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

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In this study, Fe(II)-loaded granular activated carbon (GAC) was used as a 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 the organic pollutants in the landfill leachate were investigated. In single factor experiments, the maximum Chemical Oxygen Demand (COD) removal rate reached 66.8, 66.2 and 76.3% at an Fe^{2+} dosage of 127 mg L^{-1} ($Fe^{2+}/S_2O_8{}^{2-}$ = 254 mg mol^{-1}), a persulfate concentration of 0.5 mol L^{-1} (*i.e.* $S_2O_8{}^{2-} : 12COD_0 = 1.08$) and an initial pH of 3, respectively. Obviously, pH played a more important role in the persulfate oxidation treatment than the other two factors. The synthetic experimental results showed that the COD removal rate exceeded 87.8% when the reaction conditions had a controlled Fe^{2+} dosage of 127 mg L^{-1}, persulfate concentration of 0.5 mol L^{-1} and initial pH of 3.0, simultaneously. The recycle experiments displayed that the catalytic ability of reused Fe(II)-GAC declined considerably and the COD removal rate dropped by approximately half after reusing three times. But the catalytic ability of the catalyst used could be well recovered after regeneration at 550 °C in a N_2 atmosphere. Finally, fluorescence excitation–emission matrix (EEM) spectroscopy preliminarily explained the degradation mechanism of the landfill leachate.

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 leachates are also becoming more and more severe. Once untreated leachate is let out, it could percolate the soil, infiltrate the ground water, mix with surface waters and contribute to the pollution of soil, ground and surface water.[1] Fresh landfill leachate can be well treated using biological treatments because of its good biodegradability. But according to previous research,[2] the biological oxygen demand/chemical oxygen demand (BOD/COD) ratio declines as sanitary landfill age increases. When landfills are put into use for more than 10 years, the BOD/COD ratio is lower than 0.1, implying poor biodegradability. Therefore biological treatment is not appropriate for mature landfill leachate treatment. In order to effectively deal with such leachates, many physical/chemical treatment methods are applied.[3–6]

Advanced oxidation processes (AOPs) are the most common physical/chemical treatment technologies, these 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 have focused on persulfate oxidation technology,[7,8] but there is a problem in the persulfate degradation of organic matters that needs to be solved. Persulfate is very stable and its reaction with organics is very slow at room temperature. To improve the degradation efficiency for organic matter, it is necessary to activate the persulfate. During the activation process sulfate radicals ($SO_4{}^{-\bullet}$, $E_0 = 2.5$–3.1 V)[9] are generated, which are stronger oxidants than hydroxyl radicals ($^{\bullet}OH$, $E_0 = 2.8$ V) and can degrade most of the organics. Research shows that persulfates can be activated by photocatalysis, thermocatalysis and transition metals.[10] The mechanisms of the activation processes are as follows.[11]

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

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

Microwave catalyzed persulfate oxidation of landfill leachate has been studied and achieved good results.[8] The persulfate

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oxidation technique is also used for the degradation of Orange G, diethyl phthalate,[12] carbamazepine[13] and other recalcitrant organic matter.[14–16] But there is little research on Fe(II) activated persulfate oxidation of landfill leachates.

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, long-term stability at high temperature, mechanical stability and resistance to attrition, non-selectivity in most cases, and physical and chemical stability under a wide range of conditions. Besides, heterogeneous catalysts have another advantage in 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 the different organic matter fractions from various environmental samples.[32]

In this study, Fe(II)-loaded granular activated carbon as a heterogeneous persulfate catalyst was used in the treatment of mature landfill leachate. Fe^{2+} is proved to be 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 recycling and regeneration of the Fe(II)-GAC catalyst was carried out to evaluate the advantages of a heterogeneous persulfate catalyst. Finally, the cost of the Fe(II)-GAC catalyzed persulfate oxidation was compared with that of the photocatalytic and thermocatalytic persulfate oxidations.

