (Dpd). *Water Res.* 22 (9), 1109–1115.
- Balázs, N., Zoltán, G., 2013. Reduction of dimethylarsinic acid to the highly toxic dimethylarsinous acid by rats and rat liver cytosol. *Chem. Res. Toxicol.* 26 (3), 432–443.
- Cao, C.Y., Qu, J., Yan, W.S., Zhu, J.F., Wu, Z.Y., Song, W.G., 2012. Low-cost synthesis of flowerlike α -Fe 2O_3 nanostructures for heavy metal ion removal: adsorption property and mechanism. *Langmuir ACS J. Surf. Colloids* 28 (9), 4573–4579.
- Chen, M., Shen, X., Wu, Q.H., Li, W., Diao, G.W., 2015. Template-assisted synthesis of core-shell α -Fe $2\text{O}_3/\text{TiO}_2$ nanorods and their photocatalytic property. *J. Mater. Sci.* 50 (1), 4083–4094.
- Chen, W.R., Huang, C.H., 2012. Surface adsorption of organoarsenic roxarsone and arsanilic acid on iron and aluminum oxides. *J. Hazard. Mater.* 27–228, 378–385.
- Han, J., Lee, S., Choi, K., Kim, J., Ha, D., Lee, C.G., An, B., Lee, S.H., Mizuseki, H., Choi, J.W., Kang, S., 2016. Effect of nitrogen doping on titanium carbonitride-derived adsorbents used for arsenic removal. *J. Hazard. Mater.* 302, 375–385.
- Hu, C.Z., Chen, Q.X., Liu, H.J., Qu, J.H., 2015a. Coagulation of methylated arsenic from drinking water: influence of nitrogen doping on titanium carbonitride-derived adsorbents used for arsenic removal. *J. Hazard. Mater.* 293, 97–104.
- Hu, C.Z., Liu, H.J., Chen, G.X., Qu, J.H., 2012. Effect of aluminum speciation on arsenic removal during coagulation process. *Sep. Purif. Technol.* 86, 35–40.
- Hu, P., Liu, Y.K., Jiang, B., Zheng, X., Zheng, J.T., Wu, M.B., 2015b. High-efficiency simultaneous oxidation of organoarsenic and immobilization of arsenic in fenton enhanced plasma system. *Ind. Eng. Chem. Res.* 54 (33), 8277–8286.
- Hug, S.J., Leupin, O., 2003. Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environ. Sci. Technol.* 37 (12), 2734–2742.
- Huminc, A., Huminc, G., Fleaca, C., Dumitache, F., Morjan, I., 2015. Thermal conductivity, viscosity and surface tension of nanofluids based on FeC nanoparticles. *Powder Technol.* 284, 78–84.
- Jung, B.K., Jun, J.W., Hasan, Z., Jhung, S.H., 2015. Adsorptive removal of p-arsanilic acid from water using mesoporous zeolitic imidazolate framework-8. *Chem. Eng. J.* 267, 9–15.
- Lewin, E., Persson, P.O.A., Lattemann, M., Stuber, M., Gorgoi, M., Sandell, A., Ziebert, C., Schadfers, F., Braun, W., Halbritter, J., Ulrich, S., Eberhardt, W., Hultman, L., Siegbahn, H., Svensson, S., Jansson, U., 2008. On the origin of a third spectral component of C1s XPS-spectra for nc-TiC/a-C nanocomposite thin films. *Surf. Coat. Technol.* 202 (15), 3563–3570.
- Li, J.X., Wen, W.W., Xu, G.G., Zou, M.Z., Huang, Z.G., Guan, L.H., 2015. Fe-added Fe 3C carbon nanofibers as anode for Li ion batteries with excellent low-temperature performance. *Electrochim. Acta* 153, 300–305.
- Lim, S.F., Zheng, Y.M., Chen, J.P., 2009. Organic arsenic adsorption onto a magnetic sorbent. *Langmuir ACS J. Surf. Colloids* 25 (9), 4973–4978.
