



Journal of Nanoscience and Nanotechnology Vol. 18, 8252–8257, 2018 www.aspbs.com/jnn

A Facile Strategy to Fabricate Nanoscale Zero-Valent Iron Decorated Graphene Oxide Composite for Dechloridation of Trichloroacetic Acid in Water

Huixuan Zhang¹, Xinyi Zhang¹, Ruonan Guo¹, Qingfeng Cheng², and Xiuwen Cheng^{1,*}

¹ Key Laboratory of Western China's Environmental Systems (Ministry of Education), College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730000, P. R. China

² College of Resources and Environment, Chengdu University of Information Technology, Chengdu 610225, P. R. China

In this study, nanoscale zero-valent iron decorated graphene oxide (NZVI/GO) composite was fabricated through a reduction process in the presence of sodium borohydride (NaBH₄) solution. Subsequently, physicochemical properties of the NZVI/GO composites were characterized by scanning electron microscope (SEM), transmission electron microscopy (TEM), N₂ adsorption/desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transformation infrared spectroscopy (FT-IR) and Raman spectra. Results indicated that Fe species existed in the form of Fe⁰, which uniformly dispersed on the surface of GO. Furthermore, the performance of NZVI/GO was evaluated by the degradation of tichloroacetic acid (TCAA). TCAA can be rapidly degraded by NZVI/GO. This paper provides a promising strategy to synthesize versatile catalyst which would be potentially applied in sewage treatment to degrade chlorinated organic compounds.

Keywords: Nanoscale Zero-Valent Iron, Graphene Oxide, Tichloroacetic Acid, Degradation.

1. INTRODUCTION

Trichloroacetic acid (TCAA), as one of the chlorinated organic compounds (COCs), is a non-biodegradable pollutant detected in aquatic ecosystem throughout the world, including surface and ground water.¹ So it has become a focus which attached much attention in environmental research in recent years. Also, due to the high solubility and different natural sources as well as anthropological sources, the presence of TCAA and other chloroacetic acids (CAAs) which are in water and soil causes a serious risk to human beings.² As one of disinfection by-products (DBPs), the exposure to TCAA and other CAAs are very wide. Cardador and Gallego evaluated the exposure of swimmers and workers to haloacetic acids (HAAs) in indoor and outdoor pools through the analysis of urine samples, finding that TCAA and DCAA might reach the maximum concentration level set by the U.S. EPA for haloacetic acids (HAAs).³ Traditional bioremediation method has been applied in the degradation of HAAs, including CAAs. However, it is unsuccessfully especially

for TCAA since it has being the most recalcitrant among them in water.⁴

Apart from these methods, phase-transfer techniques such as adsorption also are promising technologies, which can result in good effects. Among traditional conventional adsorbents for the removal of TCAA, graphene oxide (GO) has attached much attention due to its properties such as large specific surface areas, superior mechanical properties, strong adsorption capacity and special physicochemical properties.^{5,6} As a novel carbon nanomaterial, graphene oxide has many functional groups such as hydroxyl, carboxyl and epoxy groups. These functional groups not only improve the dispersibility of graphene oxide, but also play a very important role in the adsorption of various contaminants.⁷ However, adsorption simply transfers contaminants from one phase to another while the pollutants themselves are not degraded.⁸ Therefore, finding an environmental-friendly approach to degrade the C-Halogen bond which is toxic in nature, is very urgent.

Nanoscale zero-valent iron (NZVI) material, as a kind of strong reducing agent who's standard electrode potential is -0.43 V, has been successfully used to eliminate a variety

^{*}Author to whom correspondence should be addressed.

Zhang et al.

of organic and inorganic pollutants in environment, such as chlorinated solvents,⁹ the dye effluents,¹⁰ polychlorinated biphenyls^{11, 12} and heavy metals^{13–15} due to its large specific surface area, strong surface activity and relatively low price. However, owing to the high surface energy and magnetism among particles of NZVI, it suffers strong aggregation and fast oxidation in air. This can lead to a decrease both in adsorption sites and reactive sites, so the effective contact areas between target pollutants and NZVI become smaller, resulting in a low reactivity of NZVI.

