

Heterogeneous photo-assisted Fenton catalytic removal of tetracycline using Fe-Ce pillared bentonite

ZHANG Ya-ping(张亚平), JIA Cheng-guang(贾成光), PENG Ran(彭然), MA Feng(马丰), OU Guang-nan(欧光南)

College of Biology Engineering, Jimei University, Xiamen 361021, China

© Central South University Press and Springer-Verlag Berlin Heidelberg 2014

Abstract: In the present work, a novel heterogeneous photo-Fenton catalyst was prepared by iron and cerium pillared bentonite. The catalyst Fe-Ce/bentonite was characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), Brunauer-Emmett-Teller (BET) and scanning electron microscopy (SEM) methods. It is found that Fe and Ce intercalate into the silicate layers of bentonite successfully. Tetracycline was removed by heterogeneous photo-Fenton reaction using the catalyst in this work. The effects of different reaction systems, hydrogen peroxide concentration, initial pH, catalyst dosage, UV power and introduction of different anions on degradation were investigated in details. The stability of catalyst was investigated through recycling experiment. The results show that removal rate of tetracycline is 98.13% under the conditions of 15 mmol/L H₂O₂, 0.50 g/L catalyst dosage, initial pH 3.0, 11 W UV lamp power and 60 min reaction time. However, the removal rate decreases after adding some anions. The hydroxyl radical plays an important role in heterogeneous photo-assisted Fenton degradation of tetracycline. The catalyst is very stable and can be recycled many times.

Key words: wastewater treatment; advanced oxidation process; photo-Fenton; antibiotics; Fe-Ce/bentonite

1 Introduction

Antibiotics are one of the most important bioactive and chemotherapeutic groups of microbiological synthesizing compounds [1]. A large number of antibiotics have been used for disease control and disinfection [2]. However, their improper use has resulted in a new environmental problem [3–4]. In recent researches, residues of antibiotics have been detected in different water samples, including municipal wastewater, riverine water, lake water, and even groundwater [5–6]. Tetracycline (TC, C₂₂H₂₄N₂O₈), a representative of the broad-spectrum antimicrobial drugs, could be a good method to treat infection caused by mycoplasma, chlamydia, gram-positive bacteria, gram-negative bacteria, and has become the second most widely used antibiotics in the world [7]. However, only a small amount of TC is metabolized or absorbed by the body, most of the unchanged forms of the drug are eliminated in faeces and urine [8]. The release of TC into nature environment increases the potential for antibiotic resistance among microbial populations, and the degradation by-products have been proven even more

toxic than the parents [9]. Therefore, it is urgent to develop efficient and economical technologies to remove TC from the environment.

In recent years, many researchers were focused on removal of TCs from waste antibiotic effluents. Various techniques such as ozonation [10], photo-Fenton process [11], photoelectrocatalytic degradation [12–13] and adsorption [14–15] have been reported. The Fenton reaction is considered suitable for the treatment of a variety of wastewaters due to its high efficiency, simplicity of operation and low cost. Fenton's reagent consists of ferrous salt such as FeSO₄ or any other ferrous complex and H₂O₂. This mixture results in Fe²⁺ catalytic decomposition of H₂O₂ and proceeds via a free radical chain process which produces hydroxyl radicals (\cdot OH) [16]. However, the classic Fe²⁺ based Fenton system requires operation at pH < 3.0 to prevent the precipitation of Fe²⁺ and Fe³⁺ so that a large excess of Fe salts in traditional Fenton systems can not be recycled, producing large amounts of chemical sludge [17]. The sludge that contains many iron ions after completion of homogeneous photo Fenton reaction need to be treated, which is the major reason to restrict its practical application. Therefore, many researchers are devoted to

Foundation item: Project(51004053) supported by National Natural Science Foundation of China; Project(2009J01033) supported by Natural Science Foundation of Fujian Province, China; Project(3502Z20116008) supported by the Science and Technology Research Project of Xiamen City, China; Project(JA11146) supported by Program for Fostering Distinguished Young Scholars in University of Fujian Province, China; Project(2011B003) supported by the Foundation for Young Professors of Jimei University, China

Received date: 2012-07-27; **Accepted date:** 2012-09-20

Corresponding author: ZHANG Ya-ping, PhD; Tel: +86-13695003016; E-mail: ypzhang@jmu.edu.cn

research and develop the heterogeneous catalyst. Especially, some achievements have been reported on the metal ion pillared bentonite [18–19].

Early study has shown that electron transfer between iron and cerium could enhance the catalytic activity [20]. Therefore, according to the previous study, the pillared bentonite catalysts of iron and cerium were prepared. Fe-Ce/bentonite was used as catalyst to remove the tetracycline through photo-assisted Fenton reaction for a deep discussion on the effect of tetracycline removal.