- Nie, Y.L., Hu, C., Qu, J.H., Hu, X.X., 2008. Efficient photodegradation of Acid Red B by immobilized ferrocene in the presence of UVA and H_2O_2 . *J. Hazard. Mater.* 154 (1–3), 146–152.
- Nie, Y.L., Hu, C., Qu, J.H., Zhou, L., Hu, X.X., 2007. Photoassisted degradation of azodyes over FeOxH 2x -3/Fe0 in the presence of H_2O_2 at neutral pH values. *Environ. Sci. Technol.* 41 (13), 4715–4719.
- Nie, Y.L., Li, N.N., Hu, C., 2015. Enhanced inhibition of bromate formation in catalytic ozonation of organic pollutants over Fe-Al LDH/Al 2O_3 . *Sep. Purif. Technol.* 151, 256–261.
- Rivera-Reyna, N., Hinojosa-Reyes, L., Guzman-Mar, J.L., Cai, Y., O'Shea, K., Hernandez-Ramirez, A., 2013. Photocatalytic removal of inorganic and organic arsenic species from aqueous solution using zinc oxide semiconductor. *Photochem. Photobiol. Sci.* 12 (4), 653–659.
- Sorlini, S., Gialdini, F., 2010. Conventional oxidation treatments for the removal of arsenic with chlorine dioxide, hypochlorite, potassium permanganate and monochloramine. *Water Res.* 44 (19), 5653–5659.
- Tresintsi, S., Simeonidis, K., Vourlias, G., Stavropoulos, G., Mitras, M., 2012. Kilogram-scale synthesis of iron oxy-hydroxides with improved arsenic removal capacity: study of Fe(II) oxidation-precipitation parameters. *Water Res.* 46 (16), 5255–5267.
- Velez, D., Ybanez, N., Montoro, R., 1996. Monomethylarsonic and dimethylarsinic acid contents in seafood products. *J. Agric Food Chem.* 44 (3), 859–864.
- Xie, X.D., Hu, Y.A., Cheng, H.F., 2016. Rapid degradation of p-arsanilic acid with simultaneous arsenic removal from aqueous solution using Fenton process. *Water Res.* 89, 59–67.
- Xu, T.L., Cai, Y., O'Shea, K., 2007. Adsorption and photocatalyzed oxidation of methylated arsenic species in TiO_2 Suspensions. *Environ. Sci. Technol.* 41 (15), 5471–5477.
- Xu, Z.H., Jing, C.Y., Li, F.S., Meng, X.G., 2008. Mechanisms of photocatalytic degradation of monomethylarsonic and dimethylarsinic acids using nanocrystalline titanium dioxide. *Environ. Sci. Technol.* 42 (7), 2349–2354.
- Yan, L., Yin, H.H., Zhang, S., Leng, F.F., Nan, W.B., Li, H.Y., 2010. Biosorption of inorganic and organic arsenic from aqueous solution by *Acidithiobacillus ferrooxidans* BY-3. *J. Hazard. Mater.* 178 (1–3), 209–217.
- Yang, L., Hu, C., Nie, Y.L., Qu, J.H., 2009. Catalytic ozonation of selected pharmaceuticals over mesoporous alumina-supported manganese oxide. *Environ. Sci. Technol.* 43 (7), 2525–2529.
- Zhang, G.S., Qu, J.H., Liu, H.J., Liu, R.P., Wu, R.C., 2007. Preparation and evaluation of a novel Fe-Mn binary oxide adsorbent for effective arsenite removal. *Water Res.* 41 (9), 1921–1928.
- Zheng, Y.M., Yu, L., Chen, J.P., 2012. Removal of methylated arsenic using a nanostructured zirconia-based sorbent: process performance and adsorption chemistry. *J. Colloid Interface Sci.* 367 (1), 362–369.