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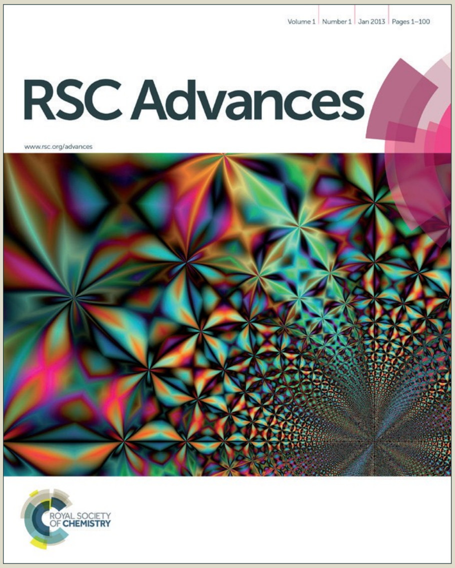

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Granular activated carbon supported iron as heterogeneous persulfate catalyst for the pretreatment of mature landfill leachate

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Abstract

In this study, Fe(Ⅱ)-loaded granular activated carbon(GAC) was used as heterogeneous persulfate catalyst for the pretreatment of mature landfill leachate. The effects of Fe^{2+} dosage, persulfate concentration and initial pH on the degradation of organic pollutants in landfill leachate were investigated. In single factor experiment, the maximum Chemical Oxygen Demand (COD) removal rate reached 66.8, 66.2 and 76.3% at Fe^{2+} dosage 127mg/L ($Fe^{2+}/S_2O_8^{2-}$ = 254 mg/mol), persulfate concentration 0.5 mol/L (i.e. $S_2O_8^{2-}$:12COD_0 = 1.08) and initial pH 3, respectively. Obviously, pH played more important role in persulfate oxidation treatment than another two factors. The synthetic experimental results showed that COD removal rate exceeded 87.8% when the reaction conditions controlled at the Fe^{2+} dosage 127mg/L, persulfate concentration 0.5mol/L and initial pH 3.0, simultaneously. Meanwhile, the recycle experiments displayed that the catalytic ability of reused Fe(Ⅱ)-GAC considerably declined and COD removal rate dropped approximate a half after reusing three times. But the catalytic ability of catalyst used could well recovered after regeneration at 550 ℃ in N_2 atmosphere. Finally, fluorescence excitation-emission matrix (EEM) spectroscopy preliminarily explained the degradation mechanism of landfill leachate.

Keywords: Landfill leachate, Heterogeneous persulfate oxidation, Fe(Ⅱ)-GAC catalysts, Recycle

1. Introduction

Sanitary landfill is the main municipal solid waste (MSW) disposal method in China. With the explosive growth of urbanization and population, billions of tons of MSW are dumped in landfills in China every year. Meanwhile, a great deal of leachates are generated, the emission standards of landfill leachate are also becoming more and more severe. Once untreated leachate let out, it could percolate the soil, infiltrate the ground water and mix with surface waters and contribute to the pollution of soil, ground and surface water [1]. Fresh landfills leachate can be well treated by biological treatment because of the good biodegradability. But according to previous research [2], biological oxygen demand/chemical oxygen demand (BOD/COD) ratio declined as sanitary landfill age increased. Especially, when landfills are put into use more than 10 years, the BOD /COD ratio is lower than 0.1, implying the poor biodegradability. Therefore biological treatment is not appropriate for mature landfill leachate treatment. In order to effectively deal with such leachate, many physical/chemical treatment methods are applied. [3, 4,5, 6]

Advanced oxidation processes (AOPs) are the most common physical/chemical treatment technologies, which include Fenton oxidation, Fenton-like oxidation, photochemical oxidation, wet catalytic oxidation, chemical oxidation, ozone oxidation and electrochemical oxidation. In recent years more and more researchers focus on persulfate oxidation technology [7, 8], but there is a problem in persulfate degradation of organic matters needed to solve. Persulfate is very stable and reaction with organics is very slow at room temperature. To improve the degradation efficiency of organic matters, it is necessary to activate the persulfate. During activated process, a new substance sulfate radicals (SO_4^{-}•, E_0=2.5-3.1V) [9] are generated, which are the stronger oxidants than hydroxyl radicals (•OH, E_0=2.8V) and can degrade most of the organics. Research shows that persulfate can be activated by the photocatalysis, thermocatalysis and transition metal [10].The mechanisms of activated process is as follows. [11]

$$S_2O_8^{2-}\text{+heat/UV} \rightarrow 2SO_4^{-}\bullet \qquad (1.1)$$

$$S_2O_8^{2-}+Me^{n+} \rightarrow Me^{(n+1)+}+SO_4^{2-}+SO_4^{-}\bullet \qquad (1.2)$$

Microwave catalyzes persulfate oxidation of landfill leachate had been studied and achieved good results. [8] Persulfate oxidation technique is also used for the degradation of Orange G and diethyl phthalate [12], carbamazepine [13] and other recalcitrant organic matters. [14-16] But researches on Fe(Ⅱ) activated persulfate oxidation of landfill leachate are few.

