Removal of methylene blue from water by magnetic Fe^0/Fe_3O_4/graphene composites

Shan Chong[a], Ting Huang[b], Guangming Zhang[b,c],*, Jianbin Guo[d], Xueyan Li[e]

[a]*State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology(Beijing), Beijing 100083, China, email: 396185870@qq.com*
[b]*School of Environment & Natural Resource, Renmin University of China, Beijing 100872, China, email: jason_huangting@163.com (T. Huang)*
[c]*School of Energy & Environmental Engineering, Hebei Institute of Technology, Tianjin, 300401, China, Tel. +86 10 82502680; email: zgm@ruc.edu.cn (G. Zhang)*
[d]*School of Soil and Water Conservation, Beijing Forestry University, Beijing, 100083, China, email: jianbinguo@bjfu.edu.cn*
[e]*School of Environmental Science & Engineering, Suzhou University of Science and Technology, Suzhou 215009, China, email: lxyhit@sina.com*

ABSTRACT

A magnetic Fe^0/Fe_3O_4/graphene was prepared and used to remove methylene blue, a typical dye, from water. The feasibility study on removal efficiency of methylene blue was carried by graphene, Fe^0, Fe_3O_4 and Fe^0/Fe_3O_4/graphene separately. Results showed that excellent synergetic effect among Fe^0, Fe_3O_4 and graphene existed in the composite. The composite could remove methylene blue in neutral pH conditions and 91.6% methylene blue was removed within 20 min at Fe^0/Fe_3O_4/graphene dosage of 1.0 g/L and initial concentration of 50 mg/L. 50% TOC removal efficiency of methylene blue after reaction was achieved, showing that chemical degradation occurred. The concentration of dissolved Fe was less than 2 mg/L, which was much less than the amount of Fe in Fe^0/Fe_3O_4/graphene, showing an excellent chemical stability. In order to study the surface morphology and phase composition of the composite, BET, XRD and SEM analyses were performed. The results showed that the composite was not simply a mixture of Fe, Fe_3O_4 and graphene, but was a composite with stable structure and large specific surface area (45 m^2/g). A potential mechanism involving microstructure of the composite and reaction behavior was proposed based on the experimental results.

Keywords: Fe^0/Fe_3O_4/graphene; Methylene blue; Removal; Reduction

1. Introduction

Dye wastewater pollution has been a critical issue in recent years due to the massive production and applications [1,2]. Methylene blue is one of the most commonly used dyes in various industries such as textile, leather, paper, pharmaceutical and food industries [3]. Methylene blue is a cationic dye with great stability and higher toxicity over anionic dyes [4]. It may cause burns to the eyes of human and animals, nausea and mental confusion [5]. Thus, the effluents pose a potential threat to environment and human health due to their toxicity and carcinogenic effects. Traditional biological, physical, and chemical methods are available for the removal of methylene blue [6–8]. However, they have limited effect and commonly lead to high cost and accumulation of sludge, which further leads to secondary pollution. Therefore, it is important to develop an efficient, energy-saving and inexpensive dye wastewater treatment process.

* Corresponding author.

The application of zero valent iron (Fe^0) has attracted wide attentions for pollutants removal due to low cost, low toxicity and abundance of raw materials [9–11]. However, the drawback of strong aggregation tendency for Fe^0 under environmental conditions limits its application in wastewater treatment [12]. To address this issue, some studies use different kinds of support materials to disperse Fe^0 particles, such as kaolinite, gel beads and graphene [13–16]. Chen et al. [17] investigated the multifunctional kaolinite-supported nanoscale zero-valent iron used for the adsorption and degradation of crystal violet in aqueous solution; 97.23% of crystal violet was removed after 30 min and the removal mechanism was proposed involving adsorption of crystal violet to the material phase and reduction of crystal violet by Fe^0 in composite. The modification of Fe^0 has an excellent performance in dyes removal in water. However, Fe^0 may easily agglomerate in water.

Loading Fe^0 on graphene will not only prevent the agglomeration of Fe^0 but also provide good adsorption ability. Moreover, Fe_3O_4 can be easily separated from water with an external magnetic field due to its super-paramagnetic property. The reaction activity of Fe^0 can be affected in the weak magnetic field environment due to its ferromagnetic characteristic and the reducibility of Fe^0 can be better demonstrated due to the uniform dispersion in the composite. Therefore, the combination of Fe^0, graphene and Fe_3O_4 can keep the features of high reduction ability, anti-aggregation performance and magnetic property, which will be an efficient and green material in wastewater treatment. In the previous study, we synthesized Fe^0/Fe_3O_4/graphene by a one-step method [18], the composite had a layered structure with Fe crystals highly dispersed in the inter-layers of graphene, and could be easily separated and re-dispersed for reuse. The composite was applied in dye wastewater treatment and showed good decolorization of multiple dyes.

This paper studied in details the degradation process and the reaction mechanism of methylene blue removal by Fe^0/Fe_3O_4/graphene composite. The effects of Fe^0/Fe_3O_4/graphene dosage and initial concentration of methylene blue were investigated. TOC changes were analyzed to evaluate the degree of mineralization of methylene blue. H_2O_2 addition was performed to analyze the main role of Fe^0/Fe_3O_4/graphene. The chemical stability of Fe^0/Fe_3O_4/graphene in removal of methylene blue was also evaluated.

2. Materials and methods

2.1. Materials

Expandable graphite was purchased from Qingdao Taine (China). Methylene blue ($C_{16}H_{24}ClN_3O_3S$) was purchased from Sinopharm (China). $FeCl_3·6H_2O$, $FeSO_4·7H_2O$, $KMnO_4$, $NaNO_3$, $NaBH_4$, NaOH were obtained from Xilong (China). H_2O_2 (30%), $NH_3·H_2O$ (28%), HCl (37%), H_2SO_4 (98%) were supplied by Beijing Chemical (China). N_2 gas was obtained from Beijing Aolin (China).