2 Materials and methods

2.1 Materials

Standard of tetracycline used in the experiment was obtained from Shanghai Biochemical Reagent Co., Ltd. H_2O_2 , ferric nitrate and cerium nitrate were of analytical reagent (AR) grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Bentonite that was obtained from Xinjiang Province in China was through Na-modification before used.

2.2 Experimental methods

2.2.1 Preparation of catalyst

Firstly, mixed solution containing 0.20 mol/L of $[Fe^{3+}]$ and $[Ce^{3+}]$ was placed in 80 °C water bath and molar ratio of $[OH^-]/([Fe^{3+}]+[Ce^{3+}])$ was adjusted to 2.0 (by addition of 0.20 mol/L of NaOH). Secondly, the liquid mixture was aged at the room temperature for 2 d after stirring for 2 h, and then was added dropwise into 2% clay slurry to make $([Fe^{3+}]+[Ce^{3+}])$ /bentonite reach 2.0 mmol/g. Thirdly, the clay slurry was placed in 80 °C water bath to age for 1 d, and then centrifuged and washed several times with deionized water to remove chlorine ions. Lastly, the precipitation was dried at 80 °C, ground to pass through 250 μm sieve and calcined 3 h at 400 °C.

2.2.2 Catalyst characterization

X-ray diffraction (XRD) patterns of Na-bentonite and Fe-Ce/bentonite were conducted in a X-Pert Pro Diffractometer (PANalytical Corporation, Netherlands) with a $Cu K_{\alpha}$ radiation at 40 kV and 20 mA. The chemical compositions of Na-bentonite and Fe-Ce/bentonite samples were determined by PANalytical Axios wavelength-dispersive X-ray fluorescence spectrometer (PANalytical Corporation, Netherlands). Scanning electron microscopy (SEM) images were recorded using LEO 1530 field emission scanning electron microscope (LEO Corporation, Germany). Brunauer-Emmett-Teller (BET) surface areas were determined with ASAP-2020 automatic specific surface area and pore size analyzer (Micromeritics, USA) by nitrogen adsorption at 77 K.

2.2.3 Wastewater treatment & analytical method

Batch experiments were conducted in the photocatalytic fluidized-bed (1.5 L). The wavelength of ultraviolet lamp was 254 nm and the reaction temperature was kept at 25 °C. The pH of simulated wastewater was controlled by adding H_2SO_4 or NaOH solution. The wastewater was aerated for 5 min after adding a certain amount of catalyst. A given amount of H_2O_2 was then mixed into the solution and the lamp was turned on at the same time. The samples were taken at selected intervals and filtered through a 0.45 μm filter film to remove catalyst particles before analyses of the solution.

The concentration of tetracycline was determined with UV-Vis spectrophotometry. The chemical oxygen demand for the samples was measured using potassium dichromate method (COD_{Cr}).

3 Results and discussion

3.1 Characterization of catalysts

3.1.1 XRD characterization

The XRD patterns of Fe-Ce/bentonite and Na-bentonite are compared in Fig. 1. Diffraction peaks at 2θ angles of 33.2°, and 35.7° assigned to α - Fe_2O_3 are distinctly observed by comparing the XRD pattern of Fe-Ce/bentonite with that of Na-Bentonite. The decrease in the intensity of diffraction peak at $2\theta=22^\circ$ suggests that the content of SiO_2 decrease after Fe and Ce pillaring. However, due to very small amount of Ce added and uniform Ce distribution, there are no diffraction peaks to be observed in Fig. 1. Moreover, many peaks of impurities in Na-bentonite weaken or disappear after pillaring.

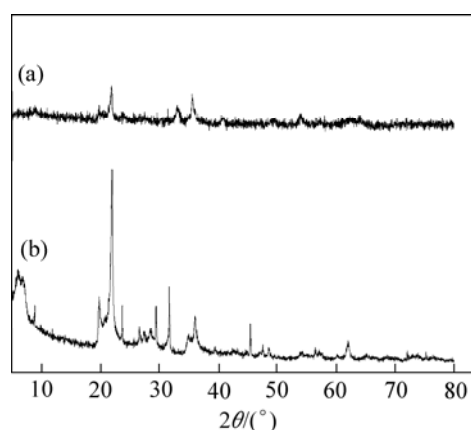


Fig. 1 XRD patterns of Fe-Ce/bentonite(a) and Na-bentonite(b)

3.1.2 XRF characterization

The chemical properties of both Na-bentonite and Fe-Ce/bentonite are shown in Table 1. The major chemical components are SiO_2 , Al_2O_3 and Fe_2O_3 . The

Table 1 Comparison of chemical compositions of Na-bentonite and Fe-Ce/bentonite (mass fraction, %)

Sample	Fe ₂ O ₃	Ce ₂ O ₃	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cl
Na-bentonite	2.17	—	7.43	1.34	14.32	66.80	0.76	2.61	4.02
Fe-Ce/bentonite	49.59	1.26	0.29	0.67	8.58	38.49	0.39	0.08	0.13

Fe₂O₃ content in Fe-Ce/Bentonite is higher than that in Na-bentonite, whereas the SiO₂, Na₂O, CaO and Al₂O₃ contents in Fe-Ce/Bentonite are lower. The existence of Fe³⁺ ions is important for determining a good efficiency of Fenton reagent, thus, higher Fe₂O₃ content and lower CaO content may be preferred for heterogeneous Fenton process [21]. Moreover, Ce₂O₃ is also observed in Fe-Ce/bentonite (1.26%). The Ce³⁺ ions can enhance the catalytic activity further by means of interaction with Fe ions.