AOPs can be classified as homogeneous or heterogeneous. [17] Compared to homogeneous catalysts, heterogeneous catalysts [18] have many advantages, such as high activity, resistance to poisoning and long-term stability at high temperature, mechanical stability and resistance to attrition, non-selectivity in most cases, and physical and chemical stability under wide range of condition. Besides, heterogeneous catalysts have another advantage, easily separating from the aqueous solution. [17]

Fluorescence excitation-emission matrix (EEM) spectroscopy has become an important analysis method to characterize complex environmental samples. The advantages of EEM fluorescence spectroscopy are that the fluorescence enables rapid, non-invasive and accurate characterisation of different organic matter fractions from various environmental samples. [32]

In this study, Fe(Ⅱ)-loaded granular activated carbon as heterogeneous persulfate catalyst was used in the treatment of mature landfill leachate. Fe^{2+} is proved an active catalyst for persulfate [11] and GAC also has a certain absorption capacity, so the combined effects of Fe^{2+} and GAC were investigated. The recycle and regeneration of Fe(Ⅱ)-GAC catalyst was carried out to evaluate the advantages of heterogeneous persulfate catalyst . Finally, the cost of Fe(Ⅱ)-GAC catalyze persulfate oxidation was compared with that of photo-catalytic and thermo-catalytic persulfate oxidation.

2. Material and methods

2.1 Chemicals and landfill leachate

All chemicals used in this study were of analytical grade. Sodium persulfate ($Na_2S_2O_8$, 98%), Silver sulfate (Ag_2SO_4, 99.7%), KI (99%), NaOH (96%), $C_4H_4KNaO_6{\cdot}4H_2O$ (99%) and HgI_2 (99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). GACs were purchased from the Aladdin chemistry Co., Ltd (Shanghai, China). Ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 99%), Ammonium iron (II) sulfate ($(NH_4)_2Fe(SO_4)_2$, 99.5%) were purchased from Tianjin HengXing Chemical Reagent Co., Ltd. (Tianjin, China). Potassium dichromate ($K_2Cr_2O_7$, 99.8%) were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd (Tianjin, China). H_2SO_4 (98%) were purchased from Zhuzhou XingKong Chemical Reagent Co., Ltd.

Landfill leachate used in this study was collected from Changsha municipal solid waste disposal site, Hei mi feng, Changsha, China. The site has been in operation since 2003. [19] The leachate collected was transferred to laboratory immediately and stored in a refrigerator at 4℃. The main physico-chemical characteristics of the raw landfill leachate were presented in Table 1. According to the landfill leachate classification of previous researchers [2, 20], the leachate belongs to mature leachate for lower BOD_5/COD ratio(<0.12). [20]

2.2 Preparation of catalysts

The catalysts, Fe(Ⅱ)-GACs, were prepared according to the method developed by Laiju et al [21] with some necessary modifications. At first, GACs washed by 10% (v/v) H_2SO_4 for 3 times and then cleaned by ultrapure water. After filtration, GACs were dried in oven at 65℃ for 2h. Then the pretreated GACs were added to a beaker including 50 mL ferrous ion solution with a certain concentration in an ultrasonic cleaner (100W, 20kHz, 25℃) for 30 min in order to make the ferrous ion even load in GACs. After dried in vacuum drying oven (DZ-2BCII TAISITE, China) at 65℃ for 2h, the newly formed Fe(Ⅱ)-GACs were calcined in a tube furnace (SK-G06123K, Tianjin Zhonghuan, China) with programmed gradually warming up to a certain temperature in N_2 atmosphere for 4h. Finally, the samples naturally cooled down to ambient temperature in N_2 atmosphere and were stored in sealed vacuum drier for further experiments.

2.3 Heterogeneous persulfate oxidation experiments

Heterogeneous persulfate oxidation experiments were conducted in 500 mL glass beaker on a rotary shaker as the batch model. 1.0 g Fe(Ⅱ)-GAC catalyst and a certain quality of $Na_2S_2O_8$ were simultaneously added to 100 mL landfill leachate. The temperature and rotary shaker speed were controlled at 25℃ and 250 r/min, respectively. The initial pH of leachate was adjusted by 1.0 mol/L H_2SO_4 and 1.0 mol/L NaOH and pH was detected using a pH meter (pHS-3C model, Leici, China). The sample taken at a constant time interval was filtered using a syringe filter with 0.22-μm micropore filter membrane (LC+PVDF membrane, ANPEL Laboratory Technologies Inc., China) and further analyzed. COD was measured by microwave digestion method. The removal efficiency, R (%), of COD was calculated by the following equation:

$$\mathrm{R}(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (1.3)$$

Where C_0 (mg/L) was the initial concentration of COD for leachate, and C_t (mg/L) stood for the concentration of COD at t min.

3. Results and discussion

3.1 Effect of calcination temperature

Research shows that calcination temperature significantly affects the physicochemical properties and the phase composition of catalysts, which further affect the catalytic performance. [22, 23] Before heterogeneous persulfate oxidation experiments, the optimum calcination temperature for the preparation of Fe(Ⅱ)-GAC catalyst was demonstrated. The samples calcined at 350, 450 and 550℃ respectively were characterized by inductively coupled plasma (ICP, Spectro Blue Sop, German) and emission scanning electron microscope (ESEM, FEI Quanta 200, Chech). The percentage composition of iron ion and the ESEM images of Fe(Ⅱ)-GAC catalysts calcined at different temperature were presented in Table 2 and Fig. 1. From Table 2, it is obviously found that the iron ion content of Fe(Ⅱ)-GAC catalysts calcined at 550℃ is more than that of 350℃and 450℃. ESEM images displays that the surface of calcined catalysts formed a rougher layer than the uncalcined catalysts, and the higher the calcination temperature is, the rougher the surface of catalysts becomes. It indicated that the physicochemical properties of catalyst occur the remarkable change after calcination, further resulted in the absorption capacity of catalysts increased. [24] BET (Nova, Quantachrome, USA) analysis shows that the surface area of catalysts increases from 522.45 m^2/g (before calcination) to 630.54m^2/g (after calcination at 550℃) and the rate of increase is approximately 20%.

