

Enhanced Fenton-like removal of nitrobenzene via internal microelectrolysis in nano zerovalent iron/activated carbon composite

Sihai Hu, Yaoguo Wu, Hairui Yao, Cong Lu and Chengjun Zhang

ABSTRACT

The efficiency of Fenton-like catalysis using nano zerovalent iron (nZVI) is limited by nZVI aggregation and activity loss due to inactive ferric oxide forming on the nZVI surface, which hinders electron transfer. A novel iron-carbon composite catalyst consisting of nZVI and granular activated carbon (GAC), which can undergo internal iron-carbon microelectrolysis spontaneously, was successfully fabricated by the adsorption-reduction method. The catalyst efficiency was evaluated in nitrobenzene (NB) removal via the Fenton-like process (H_2O_2 -nZVI/GAC). The results showed that nZVI/GAC composite was good for dispersing nZVI on the surface of GAC, which permitted much better removal efficiency (93.0%) than nZVI (31.0%) or GAC (20.0%) alone. Moreover, iron leaching decreased from 1.28 to 0.58 mg/L after reaction of 240 min and the oxidation kinetic of the Fenton-like reaction can be described well by the second-order reaction kinetic model ($R^2 = 0.988$). The composite catalyst showed sustainable catalytic ability and GAC performed as a medium for electron transfer in internal iron-carbon microelectrolysis to promote Fe^{2+} regeneration and $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycles. Therefore, this study represents an important method to design a low cost and high efficiency Fenton-like catalyst in practical application.

Key words | enhancement, Fenton-like, microelectrolysis, nitrobenzene, nZVI/GAC composite

Sihai Hu

Yaoguo Wu (corresponding author)

Hairui Yao

Cong Lu

Chengjun Zhang

Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, Department of Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710072, China
E-mail: wuygal@163.com

INTRODUCTION

Nitrobenzene (NB) is deemed a priority control pollutant by the US Environmental Protection Agency (EPA) and other countries due to its high chemical stability, low biodegradability, and high toxicity (Roy *et al.* 2013). To date, a range of chemical and biological methods have been developed for aqueous NB treatment, such as advanced oxidation process (AOPs), microelectrolysis, and biological anaerobic process (Patil *et al.* 2011; Wang *et al.* 2011). As one of the important AOPs, the Fenton reaction has a good prospect for NB treatment because of the advantages of high mineralization efficiency, easy implementation, and cost saving (Bokare & Choi 2014). Recently, nano zerovalent iron (nZVI, Fe^0) has been reported to be more effective in activation of hydrogen peroxide (H_2O_2) to generate hydroxyl radicals ($\cdot\text{OH}$) than classified soluble ferrous ions (Fe^{2+}) in the Fenton-like process (Fu *et al.* 2014). Nevertheless, nZVI as a Fenton-like catalyst is limited because of Fe^{2+} regeneration difficulty and activity loss due to inactive ferric oxides

forming on the nZVI surface. In addition, lack of stability, easy aggregation, and difficult separation from treated solution are problems of nZVI use in actual application (Messele *et al.* 2014).

Activated carbon (AC) as a support has been proved to be effective for increasing dispersion and impeding aggregation of metallic nanoparticles (Xiao *et al.* 2014). Recently, many studies have indicated that an iron-carbon microelectrolysis system can be formed between AC and iron spontaneously when iron (anode) and AC (cathode) particles are mixed and contact with each other (Dou *et al.* 2010; Mackenzie *et al.* 2012; Luo *et al.* 2014). The activity of the Fenton-like reaction enhanced by iron-carbon microelectrolysis to remove dyes (Yao *et al.* 2013; Singh *et al.* 2014; Sun *et al.* 2014), trichloroethylene (Su *et al.* 2013), ionic liquids (Zhou *et al.* 2013), Cr(VI) (Wu *et al.* 2013), etc. have been investigated through combining Fe^0 or common iron powder with AC. These results revealed that catalytic

oxidation efficiency of the Fenton-like catalyst was significantly intensified when carbon was involved in the catalyst. This phenomenon can be explained by the internal iron-carbon microelectrolysis effect that exists in such an iron-AC combination system where AC acts as a migration medium for electrons, accelerating *in situ* regeneration of Fe^{2+} (Su *et al.* 2013; Singh *et al.* 2014; Sun *et al.* 2014). Thus, the fast cycle of Fe^{3+} and Fe^{2+} on AC surface will provide continuous Fe^{2+} to catalyze H_2O_2 to generate active $\cdot\text{OH}$, which is a great potential advantage for practical NB wastewater treatment. In addition, it has been confirmed that AC is a good Fenton catalyst for NB degradation (Tan *et al.* 2013).