2.2. Preparation of Fe^0/Fe_3O_4/graphene composite

Fe^0/Fe_3O_4/graphene was synthesized by a one-step reduction method as in earlier study [18]. The graphene oxide was prepared first following a hydrothermal method [19]. $FeCl_3·6H_2O$ and $FeSO_4·7H_2O$ were mixed with graphene oxide in solution under N_2 purging. A stoichiometric amount of $NH_3·H_2O$ was added to form Fe_3O_4/graphene oxide. Then, $FeSO_4·7H_2O$ solution was mixed with the fresh Fe_3O_4/graphene oxide in solution. A stoichiometric amount of $NaBH_4$ was added dropwise to form Fe^0/Fe_3O_4/graphene. After washing for several times until neutral pH, Fe^0/Fe_3O_4/graphene was separated by a magnet and dried in vacuum oven at 50°C for 24 h.

2.3. Characterization of Fe^0/Fe_3O_4/graphene

Specific surface area and pore volume of samples were measured by BeiShiDe 3H-2000PS2 analysis instrument. The surface morphology of samples was determined by Hitachi S 4700 scanning electron microscope analyzer. (Hitachi High-Technologies Corporation, Japan). X-ray diffraction (XRD) peak was investigated by Rigaku D/max-rc diffractometer (Rigaku Corporation, Japan).

2.4. Experiments

The experiments were conducted as follows: the methylene blue solutions were first adjusted to the desired pH with NaOH and H_2SO_4 dilute solution. Then, a certain dose of Fe^0/Fe_3O_4/graphene was quickly introduced into the solution. Subsequently, the mixed solution was stirred continuously with an electronic stirrer. 1.0 mL of the sample was taken at set interval and filtrated with a 0.45 μm membrane filter. The obtained clear sample was analyzed immediately with UV spectrometer. Control experiments were also performed under the same conditions.

Determination of methylene blue was performed by a Shimadzu UV2500 spectrometer and the λ_{max} of methylene blue was 664 nm (Shimadzu Corporation, Japan). The leached Fe ions were measured by graphite furnace atomic absorption spectrometric method with a Hitachi Z-2000 atomic absorption spectrophotometer (AAS) using iron lamp as light resource. TOC was measured by M5301C total organic carbon analyzer.

3. Results and discussion

3.1. Characterization

3.1.1. BET

The powder of Fe^0/Fe_3O_4/graphene was detected by Brunauer−Emmett−Teller (BET) measurements. The specific surface area of the Fe^0/Fe_3O_4/graphene powder before use was 45.1455 m²/g, pore volume was 0.0934 mL/g and the aperture was 8.28 nm. Compared with the specific surface area of pure Fe^0 (35.16 m²/g) and Fe_3O_4 (28.9 m²/g) according to the literature [13,20], the specific surface area of the Fe^0/Fe_3O_4/graphene powder was 45.1455 m²/g, which was higher than both pure Fe^0 and Fe_3O_4. After use, the specific surface area of Fe^0/Fe_3O_4/graphene decreased to 8.0479 m²/g after reaction of Fe^0/Fe_3O_4/graphene and methylene blue. The pore volume of Fe^0/Fe_3O_4/graphene increased nearly doubled from 0.0934 to 0.162 mL/g and the aperture had more than doubled from 8.28 to 17.47 nm after use. The significant difference indicated

that chemical reactions occurred on the surface and inside of Fe^0/Fe_3O_4/graphene composite. The solid iron of Fe^0 and Fe_3O_4 in Fe^0/Fe_3O_4/graphene changed to soluble Fe^{2+} and Fe^{3+} in the reaction process. The dissolution of iron led to the increase of pore volume and aperture in Fe^0/Fe_3O_4/graphene.

3.1.2. X-ray diffraction

XRD characterization is an important means to study the phase composition of materials. In this study, we compared the XRD peaks of Fe^0/Fe_3O_4/graphene with graphene, Fe^0, Fe^0/Fe_3O_4, Fe^0/graphene and Fe_3O_4/graphene, respectively. The spectra are shown in Fig. 1. Clearly, the composite was different from all above compounds and not a mere mixture of these compounds. Comparing with literature, the composite was a little different from Fe_3O_4 [21,22]. As shown in Fig. 1, the peaks of Fe^0/Fe_3O_4/graphene were closer to the diffraction peaks of Fe_3O_4/graphene, and the peak strength of Fe^0 was relatively weak, mainly because Fe^0 did not occupy a high proportion in the composite.