The catalysts calcined at different temperature were used to activate the persulfate for the mature landfill leachate treatment and the results presented in Fig.2. With the increasing calcination temperature, the removal efficiency of COD improves accordingly. When the calcination temperature is 550℃, the removal rate reaches the maximum (59.3%). Özdemir et al. reported that high calcination temperatures enhanced interaction of metal oxide with support. [25] So the higher calcination temperature not only is in favor of the physicochemical properties of support (GAC), but also enhances the immobilization of Fe(Ⅱ). In subsequent experiments, the Fe(Ⅱ)-GAC calcined at 550℃ will be chosen as the catalyst.

3.2 Effects of persulfate concentration

To evaluate the effect of persulfate concentration, 0.238, 2.38, 4.76, 11.9 and 23.8g $Na_2S_2O_8$ was added into 100 mL landfill leachate with 1g Fe(Ⅱ)-GAC catalyst, where the persulfate concentration was 0.01, 0.1, 0.2, 0.5, 1.0 mol/L respectively. As shown as Fig. 3, the removal rate of COD increases as the persulfate concentration increases. The maximum removal rate of 66.2% was achieved at persulfate concentration of 0.5 mol/L. The persulfate concentration further raised to 1.0mol/L, the COD removal efficiency was not significant improvement. Basicly, the COD removal efficiency increases as the concentration of $Na_2S_2O_8$ increases. [26] However, the detailed mechanisms of sulfate radical attack of leachate organic matters are not well understood. the pathways of organic degradation are difficultly determined. [7] Meanwhile, the lesser Fe(Ⅱ)-GAC catalyst (1g/100 mL) limits the activation of high concentration persulfate, resulting in the decrease of COD removal efficiency.

3.3 Influence of ferrous concentration

Fe^{2+} can active persulfate generated sulfate free radical (Eq. 1.4) but excess Fe^{2+} also can react with sulfate free radical (Eq. 1.5). [11]

Slow: $$S_2O_8^{2-}+Fe^{2+} \rightarrow Fe^{3+}+SO_4^{2-}+SO_4^{-}\bullet \qquad (1.4)$$

Fast: $$SO_4^{-}\bullet+Fe^{2+} \rightarrow Fe^{3+}+SO_4^{2-} \qquad (1.5)$$

Integrated two equations is:

$$S_2O_8^{2-}+2Fe^{2+} \rightarrow 2Fe^{3+}+2SO_4^{2-} \qquad (1.6)$$

It can be seen from the Eq.1.6, excessive Fe^{2+} will reduce the utilization of sulfate free radical. Thereby the controlling of ferric dosage is very important in persulfate oxidation process. In this study, we maintained the fixed amount of catalyst (1g/100 mL) in heterogeneous persulfate oxidation experiments. So the amount of immobilized Fe(Ⅱ) on GAC determined the ferric dosage. Before Fe(Ⅱ)-GAC was calcined in tube furnace, GAC was immersed in 50 mL ferrous solution with the concentrations of 0.05, 0.1, 0.2, 0.5 and 1.0 mol/L under ultrasonic treatment (100W, 20kHz, 25℃). These catalysts calcined at 550℃were sent to ICP analysis and the iron content in catalyst (w/w, %) was listed in Table 3. Obviously, high ferrous concentration caused more immobilization of Fe(Ⅱ) on GAC. The highest iron content in Fe(Ⅱ)-GAC reached 3.98% when the ferrous concentration was 1.0 mol/L. Fig. 4 shows the COD removal with different ferrous concentration. Similar to previous researches, the change of COD removal efficiency was not linear increase with the Fe^{2+} dosage. When Fe^{2+} dosage was moderate 127mg/L ($Fe^{2+}/S_2O_8^{2-}$ = 254 mg/mol), the removal rate of COD was the highest (66.8%). The results demonstrated that Fe^{2+} has a great influence on persulfate of generating sulfate free radicals, which too much or less Fe^{2+} is negative to produce sulfate free radicals. [9, 27]

3.4 Influence of initial pH

It is well known that pH can remarkably affect the Fe(Ⅱ) activated persulfate oxidation of refractory organic contaminants. [7] The effect of initial pH on the removal of COD by Fe(Ⅱ)-GAC activated persulfate oxidation at room temperature is shown Fig. 5. When the initial pH fluctuated between 3 and 11, the COD removal efficiency decreased with the increasing pH. It is interesting that the COD removal exhibits higher performance at pH 11. However, the maximum COD removal of 76.3% was achieved at pH 3**.** It can be explained by following equations, namely, persulfate is activated effectively by Fe(Ⅱ) and generated more sulfate radicals under acidic conditions. [11]

$S_2O_8^{2-}$+H^+→ $HS_2O_4^-$ (1.7)

$HS_2O_4^-$→ SO_4^-•+SO_4^{2-} + H^+ (1.8)

SO_4^-• formed can produce a rapid attack on any oxidizable agents including organic contaminants. [28] But too more H^+ will inhibit the formation of sulfate radicals (Eq. 1.8). Also, the presence of SO_4^-• in aqueous solution can result in radical interconversion reactions to produce the hydroxyl radical (•OH, E_0=2.8V) in accordance with the Eqs. 1.9 and 1.10. [28, 29] That is why the removal COD also keeps high level under the alkaline condition (pH=11).