3.1.3 BET characterization

The BET surface areas of Fe-Ce/bentonite and Na-bentonite are given in Table 2. The Na-bentonite exhibits a surface area of 38.38 m²/g. While the Fe-Ce/bentonite surface area is greatly enlarged after the iron and cerium clusters being intercalated into the bentonite layers, and the value of BET surface area reaches to 69.38 m²/g. Larger surface area can provide better adsorption ability and more activity sites. Moreover, average pore diameter and total pore volume of Fe-Ce/bentonite are larger compared with Na-bentonite. These reveal that Fe-Ce/bentonite has higher catalytic efficiency.

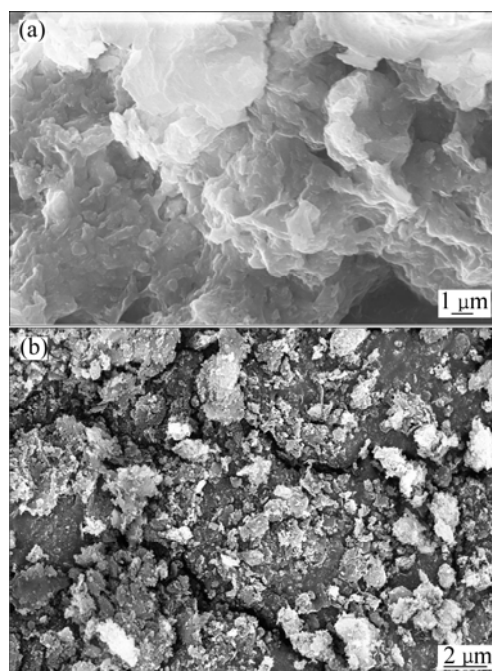
Table 2 BET surface area and pore structure data of different samples

Sample	BET area/ (m ² ·g ⁻¹)	Average pore diameter/nm	Total pore volume/(cm ³ ·g ⁻¹)
Na-bentonite	38.38	9.16	0.14
Fe-Ce/bentonite	69.38	11.23	0.26

3.1.4 SEM analysis

Figure 2 shows the SEM images of bentonite before and after pillaring. It can be seen that the unpillared bentonite (Fig. 2(a)) owns many prominent lamellar structures and outline clear, but its structure is irregular. The pillared bentonite (Fig. 2(b)) has a small and well-distributed lamella structure which is loose and smashed so that its surface area is increased significantly. That is in line with the result of BET characterization. Compared with the unpillared bentonite, some lamella has rolled and peeling of the lamella is very obvious. A possible reason is that poly-hydroxy cations from Fe and Ce hydrolysis pass into the bentonite lamella through ion exchange, which increases the basal spacing, and when the basal spacing reaches a certain value, the original layer gravity is broken to make the lamella roll and strip [22–23]. In addition, it can be seen from the pillared

bentonite (Fig. 2(b)) that there are many small particles, which are the polymers of Fe₂O₃ and Ce₂O₃ formed during roasting in the bentonite layer.

**Fig. 2** SEM micrographs of bentonite before and after pillaring: (a) Na-bentonite; (b) Fe-Ce/Bentonite

3.2 Effect of different reaction systems

The removal of tetracycline were carried out by UV+H₂O₂+Fe-Ce/bentonite, UV+H₂O₂, H₂O₂+Fe-Ce/bentonite in dark, UV+Fe-Ce/bentonite and UV light only, and the results are shown in Fig. 3. The tetracycline removal rate is only 11.14% with UV irradiation in the absence of H₂O₂ and catalyst, indicating that tetracycline is not sensitive to the UV light. The removal rate is only 18.61% when the solution is treated with UV and Fe-Ce/bentonite. The H₂O₂ and Fe-Ce/bentonite process is also insufficient to achieve excellent removal efficiency (31.94%). With UV and H₂O₂, removal efficiency is 83.76% after 60 min. When the reaction is carried out in UV, H₂O₂ and Ce-Fe/Bentonite system, the best removal efficiency rate is observed (98.13%).