3.1.3. SEM

The SEM images of GO, Fe^0/GO, Fe_3O_4/GO and Fe^0/Fe_3O_4/GO are shown in Fig. 2. Graphene oxide (GO) displayed a layer structure with smooth surface. Fe particles tended to aggregate rather than uniformly distributed when Fe^0 and Fe_3O_4 were loaded on GO, respectively. On the other hand, Fe^0 and Fe_3O_4 particles in Fe^0/Fe_3O_4/GO were distributed evenly in the layered structure of GO, avoiding the agglomeration of iron and ferric oxygen particles due to their magnetic properties.
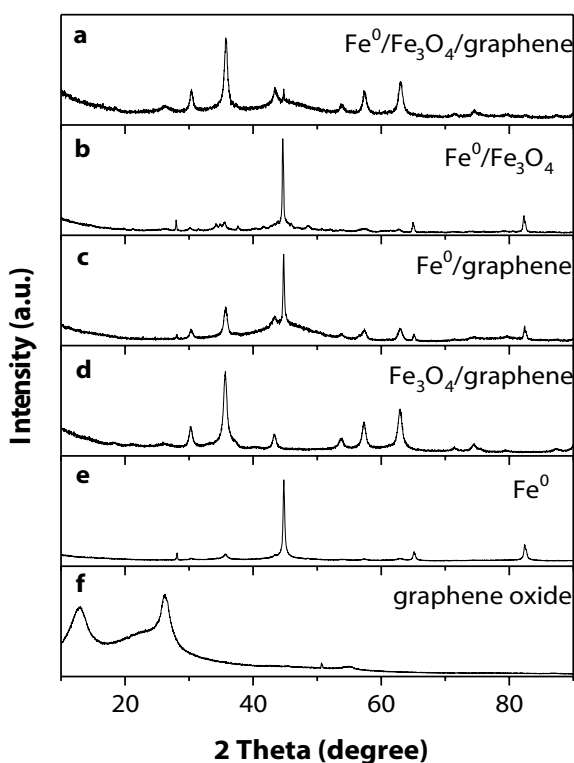

Fig. 1. XRD peaks of graphene, Fe^0, Fe^0/Fe_3O_4, Fe^0/graphene, Fe_3O_4/graphene and Fe^0/Fe_3O_4/graphene.

3.2. Effectiveness of Fe^0/Fe_3O_4/graphene in methylene blue removal

To evaluate the feasibility study of Fe^0/Fe_3O_4/graphene, comparison on removal efficiency of methylene blue was carried by graphene, Fe^0, Fe_3O_4 and Fe^0/Fe_3O_4/graphene separately. As shown in Fig. 3a, methylene blue removal efficiency of graphene and Fe_3O_4 was 23.2% and 8.4%, respectively, which was mainly attributed to the adsorption activity of graphene and Fe_3O_4. Fe^0 showed a very quick reaction, the removal efficiency reached 71.5% within 20 min. Fe^0/Fe_3O_4/graphene showed a very good removal (91.6% within 20 min), which was higher than Fe^0. Therefore, synergetic effect existed among Fe^0, Fe_3O_4 and graphene in Fe^0/Fe_3O_4/graphene. This could be ascribed to the reactions of Fe^0, Fe_3O_4 and graphene in the composite, which could reduce and adsorb methylene blue from aqueous solution [23]. Note there was a slight decrease of methylene blue from 15 to 20 min, which might be due to the combination of adsorption and redox reaction. The activities of adsorption and desorption always existed in the reaction process, and the slight decrease in the reaction rate at 20 min might be caused by desorption. At this time, the reaction did not fully reach a stable state. So we extended the reaction time to 40 min in subsequent experiments.

Most processes for methylene blue removal need intensive energy and chemical and involve complex operation, such as photo-catalysis [24,25], photo-Fenton [22,26] and heterogeneous Fenton process [8,27]. In comparison, this method is very simple and highly effective, needs no extra energy, which makes it an efficient, green and sustainable approach in methylene blue wastewater treatment.

The typical UV-Vis spectra of methylene blue during removal process are shown in Fig. 3b. The maximum absorbance band of methylene blue was at 664 nm and other absorbance bands occurred at 200–350 nm. The bands at 664 and 200–350 nm all became weaker in the removal process. The phenomenon indicated that methylene blue was removed as the reaction progressed. Similar spectra were also reported in other studies of methylene blue removal. Wang et al. [28] studied the degradation of methylene blue in aqueous solution by $CuFe_2O_4$ nano particles. The result showed that the absorbance of methylene blue aqueous solution at 665 nm also sharply decreased with reaction progress [28]. Li et al. [29] also investigated the visible-light photocatalytic degradation of methylene blue using MoS_2–reduced graphene oxide composites and found the similar changes of UV-Vis spectra of methylene blue. The phenomenon showed that Fe^0/Fe_3O_4/graphene was an effective material in methylene blue removal process.