All pHs: SO_4^-•+H_2O→ SO_4^{2-}+•OH + H^+ (1.9)

Alkaline pH: SO_4^-•+OH^-→ SO_4^{2-} +•OH (1.10)

pH plays a more complex role in persulfate oxidation of contaminants. [28, 30, 31] In previous researches, the highest COD removal in persulfate oxidation of landfill leachate was achieved at pH 3 [31], but the optimal TCE degradation by persulfate oxidation occurred at near neutral pH (i.e., pH 7) [28], meanwhile the maximum degradation rate of sulfamethazine (SMZ) induced by persulfate oxidation appeared at pH 9. [30] Reaction mechanisms of SO_4^-• and HO• with organic compounds could be quite different. The reaction between SO_4^-• and organic compounds is primarily through electron transfer, H-atom abstraction and addition-elimination, whereas HO• reacts with organic compounds preferentially via the addition of C=C double bonds and abstracting H from C-H, N-H, or O-H bonds. [11, 30] Therefore, pH affects the persulfate oxidation by altering the predominant oxidizing species in solution, further bringing about different mechanism for pollutants degradation. Furthermore, pH also can change the speciation of target pollutants. [30]

3.5 Optimum synthetic experiment

Based on the experimental results above, we carried out the optimum synthetic experiment of Fe(Ⅱ)-GAC catalytic persulfate oxidation for mature landfill leachate treatment at pH 3, Fe^{2+} dosage 127mg/L ($Fe^{2+}/S_2O_8^{2-}$ =254 mg/mol) and persulfate concentration 0.5 mol/L (i.e. $S_2O_8^{2-}$:$12COD_0$=1.08). The COD removal rate achieves to 87.8% under optimal conditions. Compared with heat-activated persulfate oxidation for landfill leachate treatment, the optimal COD removal rate 91% is higher than in this study at $S_2O_8^{2-}$:$12COD_0$=2, 50℃ and pH 4 [7], but more persulfate and energy consumption occurred in this process to achieve similar performance. Under the similar reaction conditions, the maximum removal rates of COD were 66.0, 59.3 and 87.8% at the reaction time of 120 min in Fe^{2+}/PS, PS/GAC and PS/Fe(Ⅱ)-GAC system, respectively (Fig. 6(a)). High correlation coefficient (R^2) suggests that COD degradation in all catalytic system could be well expressed by the pseudo-first-order kinetics within first 30min (Fig. 6(b)). The rate constant (k) for the PS/Fe(Ⅱ)-GAC system is 0.0596 min^{-1}, which is 2.18 and 2.41 times than that of Fe^{2+}/PS and PS/GAC system. These results suggested that Fe(Ⅱ)-GAC catalytic combined the catalysis of Fe(Ⅱ) and adsorption of GAC and enhanced the persulfate oxidation of landfill leachate.

3.6 Recycle and regeneration of Fe(Ⅱ)-GAC catalysts

Fe(Ⅱ)-GAC catalysts used was separated from solution by filtrating and cleaned with ultrapure water. Then the catalysts was dried in vacuum drying oven at 65℃ and calcined in tube furnace at 550℃ under N_2 atmosphere for 1h. The catalysts were reused in the persulfate oxidation of mature landfill leachate treatment. Three recycle experimental results were presented in Fig. 7. As shown in Fig. 7, the catalytic performance of Fe(Ⅱ)-GAC gradually declines with the time of recycle. When the Fe(Ⅱ)-GAC was reused three time, the COD removal rate dropped almost a half . But when the reused catalysts put in ferrous solution with ultrasonic treatment and calcined in 550℃under N_2 atmosphere to regenerate, the catalytic performance of Fe(Ⅱ)-GAC can be recovered and the COD removal rate achieved the level as the fresh catalyst. The perfect renewable characteristics of Fe(Ⅱ)-GAC exhibits its advantage in the heterogeneous persulfate oxidation. The detection result of iron ion before and after persulfate oxidation showed that the amount of ferrous and ferric ions leached was considerably little (date no shown), which is similar to previous researches [12, 21]. It also proved that persulfate was mainly heterogeneous activated by Fe(Ⅱ)-GAC instead of Fe^{2+} in aqueous solution.

3.7 3D-EEM fluorescence spectra analysis

In this study, three-dimensional excitation and emission matrix (3D-EEM) fluorescence spectroscopy (F-4600, HITACHI, Japan) was applied to analysis the dissolved organic matter (DOM) in landfill leachate before and after persulfate oxidation. Fluorescence data were collected by scanning excitation wavelengths in the range from 300 to 700 nm in 5 nm steps, and detecting the emitted fluorescence in 5nm steps between 300 and 700 nm. [32] The EEM fluorescence spectra are illustrated in Fig. 8.

Generally, EEM fluorescence spectra exhibit increased intensities in particular regions and these fluorescence regions can be attributed to both natural fluorescence (humic- and fulvic-like), defined as peaks A and C and microbial derived organic matter (tryptophan- and tyrosine-like fluorescence, defined as peaks T and B) at shorter emission wavelengths (Table 4). [33, 34]

As shown in Fig. 8, the EEM fluorescence spectra peaks of landfill leachate before and after persulfate oxidation are mainly on Ex. 355-375nm/Em. 420-455nm. This demonstrated that the major constituent of landfill leachate is humic (highly colored) [35] and the spectra of leachate after treatment has no new peaks, indicating that no new organics are generated in persulfate oxidation. [36] The color depth of the peaks demonstrated that the concentration of organics decreased after persulfate treatment and the humic-like organics were well decomposed with the increasing of persulfate concentration.