As far as we know, the Fenton-like catalysis using a composite of nZVI and AC for NB removal has not been investigated up to now. Moreover, AC is often used in the form of granular activated carbon (GAC), which is the most widely used adsorbent for water treatment. Therefore, nZVI/GAC composite was prepared by adsorption-liquid phase reduction, and its performance for NB removal from aqueous solution was evaluated by the Fenton-like system (H_2O_2 -nZVI/GAC), with the aim of exploring a novel heterogeneous Fenton-like catalyst for refractory organic wastewater treatment in a cost-effective way.

MATERIALS AND METHODS

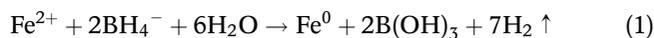
Materials

GAC derived from biomass was purchased from Gongyi Tongxin Water Treatment Material Co., Ltd (Henan, China). Before use, the GAC was soaked in 1 M HNO_3 for 24 h followed by repeated rinsing with deionized water (resistance > 18 M Ω) and then dried at 105 °C. Other reagents used in this study were purchased from the Xi'an Chemical Corporation (Xi'an, China) and were of analytical grade.

Preparation of nZVI/GAC composite

The composite of nZVI/GAC was prepared by adsorption-liquid phase reduction method according to Xiao *et al.* (2014). Briefly, 1.0 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 5.0 g of GAC were mixed in 200 mL of degassed deionized water. The mixture was treated with ultrasound for 15 min, and then stirred vigorously at ambient temperature for over 12 h to achieve GAC saturated adsorption of Fe^{2+} . The slurry was diluted five times with a mixture of ethanol and deionized water (1:1 v/v). To ensure complete reduction of Fe^{2+} ,

25 mL of 1 M NaBH_4 solution was added at 30 drops/min while stirring. The reduction reaction is as follows:



After reduction, the black solids were separated from the solution using a vacuum filtration flask (0.45 μm membrane filter) and washed several times with degassed deionized water to remove residual sulfate, then vacuum-dried at 60 °C and stored in a N_2 -purged desiccator. Unsupported nZVI particles were also prepared in a similar way without GAC, and in all syntheses, N_2 was bubbled into solution during the entire process to maintain an inert atmosphere. The nZVI loaded amount on GAC was 64.3 $\mu\text{mol/g}$ calculated according to the procedure reported by Zhu *et al.* (2009).

Batch experiments

The model wastewater was prepared by dissolving NB (>99%) in deionized water with final concentration of 40 mg/L. Then, 200 mL of wastewater was placed in a 250-mL brown flask and pH values were adjusted to 3.0, 4.0, and 5.0 with 1 M H_2SO_4 . The dosages of 0.2, 0.4, and 0.6 g/L nZVI/GAC and 2.5, 5.0, and 10.0 mmol/L H_2O_2 solutions were added according to the designed Fe^{2+} and H_2O_2 molar ratio, and the initial dissolved oxygen of the mixed solution was 7.24 mg/L. The flask was capped and stirred on a thermostatic magnetic stirrer at 300 rpm with temperature of 25 °C and sampled regularly with intervening time of 15 or 30 min. The dosages of bare nZVI and GAC were equivalent to that in the nZVI/GAC composite, which were determined by nZVI loading in the composite. All experiments were conducted in triplicate and analysis showed that relative errors were lower than $\pm 5\%$.

Analysis

Scanning electron microscopy (SEM) (Vega 3 LMH, Tescan, Czech) was used to view the morphology and surface characteristics of nZVI/GAC composite. The NB concentrations were determined using a high-performance liquid chromatograph equipped with a Waters symmetry C-18 column (150 mm \times 4.6 mm i.d., 5 μm). The mobile phase was a mixture of methanol and 5 mM H_3PO_4 in the ratio of 3:2 (v/v) (isocratic). The flow rate was set at 1 mL/min and detection wavelength was set to 267.5 nm, and the column temperature was maintained at 25 °C. The samples were filtered through

0.45 μm filters and then 20 μL was injected manually through an injection port. All the prepared samples were taken for analysis immediately.

RESULTS AND DISCUSSION

The morphology of nZVI/GAC composite

Figure 1(a) shows that GAC had an abundance of pores which could provide a good possibility for nZVI particles to be trapped inside. Figure 1(b) implies that, in the absence of GAC, iron particles were found to agglomerate and link as chains due to the large surface energy of nanoparticles. In comparison, as is revealed in Figure 1(c), iron particles were well dispersed on the surface or pores of GAC carrier without aggregation, and the particles size were 40–100 nm by comparison with a standard ruler. The SEM images confirmed the presence of both iron and GAC in the composite, and the iron particles were uniformly dispersed over the GAC matrix with a nanometre scale. Therefore, nZVI particles are able to distribute over GAC at nanoscale. Moreover, the results also demonstrate that GAC is a good carrier of nano-iron and has capability to prevent nano-iron particles from aggregating together to form chains. Hence, the good dispersion of nZVI will enlarge its surface area providing a better catalysis for H_2O_2 to generate active $\cdot\text{OH}$ to enhance the Fenton-like effect.

