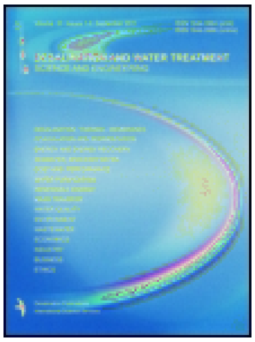

Desalination and Water Treatment

ISSN: 1944-3994 (Print) 1944-3986 (Online) Journal homepage: http://www.tandfonline.com/loi/tdwt20

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To cite this article: Jiang Sheng-tao, Zhu Jian-zhong, Bai Shu-li, Guan Yu-jiang & Yao Jun (2016) Research on Fe-loaded ZSM-5 molecular sieve catalyst in high-concentration aniline wastewater treatment, Desalination and Water Treatment, 57:2, 791-798, DOI: 10.1080/19443994.2014.968628

To link to this article: http://dx.doi.org/10.1080/19443994.2014.968628

Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.968628

57 (2016) 791–798
January

Research on Fe-loaded ZSM-5 molecular sieve catalyst in high-concentration aniline wastewater treatment

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Received 1 January 2014; Accepted 18 September 2014

ABSTRACT

Fe-ZSM-5 molecular sieve catalysts were fabricated and characterized through scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction techniques. Researches were developed within a heterogeneous Fenton-like catalysis system established with Fe-ZSM-5 molecular sieve catalyst and H_2O_2, with regard to the effects of pH, H_2O_2 dosage, inlet concentration of aniline, and catalyst dosage on extent of removal and reaction rate, and preliminarily revealed the mechanisms of degradation in aniline wastewater. Outcomes have demonstrated that Fenton-like Fe-ZSM-5 molecular sieve catalysts are functionally stable and recyclable in which the extents of removal of aniline, COD_{Cr} and TOC are 96.4, 92.5, and 72.5%, respectively; with 3 g catalyst dosed into 500 mL aniline wastewater of 200 mg L^{-1} in concentration, pH 4, and H_2O_2 of $0.5Q_{th}$ (0.31 mL L^{-1}), the Fenton-like conditions could not only break up the inner structures of aniline, but also catalyze the products in further mineralization to CO_2 and H_2O.

Keywords: Fe-ZSM-5 molecular sieve; Aniline wastewater; Fenton-like; Degradation

1. Introduction

Aniline, also known as benzamine, with the molecular formula of C_6H_7N, is an important material and intermediate in chemical industry, and is widely used in industries including medical, pesticide, chemical, dyes, etc. [1,2] Aniline is a type of highly toxic substance of low biodegradability, and could cause purpura being rapidly absorbed by man through skin and respiration, which led to its being listed as one of the prioritized to-be-controlled environmental pollutants in China. Aniline enters into the environment mainly from wastewater of the above-mentioned industries, which usually contains a huge amount of aniline. Due to the toxicity of aniline and the characteristics of aniline wastewater, including high concentration and low biodegradability, and that the upper limit is set at 2 mg L^{-1} for industrial wastewater emission according to the Grade II requirements in National Comprehensive Standards for Pollution Emission, aniline wastewater treatment is even harder to achieve compliance, and has brought about much focus both in real practice and in studies [3–5]. There have already been many reports regarding different treatment

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approaches, such as biodegradation [6], absorption [7,8], photocatalysis [9], and electro-Fenton [10], which yet have not been proved satisfactory in all ways regarding efficiency, cost, feasibility, etc. In recent years, heterogeneous Fenton-like catalysis, as a typical type of advanced oxidation technique, has brought about universal interest among researchers [11–13].

ZSM-5 molecular sieve is a type of artificial silicon-rich zeolite, with Si/Al ratio ($SiO_2/A1_2O_3$) ranging from 25 to 200, and is usually used as a catalyst carrier in the petrochemical industry, fine chemicals industry, etc. Considering the superiorities of ZSM-5 molecular sieve as catalyst carrier, Fajerwerg et al. [14,15], for the first time, fabricated Fenton-like Fe-ZSM-5 catalysts and established heterogeneous Fenton-like systems with Fe-ZSM-5 catalysts and H_2O_2, which realized highly efficient degradation of phenol wastewater. On the basis of above, Shu-xiang et al. [16] conducted researches regarding the effects of different Si/Al rates on phenol degradation and the lifespan of Fe-ZSM-5 catalysts. Studies so far have demonstrated that compared to the traditional Fenton reagents, Fe-ZSM-5 molecular sieve catalysts are very low in iron ion release, which avoids secondary pollution and enables repeated recycling and reuse. However, studies so far haven't gone deep enough into the interface effects and reaction mechanisms of the pollutants and catalysts in the heterogeneous Fenton-like systems, and haven't reported about using Fe-ZSM-5 molecular sieve catalysts for high-concentration aniline wastewater degradation.