The COD_{Cr} of two systems (UV+H₂O₂ and UV+H₂O₂+Fe-Ce/bentonite) were measured at the same time. The removal of tetracycline by heterogeneous Fe-Ce/bentonite obtains the best removal effects, and the UV/H₂O₂ process follows. When 60 min has passed, the COD_{Cr} concentration reduces from 324 mg/L to 34 mg/L in the heterogeneous Fe-Ce/bentonite process,

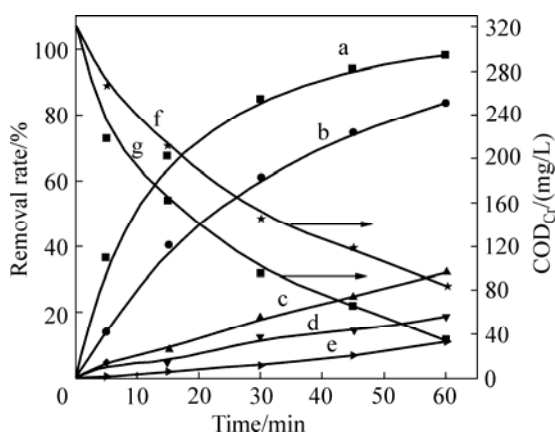


Fig. 3 Effect of different processes on removal of tetracycline and changes of COD_{Cr} in figure. (Reaction conditions: initial concentration of hydrogen peroxide, [H₂O₂]₀=15 mmol/L, pH=3.0, catalyst dosage=0.50 g/L, UV lamp power=11 W and reaction time=60 min. a—UV+H₂O₂+Fe-Ce/bentonite; b—UV+H₂O₂; c—H₂O₂+Fe-Ce/bentonite; d—UV+Fe-Ce/bentonite; e—UV light only; f—COD_{Cr} of UV+H₂O₂; g—COD_{Cr} of UV+H₂O₂+Fe-Ce/bentonite)

and the removal rate of tetracycline reaches 89.43%, which shows that the mineralization level of tetracycline is higher in this system.

Meanwhile, the studies on ultraviolet-visible absorption spectra according to the UV/H₂O₂ process and heterogeneous Fe-Ce/bentonite process were conducted, respectively (Fig. 4). It can be seen that the maximum absorption peaks of tetracycline in the UV-visible range is at 274 nm and 356 nm. In the UV spectroscopy of tetracycline removal using the UV/H₂O₂ process and heterogeneous Fe-Ce/bentonite process, the maximum absorption peaks decrease significantly as the reaction proceeds. At the same reaction time, the heterogeneous Fe-Ce/bentonite process declines in a greater degree

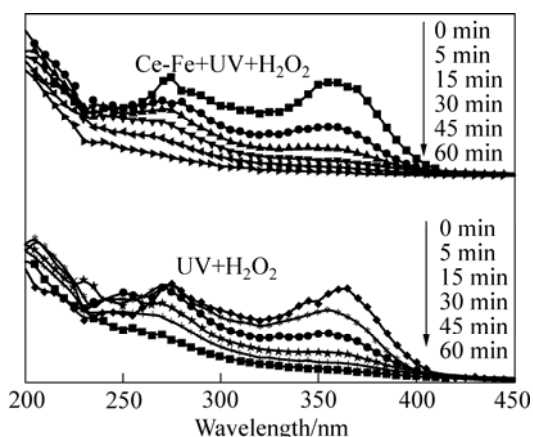


Fig. 4 Absorption spectra of UV-visible in removal process of tetracycline. (Reaction conditions: initial concentration of hydrogen peroxide, [H₂O₂]₀=15 mmol/L, pH=3.0, catalyst dosage=0.50 g/L, UV lamp power=11 W and reaction time=60 min)

compared with the UV/H₂O₂ process, which indicates that the heterogeneous Fe-Ce/bentonite treatment obtains the best efficiency of removal, and UV/H₂O₂ process follows. After 60 min, the absorption peaks at 274 nm and 356 nm of the heterogeneous Fe-Ce/bentonite process almost disappears, suggesting that the ring structure of tetracycline is seriously damaged during the reaction.

3.3 Effect of H₂O₂ dosage

The effect of H₂O₂ dosage on the removal of tetracycline was examined by varying the initial concentration of H₂O₂ from 5 to 25 mmol/L and the results are shown in Fig. 5. At low H₂O₂ concentrations of 5 mmol/L and 10 mmol/L, the removal rates of tetracycline are low because of the insufficient •OH in aqueous solution. As the H₂O₂ concentration increases to 15 mmol/L, the tetracycline removal is obviously enhanced, because more radicals are formed. However, for higher concentrations (20 mmol/L and 25 mmol/L), the removal rate decreases. This is because the H₂O₂ molecule can occur with •OH rapidly [24]:



Therefore, excess H₂O₂ in the reaction system captures a large number of •OH, reducing the probability of •OH attacking organic molecules.