Enhancement of nZVI/GAC composite as Fenton-like catalyst for NB removal

To compare the enhancement of nZVI/GAC, control experiments were conducted using nZVI and GAC individually with the same amount as in nZVI/GAC composite. As

shown in Figure 2(a), the best removal effect was achieved for nZVI/GAC composite as Fenton-like catalyst. With an initial NB concentration of 40 mg/L, the removal ratio is 93.0%, 31.0% and 20.0% at 240 min for the composite, nZVI and GAC respectively. Obviously, the degradation rate is higher for the composite than for GAC or nZVI and higher than the sum of them as well. Also, the experimental results reveal that the catalytic activity for H_2O_2 decomposition of nZVI mainly occurred within 30 min; however, by comparison, when nZVI/GAC acted as a catalyst, NB still could be removed after 60 min, illustrating that the catalytic durability and stability of nZVI were improved dramatically after combination with GAC. This phenomenon strongly suggests that NB removal is enhanced with GAC involvement, and the combination of GAC and nZVI is excellent for the Fenton-like process because of synergetic effects existing in this composite, which is confirmed by the result that the removal ratio for the composite was higher than the total of GAC and nZVI individually.

The enhancement of NB degradation by the Fenton-like catalyst can be attributed to the involvement of GAC, making it possible for nZVI and GAC to spontaneously form an iron-carbon microelectrolysis system. In this case, the regeneration rate of Fe^{2+} can be speeded up via Fe^{3+} reacting with Fe^0 on the surface or in the pores of nZVI/GAC composite (Equation (2)), which intensified $\cdot\text{OH}$ formation (Equation (3)). Therefore, GAC as a medium for electron transfer accelerates the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle, and iron utilization efficiency is improved and iron leaching is reduced as well.

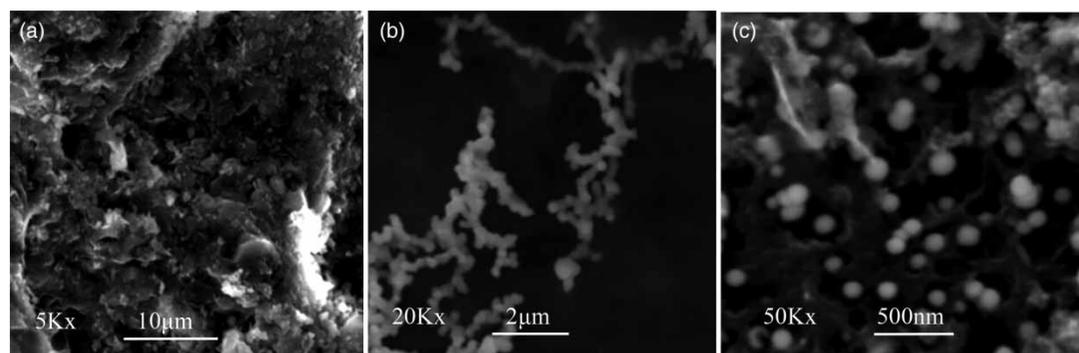
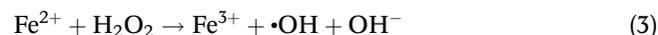


Figure 1 | The morphology of GAC (a), nZVI (b) and nZVI/GAC composite (c).