Apart from the properties described above of the graphene oxide, it also can be considered as a convenient support material for the nanoparticles. In order to overcome agglomeration and passivation of NAVI, NZVI could be fixed on the surface of GO. On the one hand, GO can effectively inhibit the aggregation of metal nano-particles.¹⁶ Magdalena et al.¹⁷ prepared reduced graphene oxide with metal or metal oxide nanoparticles by using various methods, finding that GO can be successfully used as a template for direct synthesis of metal or metal oxide nano-particles on its surface with a homogenous distribution.^{18, 19} Zhang et al.²⁰ synthesized silver phosphate/graphene oxide (Ag₃PO₄/GO) composite by ultrasound-precipitation processes, which can degrade tetrabromosphenol A (TBBPA) successfully. On the other hand, the GO-supported nanometer iron material can be recycled due to the magnetic properties of NZVI. What's more, the price of NZVI materials is cheaper while the ing NZVI on GO can reduce the cost of materials and improve its economy.

In this study, GO was firstly prepared by ultrasonic method, then the NZVI/GO composites were fabricated via liquid-phase reduction methods with borohydride salt. Afterwards, physicochemical properties of GO-NZVI composites were systematically investigated through series of characterizations. Furthermore, the performance of NZVI/GO was evaluated by degradation of TCAA. The results showed that NZVI/GO exhibited higher degradation performance. Besides, the possible degradation pathways of TCAA by identifying the corresponding degradation intermediates were further elucidated.

2. MATERIALS AND METHODS

2.1. Materials and Reagents

Ferrous sulfate hepta-hydrate (FeSO₄ \cdot 7H₂O), sodium nitrate (NaNO₃), graphite powder (purity, >99.5%), concentrated sulfuric acid, potassium hypermanganate (KMnO₄), ethanol (C₂H₅OH), hydrogen peroxide (H₂O₂), sodium borohydride (NaBH₄), and trichloroacetic acid (TCAA) were analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. All these chemicals were used as received without any further purification. MQ water was used throughout this experiment.

J. Nanosci. Nanotechnol. 18, 8252-8257, 2018

2.2. Synthesis of NZVI/GO Composites

Normally, GO was synthesized by using chemical oxidation process. First, 25 mL concentrated sulfuric acid was added into 1.0 g graphite powder and 0.5 g sodium nitrate under stirring in ice-water bath. Second, in order to control the temperature which was 293 K of the suspension, 3.0 g potassium hypermanganate ($KMnO_4$) was dropwise added. After these, the mixture obtained was transferred to a water bath whose temperature is 308 K under mechanical stirring for 90 min. Subsequently, 10 mL 30 wt% hydrogen peroxide (H₂O₂) was added slowly. Next, 50 mL 5 wt% hydrochloric acid was used to purify the mixture. Then, the as-obtained mixture was washed by 200 mL MQ-water and then filtrated to form a neutral solution. Eventually, the powder was dried for 24 h at 333 K.

In order to obtain the NZVI/GO composite, further experiment needs to be performed. In detail, 0.5 g GO was dispersed in MQ-water (250 mL) under ultrasound for 2 h so that GO can be fully peeled off. Afterwards, the above solution was placed in a three-necked flask. Next, 0.92 g $FeSO_4 \cdot 7H_2O$ was added to the solution stirring for 15 min. Then, 0.2 g NaBH₄ was added to the mixture under the condition of 80 °C water bath. After 4 h reaction, the product was washed twice or 3 times with absolute ethanol and then dried at 60 °C. Finally, the product was sealed and stored. NZVI immobilized in the surface of GO was prepared according to Eq. (1).

(1)

2.3. Characterization

Apparent morphology of GO and NZVI/GO was recorded by scanning electron microscopy (SEM) at 20 kV. The particle size of the catalyst was analyzed by transmission electron microscopy (TEM). X-ray diffraction (XRD) measurements were performed using a Rigaku D/Max IIIB diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm). The X-ray photoelectron spectroscopy spectra were carried out at 10 kV and 5 mA under 10-8 Pa residual pressure using a thermo ESCALAB 250 electron spectrometer (Al K α X-ray source, 1486.6 eV) with multidetection analyzer. Raman spectrum was carried out by using a Jobin Yvon HR800 Raman spectrophotometer (equipped with Ar laser excitation wavelength of 457.9 nm). Fourier transformed infrared spectroscopy (FT-IR) was measured on Spectrum One apparatus, in which KBr standards were used as reference.