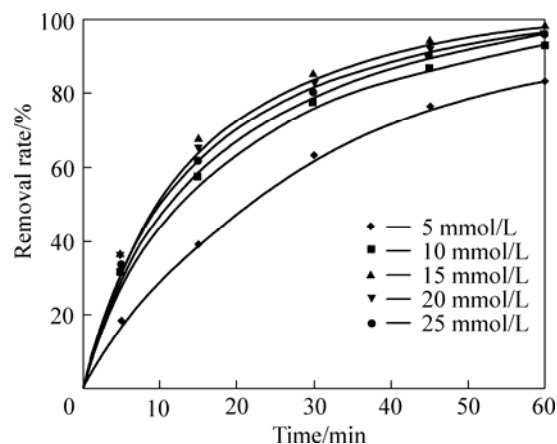


Fig. 5 Effect of H₂O₂ dosage on removal of tetracycline. (Reaction conditions: pH=3.0, catalyst dosage is 0.50 g/L, UV lamp power is 11 W and reaction time is 60 min)

3.4 Effect of catalyst dosage

The influence of catalyst dosage on removal efficiency of tetracycline versus time is illustrated in Fig. 6. Figure 6 shows that when the Fe-Ce/bentonite dose increases from 0.10 to 0.50 g/L, the removal of tetracycline is moderately accelerated. When the catalyst amount increases to 0.50 g/L, the removal rate of tetracycline reaches 98.13%. Nevertheless, the tetracycline removal is not enhanced but a little decreased when the Fe-Ce/bentonite dose increases to

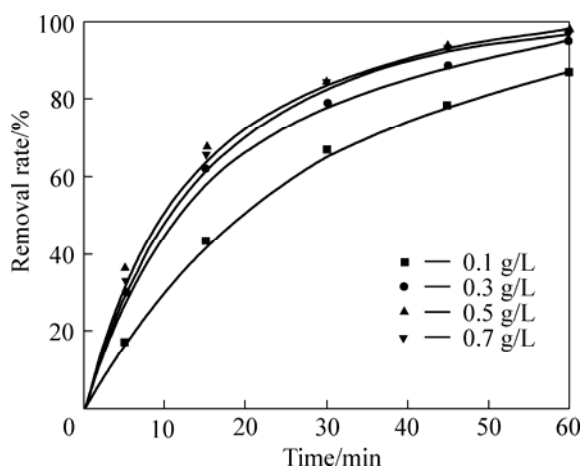


Fig. 6 Effect of catalyst dosage on removal of tetracycline. (Reaction conditions: initial concentration of hydrogen peroxide, $[H_2O_2]_0$ is 15 mmol/L, pH=3.0, UV lamp power is 11 W and reaction time is 60 min)

0.70 g/L. This behavior may be explained by the fact that higher dosage make much $\bullet OH$ radicals react with themselves, instead of tetracycline in the water, or the UV light which transmits in the reaction system is blocked by an excess of catalyst, thereby the amount of $\bullet OH$ free radicals reduces, resulting in the decrease of the removal of tetracycline.

3.5 Effect of initial pH

The effect of initial pH value on the removal of tetracycline is studied in the pH range of 3.0–9.0 and the results are shown in Fig. 7. When initial pH value changes from 3.0 to 9.0, the removal rate decreases, and the removal rates are 98.13%, 93.28%, 91.21% and 88.43%. High removal rates of tetracycline are obtained at these initial pH, indicating that Fe-Ce/bentonite catalyst fits with a wide range of pH.

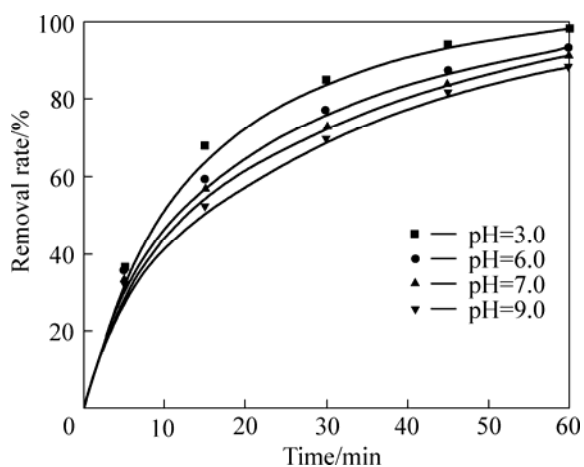


Fig. 7 Effect of initial pH on removal of tetracycline. (Reaction conditions: initial concentration of hydrogen peroxide, $[H_2O_2]_0$ is 15 mmol/L, catalyst dosage is 0.50 g/L, UV lamp power=11 W and reaction time is 60 min)

3.6 Effect of UV power

The effects of different light intensities on the reaction were studied through changing the UV lamp power, and the results are shown in Fig. 8. It can be seen that the removal rate of tetracycline increases with the increase in UV lamp power. After 60 min, the removal rates of tetracycline are 83.47%, 98.13% and 99.31% at power densities of 8 W, 11 W and 2×11 W. When the light intensity ranges from 11 W to 2×11 W, the removal rate of tetracycline has no significant increase. The reason is presumably that as the light intensity constantly increases, the ultraviolet light absorption of catalyst gradually reaches saturation.