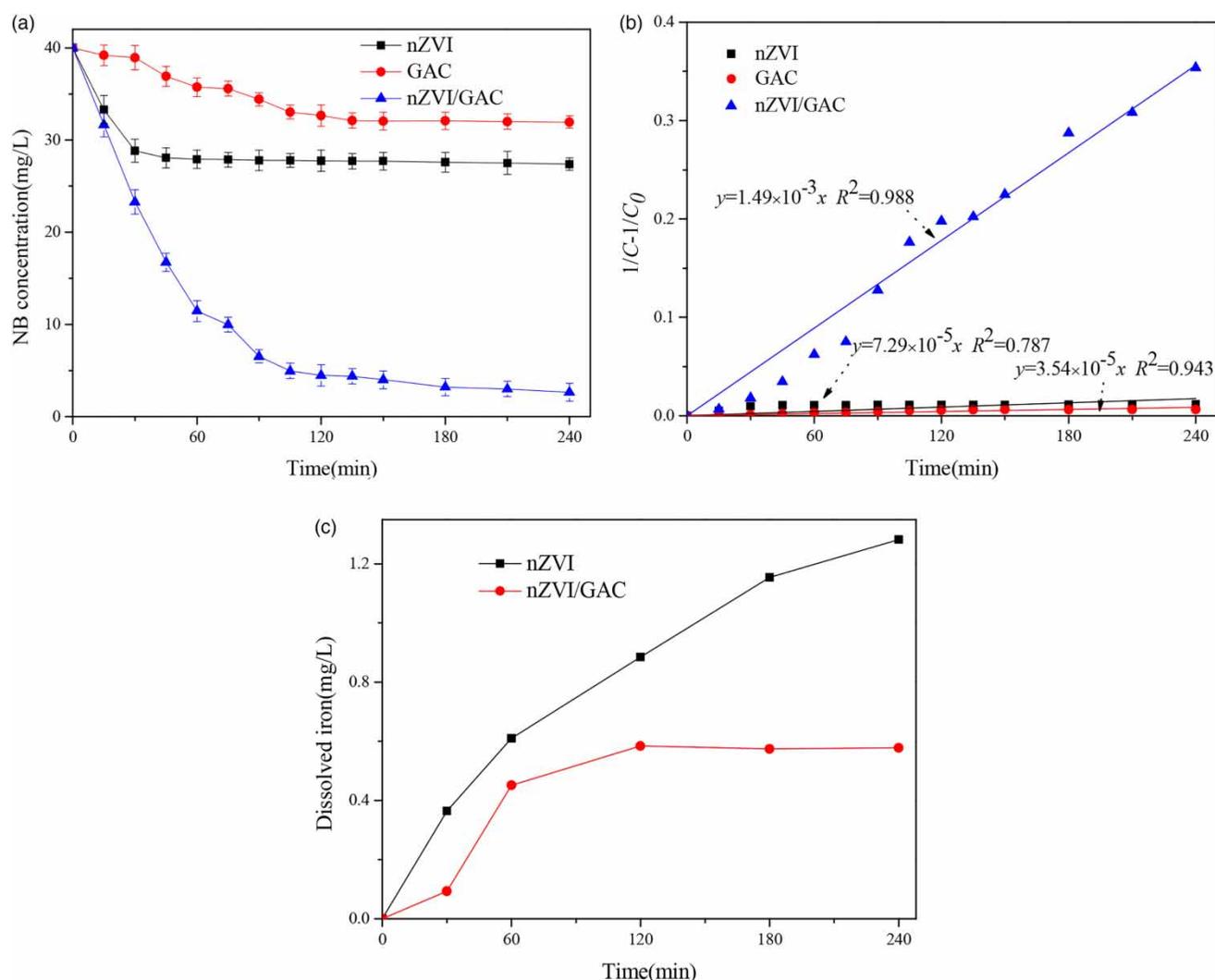


Figure 2 | The concentration change of NB (a), degradation kinetics (b) and dissolved iron (c) with reaction time.

The Fenton-like reaction can be described as a pseudo-second-order reaction with respect to NB concentration as given in Equation (4):

$$v = -dc/dt = k_{obs}c^2 \quad (4)$$

where v is the reaction rate, c and t are NB concentration of reaction process and reaction time respectively, and k_{obs} is the observed second-order reaction rate constant, which is the slope of the regression lines obtained by plotting a linear regression graph with respect to NB concentration and reaction time according to Equation (5):

$$1/c - 1/c_0 = k_{obs}t \quad (5)$$

where c_0 is equal to initial NB concentration. The relationship between $1/c$ and reaction time is presented in

Figure 2(b). A linear regression of the first-order kinetic Equation (5) is performed for each group of data. The k_{obs} values are $7.29 \times 10^{-5} \text{ mg}^{-1} \text{ L min}^{-1}$, $3.54 \times 10^{-5} \text{ mg}^{-1} \text{ L min}^{-1}$, and $1.49 \times 10^{-3} \text{ mg}^{-1} \text{ L min}^{-1}$ for nZVI, GAC, and nZVI/GAC composite respectively. Compared to nZVI or GAC individually, k_{obs} prominently increased for nZVI/GAC. The difference between k_{obs} for nZVI and nZVI/GAC composite means that k_{obs} is significantly affected by the kind of catalysts. Moreover, the data for nZVI/GAC composite fits to the nonlinear model well ($R^2 = 0.988$), which provides strong evidence that the removal by the composite is the pseudo-second-order reaction.

Furthermore, dissolved iron was monitored for both nZVI and nZVI/GAC composite as a Fenton-like catalyst (Figure 2(c)). For the composite, dissolved iron was $<0.6 \text{ mg/L}$; by comparison with nZVI, the amount was

reduced to half (from 1.28 to 0.58 mg/L) (Figure 2(c)), indicating that iron utilization efficiency was obviously raised and iron leaching was reduced because of the high adsorption capacity of GAC in the Fenton-like reaction.

Effect of nZVI/GAC composite dosages on Fenton-like NB removal

Studies have shown that an extreme dosage of iron can contribute to significant improvement in NB removal efficiency by the Fenton-like reaction (Bokare & Choi 2014); however, it can easily cause an obvious increase in iron leaching and iron sludge simultaneously (Segura *et al.* 2013). Thus, excessive iron dosage tends to need a further treatment for the effluent before its discharge into water (Gogate & Pandit 2004). As demonstrated in Figure 3(a), NB degradation efficiency increased with the catalyst dosage up to 0.4 g/L, but then slightly decreased upon further addition of the catalyst; correspondingly, the k_{obs} increased from 8.36×10^{-4} to $1.66 \times 10^{-3} \text{ mg}^{-1} \text{ L min}^{-1}$ and then decreased to $1.33 \times 10^{-4} \text{ mg}^{-1} \text{ L min}^{-1}$ as shown in Figure 3(b). The fairly good removal efficiency was achieved when the catalyst dosage was 0.4 g/L under the experimental conditions, and degradation kinetics could be well described using the pseudo-second-order reaction ($R^2 = 0.95$).