3.3. Effects of reactant dosage and methylene blue initial concentration

3.3.1. Effect of Fe^0/Fe_3O_4/graphene dosage

Reagent concentration is a determinative parameter in chemical reactions. The effect of Fe^0/Fe_3O_4/graphene dosage was investigated and the results are shown in Fig. 4. The removal efficiency of methylene blue increased significantly from 14.9% to 90.5% with the composite dosage increasing from 0.3 to 1.0 g/L. As the reaction occurred at the interface of the composite and water, the more composite addition, the
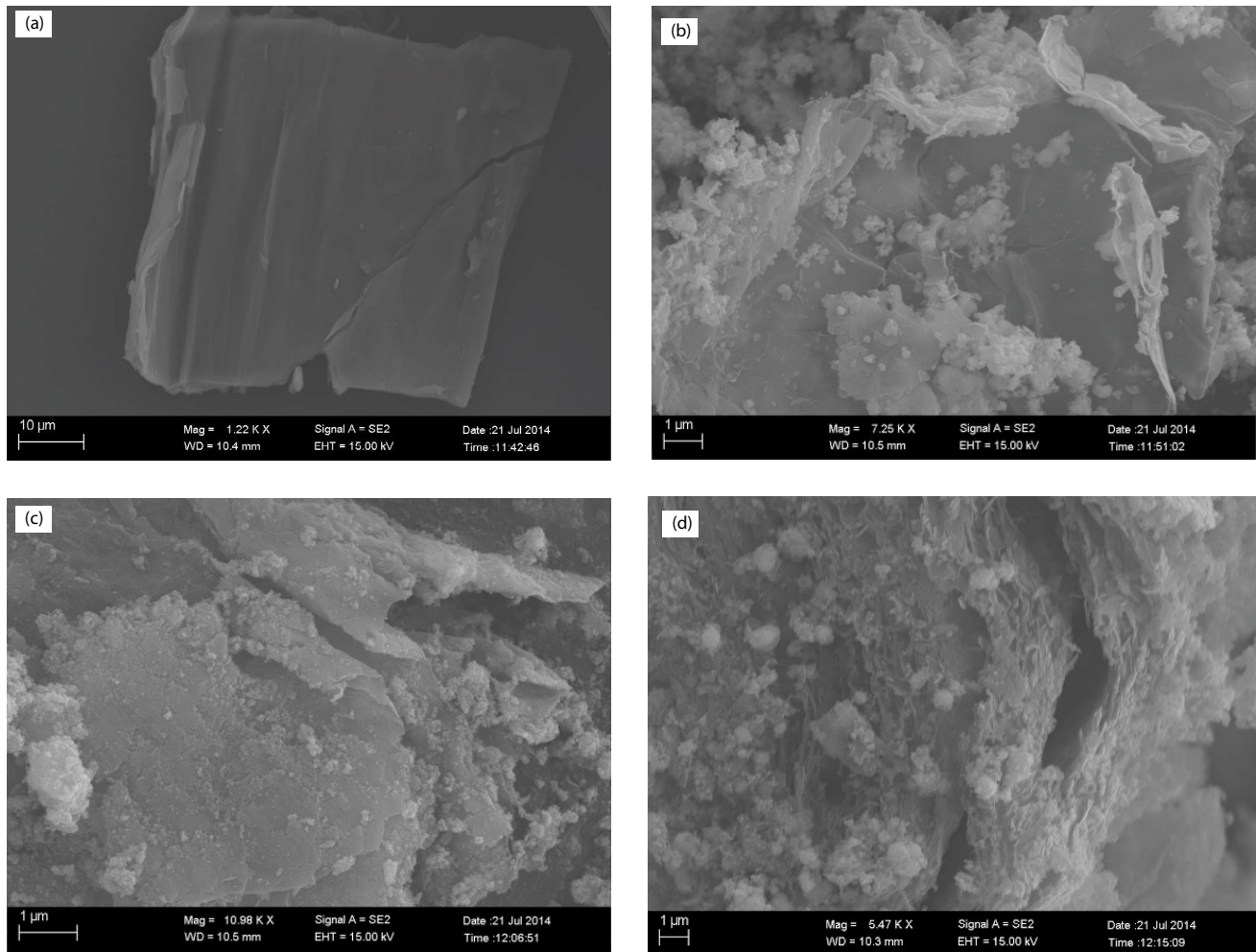
Fig. 2. SEM images of (a) GO, (b) Fe^0/GO, (c) Fe_3O_4/GO, and (d) Fe^0/Fe_3O_4/GO.

more adsorptive and reactive sites were obtained. Besides, the composite dosage might be correlated with the amount of transferring electrons in reaction, which played important roles in redox processes [30]. Fe^0/Fe_3O_4/graphene showed an excellent performance at dosage of 1.0 g/L, so 1.0 g/L was chosen as the best condition for following experiments.

3.3.2. Effect of methylene blue initial concentration

Initial concentration of methylene blue also influences its removal and the results are summarized in Fig. 5. The removal efficiency of methylene blue increased at first and then decreased with the initial concentration increasing from 20 to 100 mg/L. The concentration range was chosen according to literatures and our preliminary experiments [5,18,26]. In general, the reaction was benefitted by higher reagent concentration as more methylene blue molecules aggregated at the active sites and facilitated the electron transferring. Su et al. [31] also found a similar phenomenon in degradation of amoxicillin using sulphate radicals under ultrasound irradiation. But excessive amount of methylene blue molecules would cover the active sites and then hinder the electron transferring, which was adverse to the reaction.

The highest removal efficiency of 91.5% was achieved at 50 mg/L.