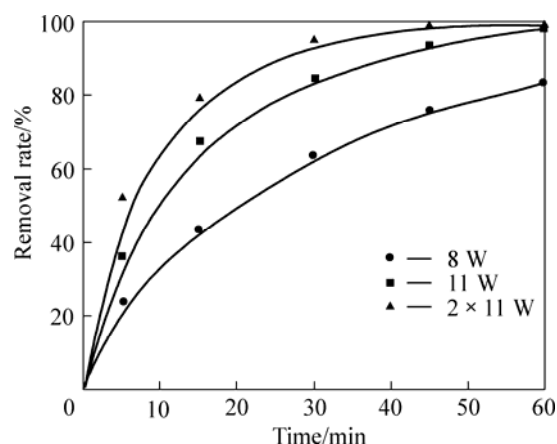


Fig. 8 Effect of UV power on removal of tetracycline. (Reaction conditions: initial concentration of hydrogen peroxide, $[H_2O_2]_0$ is 15 mmol/L, pH=3.0, catalyst dosage is 0.50 g/L and reaction time is 60 min)

3.7 Effect of anion

In fact, there are usually a certain concentration of anions in the solution, especially NO_3^- , SO_4^{2-} , Cl^- and some organic acids ions, and these factors would affect the production of $\bullet OH$ in the advanced oxidation processes [25]. The effect of anions on the rate of removal is shown in Fig. 9. It can be seen that the removal rate of tetracycline decreases significantly when Cl^- or NO_3^- ions are present in the system. The tetracycline removal decreases less in the system containing SO_4^{2-} ions, as compared to Cl^- or NO_3^- tests. The main reasons may be that part of the hydroxyl radicals can react with Cl^- (Eq. (2)) to be consumed, and that ultraviolet light is absorbed strongly by NO_3^- ions not to get through the solution effectively, resulting in the decrease of $\bullet OH$ produced by H_2O_2 photolysis [26]. In the solution containing SO_4^{2-} , HSO_4^- can react with $\bullet OH$ (Eq. (3)), but the reaction rate constant is so small that the SO_4^{2-} has little effect on the reaction system. Therefore, the depression of three kinds of ions on the removal of tetracycline follows this order: NO_3^- , Cl^- , SO_4^{2-} .



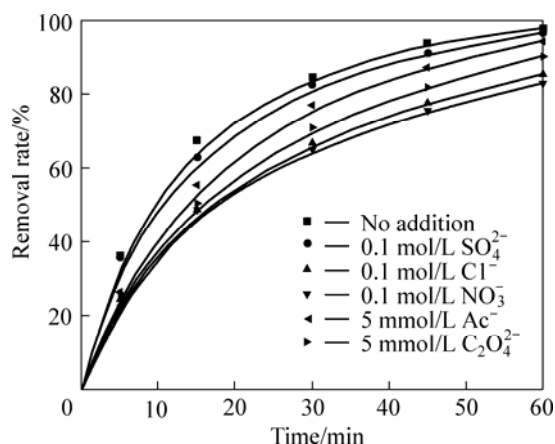


Fig. 9 Effect of anion on removal of tetracycline by Ce-Fe/bentonite photo-Fenton system. (Reaction conditions: initial concentration of hydrogen peroxide, $[\text{H}_2\text{O}_2]_0$ is 15 mmol/L, pH=3.0, catalyst dosage is 0.50 g/L, UV lamp power is 11 W and reaction time is 60 min)

The removal of tetracycline decreases after adding $\text{C}_2\text{O}_4^{2-}$ and Ac^- (Fig. 9). For example, after 30 min, the removal of tetracycline is 84.88% without $\text{C}_2\text{O}_4^{2-}$ and Ac^- , while the removal rate of tetracycline are only 77.24% and 71.06% when adding $\text{C}_2\text{O}_4^{2-}$ and Ac^- . The reason is presumably that pH of solution is changed after adding the organic acid ions to cause a decrease in the activity of catalyst.

3.8 Catalyst recycling experiment

The catalyst was separated from solution by centrifugation, washed with deionized water for several times, dried and then used for next run to study its reusability. The results are shown in Fig. 10. The catalytic efficiency of the Fe-Ce/bentonite catalyst is