It has been reported that an excess of ferrous ions will consume $\cdot\text{OH}$; for this reason, in this experiment no improvements have been attained when nZVI/GAC dosage was increased to 0.6 g/L at H_2O_2 concentration of 2.5 mmol/L (Figure 3). The same phenomenon was reported

by Liao *et al.* (2009) as well. The inhibition effect of iron species is considered as the reason for this decrease because the scavenging of $\cdot\text{OH}$ or other radicals will occur when excessive metal species exist, which can be expressed by the following equations.



Effect of hydrogen peroxide concentrations on Fenton-like NB removal

The effect of initial H_2O_2 concentrations on the Fenton-like reaction catalyzed by nZVI/GAC composite was observed by varying H_2O_2 concentration from 2.5 to 10.0 mmol/L, and the results are presented in Figure 4.

As shown in Figure 4, the concentration of NB decreased with reaction time and removal efficiency significantly increased when H_2O_2 concentration increased from 2.5 to 5.0 mmol/L, but decreased for further increase to 10.0 mmol/L. The k_{obs} was $8.36 \times 10^{-4} \text{ mg}^{-1} \text{ L min}^{-1}$, $2.49 \times 10^{-3} \text{ mg}^{-1} \text{ L min}^{-1}$ and $1.91 \times 10^{-3} \text{ mg}^{-1} \text{ L min}^{-1}$, respectively (Figure 4(b)), whereas correlation coefficient (0.88) slightly decreased for H_2O_2 concentration of 5.0 mmol/L. This means that H_2O_2 dosage affects the kinetics of the Fenton-like process markedly and the enhancement to NB removal is related to $\cdot\text{OH}$ yield. However, it should be pointed out that the oxidation rate decreased when the concentration of H_2O_2 exceeded 5.0 mmol/L (Figure 4(b)). This can be explained by the

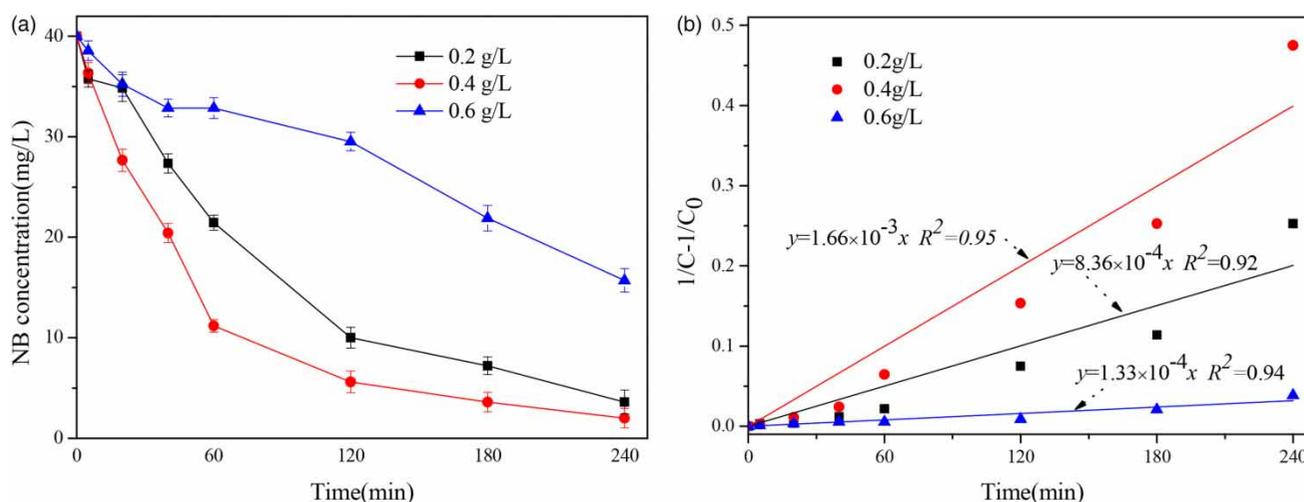


Figure 3 | The effects of nZVI/GAC composite dosage on Fenton-like NB removal (a) and degradation kinetics (b).