2.4. Dechlorination of Trichloroacetic Acid by NZVI/GO

TCAA dechlorination was conducted in 50 mL glass vials with some dose of NZVI/GO. And the glass vials allowed for about a 10 mL headspace. The vials were sealed with Telfon-lined rubber septa and aluminum cap immediately and then placed on an orbital shaker under stirring at room A Facile Strategy to Fabricate NZVI/GO Composite for Dechloridation of Trichloroacetic Acid in Water

Zhang et al.

temperature. This process ran through the dechlorination experiment. At selected time intervals, duplicate sample vials were sacrificed and liquid samples were taken with a gas-tight syringe and then filtered through a 0.22 mm Millipore syringe filter for subsequent analyses. All experiments were performed in triplicate. If there was not any special instruction, the solution used in this study was prepared by deionized water.

3. RESULTS AND DISCUSSION

3.1. SEM and TEM Analysis

The microstructures and morphologies presented in the prepared GO and NZVI/GO composite were investigated by SEM, and the results were shown in Figures 1(a) and (b), respectively. From Figure 1(a), GO had irregular layer or sheet structure, and its surface had some folds owing to the outer layer of the oxidation process in the peeling off part of the formation of a large number of different sizes of graphite sheet. As seen from Figure 1(b), a large number of small zero-valent iron nanoparticles evenly dispersed on the surface of GO. But there was still a small amount of nanoscale zero-valent iron aggregated particles due to magnetic interaction. Figure 2 showed the TEM image of NAVI/GO samples. Similar to the SEM of NZVI/GO composite, GO showed a transparent, wrinkled structure and folding back of the edges. And NZVI had a low degree of aggregation. This indicates that GO sheets could not only act as supports for the growth of the NZVI but also function as stabilizing agent for preventing the agglomeration of the as grown NZVI. The specific surface areas (SSA) of NZVI were measured by using a BET-N₂ surface area analyzer. Hardiljeet et al.²¹ measured that the freshly prepared NZVI had a specific surface area of 26.3 $m^2 \cdot g^{-1}$. However, the specific surface area measured in this study was 65 m² \cdot g⁻¹. This might be due to the presence of GO, inhibited the accumulation of nanoscale zero-valent iron to a certain extent, which were in accordance with the SEM and TEM results.

3.2. XRD Analysis

In order to confirm the existence of NZVI on the surface of GO, XRD patterns were measured and showed in Figure 3. Noted, GO showed a strong diffraction peak at 2 theta = 11.8 degrees ascribed to the presence of abundant



Figure 1. The typical top-view SEM image of GO (a) and NAVI/GO (b) samples.



Figure 2. The TEM image of NAVI/GO samples.

oxygen containing functional groups on the surfaces of the GO sheets. Besides, the diffraction peak at 2 theta = 46.5 degrees, corresponding to the formation of iron as the form of zero-valent (Fe⁰ state 110), suggesting Fe²⁺ was reduced by the potassium borohydride. Furthermore, the peak at 2 theta = 65.1 degrees represented Fe₂O₃ produced. What's more, the peak of the reduced graphene oxide (rGO) was not found, indicating that the graphene oxide was only used as a carrier in the process and did not participate in the reaction.

3.3. XPS Analysis 6:44

Figure 4 exhibited the results from the X-ray photoelectron spectroscopy (XPS) characterization of the NZVI/GO, which presented spectra of Fe 2*p*. A feature peak around 706.7 eV could be observed, corresponding to the 2*p*3/2 peaks of zero-valent iron (Fe⁰),²² which indicated that Fe⁰ did exist on the surface of GO. Besides, the peaks at 720.5 eV suggested the presence of γ -Fe₂O₃, indicating that a part of NZVI had been oxidized on the surface of GO. This might be due to the existence of graphene oxide, inhibiting the aggregation of zero-valent iron nanoparticles, making the contact area between zero-valent iron



Figure 3. XRD pattern of NZVI/GO composite.

J. Nanosci. Nanotechnol. 18, 8252-8257, 2018



Figure 4. XPS spectrum of Fe 2p of the GO/NZVI composite.

nano-particles and the outside become larger, thus making NZVI easier to be oxidized.