3.8 Cost of Fe(Ⅱ)-GAC catalysts method

According to optimal conditions of Fe(Ⅱ)-GAC catalytic persulfate oxidation, 100mL landfill leachate treatment need about 1g GAC, 11.9g persulfate, 2.78g $FeSO_4·7H_2O$, 3mL H_2SO_4 and considering energy consumption. Based on the price in China (GAC 150 US$/t, $FeSO_4·7H_2O$ 65 US$/t, persulfate 130US$/t and H_2SO_4 90 US$/t), the cost was estimated to about 82US$ for 1000 gallons leachate. Compared with the cost of other AOPs treatments US$ 50 to US$ 800 per 1000 gallons [4, 37], it demonstrated that Fe(Ⅱ)-GAC catalyst has a great potential in landfill leachate treatment.

4. Conclusions

In this study, granular activated carbon supported iron was used as heterogeneous persulfate catalyst to pretreat the mature landfill leachate. The optimal experiment conditions for Fe(Ⅱ)-GAC catalytic persulfate oxidation were pH 3, Fe^{2+} dosage 127mg/L ($Fe^{2+}/S_2O_8^{2-}$=254mg/mol) and persulfate concentration 0.5 mol/L (i.e. $S_2O_8^{2-}$:12COD_0=1.08), in which the maximum COD removal rate of 87.8% was achieved. The kinetic study demonstrated that the persulfate activated by Fe(Ⅱ)-GAC was rapid process and the COD removal in all the experiments reached the best about 30 minutes because $SO_4^{-}\cdot$ formed can produce a rapid attack on any oxidizable agents including organic contaminants. The catalytic performance of Fe(Ⅱ)-GAC gradually declines with the time of recycle and the COD removal rate dropped approximate a half after three times reuse. The regenerated Fe(Ⅱ)-GAC could be regenerated through the calcination at 550 ℃ under N_2 atmosphere. 3D-EEM analysis demonstrated that the major constituent of landfill leachate is humic acid and the humic-like organics were decomposed by sulfate free radical from Fe(Ⅱ)-GAC activated persulfate.

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Table caption

Table 1. Characteristics of raw landfill leachate.

Table 2. ICP-MS analysis of iron content in Fe(Ⅱ)-GAC calcined at different temperature.

Table 3. Iron content in Fe(Ⅱ)-GAC immersed with different ferrous concentration solution.

Table 4. Excitation and emission wavelength pairs for principal peak fluorescence intensities.

Figure caption

Fig. 1. ESEM images of Fe(Ⅱ)-GAC calcined at different temperature. Uncalcined (a), 350℃ (b), 450℃ (c) and 550℃ (d).

Fig. 2. Influence of calcination temperature on persulfate oxidation of COD. Reaction conditions: Fe(Ⅱ)-GAC 10 g/L, persulfate concentration 0.1 mol/L, pH not adjusted.

Fig. 3. COD removal under different persulfate concentrations. Reaction conditions: Fe(Ⅱ)-GAC 10 g/L, landfill leachate 100 mL, pH not adjusted.

Fig. 4. Effect of immersed ferrous concentration on the COD removal. Reaction conditions: Fe(Ⅱ)-GAC 10 g/L, landfill leachate 100 mL, persulfate concentration 0.5mol/L, pH not adjusted.

Fig. 5. Effect of initial pH on the COD removal. Reaction conditions: Fe(Ⅱ)-GAC 1.0 g/L, landfill leachate 100 mL, persulfate concentration 0.1mol/L, temperature 25℃.

Fig. 6. (a) Comparison of COD removal by persulfate oxidation with different catalysts (pH 3, Fe^{2+} dosage 127mg/L, persulfate concentration 0.5 mol/L). (b) Pseudo-first-order kinetic curves for COD degradation.

Fig. 7. Recycle and regeneration of Fe(Ⅱ)-GAC catalysts.

Fig. 8. 3DEEM fluorescence spectra of (a) raw landfill leachate (peak Ex.375 nm/Em.455 nm), (b) leachate treated with 0.2 mol/L persulfate (peak Ex.360 nm/Em.435 nm), (c) leachate treated with 0.5 mol/L persulfate (peak Ex.355 nm/Em.425 nm) and (d) leachate treated with 1.0 mol/L persulfate (peak Ex.360 nm/Em.420 nm).

Table 1. Characteristics of raw landfill leachate.

Parameter	Value
TOC(mg/L)	2965±3.01%
COD (mg/L)	9163±4.35%
BOD_5(mg/L)	956±3.11%
BOD_5/COD	0.10
NH_4^+-N(mg/L)	1845±1%
NO_3^--N(mg/L)	18.1±6.63%
NO_2^--N(mg/L)	0.71±0.56%
SS(mg/L)	441±2.04%
pH	7.82
Conductivity(us/cm)	16750±2.48%
Turbidity(NTU)	1222±2.62%

Table 2. ICP-MS analysis of iron content in Fe(Ⅱ)-GAC calcined at different temperature.

Temperature(℃)	Blank[a]	350	450	550
Fe ion/g Fe(Ⅱ)-GAC (%)	0.16	0.60	0.53	0.68

a. no any treatment

Table 3. Iron content in Fe(Ⅱ)-GAC immersed with different ferrous concentration solution.

Ferrous solution concentration(mol/L)	Fe(%)/g Fe(Ⅱ)-GACs
0	0.16
0.01	0.48
0.05	0.52
0.1	0.97
0.2	1.27
0.5	2.71
1.0	3.98

Table 4. Excitation and emission wavelength pairs for principal peak fluorescence intensities.