of peroxide to completely mineralize aniline to CO_2, and $1.0Q_{th}$ = (0.61 mL of 30% H_2O_2 dosage)/(per L of aniline wastewater).

3. Results and discussion

3.1. Characterization of catalysts

The Fe-ZSM-5 catalyst was prepared by high temperature solid-state reaction using the ZSM-5 molecular sieves [14]. The microstructures of ZSM-5 and Fe-ZSM-5 were observed by SEM as shown in Fig. 1. By comparison between ZSM-5 and Fe-ZSM-5, we can see that the microstructures of these two have no significant difference. But it can be seen from the pictures that Fe-ZSM-5 is relatively rougher than ZSM-5, showing a tendency of further bonding between the particles.

The EDS analysis of ZSM-5, presented in Fig. 2 and Table 1, showed 6.95% C, 53.54% O, 38.17% Si and 1.34% Al atomic weight consisting of the ZSM-5. Likewise, the EDS analysis of Fe-ZSM-5, presented in Fig. 2 and Table 1, showed 9.38% C, 60.50% O, 24.85% Si, 4.39% Fe, and 0.88% Al atomic weight consisting of the Fe-ZSM-5. The iron peak, which does not exist in Fig. 2(a) and does exist in Fig. 2(b), proves that iron has been introduced into Fe-ZSM-5 molecular sieve catalysts. Judging from the atomic weight percentage shown in Table 1, Fe-ZSM-5, as compared with ZSM-5, contains iron that takes up 4.39% of all weight, which that means iron has been successfully loaded onto ZSM-5 molecular sieves [15,16].

The XRD pattern for ZSM-5 and Fe-ZSM-5 is presented in Fig. 3. As could been seen, there are five distinctive peaks at 20.87˚, 23.09˚, 23.13˚, 23.31˚, and 23.93˚ for ZSM-5 and Fe-ZSM-5, respectively, which means that ZSM-5 and Fe-ZSM-5 are formed with good crystal structures [16]. The diffraction peaks of ZSM-5 at featured locations are much higher than that of Fe-ZSM-5, which shows that iron has been dispersed on the ZSM-5 molecular sieves and has formulated a certain degree of crystal build-up.

3.2. Influential factors on Fenton-like reactions

3.2.1. Effects of pH on aniline removal

Heterogeneous systems were established with Fe-ZSM-5 catalysts and H_2O_2, and were used to degrade 500 mL wastewater of 200 mg L^{-1} aniline concentration,

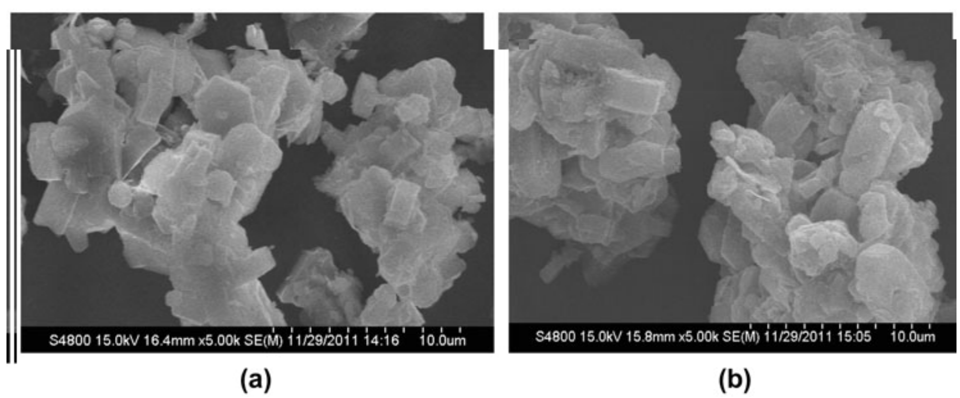


Fig. 1. The SEM partners of ZSM-5 and Fe-ZSM-5. (a) The SEM partners of ZSM-5 and (b) The SEM partners of Fe-ZSM-5.