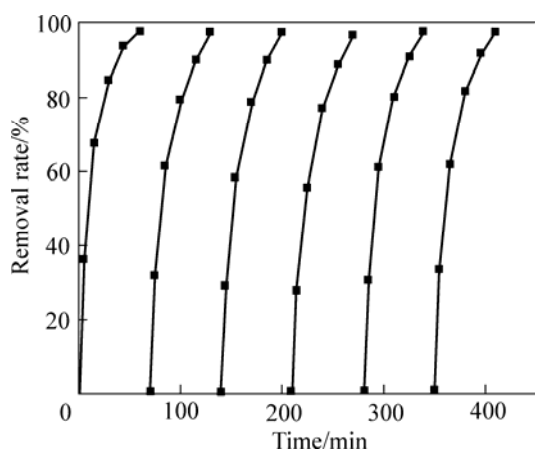


Fig.10 Effect of recycle of catalysts. (Reaction conditions: initial concentration of hydrogen peroxide, $[\text{H}_2\text{O}_2]_0$ is 5 mmol/L, pH=3.0, catalyst dosage is 0.50 g/L, UV lamp power is 11 W and reaction time is 60 min) still more than 97% after recycling six times and the

catalytic performance is not affected by repeated times. Thus, the stable performance of the Fe-Ce/bentonite catalyst reveals that the leakage of metal ions from the catalyst during each run can be negligible.

4 Conclusions

1) An efficient heterogeneous photo-Fenton catalyst Fe-Ce/bentonite is successfully prepared by using an impregnation method. The catalyst is characterized by XRD, XRF and BET analyses, and the results suggest that iron and cerium exist in the bentonite successfully, and the surface area, average pore diameter and total pore volume of the Fe-Ce/bentonite catalyst increase compared to those of the Na-bentonite, which is in favor of the catalytic property of the Fe-Ce/bentonite catalyst.

2) The Fe-Ce/bentonite shows good catalytic property for removal of tetracycline in aqueous solution in the presence of H_2O_2 under UV irradiation. The structure of tetracycline is strongly destroyed. The degradation could occur efficiently over a wide pH range of 3.0–9.0. Different anions have different impacts on the removal of tetracycline, and the effect of three kinds of inorganic anions on the removal follows this order: NO_3^- , Cl^- , SO_4^{2-} ; and the effect of organic anions follows this order: Ac^- , $\text{C}_2\text{O}_4^{2-}$.

3) The catalyst has good stability for the degradation of tetracycline after six recycles, and has great potential application value. However, heterogeneous photo-assisted Fenton process for the removal of tetracycline wastewater is under UV irradiation. The artificial UV apparatus are expensive and often unstable, and consume large quantities of electrical power, so the Fe-Ce/bentonite catalyst will be improved to utilize sunlight or visible light irradiation as the light source efficiently in further work.

References

- [1] JOSHI S. HPLC separation of antibiotics present in formulated and unformulated samples [J]. *Journal of Pharmaceutical and Biomedical Analysis*, 2002, 28(5): 795–809.
- [2] TONG Lei, LI Ping, WANG Yan-xin, ZHU Kuan-zheng. Analysis of veterinary antibiotic residues in swine wastewater and environmental water samples using optimized SPE-LC/MS/MS [J]. *Chemosphere*, 2009, 74(8): 1090–1097.
- [3] CHRISTIAN T, SCHNEIDER R J, FÄRBER H A, SKUTLAREK D, MEYER M T, GOLDBACH H E. Determination of antibiotics residues in manure, soil, and surface waters [J]. *Acta Hydrochimica et Hydrobiologica*, 2003, 31(1): 36–44.
- [4] GIGER W, ALDER A C, GOLET E M, KOLHER H P E, MCARDELL C S, MOLNAR E, SIEGRIST H, SUTER M J F. Occurrence and fate of antibiotics as trace contaminants in wastewaters sewage sludge and surface waters [J]. *CHIMIA International Journal for Chemistry*, 2003, 57(7): 485–491.
- [5] BATT A L, SNOW D D, AGA D S. Occurrence of sulfonamide