Peak	λ_{Ex} (nm)	λ_{Em} (nm)
Humic		
A	237–260	400–500
Humic (highly coloured)		
C	300–370	400–500
C1	320–340	410–430
C2	370–390	460–480
Tyrosine		
B1	225–237	309–321
B2	275	310
Tryptophan		
T1	275	340
T2	225–237	340–381
Humic (marine)		
M	290–310	370–410

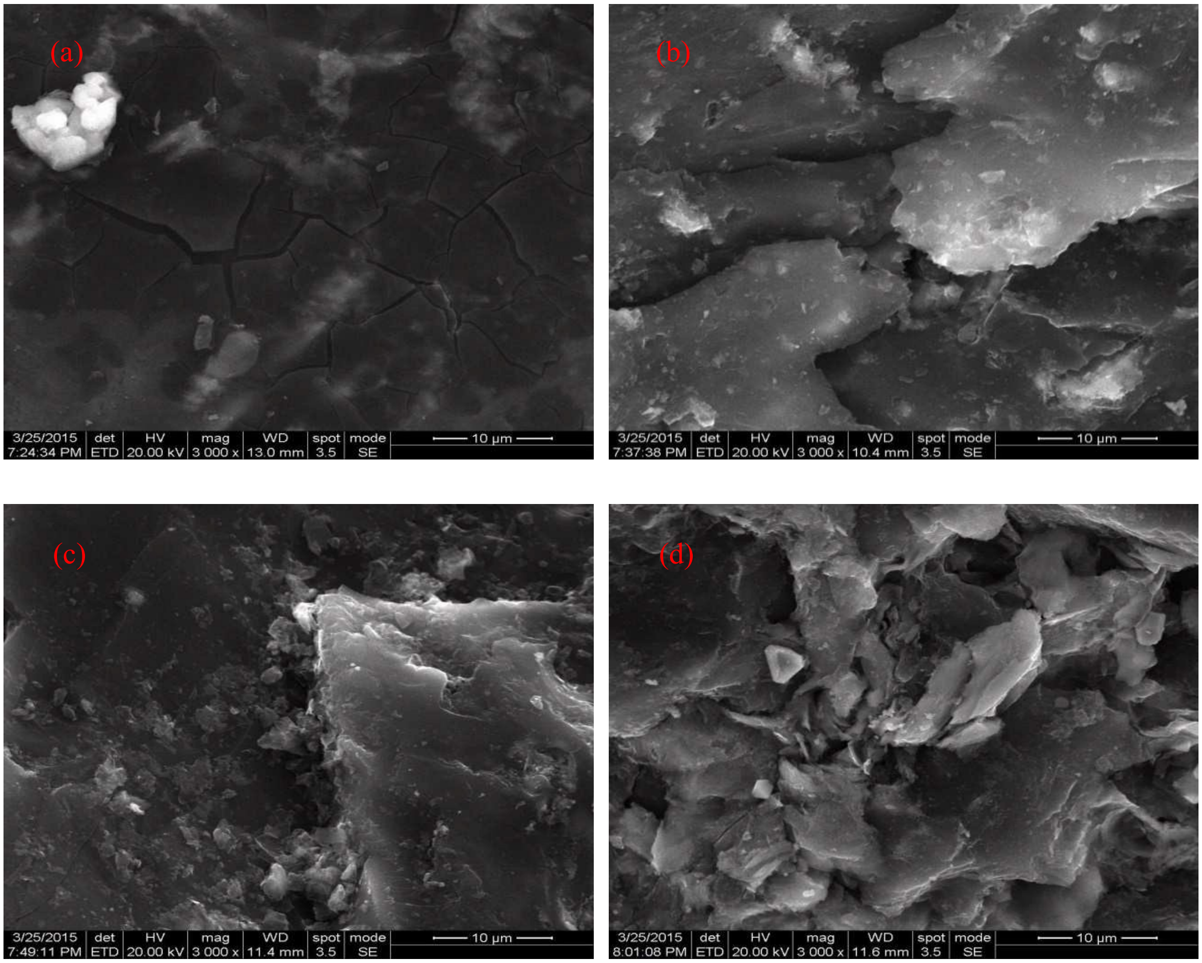


Fig. 1. ESEM images of Fe(Ⅱ)-GAC calcined at different temperature. Uncalcined (a), 350℃ (b), 450℃ (c) and 550℃ (d).

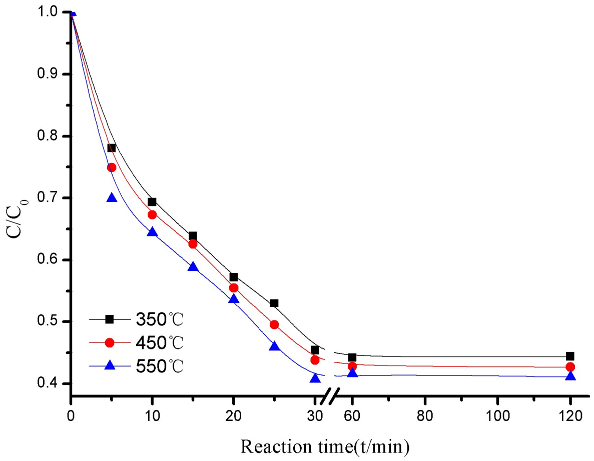


Fig. 2. Influence of calcination temperature on persulfate oxidation of COD. Reaction conditions: Fe(Ⅱ)-GAC 10 g/L, persulfate concentration 0.1 mol/L, pH not adjusted.