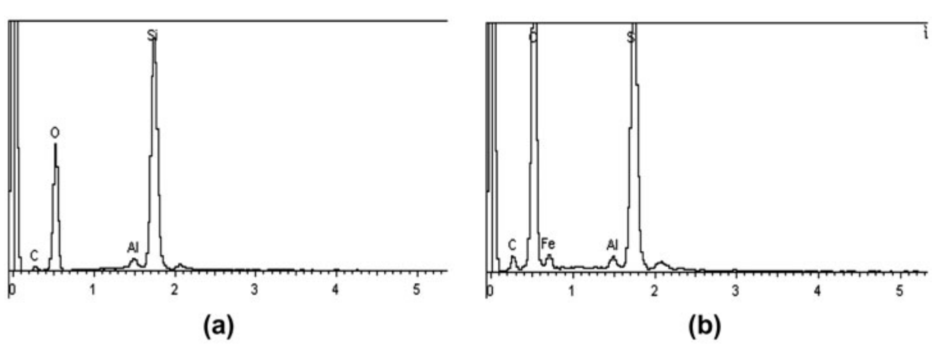


Fig. 2. The EDS partners of ZSM-5 (a) and Fe-ZSM-5 (b).

Table 1
Comparison of ZSM-5 and Fe-ZSM-5 atomic weight percent

Weight percentage (%)	Fe	C	O	Al	Si
ZSM-5	0	6.95	53.54	1.34	38.17
Fe-ZSM-5	4.39	9.38	60.50	0.88	24.85

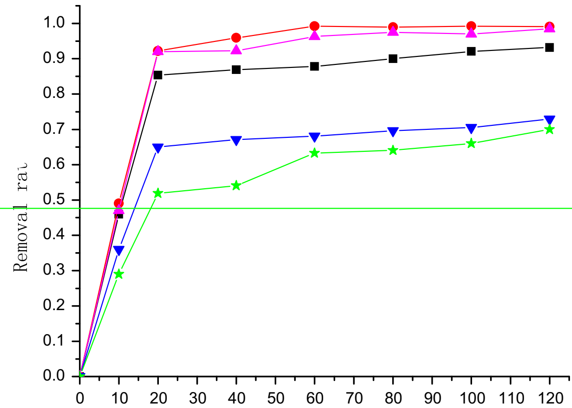
the results of which are shown in Fig. 4. Under room temperature with H_2O_2 dosage of $Q_{th} = 0.61$ mL L^{-1} (theoretical dosage), and catalysts' dosage of 3.0 g, the extent of removal of aniline was determined as 93.2, 99.1, 98.5, 72.9 and 70% respectively in accordance with pH set at 2, 4, 6, 8 and 10, following an order of pH 4 > pH 2 > pH 6 > pH 8 > pH 10. These experiments demonstrate that the heterogeneous Fenton-like systems established with Fe-ZSM-5 catalysts and H_2O_2 could perform good treatment when pH ranges from 2 to 10, and compared with traditional Fenton reactions, heterogeneous Fenton-like reactions adapt to a wider range of pH.

3.2.2. Effects of catalyst dosage on aniline removal

With pH set at 4, H_2O_2 dosage of $0.5Q_{th} = 0.31$ mL L^{-1}, and Fe-ZSM-5 dosage of 0, 0.75, 1.5, 3.0 respectively, the results of heterogeneous catalysis oxidation on 500 mL wastewater of 200 mg L^{-1} aniline concentration are shown in Fig. 5. It was demonstrated that with no catalyst, the extent of removal of aniline was only 2.6%, which means H_2O_2 is not only strong at oxidizing but also degrading aniline; with catalyst dosages of 0.75, 1.5, and 3 g, respectively, the extent of removal went up to 36.5, 71.6 and 96.4%, which shows a significant raise of the extent of removal of aniline, as more catalysts were dosed into the heterogeneous Fenton system. The experiment shows that with more catalysts in the heterogeneous catalysis oxidation system, there is more active surface in a given volume, which increases the chance of collision with H_2O_2 to generate a free hydroxyl ($HO^{\bullet}$), and brings about higher efficiency and rate of aniline degradation [18].