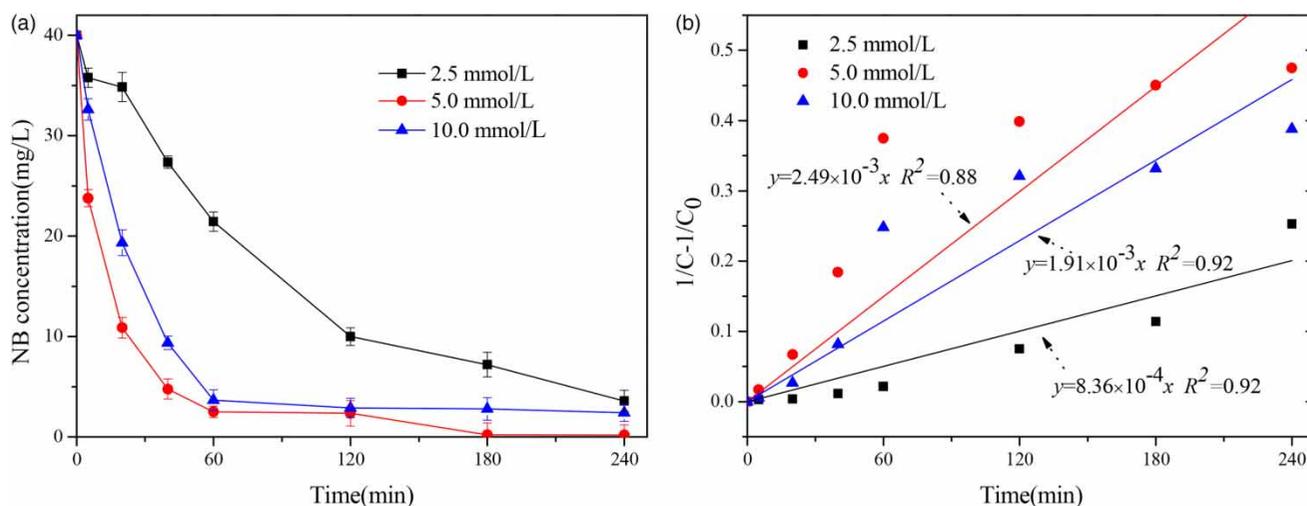


Figure 4 | The effect of H₂O₂ concentration on Fenton-like NB removal (a) and degradation kinetics (b).

scavenging of •OH at a higher H₂O₂ dosage, leading to a decrease in the number of •OH in the solutions (Chen *et al.* 2009).



Effect of initial pH values on Fenton-like NB removal

According to previous research, pH value is an important reaction parameter affecting Fenton removal of NB

(Bokare & Choi 2014). An optimum working pH range is 2.8–3.2 for classical Fenton reaction, and widening the pH range is required for practical application (Bokare & Choi 2014; Fu *et al.* 2014). Thus, typical experiments at pH 3.0, 4.0 and 5.0 were carried out individually to check the extent of Fenton-like removal efficiency with nZVI/GAC composite as the catalyst.

The obtained results showed that for all pH values tested, NB concentration decreased with reaction time (Figure 5(a)). The k_{obs} values of the Fenton-like reaction increased from 1.4×10^{-3} to $2.28 \times 10^{-3} \text{ mg}^{-1} \text{ L min}^{-1}$ for pH increase from 3.0 to 4.0, but then decreased to $1.7 \times 10^{-3} \text{ mg}^{-1} \text{ L min}^{-1}$ when pH increased to 5.0 (Figure 5(a)), and for all pHs, the Fenton-like oxidation could be well described

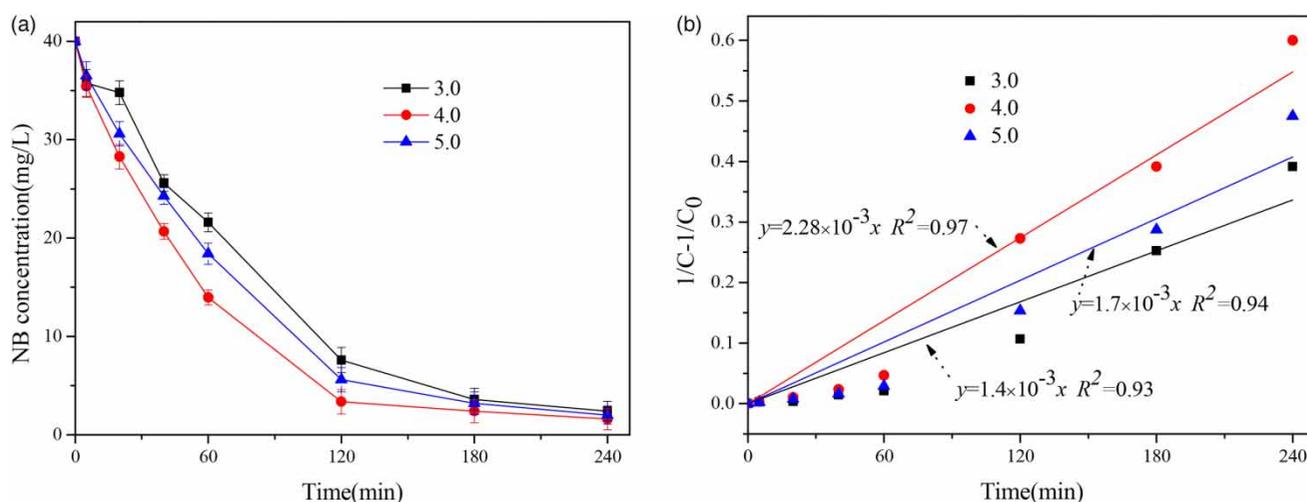


Figure 5 | The effect of initial pH on Fenton-like NB removal (a) and degradation kinetics (b).