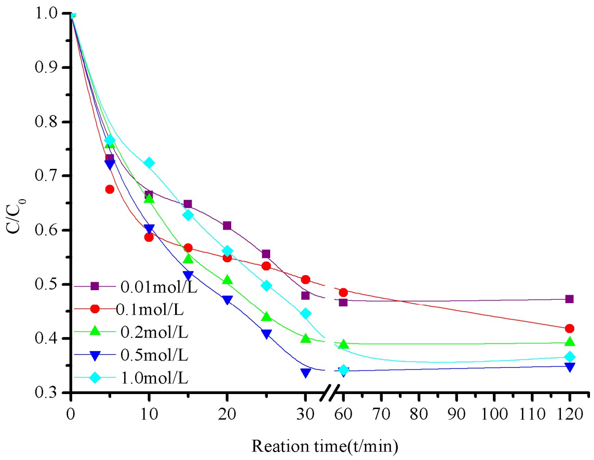


Fig. 3. COD removal under different persulfate concentrations. Reaction conditions: Fe(Ⅱ)-GAC 10 g/L, landfill leachate 100 mL, pH not adjusted.

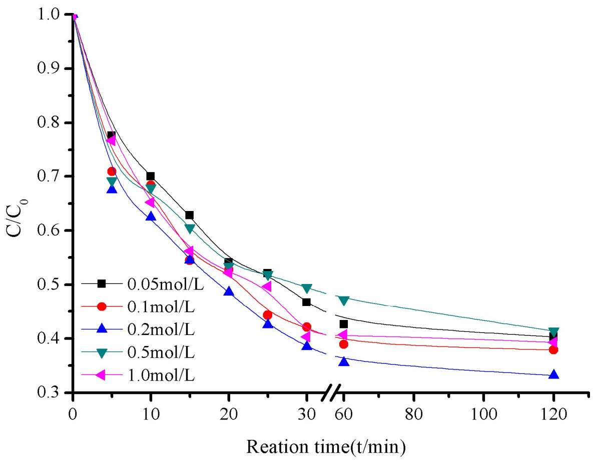


Fig. 4. Effect of immersed ferrous concentration on the COD removal. Reaction conditions: Fe(Ⅱ)-GAC 10 g/L, landfill leachate 100 mL, persulfate concentration 0.5 mol/L, pH not adjusted.

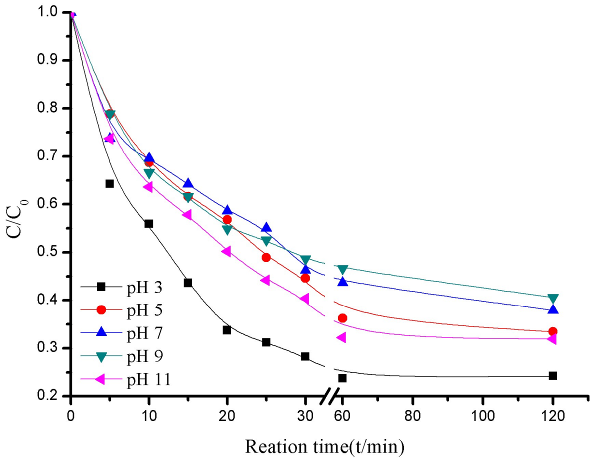
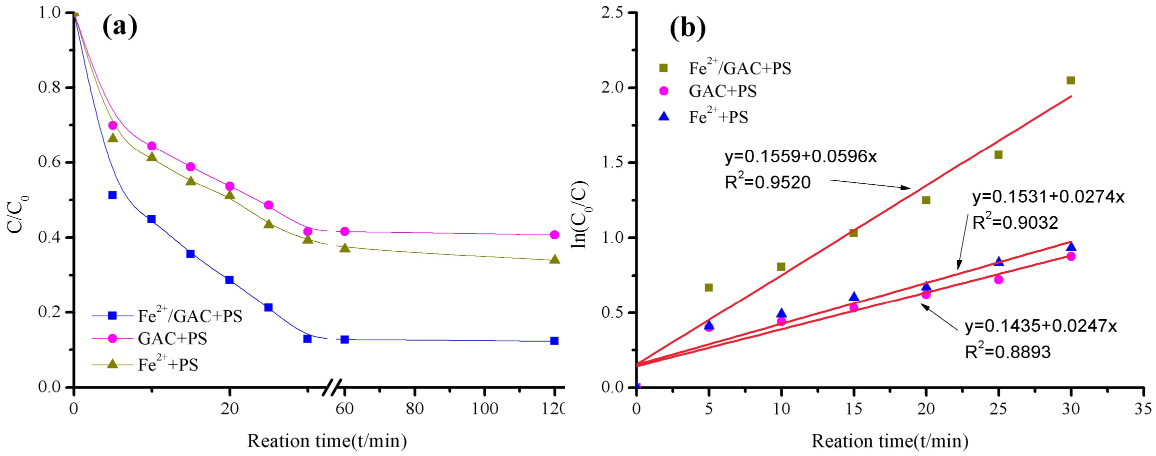


Fig. 5. Effect of initial pH on the COD removal. Reaction conditions: Fe(Ⅱ)-GAC 10 g/L, landfill leachate 100 mL, persulfate concentration 0.1mol/L, temperature 25℃.