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%), $C_4H_4KNaO_6\cdot4H_2O$ (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 ($FeSO_4\cdot7H_2O$, 99%), and 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%) was purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd (Tianjin, China). H_2SO_4 (98%) was purchased from Zhuzhou XingKong Chemical Reagent Co., Ltd.

The landfill leachate used in this study was collected from the 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 the laboratory immediately and stored in a refrigerator at 4 °C. The main physico-chemical characteristics of the raw landfill leachate are presented in Table 1. According to the landfill leachate classification of previous researchers,[2,20] the leachate belongs to the mature leachate class due to its lower BOD_5/COD ratio (<0.12).[20]

Table 1 Characteristics of raw landfill leachate

Parameter	Value
TOC (mg L^{-1})	2965 ± 3.01%
COD (mg L^{-1})	9163 ± 4.35%
BOD_5 (mg L^{-1})	956 ± 3.11%
BOD_5/COD	0.10
NH_4^+–N (mg L^{-1})	1845 ± 1%
NO_3^-–N (mg L^{-1})	18.1 ± 6.63%
NO_2^-–N (mg L^{-1})	0.71 ± 0.56%
SS (mg L^{-1})	441 ± 2.04%
pH	7.82
Conductivity (μs cm^{-1})	16 750 ± 2.48%
Turbidity (NTU)	1222 ± 2.62%

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, the GACs were washed using 10% (v/v) H_2SO_4 3 times and were then cleaned using ultrapure water. After filtration, the GACs were dried in an oven at 65 °C for 2 h. Then the pretreated GACs were added to a beaker containing 50 mL of ferrous ion solution with a certain concentration in an ultrasonic cleaner (100 W, 20 kHz, 25 °C) for 30 min in order to make the ferrous ions evenly load onto the GACs. After drying in a vacuum drying oven (DZ-2BCII TAISITE, China) at 65 °C for 2 h, the newly formed Fe(II)-GACs were calcined in a tube furnace (SK-G06123K, Tianjin Zhonghuan, China) programmed to gradually warm up to a certain temperature under a N_2 atmosphere for 4 h. Finally, the samples were allowed to naturally cool down to ambient temperature under a N_2 atmosphere and were stored in a sealed vacuum drier for further experiments.

2.3 Heterogeneous persulfate oxidation experiments

Heterogeneous persulfate oxidation experiments were conducted in a 500 mL glass beaker on a rotary shaker as the batch model. 1.0 g of Fe(II)-GAC catalyst and a certain quantity of $Na_2S_2O_8$ were simultaneously added to 100 mL of landfill leachate. The temperature and rotary shaker speed were set at 25 °C and 250 rpm, respectively. The initial pH of the leachate was adjusted using 1.0 mol L^{-1} H_2SO_4 and 1.0 mol L^{-1} NaOH and the pH was detected using a pH meter (pHS-3C model, Leici, China). Samples taken at a constant time interval were filtered using a syringe filter with a 0.22 μm micropore filter membrane (LC + PVDF membrane, ANPEL Laboratory Technologies Inc., China) and further analyzed. The COD was measured using the microwave digestion method. The removal

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

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

[a] No treatment.