3.4. Proposed reaction mechanism

3.4.1. Effect of H_2O_2 addition

Studies showed that methylene blue could be removed efficiently in heterogeneous Fenton-like system, which is formed by H_2O_2 and Fe-containing materials in water [27,32]. Thus, we added H_2O_2 with Fe^0/Fe_3O_4/graphene expecting to obtain better removal performance of methylene blue and the results are shown in Fig. 6. Clearly, the addition of H_2O_2 sharply decreased the methylene blue efficiency from 91.5% to 22.1%, showing that H_2O_2 inhibited the activity of Fe^0/Fe_3O_4/graphene significantly. The reason mainly attributed to the redox reaction between the composite and H_2O_2, which weakened the reduction capability of the composite. Besides, H_2O_2 molecules in solution may occupy the active sites on Fe^0/Fe_3O_4/graphene, which affected the adsorption of methylene blue in solution. Fe^0 in Fe^0/Fe_3O_4/graphene was oxidized by H_2O_2 to generate trivalent ions, indicating that reduction can no longer participate in the methylene blue removal process. Thus, the addition of H_2O_2 completely
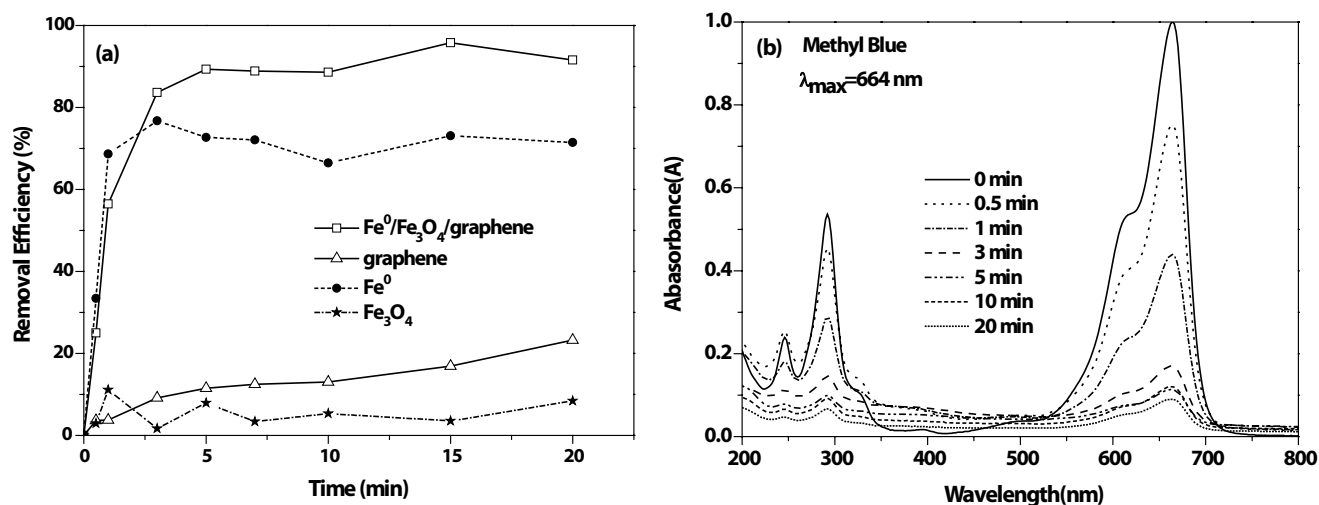
Fig. 3. Removal of methylene blue by various reagents: (a) removal efficiency vs. reaction time and (b) UV/Visible adsorption spectra, [methylene blue] = 15 mg/L, pH = 5, [reagent dosage] = 1.0 g/L.
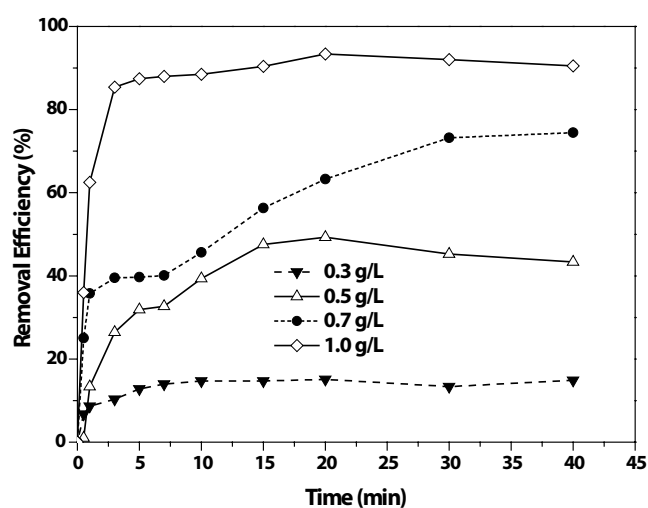

Fig. 4. Effect of Fe^0/Fe_3O_4/graphene dosage on methylene blue removal, [methylene blue] = 15 mg/L, pH = 5.
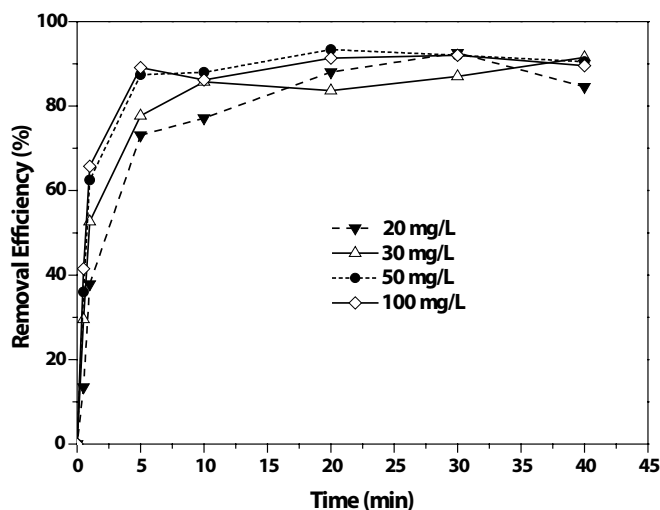

Fig. 5. Effect of methylene blue initial concentration in removal process, [Fe^0/Fe_3O_4/graphene] = 1.0 g/L, pH = 5.

inhibited the reduction role of Fe^0/Fe_3O_4/graphene, which further indicated that reduction of Fe^0/Fe_3O_4/graphene dominated the removal process.

3.4.2. TOC removal in reaction process

In order to further investigate the mineralization of methylene blue in solution, TOC removal in reaction process was determined and the results are shown in Fig. 7. TOC removal efficiency reached 54.0% after 40 min, at the same time, methylene blue removal efficiency reached 90.5%. The changes of TOC may be due to the adsorption of methylene blue on Fe^0/Fe_3O_4/graphene and mineralization of methylene blue in solution. However, the difference of 36.5% between TOC and methylene blue removal efficiency indicated that the intermediates of methylene blue generated and still existed in the solution without further mineralization. Liu et al. [26] studied the heterogeneous

photo-Fenton degradation of methylene blue with Fe_2O_3/graphene oxide catalyst, and almost all of methylene blue were removed with corresponding 56% TOC removed in 80 min. The generation of inorganic ions (SO_4^{2-} and NO_3^-) was detected in the reaction process [33]. The results further verified the degradation of methylene blue by Fe^0/Fe_3O_4/graphene in the reaction process. 90.5% methylene blue removal efficiency and 54.0% TOC removal efficiency suggested that Fe^0/Fe_3O_4/graphene was an efficient material in methylene blue removal process. The big gap between TOC removal and decolorization further proved that this was a reduction and not adsorption process.