3.2.3. Effects of H_2O_2 dosage on aniline removal

With pH set at 4, catalysts' dosage of 3 g, the results of heterogeneous catalysis oxidation on 500 mL wastewater of 200 mg L^{-1} aniline concentration in accordance with different H_2O_2 dosage are shown in Fig. 6. It was demonstrated that within 120 min, the extent of removal of aniline was 99.2, 96.2, 94.8, 93.3, and 81.2%, respectively, in accordance with H_2O_2 dosage of Q_{th} (0.61 mL L^{-1}), $0.8Q_{th}$ (0.49 mL L^{-1}), $0.6Q_{th}$ (0.37 mL L^{-1}), $0.5Q_{th}$ (0.31 mL L^{-1}), and $0.3Q_{th}$ (0.18 mL L^{-1}), and this H_2O_2 dosage does impact the extent of removal of aniline. As H_2O_2 dosage decreases, the extent of removal of aniline goes down, which is fairly obvious from the dosage that goes down from $0.5Q_{th}$ (0.31 mL L^{-1}) to $0.3Q_{th}$ (0.18 mL L^{-1}). However, it was also demonstrated that even though H_2O_2 concentration is low, a heterogeneous Fenton-like system established with Fe-ZSM-5 and H_2O_2 is still strong at oxidizing and degrading aniline wastewater, with the extent of removal always



above 80%, which means a lot in bringing down the running cost in treatment projects.

3.2.4. Effects of initial aniline concentration on aniline removal

With pH set at 4, H_2O_2 dosage of $0.5Q_{th}$ (0.31 mL L^{-1}) and catalyst' dosage of 3.0 g, the results of heterogeneous Fenton-like catalysis oxidation on wastewater of different initial aniline concentrations are shown in Fig. 7.

Fig. 7 shows that with initial aniline concentration at 100, 200, 300, and 400 mg L^{-1}, respectively, the extent of removal gets 94.7, 90.7, 76.3, and 54.1% accordingly within 20 min, and 100, 96.4, 92.1, and 74% within 120 min, respectively. The results demonstrated that with a fixed dosage of H_2O_2 and catalysts, a heterogeneous Fenton-like system performs a good degradation for aniline wastewater ranging from 100 to 400 mg L^{-1}, and reaches the best at 100 mg L^{-1}. With an increase in initial concentration, the extent of removal goes down, as the quantity of effective active matter ·OH generated is limited to the dosage of H_2O_2 and thus, restrains the capacity of degrading aniline.

3.2.5. Efficiency of catalyst recycling and reuse

With pH set at 4, H_2O_2 dosage of $0.5Q_{th}$ (0.31 mL L^{-1}) and catalysts' dosage of 3 g, we carried out experiments on catalyst recycling and reuse on 500 mL wastewater of 200 mg L^{-1} aniline concentration. After each 120 min of reaction, the used catalysts were filtered out and put into use for the next round, the results of which are shown in Table 2. It indicates that there was an obvious slow drop in efficiency a the recycles progressed and the aniline extent of removal was kept above 93%. Iron dissolution was also tested during the experiments through phenanthroline spectrophotometry [19], which identified no iron concentration (while the minimum threshold is 0.03 mg L^{-1}) and thus, testified that during the experiments, iron on ZSM-5 molecular sieves was firmly loaded, and these Fe-ZSM-5 catalysts have relatively long lifespans with stable properties, being recyclable and reusable, and practically valuable.

3.3. COD_{Cr}, TOC and aniline removal efficiency

For 500 mL wastewater of 200 mg L^{-1} aniline concentration, with pH set at 4, H_2O_2 dosage of $0.5Q_{th} = 0.31$ mL L^{-1}, and catalysts' dosage of 3 g, the extents of removal of COD_{Cr}, TOC, and aniline are shown in Fig. 8. It was demonstrated that in the Fenton-like system, the benzene structure in aniline is destroyed and further mineralized. After the reactions,