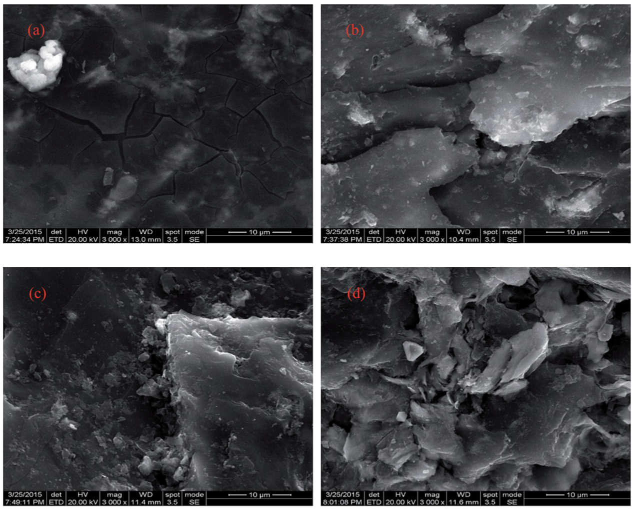

Fig. 1 ESEM images of Fe(II)-GAC calcined at different temperatures. Uncalcined (a), 350 °C (b), 450 °C (c) and 550 °C (d).

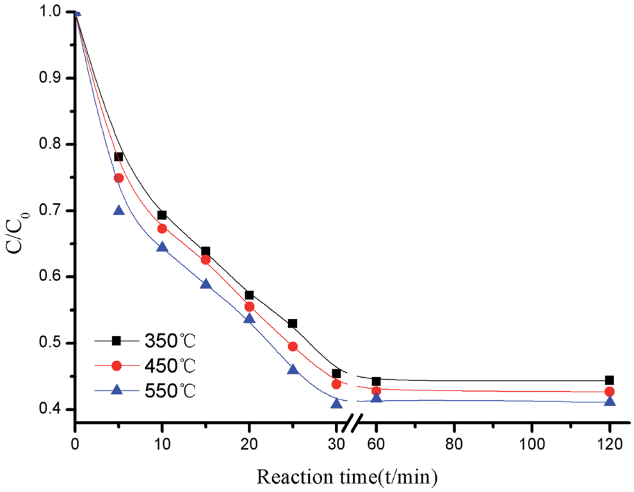

Fig. 2 Influence of calcination temperature on persulfate oxidation of COD. Reaction conditions: Fe(II)-GAC 10 g L^{-1}, persulfate concentration 0.1 mol L^{-1}, pH not adjusted.

efficiency, R (%), of the COD was calculated using the following equation:

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

where C_0 (mg L^{-1}) was the initial concentration of the COD for the leachate, and C_t (mg L^{-1}) stood for the concentration of the COD at t min.

3. Results and discussion

3.1 Effect of calcination temperature

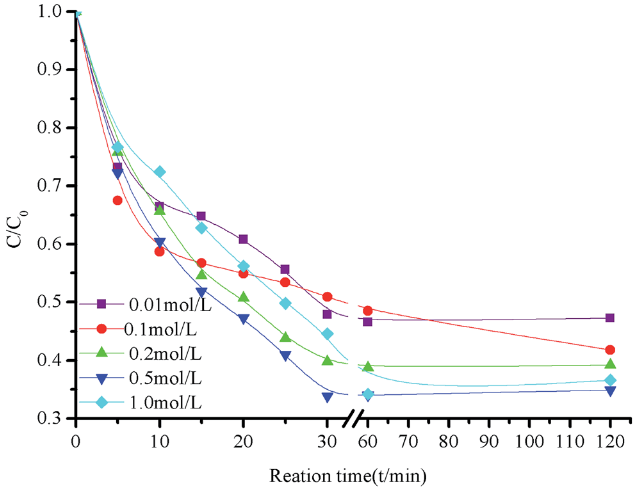

Fig. 3 COD removal under different persulfate concentrations. Reaction conditions: Fe(II)-GAC, 10 g L^{-1}; landfill leachate, 100 mL; pH, not adjusted.