3.4. FT-IR Analysis

The FT-IR spectra of the NZVI/GO composites were shown in Figure 5. As for GO, the characteristic bands appeared for hydroxyl ('OH) (stretching at 3400 cm^{-1}), alkoxy C–O (vibrating at 1050 cm⁻¹), epoxy group (C–O) at 1137 cm⁻¹, carbonyl (C=O) at 1730 cm⁻¹, the bending vibration peak of unsaturated double bonds (C=C) and C-OH at 1618 cm⁻¹, which may be due to interstitial water presented in the GO sheet, which was consistent with the fact that the GO cannot be completely dried.^{23, 24} These oxygen-containing groups resulted in the increase of the interlayer spacing between graphite sheets. As for NZVI/GO, the weakening of the peak at 3400 cm⁻¹ for graphene suggested that treatment removed the oxygen from the hydroxyl groups so that the C-O peak became weaker compared to graphene oxide.²⁵ The peak near 1400 cm⁻¹ could be attributed to bands associated with Fe₃O₄, Fe₂O₃ and FeOOH formation surrounding Fe^{0.26} Besides, the C=O band disappeared and the intensity of C-O-C band decreased in the spectrum of the NZVI/GO, which indicated that the oxygen-containing

Figure 5. FT-IR spectra of NZVI/GO composites.

J. Nanosci. Nanotechnol. 18, 8252-8257, 2018

functional groups in the GO were effectively reduced in the NZVI/GO. These results above confirmed that NZVI/GO were well prepared via this method.

3.5. Raman Analysis

Figure 6 showed the Raman spectra of GO and NZVI/GO composite. As shown in Figure 6, the presence of the intense D-band at 1362.5 cm⁻¹ (the band referring to lattice distortion) and the normal G-band at 1582.8 cm⁻¹ were both Raman characteristic peaks of C atoms. Among them, the D-band was attributed to the high level of oxidation which resulted in defects on GO nanosheets surface and lattice distortion. According to the Raman spectra of NZVI/GO composite, it was noticed that D band and G band have a little blue shift to a certain degree, which could be attributed to the synergistic effect between GO and NZVI. What's more, we found that the value of ID/IG ratio (the intensity ratio of D-band and G-band, as an indicator of structural defects) increased from 0.785 for GO to 0.937 for NZVI/GO composites, which may be due to the change in the microstructure of graphitized structures.^{27, 28}

3.6. The Degradation of TCCA by NZVI/GO

Further experiments were performed to investigate the performance of NZVI/GO composite via trichloroacetic acid (TCAA) degradation. As shown in Figure 7, the concentration of TCAA gradually decreased over time and its concentration was nearly reduced to zero at about 160 min, which indicated that NZVI/GO composites had a good degradation effect on TCAA. This may be due to the impact of pH_{PZC} (pH at point of zero charge) of NZVI/GO composites. Generally speaking, the surface charge of NZVI/GO was positive at lower pH value than the pH_{PZC} and vice versa. Sun et al.²⁹ measured the pH_{PZC} of NZVI and NZVI/GO composites were 5.1 and 4.66, respectively. Therefore, acidic condition can result in positive charges on the surface of NZVI/GO composites, which will attract TCAA. Furthermore, GO also had a capacity to adsorb TCAA to a certain degree. So TCAA can be rapidly degraded by zero-valent iron nano-particles.



Figure 6. Raman spectra of GO and NZVI/GO composite.

8255

Zhang et al.



Figure 7. Decomposition of TCAA, DCAA, MCAA, acetic acid and Cl⁻ concentration during the TCAA degradation.

At the same time, with time increased, the concentration of dichloroacetic acid (DCAA) and monochloroacetic acid (MCAA) showed a first increase and then decreased. On the contrary, the concentration of acetic acid and Cl^- gradually increased as time went by. These indicated that the complete dechlorination product (acetic acid) was measured as the only final product during the degradation of TCAA by using NZVI/GO composites. Besides, both of MCAA and DCAA were intermediate products.

3.7. Degradation Mechanism for TCAA/by the merican NZVI/GO Composites

In order to better understand the degradation process of TCAA, degradation mechanism for TCAA by NZVI/GO composites was proposed. As shown in Figure 8, the zero-valent nano-particles were dispersed on graphene oxide. The process of TCAA dechlorination was divided into two stages under the presence of NZVI/GO: firstly, TCAA was adsorbed on the surface of NZVI/GO. As the graphene oxide could inhibit the accumulation of zero-valent iron



Figure 8. Reaction mechanism of TCAA by NZVI/GO composite.