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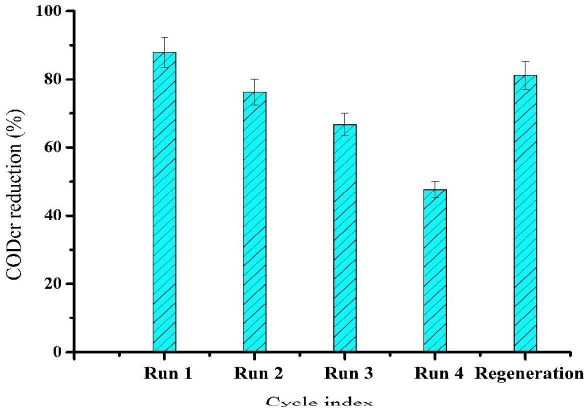
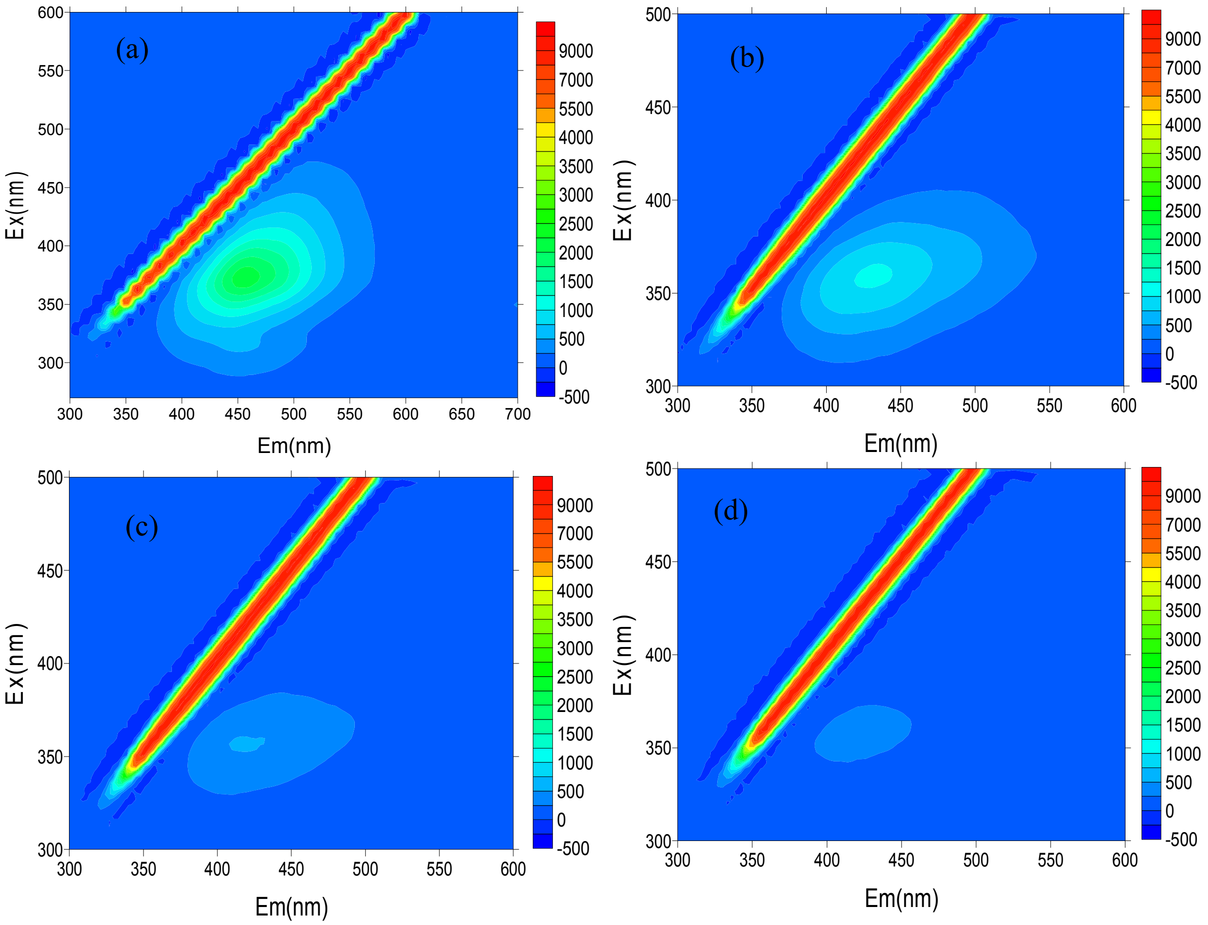


Fig. 7. Recycle and regeneration of Fe(Ⅱ)-GAC catalysts.



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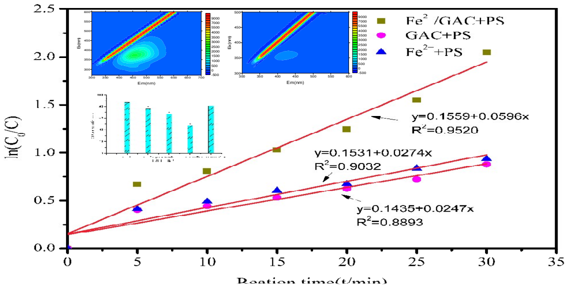
Graphical abstract



Highlights:

- Fe(Ⅱ) loaded in granular activated carbon as persulfate catalyst was first applied to landfill leachate.
- The optimum conditions for COD removal of mature landfill leachate were determined.
- The recycle experiments of the Fe(Ⅱ)-loaded GAC catalysts were conducted.
- Fluorescence excitation-emission matrix (EEM) spectroscopy was applied to explain the degradation mechanism of landfill leachate.