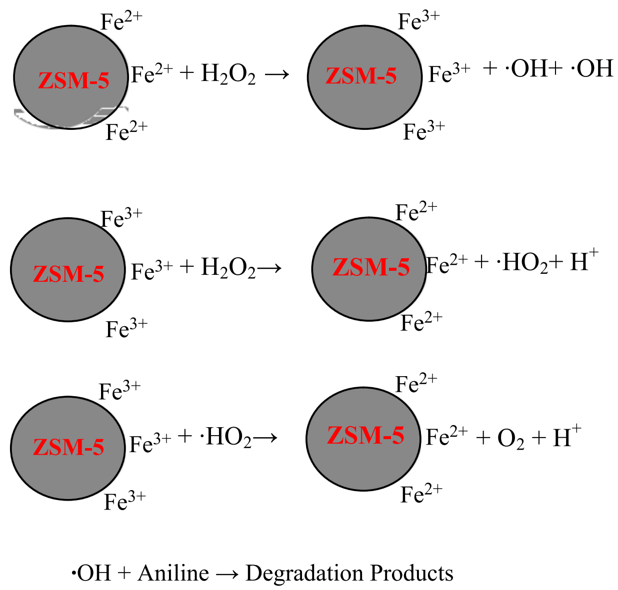


Fig. 10. Fenton-like degradation mechanism.

also the catalysis oxidation of Fe-ZSM-5 catalyst on targeted aniline is not a traditional homogeneous Fenton reaction, but probably a heterogeneous Fenton-like micro-superficial reaction.

Both Fe (Π) and Fe (Ш) loaded on ZSM-5 molecular sieves could react with H_2O_2, generating ·OH and $·HO_2$, respectively, of which the latter is weaker at oxidizing compared with the first, and could only last for a very short time in the solutions, which indicates that the oxidative degradation in Fenton-like systems is primarily brought about by ·OH [23,24]. Therefore, the reaction mechanisms of Fe-ZSM-5 Fenton-like catalysts catalyzing organics are shown in Fig. 10.

4. Conclusions

(1) Fenton-like reactions with Fe-ZSM-5 molecular sieves as catalysts have good treatment performance across a pH range from 2 to 10, which breaks the limitation in traditional Fenton reactions, in which the pH needs to be controlled to keep the reaction acidic.

(2) The catalysis oxidation of aniline wastewater by Fe-ZSM-5 molecular sieve catalysts is not a traditional homogeneous Fenton reaction, but a heterogeneous Fenton-like reaction. The oxidation and degradation in Fenton-like systems is primarily brought about by a free ·OH generated from Fe (Π) and Fe (Ш) loaded onto ZSM-5 reacting with H_2O_2, which is a micro-superficial reaction.

(3) Fe-ZSM-5 molecular sieve catalysts have stable properties, and are recyclable and reusable. Fenton-like conditions could not only break and degrade the structures of aniline, but also further mineralize the degradation products into CO_2 and H_2O with catalysis.

Acknowledgements

This work was financially supported by the Public Technology Applied Research Fund of Zhejiang Province Science and Technology Department [grant number 2013C33020] and Environmental Science and Technology Project of Zhejiang Province [grant number 2013B018].

References

[1] S. Chen, D. Sun, J.-S. Chung, Simultaneous methanogenesis and denitrification of aniline wastewater by using anaerobic–aerobic biofilm system with recirculation, J. Hazard. Mater. 169 (2009) 575–580.
[2] M. Delnavaz, B. Ayati, H. Ganjidoust, Prediction of moving bed biofilm reactor (MBBR) performance for the treatment of aniline using artificial neural networks (ANN), J. Hazard. Mater. 179 (2010) 769–775.
[3] S. Zhang, A. Li, D. Cui, J. Yang, F. Ma, Performance of enhanced biological SBR process for aniline treatment by mycelial pellet as biomass carrier, Bioresour. Technol. 102 (2011) 4360–4365.
[4] Z. Gu, M. Gao, Z. Luo, Bis-pyridinium dibromides modified organo-bentonite for the removal of aniline from wastewater: A positive role of π–π polar interaction, Appl. Surf. Sci. 290 (2014) 107–115.
[5] Y. Ren, T. Li, C. Wei, Competitive adsorption between phenol, aniline and *n*-heptane in tailrace coking wastewater, Water Air Soil Pollut. 224 (2013) 1365–1370.
[6] Q. Jin, Z. Hu, Z. Jin, L. Qiu, W. Zhong, Z. Pan, Biodegradation of aniline in an alkaline environment by a novel strain of the halophilic bacterium, *Dietzia natronolimnaea* JQ-AN, Bioresour. Technol. 117 (2011) 154–158.
[7] F. An, X. Feng, B. Gao, Adsorption of aniline from aqueous solution using novel adsorbent PAM/SiO_2, Chem. Eng. J. 151 (2009) 18–187.
[8] G. Xiao, L. Long, Efficient removal of aniline by a water-compatible microporous and mesoporous hyper-cross-linked resin and XAD-4 resin: A comparative study, Appl. Surf. Sci. 258 (2012) 6465–6471.
[9] H. Tang, J. Li, Y. Bie, L. Zhu, J. Zou, Photochemical removal of aniline in aqueous solutions: Switching from photocatalytic degradation to photo-enhanced polymerization recovery, J. Hazard. Mater. 175 (2010) 977–984.
[10] J. Anotai, C.-C. Su, Y.-C. Tsai, M.-C. Lu, Effect of hydrogen peroxide on aniline oxidation by electro-Fenton and fluidized-bed Fenton processes, J. Hazard. Mater. 183 (2010) 888–893.