3.4.3. Fe ion leaching in removal process

To investigate the stability of Fe^0/Fe_3O_4/graphene in the removal process, the leaching Fe ions during the reaction were analyzed. Fig. 8 shows that the concentrations of Fe ions
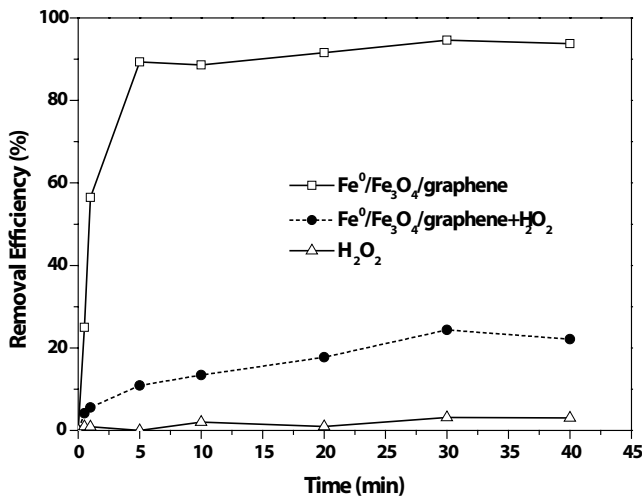
Fig. 6. Effect of H_2O_2 addition on methylene blue degradation, [methylene blue] = 50 mg/L, pH = 5, Fe^0/Fe_3O_4/graphene = 1.0 g/L, [H_2O_2] = 100 mmol/L.
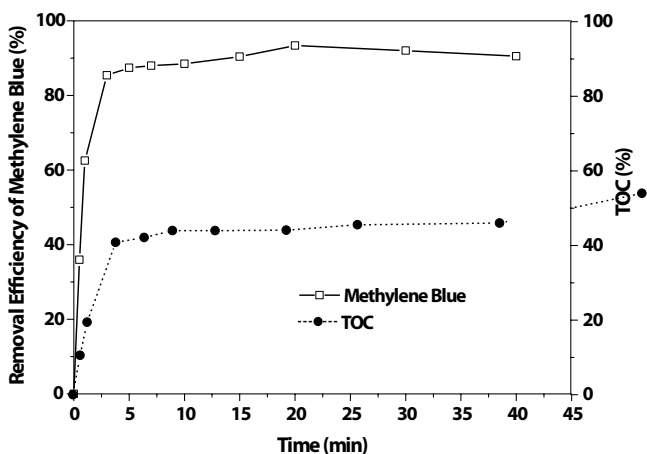

Fig. 8. Fe ions leaching in reaction process, [methylene blue] = 50 mg/L, pH = 5, Fe^0/Fe_3O_4/graphene = 1.0 g/L.

Fig. 7. TOC removal of methylene blue in reaction process [methylene blue] = 50 mg/L, pH = 5, Fe^0/Fe_3O_4/graphene = 1.0 g/L.
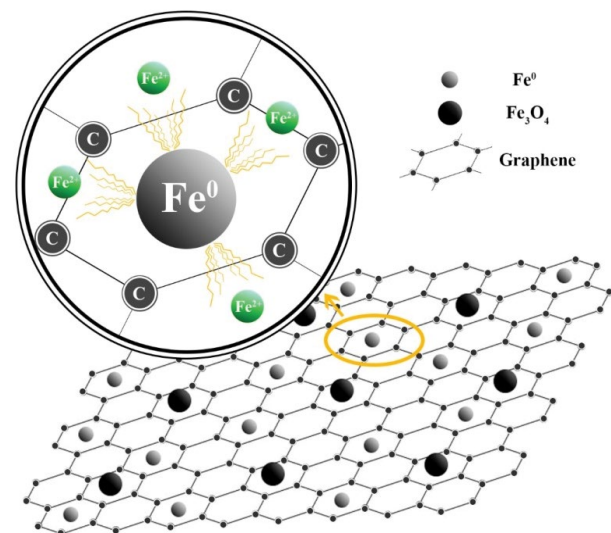
Fig. 9. Structure of Fe^0/Fe_3O_4/graphene and its function mechanism.

were less than 5.0 mg/L in the reaction process, which were much less than the amounts of Fe in Fe^0/Fe_3O_4/graphene. Interestingly, the final concentration of Fe ions was less than 2.0 mg/L after equilibrium, showing release adsorption of Fe ions during the process. The extreme low Fe ions (less than the national drinking water standard) indicated excellent chemical stability of Fe^0/Fe_3O_4/graphene during reaction.