nano-particles, so the effective contact area of zero-valent iron nano-particles and TCAA increased. Besides, the GO itself had a larger adsorption capacity to adsorb TCAA, therefore, the composite could adsorb more contaminants. Subsequently, TCAA was reduced by zero-valent iron nano-particles which dispersed on the surface of GO. Zero-valent iron nano-particles released many electrons while being corroded, corresponding reaction (2) and (3). The extremely fast conductivity and the unique twodimensional planar structure of the graphene oxide could make electrons which were released by zero-valent iron nano-particles moving rapidly and thus electrons could involve in the further reaction quickly. As a result, a part of TCAA removed chloride ions into DCAA, MCAA or directly to acetic acid (CH₂COOH) under the action of electrons (reaction (4)). Apart from these, superoxide radicals (O_2^{-}) which generated via the combination of electrons and oxygen molecules dissolved in water also had a positive effect for the degradation of TCAA and other intermediate products. Noticeably, the low pH conditions of the system and the iron ions produced by the NZVI as an effective reducing agent provided sufficient conditions for the Fenton reaction. On the one hand, in the process of corrosion of zero-valent iron nano-particles, not only divalent iron ions but also trivalent iron ions would be produced. On the other hand, trivalent iron ions could further react with zero valent iron nanoparticles thus formed divalent iron ions according to reaction (5). Oxygen molecules would be reduced by H⁺ to generate a certain amount of H_2O_2 (reaction (6)) under the action of zero-valent iron nano-particles. Afterwards, due to the Fenton reaction between trivalent iron ions and H_2O_2 , a lot of hydroxyl radicals ('OH) which had strong oxidizing capacities are generated (reaction (7)). Then trivalent iron ions produced by Fenton reaction instantly being reduced to be divalent iron ions (reaction (8)) thus forming a cycle. Finally, the resulting active species were used to dechlorinate and degrade contaminants. At the same time, the chlorine atoms from TCCA were present in the aqueous solution in the form of chloride ions, maintaining the charge balance. Therefore, this system did hardly produce any sludge.

$$\mathrm{Fe}^0 \to 3e^- + \mathrm{Fe}^{3+} \tag{2}$$

$$\mathrm{Fe}^0 \to 2e^- + \mathrm{Fe}^{2+} \tag{3}$$

$$\mathrm{RCl}_{\mathrm{n}} + e^{-} \to \mathrm{RCl}_{\mathrm{n-1}} + \mathrm{Cl}^{-} \tag{4}$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \tag{5}$$

$$O_2 + 2H^+ + 2Fe^0 \to H_2O_2 + Fe^{2+}$$
 (6)

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow OH + H_2O + Fe^{3+}$$
 (7)

$$\mathrm{Fe}^{3+} + e^- \to \mathrm{Fe}^{2+} \tag{8}$$

$$\mathcal{O}_2 + 2e^- \to \mathcal{O}_2^{\cdot -} \tag{9}$$

J. Nanosci. Nanotechnol. 18, 8252-8257, 2018

8256

Zhang et al.

4. CONCLUSIONS

A magnetic composite material consisting of zero-valent iron nano-particles and graphene oxide was synthesized and used as a catalyst for the degradation of trichloroacetic acid (TCAA). The results showed that the zero-valent iron nano-particles were dispersed on graphene oxide and the specific surface area increased. What's more, the GO could serve as a stabilizer to avoid aggregate formation of zero-valent iron nano-particles. Furthermore, NZVI/GO had a good ability to degrade trichloroacetic acid. Trichloroacetic acid was substantially completely degraded within 250 min. The final product of trichloroacetic acid degradation is acetic acid. In addition, we proposed the mechanism of the degradation of TCCA by NZVI/GO composite. It was presumed that Fenton reaction may have occurred to produce hydroxyl radicals (OH) and superoxide radicals (O_2^-) for dechlorination of TCCA. In summary, NZVI/GO composite material as a new catalyst has a good development prospects, need to be further in-depth study.

Acknowledgment: This work was kindly supported by National Natural Science Foundation of China (51508254, 41771341), Nature Science Foundation of Gansu Province of China (1506RJZA216), Opening Project of State Key Laboratory of High Performance Ceramics and Superfine Microstructure (SKL201509SIC), Open fund by Jiangsu Engineering Technology Research Center of Environmental Cleaning Materials (KFK1502), A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) and Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences.

References and Notes

- D. A. Ellis, M. L. Hanson, P. K. Sibley, T. Shahid, N. A. Fineberg, K. R. Solomon, D. C. G. Muir, and S. A. Mabury, *Chemosphere* 42, 309 (2001).
- M. Berg, S. R. Müller, J. Mühlemann, A. Wiedmer, and R. P. Schwarzenbach, *Environ. Sci. Technol.* 34, 2675 (2000).
- 3. M. J. Cardador and M. Gallego, *Environ. Sci. Technol.* 45, 5783 (2011).