Table 3 Iron content in Fe(II)-GAC immersed in different ferrous concentration solutions

Ferrous solution concentration (mol L^{-1})	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

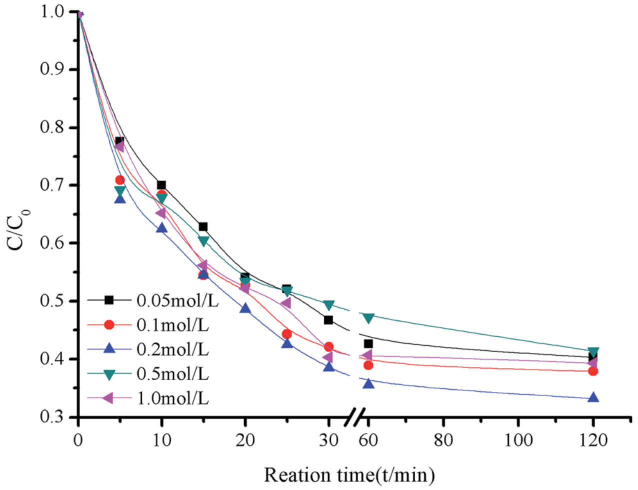

Fig. 4 Effect of immersed ferrous concentration on the COD removal. Reaction conditions: Fe(II)-GAC, 10 g L^{-1}; landfill leachate, 100 mL; persulfate concentration, 0.5 mol L^{-1}; pH, not adjusted.

Research shows that the calcination temperature significantly affects the physicochemical properties and the phase composition of catalysts, which further affects the catalytic performance.[22,23] Before the heterogeneous persulfate oxidation experiments, the optimum calcination temperature for the preparation of the Fe(II)-GAC catalyst was demonstrated. The samples calcined at 350, 450 and 550 °C were characterized

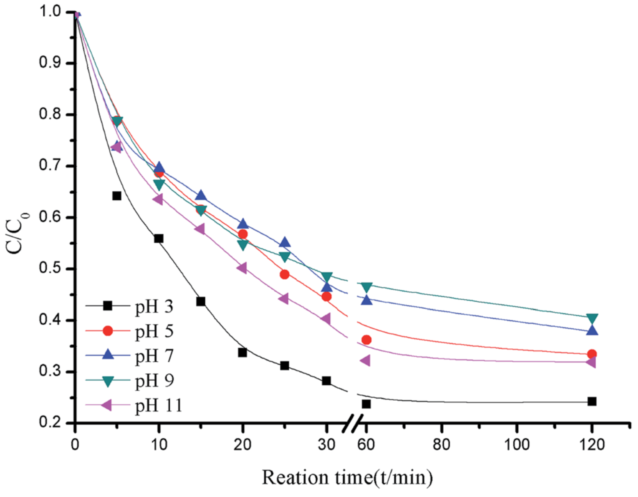

Fig. 5 Effect of initial pH on the COD removal. Reaction conditions: Fe(II)-GAC, 1.0 g L^{-1}; landfill leachate, 100 mL; persulfate concentration, 0.1 mol L^{-1}; temperature, 25 °C.

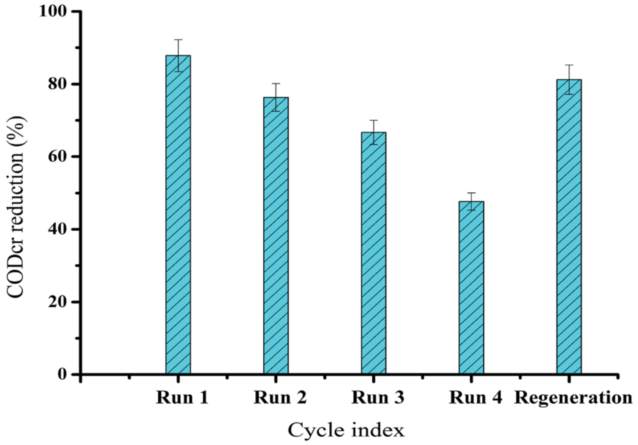

Fig. 7 Recycling and regeneration of Fe(II)-GAC catalysts.