3.5. Mechanism study

The structural morphology and function mechanism of the magnetic Fe^0/Fe_3O_4/graphene were inferred as shown in Fig. 9. Based on our previous study, the graphene with layered structure was the supporter of this composite, and Fe^0 and Fe_3O_4 particles were attached to the surface of the graphene layer homogeneously and dispersedly. This composite had a saturation magnetization of 70.394 emu/g [18]. In this composite, weak magnetic field effect can be formed
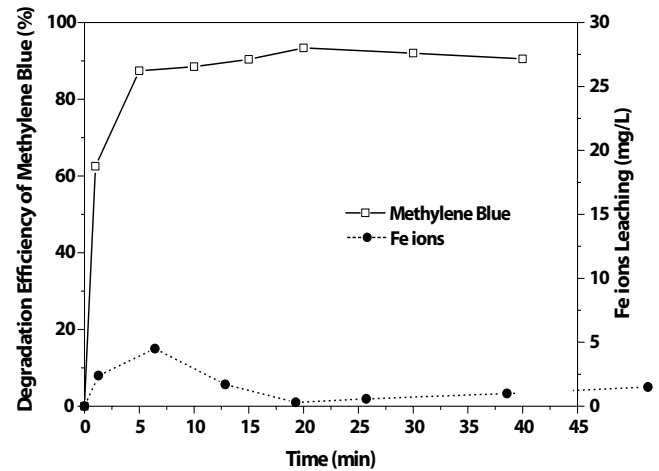
by Fe_3O_4 itself due to its super paramagnetic characteristic. Meanwhile, the reaction activity of Fe^0 can be affected in the weak magnetic field environment due to its ferromagnetic characteristic and the reducibility of Fe^0 can be better demonstrated due to the uniform dispersion in the composite.

Methylene blue molecules could be adsorbed by the graphene and iron oxides through $\pi-\pi$ interaction and electrostatic interaction, respectively. Then, the adsorbed methylene blue molecules tended to aggregate and became much easier to reduce by Fe^0. Fe^{2+} ions were released from Fe^0 while electrons transferred among Fe^0, Fe_3O_4 and graphene due to the synergistic effects in the reaction process. Thus, these molecules were degraded and intermediates were generated. Part of the intermediates was released to solution and the regenerated active sites absorbed more molecules into Fe^0/Fe_3O_4/graphene composite. Finally, methylene blue

molecules were removed due to simultaneous adsorption and degradation in water.

4. Conclusions

The removal of methylene blue in aqueous solution by magnetic Fe^0/Fe_3O_4/graphene was investigated in details. Fe^0/Fe_3O_4/graphene has the features of high reduction ability, adsorption performance and magnetic property, and synergetic effect existed among Fe^0, Fe_3O_4 and graphene in the composite. The methylene blue removal efficiency achieved 91.6% within 20 min under Fe^0/Fe_3O_4/graphene dosage of 1.0 g/L and initial concentration of 50 mg/L. 56% TOC changes verified that the decomposition of methylene blue by Fe^0/Fe_3O_4/graphene occurred in the reaction process. Fe^0/Fe_3O_4/graphene exhibited an excellent chemical stability in the reaction process.

Acknowledgments

References

[1] R. Foroutan, R. Mohammadi, B. Ramavandi, Elimination performance of methylene blue, methyl violet, and Nile blue from aqueous media using AC/CoFe2O4 as a recyclable magnetic composite, Environ. Sci. Pollut. Res., 26 (2019) 19523–19539.
[2] R. Foroutan, R. Mohammadi, S. Farjadfard, H. Esmaeili, B. Ramavandi, G.A. Sorial, Eggshell nano-particle potential for methyl violet and mercury ion removal: Surface study and field application, Adv. Powder Technol., 30 (2019) 2188–2199.
[3] H. Daraei, A. Mittal, Investigation of adsorption performance of activated carbon prepared from waste tire for the removal of methylene blue dye from wastewater, Desal. Wat. Treat., 90 (2017) 294–298.
[4] R. Kumar, R. Ahmad, Biosorption of hazardous crystal violet dye from aqueous solution onto treated ginger waste (TGW), Desalination, 265 (2011) 112–118.
[5] R. Foroutan, R. Mohammadi, J. Razeghi, B. Ramavandi, Performance of algal activated carbon/Fe_3O_4 magnetic composite for cationic dyes removal from aqueous solutions, Algal Res., 40 (2019) 1–12.
[6] J. Gulen, B. Akin, M. Ozgur, Ultrasonic-assisted adsorption of methylene blue on sumac leaves, Desal. Wat. Treat., 57 (2016) 9286–9295.
[7] S.A. Ong, L.N. Ho, Y.S. Wong, Comparison on biodegradation of anionic dye orange II and cationic dye methylene blue by immobilized microorganisms on spent granular activated carbon, Desal. Wat. Treat., 54 (2015) 557–561.
[8] Y. Zha, Z. Zhou, H. He, T. Wang, L. Luo, Nanoscale zero-valent iron incorporated with nanomagnetic diatomite for catalytic degradation of methylene blue in heterogeneous Fenton system, Water Sci. Technol., 73 (2016) 2815–2823.
[9] B.H. Moon, Y.B. Park, K.H. Park, Fenton oxidation of Orange II by pre-reduction using nanoscale zero-valent iron, Desalination, 268 (2011) 249–252.
[10] H.Y. Shu, M.C. Chang, H.H. Yu, W.H. Chen, Reduction of an azo dye Acid Black 24 solution using synthesized nanoscale zerovalent iron particles, J. Colloid Interface Sci., 314 (2007) 89–97.
[11] Y. Wang, L. Liu, G. Fang, L. Wang, F.O. Kengara, C. Zhu, The mechanism of 2-chlorobiphenyl oxidative degradation by nanoscale zero-valent iron in the presence of dissolved oxygen, Environ. Sci. Pollut. Res., 25 (2018) 2265–2272.