using the second-order kinetics model. These observations are consistent with previously reported results (Yao et al. 2013; Thankappan et al. 2015). Obviously, the nZVI/GAC catalyst has been active in the investigated pH of between 3.0 and 5.0. For example, at pH 3.0, 4.0 and 5.0, 81.0%, 91.6%, and 86.0% of NB was degraded by nZVI/GAC composite catalyst respectively after 120 min of reaction.

Figure 5 also implies that the best degradation of NB was attained at pH 4.0 and the composite will still have activity at pH over 4.0. This conclusion was remarkably well supported by the result that NB removal ratio was 86.0% at pH 5.0. This is an important advantage because it is well known that one major drawback of the homogeneous Fenton process is the narrow pH range (pH < 3.0) (Pignatello et al. 2006), because such a narrow pH range is unfavorable in practice due to the costs of acidification during processing and neutralization after treatment. The possible mechanisms are that, with the involvement of GAC, Fenton oxidation occurs mostly on the interface of the nZVI/GAC composite, and continuous regeneration of Fe^{2+} is accelerated by internal microelectrolysis, and thus, inactive ferric oxide formation is reduced, mitigating the pH-limited reaction of conventional Fenton, and it may be feasible to use a wider pH range above pH 5.0. For these reasons, further experiments will be carried out at pH over 5.0 using the promising composite catalyst for refractory organic degradation.

CONCLUSIONS

The involvement of GAC greatly improved the dispersion of nZVI and dramatically intensified NB removal with nZVI/GAC composite as Fenton-like catalyst. NB removal efficiency increased from 31.0% for nZVI alone to 93.0% for nZVI/GAC composite after reaction of 240 min, and dissolved iron decreased from >1.2 mg/L to <0.6 mg/L. Not only was the Fenton-like catalysis using nZVI/GAC composite a good combination of adsorption by GAC and Fenton oxidation by nZVI, but also some synergetic effects existed in such a composite, because GAC in the composite performed as an electron transfer medium for internal iron-carbon microelectrolysis to enhance $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycles. Therefore, although used in limited pH range, this novel composite represents an important step in the development of new inexpensive and efficient materials to remove refractory organics by the Fenton-like method, and of course the mechanism and influencing factors need to be thoroughly researched in further studies.

ACKNOWLEDGEMENTS

The project was financially supported by the National Natural Science Foundation of China (Grant No. 40872164, 41502240), fund for basic research from the Northwestern Polytechnical University (No. JCY20130145), China geological survey project (12120114056201), and graduate starting seed fund of Northwestern Polytechnical University (Z2015147).

REFERENCES

- Bokare, A. D. & Choi, W. 2014 Review of iron-free Fenton-like systems for activating H_2O_2 in advanced oxidation processes. *J. Hazard. Mater.* **275**, 121–135.
- Chen, Q. Q., Wu, P. X., Li, Y. Y., Zhu, N. W. & Dang, Z. 2009 Heterogeneous photo-Fenton photodegradation of reactive brilliant orange X-GN over iron-pillared montmorillonite under visible irradiation. *J. Hazard. Mater.* **168**, 901–908.
- Dou, X. M., Li, R., Zhao, B. & Liang, W. Y. 2010 Arsenate removal from water by zero-valent iron/activated carbon galvanic couples. *J. Hazard. Mater.* **182**, 108–114.
- Fu, F. L., Dionysiou, D. D. & Liu, H. 2014 The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. *J. Hazard. Mater.* **267**, 194–205.
- Gogate, P. R. & Pandit, A. B. 2004 A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. *Adv. Environ. Res.* **8**, 501–551.
- Liao, Q., Sun, J. & Gao, L. 2009 Degradation of phenol by heterogeneous Fenton reaction using multi-walled carbon nanotube supported Fe_2O_3 catalysts. *Colloid Surf. A: Physicochem. Eng. Asp.* **345**, 95–100.
- Luo, J. H., Song, G. Y., Liu, J. Y., Qian, G. G. & Xu, Z. P. 2014 Mechanism of enhanced nitrate reduction via microelectrolysis at the powdered zero-valent iron/activated carbon interface. *J. Colloid Interf. Sci.* **435**, 21–25.
- Mackenzie, K., Bleyl, S., Georgi, A. & Kopinke, F. D. 2012 Carbo-iron – an Fe/AC composite – as alternative to nano-iron for groundwater treatment. *Water Res.* **46**, 3817–3826.
- Messele, S. A., Soares, O. S. G. P., Órfão, J. J. M., Stüber, F., Bengoa, C., Fortuny, A., Fabregat, A. & Font, J. 2014 Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol. *Appl. Catal. B: Environ.* **154–155**, 329–338.
- Patil, D. V., Rallapalli, P. B. S., Dangi, G. P., Tayade, R. J., Somani, R. S. & Bajaj, H. C. 2011 MIL-53(Al): an efficient adsorbent for the removal of nitrobenzene from aqueous solutions. *Ind. Eng. Chem. Res.* **50**, 10516–10524.
- Pignatello, J. J., Oliveros, E. & MacKay, A. 2006 Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit. Rev. Environ. Sci. Technol.* **36**, 1–84.
- Roy, P., Periasamy, A. P., Liang, C. T. & Chang, H. T. 2013 Synthesis of graphene-ZnO-Au nanocomposites for efficient