- 4. P. Zhang, T. M. Lapara, E. H. Goslan, Y. Xie, S. A. Parsons, and R. M. Hozalski, *Environ. Sci. Technol.* 43, 3169 (2009).
- Y. T. Chen, W. Zhang, A. Hobiny, A. Alsaedi, and X. K. Wang, *Sci. China Chem.* 59, 412 (2016).
- S. J. Yu, J. Wang, S. Song, K. Y. Sun, J. Li, X. X. Wang, Z. S. Chen, and X. K. Wang, *Sci. China Chem.* 60, 415 (2017).
- 7. G. K. Ramesha, A. Vijaya Kumara, H. B. Muralidhara, and S. Sampath, *J. Colloid Interface Sci.* 361, 270 (2011).
- Z. A. Al-Othman, Inamuddin, and M. Naushad, *Chem. Eng. J.* 169, 38 (2011).
- 9. L. Zhou, T. L. Thanh, J. Gong, J. H. Kim, E. J. Kim, and Y. S. Chang, *Chemosphere* 104, 155 (2014).
- H. Ma, Y. P. Huang, M. W. Shen, D. M. Hu, H. Yang, M. F. Zhu, S. P. Yang, and X. Y. Shi, *RSC Adv.* 3, 6455 (2013).
- 11. G. Xu, J. Wang, and M. Lu, Chemosphere 117, 455 (2014).
- H. I. Gomes, C. Dias-Ferreira, L. M. Ottosen, and A. B. Ribeiro, J. Colloid Interface Sci. 433, 189 (2014).
- 13. X. Qiu, Z. Fang, X. Yan, W. Cheng, and K. Lin, *Chem. Eng. J.* 220, 61 (2013).
- 14. F. L. Fu, D. D. Dionysiou, and H. Liu, J. Hazard. Mater. 267, 194 (2014).
- 15. Y. Li, J. Li, and Y. Zhang, J. Hazard. Mater. 227-228, 211 (2012).
- 16. S. J. Tesh and T. B. Scott, Adv. Mater. 26, 6056 (2014).
- 17. M. Onyszko, K. Urbas, M. Aleksandrzak, and E. Mijowska, Pol. J.
- Chem. Technol. 4, 95 (2015). 18. J. Li, C. L. Chen, R. Zhang, and X. K. Wang, Sci. China Chem. 59, 150 (2016).
- 19. S. J. Sun, J. Wang, S. Song, K. Y. Sun, J. Li, X. X. Wang, Z. S. Chen, and X. K. Wang, *Sci. China Chem.* 60, 415 (2017).
- 20. X. Y. Zhang, H. X. Zhang, Y. Y. Xiang, S. B. Hao, Y. Y. Zhang, R. N. Guo, X. W. Cheng, M. Z. Xie, Q. F. Cheng, and B. Li, *J. Hazard. Mater.* 342, 353 (2018).
- **21.7** H. K. Boparai, M. Joseph, and D. M. O'Carroll, *J. Hazard. Mater.* Scie 186, 458 (2011).
- 22. J. T. Nurmi, P. G. Tratnyek, V. Sarathy, D. R. Baer, J. E. Amonette, K. Pecher, C. Wang, J. C. Linehan, D. W. Matson, R. Lee Penn, and M. D. Driessen, *Environ. Sci. Technol.* 39, 1221 (2005).
- 23. Y. C. Zhao, L. J. Huang, Y. X. Wang, J. G. Tang, Y. Wang, J. X. Liu, L. A. Belfiore, and M. J. Kipper, J. Alloys Compd. 687, 95 (2016).
- 24. Z. Mohammadi and M. H. Entezari, Ultrason. Sonochem. 1, 44 (2018).
- **25.** A. A. Karamani, A. P. Douvalis, and C. D. Stalikas, *J. Chromatogr. A* 1271, 1 (**2013**).
- M. Gotić and S. MusićMossbauer, J. Mol. Struct. 834–836, 445 (2007).
- 27. C. Lu, Y. L. Chung, and K. F. Chang, Water Res. 39, 1183 (2005).
- 28. D. Shao, J. Hu, C. Chen, G. Sheng, X. Ren, and X. Wang, J. Phys. Chem. C 114, 21524 (2010).
- 29. Y. B. Sun, C. C. Ding, W. C. Cheng, and X. K. Wang, J. Hazard. Mater. 280, 399 (2014).

Received: 15 December 2017. Accepted: 22 March 2018.