[11] H.-Y. Xu, M. Prasad, Y. Liu, Schorl: A novel catalyst in mineral-catalyzed Fenton-like system for dyeing wastewater discoloration, J. Hazard. Mater. 165 (2009) 1186–1192.

[12] J.-M. Leea, J.-H. Kima, Y.-Y. Chang, Y.-S. Chang, Steel dust catalysis for Fenton-like oxidation of polychlorinated dibenzo-p-dioxins, J. Hazard. Mater. 163 (2009) 222–230.

[13] N. Panda, H. Sahoo, S. Mohapatra, Decolourization of Methyl Orange using Fenton-like mesoporous Fe_2O_3–SiO_2 composite, J. Hazard. Mater. 185 (2011) 359–365.

[14] K. Fajerwerg, H. Debellefontaine, Wet oxidation of phenol by hydrogen peroxide using heterogeneous catalysis Fe-ZSM-5: A promising catalyst, Appl. Catal. B: Environ. 10 (1996) L229–L235.

[15] K. Fajerwerg, J.N. Foussard, A. Perrard, H. Debellefontaine, Wet oxidation of phenol by hydrogen peroxide: The key role of pH on the catalytic behaviour of Fe-ZSM-5, Water Sci. Technol. 35(4) (1997) 103–110.

[16] L.U. Shu-xiang, W.E.I. Jia, H.U. Yang, Catalytic oxidation of phenol in waste water with high concentration by Fe-ZSM-5 zeolite catalyst, Chin. J. Process Eng. 8(4) (2008) 751–755.

[17] GB 11889-89, Water Quality—Determination of Aniline Compounds—Spectrophotometric Method with N-(1-naphthyl) Ethylenediamine [S], (in Chinese).

[18] S.H. Tian, Y.T. Tu, D.S. Chen, Degradation of Acid Orange II at neutral pH using Fe2(MoO4)3 as a heterogeneous Fenton-like catalyst, Chem. Eng. J. 169 (2011) 31–37.

[19] F. Ji, C. Li, J. Zhang, L. Deng, Efficient decolorization of dye pollutants with LiFe(WO4)2 as a reusable heterogeneous Fenton-like catalyst, Desalination 269 (2011) 284–290.

[20] N.K. Daud, B.H. Hameed, Fenton-like oxidation of reactive black 5 solution using iron-Montmorillonite K10 catalyst, J. Hazard. Mater. 176 (2010) 1118–1121.

[21] N. Masomboon, C. Ratanatamskul, M.-C. Lu, Kinetics of 2,6-dimethylaniline oxidation by various Fenton processes, J. Hazard. Mater. 192 (2011) 347–353.

[22] I.W.C.E. Arends, R.A. Sheldon, Activities and stabilities of heterogeneous catalysts in selective liquid phase oxidations: Recent developments, Appl. Catal., A 212 (2001) 175–187.

[23] S. Chou, C. Huang, Y.H. Huang, Heterogeneous and homogeneous catalytic oxidation by supported γ-FeOOH in a fluidized-bed reactor: Kinetic approach, Environ. Sci. Technol. 35(6) (2001) 1247–1251.

[24] N. Wang, L.H. Zhu, D.L. Wang, M.Q. Wang, Z.F. Lin, Sono-assisted preparation of highly-efficient peroxidase-like Fe_3O_4 magnetic nanoparticles for catalytic removal of organic pollutants with H_2O_2, Ultrason. Sonochem. 17(3) (2010) 526–533.