- photocatalytic reduction of nitrobenzene. *Environ. Sci. Technol.* **47**, 6688–6695.
- Segura, Y., Martínez, F. & Melero, J. A. 2013 Effective pharmaceutical wastewater degradation by Fenton oxidation with zero-valent iron. *Appl. Catal. B: Environ.* **136–137**, 64–69.
- Singh, P., Raizada, P., Kumari, S., Kumar, A., Pathania, D. & Thakur, P. 2014 Solar-Fenton removal of malachite green with novel Fe⁰-activated carbon nanocomposite. *Appl. Catal. A: Gen.* **476**, 9–18.
- Su, Y. F., Cheng, Y. L. & Shih, Y. H. 2013 Removal of trichloroethylene by zero valent iron/activated carbon derived from agricultural wastes. *J. Environ. Manage.* **129**, 361–366.
- Sun, L. J., Yao, Y. Y., Wang, L., Mao, Y. J., Huang, Z. F., Yao, D. C., Lu, W. Y. & Chen, W. X. 2014 Efficient removal of dyes using activated carbon fibers coupled with 8-hydroxyquinoline ferric as a reusable Fenton-like catalyst. *Chem. Eng. J.* **240**, 413–419.
- Tan, D., Zeng, H. H., Liu, J., Yu, X. Z., Liang, Y. P. & Lu, L. J. 2013 Degradation kinetics and mechanism of trace nitrobenzene by granular activated carbon enhanced microwave/hydrogen peroxide system. *J. Environ. Sci.* **25**, 1492–1499.
- Thankappan, R., Nguyen, T. V., Srinivasan, S. V., Vigneswaran, S., Kandasamy, J. & Loganathan, P. 2015 Removal of leather tanning agent syntan from aqueous solution using Fenton oxidation followed by GAC adsorption. *J. Ind. Eng. Chem.* **21**, 483–488.
- Wang, A. J., Cheng, H. Y., Liang, B., Ren, N. Q., Cui, D., Lin, N., Kim, B. H. & Rabaey, K. 2011 Efficient reduction of nitrobenzene to aniline with a biocatalyzed cathode. *Environ. Sci. Technol.* **45**, 10186–10193.
- Wu, L. M., Liao, L. B., Lv, G. C., Qin, F. X., He, Y. J. & Wang, X. Y. 2013 Micro-electrolysis of Cr(VI) in the nanoscale zero-valent iron loaded activated carbon. *J. Hazard. Mater.* **254–255**, 277–283.
- Xiao, J. N., Yue, Q. Y., Gao, B. Y., Sun, Y. Y., Kong, J. J., Gao, Y., Li, Q. & Wang, Y. 2014 Performance of activated carbon/nanoscale zero-valent iron for removal of trihalomethanes (THMs) at infinitesimal concentration in drinking water. *Chem. Eng. J.* **253**, 63–72.
- Yao, Y. Y., Wang, L., Sun, L. J., Zhu, S., Huang, Z. F., Mao, Y. J., Lu, W. Y. & Chen, W. X. 2013 Efficient removal of dyes using heterogeneous Fenton catalysts based on activated carbon fibers with enhanced activity. *Chem. Eng. Sci.* **101**, 424–431.
- Zhou, H. M., Lv, P., Shen, Y. Y., Wang, J. J. & Fan, J. 2013 Identification of degradation products of ionic liquids in an ultrasound assisted zero-valent iron activated carbon microelectrolysis system and their degradation mechanism. *Water Res.* **47**, 3514–3522.
- Zhu, H. J., Jia, Y. F., Wu, X. & Wang, H. 2009 Removal of arsenic from water by supported nano zero-valent iron on activated carbon. *J. Hazard. Mater.* **172**, 1591–1596.

First received 11 April 2015; accepted in revised form 28 August 2015. Available online 15 September 2015