- antimicrobials in private water wells in Washington County, Idaho, USA [J]. *Chemosphere*, 2006, 64(11): 1963–1971.
- [6] GROS M, PETROVIĆ M, BARCELÓ D. Development of a multi-residue analytical methodology based on liquid chromatography–tandem mass spectrometry (LC-MS/MS) for screening and trace level determination of pharmaceuticals in surface and wastewaters [J]. *Talanta*, 2006, 70(4): 678–690.
- [7] THRIELE-BRUHN S. Pharmaceutical antibiotics compounds in soils—a review [J]. *Journal of Plant Nutrition and Soil Science*, 2003, 166(2): 145–167.
- [8] BRINZILA C I, PACHECO M J, CIRÍACO L, CIOBANU R C, LOPES A. Electrodegradation of tetracycline on BDD anode [J]. *Chemical Engineering Journal*, 2012, 209: 54–61.
- [9] JEONG J, SONG W, COOPER W J, JUNG J, GREAVES J. Degradation of tetracycline antibiotics: Mechanisms and kinetic studies for advanced oxidation/reduction processes [J]. *Chemosphere*, 2010, 78(5): 533–540.
- [10] KHAN M H, BAE H, JUNG J Y. Tetracycline degradation by ozonation in the aqueous phase: Proposed degradation intermediates and pathway [J]. *Journal of Hazardous Materials*, 2010, 181(1/2/3): 659–665.
- [11] BAUTITZ I R, NOGUEIRA R F P. Degradation of tetracycline by photo-Fenton process-Solar irradiation and matrix effects [J]. *Journal of Photochemistry and Photobiology A: Chemistry*, 2007, 187(1): 33–39.
- [12] BAI Jing, LIU Yan-biao, LI Jin-hua, ZHOU Bao-xue, ZHENG Qing, CAI Wei-min. A novel thin-layer photoelectrocatalytic (PEC) reactor with double-faced titania nanotube arrays electrode for effective degradation of tetracycline [J]. *Applied Catalysis B: Environment*, 2010, 98(3/4): 154–160.
- [13] LIU Yan-biao, GAN Xiao-jie, ZHOU Bao-xue, XIONG Bi-tao, LI Jin-hua, DONG Chao-ping, BAI Jing, CAI Wei-min. Photoelectrocatalytic degradation of tetracycline by highly effective TiO₂ nanopore arrays electrode [J]. *Journal of Hazardous Materials*, 2009, 171(1/2/3): 678–683.
- [14] CHANG P H, LI Z H, YU T L, MUNKHBAYER S, KUO T H, HUNG Y C, JEAN J S, LIN K H. Sorptive removal of tetracycline from water by palygorskite [J]. *Journal of Hazardous Materials*, 2009, 165(1/2/3): 148–155.
- [15] JI Liang-liang, CHEN Wei, DUAN Lin, ZHU Dong-qiang. Mechanisms for strong adsorption of tetracycline to carbon nanotubes: A comparative study using activated carbon and graphite as adsorbents [J]. *Environmental Science and Technology*, 2009, 43(7): 2322–2327.
- [16] XIAO Yu-tang, XU Shuang-shuang, LI Zhi-hua. Degradation of polyvinyl-alcohol wastewater by Fenton's reagent: Condition optimization and enhanced biodegradability [J]. *Journal Central South University of Technology*, 2011, 18(1): 96–100.
- [17] CHEN Qing-kong, JI Fang-ying, LIU Ting-yi, YAN Peng, GUAN Wei, XU Xuan. Synergistic effect of bifunctional Co–TiO₂ catalyst on degradation of Rhodamine B: Fenton-photo hybrid process [J]. *Chemical Engineering Journal*, 2013, 229: 57–65.
- [18] FENG Ji-yun, HU Xi-jun, YUE P L. Discoloration and mineration of orange II using different heterogeneous catalysts containing Fe: A comparative study [J]. *Environmental Science and Technology*, 2004, 38(21): 5773–5778.
- [19] CHEN Jian-xin, Zhu Li-zhong. Heterogeneous UV-Fenton catalyst degradation of dyestuff in water with hydroxyl-Fe pillared bentonite [J]. *Catalysis Today*, 2007, 126(3/4): 463–470.
- [20] ZHANG Ya-ping, WEI Chao-hai, WU Chao-fei, QIAN Zhan. Preparation and characterization of CeO₂ doped with Fe/Al₂O₃ catalyst in photo-Fenton [J]. *China Environmental Science*, 2006, 26(3): 320–323. (in Chinese)
- [21] ZHANG Ai-li, WANG Nan-nan, ZHOU Ji-ti, JIANG Ping, LIU Guang-fei. Heterogeneous Fenton-like catalytic removal of p-nitrophenol in water using acid-activated fly ash [J]. *Journal of Hazardous Materials*, 2012, 201–202: 68–73.
- [22] SUN Hong-xia, LI Jian-chao, LU Tang-jun, ZHANG Ai-xia, ZHANG Xin-ying. Performance of a novel Fe/Al cross-linked modified bentonite (MB) in decolorization of Azo dyes [J]. *Acta Mineralogica Sinica*, 2010, 30(2): 252–256. (in Chinese)
- [23] THAKREA D, RAYALUA S, KAWADEA R, MESHRAM S, SUBRT J, LABHSETWAR N. Magnesium incorporated bentonite clay for defluoridation of drinking water [J]. *Journal of Hazardous Materials*, 2010, 180(1/2/3): 122–130.
- [24] HASSAN H, HAMEED B H. Fe–clay as effective heterogeneous Fenton catalyst for the decolorization of reactive blue 4 [J]. *Chemical Engineering Journal*, 2011, 171(3): 912–918.
- [25] JIANG Cheng-chun, PANG Su-yan, JIANG Jin, OUYANG Feng, MA Jun. The effects of inorganic anions on Fenton-like reactions of atrazine and phenol [J]. *Acta Scientiae Circumstantiae*, 2008, 28(5): 982–987. (in Chinese)
- [26] DU Ying-xun, ZHOU Ming-hua, LEI Le-cheng. The role of oxygen in the degradation of p-chlorophenol by Fenton system [J]. *Journal of Hazardous Materials*, 2007, 139(1): 108–115.

(Edited by HE Yun-bin)