[12] X. Wang, P. Wang, J. Ma, H. Liu, P. Ning, Synthesis, characterization, and reactivity of cellulose modified nano zero-valent iron for dye discoloration, Appl. Surf. Sci., 345 (2015) 57–66.
[13] Z.X. Chen, Y. Cheng, Z. Chen, M. Megharaj, R. Naidu, Kaolin-supported nanoscale zero-valent iron for removing cationic dye-crystal violet in aqueous solution, J. Nanopart. Res., 14 (2012).
[14] O. Iglesias, M.A. Fernandez de Dios, E. Rosales, M. Pazos, M.A. Sanroman, Optimisation of decolourisation and degradation of Reactive Black 5 dye under electro-Fenton process using Fe alginate gel beads, Environ. Sci. Pollut. Res., 20 (2013) 2172–2183.
[15] H. Jabeen, K.C. Kemp, V. Chandra, Synthesis of nano zerovalent iron nanoparticles-Graphene composite for the treatment of lead contaminated water, J. Environ. Manage., 130 (2013) 429–435.
[16] F. Liu, J. Yang, J. Zuo, D. Ma, L. Gan, B. Xie, P. Wang, B. Yang, Graphene-supported nanoscale zero-valent iron: removal of phosphorus from aqueous solution and mechanistic study, J. Environ. Sci., 26 (2014) 1751–1762.
[17] Z. Chen, T. Wang, X. Jin, Z. Chen, M. Megharaj, R. Naidu, Multifunctional kaolinite-supported nanoscale zero-valent iron used for the adsorption and degradation of crystal violet in aqueous solution, J. Colloid Interface Sci., 398 (2013) 59–66.
[18] S. Chong, G. Zhang, H. Tian, H. Zhao, Rapid degradation of dyes in water by magnetic Fe0/Fe_3O_4/graphene composites, J. Environ. Sci., 44 (2016) 148–157.
[19] C. Bao, L. Song, W. Xing, B. Yuan, C.A. Wilkie, J. Huang, Y. Guo, Y. Hu, Preparation of graphene by pressurized oxidation and multiplex reduction and its polymer nanocomposites by masterbatch-based melt blending, J. Mater. Chem., 22 (2012) 6088–6096.
[20] F. Ghanbari, M. Ahmadi, F. Gohari, Heterogeneous activation of peroxymonosulfate via nanocomposite CeO_2-Fe_3O_4 for organic pollutants removal: the effect of UV and US irradiation and application for real wastewater, Sep. Purif. Technol., 228 (2019) 115732 1–10.
[21] M. Shafiee, R. Foroutan, K. Fouladi, M. Ahmadlouydarab, B. Ramavandi, S. Sahebi, Application of oak powder/Fe_3O_4 magnetic composite in toxic metals removal from aqueous solutions, Adv. Powder Technol., 30 (2019) 544–554.
[22] X. Yang, W. Chen, J. Huang, Y. Zhou, Y. Zhu, C. Li, Rapid degradation of methylene blue in a novel heterogeneous Fe_3O_4@rGO@TiO_2-catalyzed photo-Fenton system, Sci. Rep., 5 (2015) 10632 1–10.
[23] J. Fan, Y. Guo, J. Wang, M. Fan, Rapid decolorization of azo dye methyl orange in aqueous solution by nanoscale zerovalent iron particles, J. Hazard. Mater., 166 (2009) 904–910.
[24] J. Qin, X. Zhang, C. Yang, M. Cao, M. Ma, R. Liu, ZnO microspheres-reduced graphene oxide nanocomposite for photocatalytic degradation of methylene blue dye, Appl. Surf. Sci., 392 (2017) 196–203.
[25] G.J. Rani, M.A.J. Rajan, G.G. Kumar, Reduced graphene oxide/$ZnFe_2O_4$ nanocomposite as an efficient catalyst for the photocatalytic degradation of methylene blue dye, Res. Chem. Intermediat., 43 (2017) 2669–2690.
[26] Y. Liu, W. Jin, Y. Zhao, G. Zhang, W. Zhang, Enhanced catalytic degradation of methylene blue by alpha-Fe_2O_3/graphene oxide via heterogeneous photo-Fenton reactions, Appl. Catal., B, 206 (2017) 642–652.
[27] S.H. Yoo, D. Jang, H.I. Joh, S. Lee, Iron oxide/porous carbon as a heterogeneous Fenton catalyst for fast decomposition of hydrogen peroxide and efficient removal of methylene blue, J. Mater. Chem. A, 5 (2017) 748–755.
[28] L. Wang, G. Hu, Z. Wang, B. Wang, Y. Song, H. Tang, Highly efficient and selective degradation of methylene blue from mixed aqueous solution by using monodisperse $CuFe_2O_4$ nanoparticles, RSC Adv., 5 (2015) 73327–73332.
[29] J. Li, X. Liu, L. Pan, W. Qin, T. Chen, Z. Sun, MoS_2-reduced graphene oxide composites synthesized via a microwave-assisted method for visible-light photocatalytic degradation of methylene blue, RSC Adv., 4 (2014) 9647–9651.

[30] X. Lv, X. Xue, G. Jiang, D. Wu, T. Sheng, H. Zhou, X. Xu, Nanoscale Zero-Valent Iron (nZVI) assembled on magnetic Fe_3O_4/graphene for Chromium (VI) removal from aqueous solution, J. Colloid Interface Sci., 417 (2014) 51–59.

[31] S. Su, W. Guo, C. Yi, Y. Leng, Z. Ma, Degradation of amoxicillin in aqueous solution using sulphate radicals under ultrasound irradiation, Ultrason. Sonochem., 19 (2012) 469–474.

[32] X. Li, Y. Kong, S. Zhou, B. Wang, In situ incorporation of well-dispersed Cu-Fe oxides in the mesochannels of AMS and their utilization as catalysts towards the Fenton-like degradation of methylene blue, J. Mater. Sci. 52 (2017) 1432–1445.

[33] H. He, S. Yang, K. Yu, Y. Ju, C. Sun, L. Wang, Microwave induced catalytic degradation of crystal violet in nano-nickel dioxide suspensions, J. Hazard. Mater., 173 (2010) 393–400.