using inductively coupled plasma (ICP, Spectro Blue Sop, German) and emission scanning electron microscopy (ESEM, FEI Quanta 200, Chech). The percentage composition of iron ions and the ESEM images of the Fe(II)-GAC catalysts calcined at different temperatures are presented in Table 2 and Fig. 1. From Table 2, it is obviously found that the iron ion content of the Fe(II)-GAC catalysts calcined at 550 °C is more than that of those calcined at 350 °C and 450 °C. The ESEM images display that the surface of the calcined catalysts formed a rougher layer than the uncalcined catalysts, and the higher the calcination temperature is, the rougher the surface of the catalyst becomes. This indicated that the physicochemical properties of a catalyst undergo a remarkable change after calcination, further resulting in the absorption capacity of the catalysts increasing.[24] BET (Nova, Quantachrome, USA) analysis shows that the surface area of the catalysts increases from 522.45 $m^2\ g^{-1}$ (before calcination) to 630.54 $m^2\ g^{-1}$ (after calcination at 550 °C) and the rate of increase is approximately 20%.

The catalysts calcined at different temperatures were used to activate the persulfate for the mature landfill leachate treatment and the results are presented in Fig. 2. With the increasing calcination temperature, the removal efficiency of the COD improves accordingly. When the calcination temperature is 550 °C, the removal rate reaches the maximum (59.3%). Özdemir *et al.* reported that high calcination temperatures enhanced the interaction of metal oxides with a support.[25] So the higher calcination temperature is not only in favor of the physicochemical properties of the support (GAC), but also enhances the immobilization of Fe(II). In subsequent experiments, the Fe(II)-GAC calcined at 550 °C 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 or 23.8 g of $Na_2S_2O_8$ was added into 100 mL landfill leachate with 1 g of the Fe(II)-GAC catalyst, where the persulfate

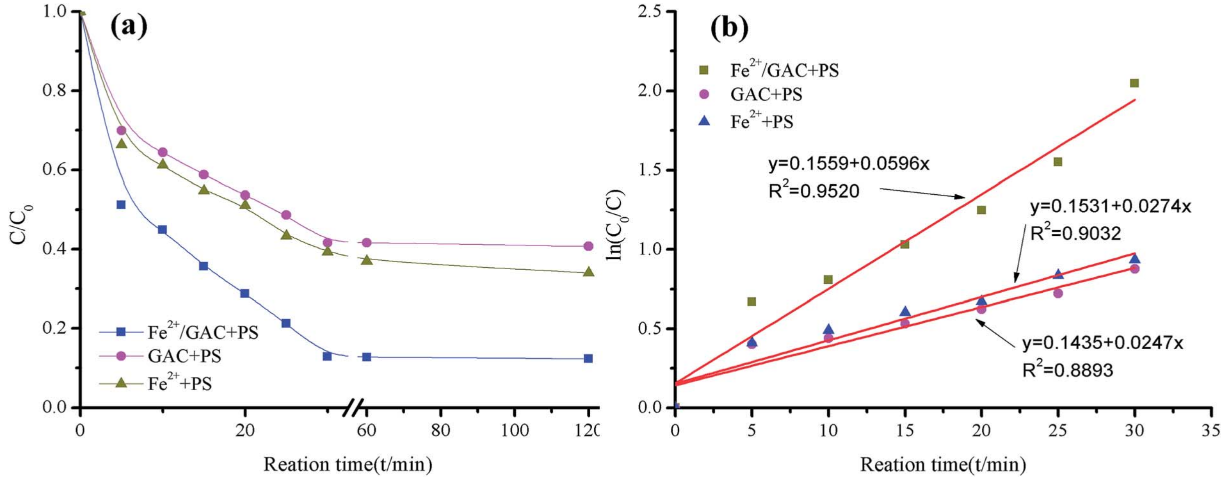

Fig. 6 (a) Comparison of COD removal by persulfate oxidation with different catalysts (pH 3, Fe^{2+} dosage 127 mg L^{-1}, persulfate concentration 0.5 mol L^{-1}). (b) Pseudo-first-order kinetics curves for COD degradation.

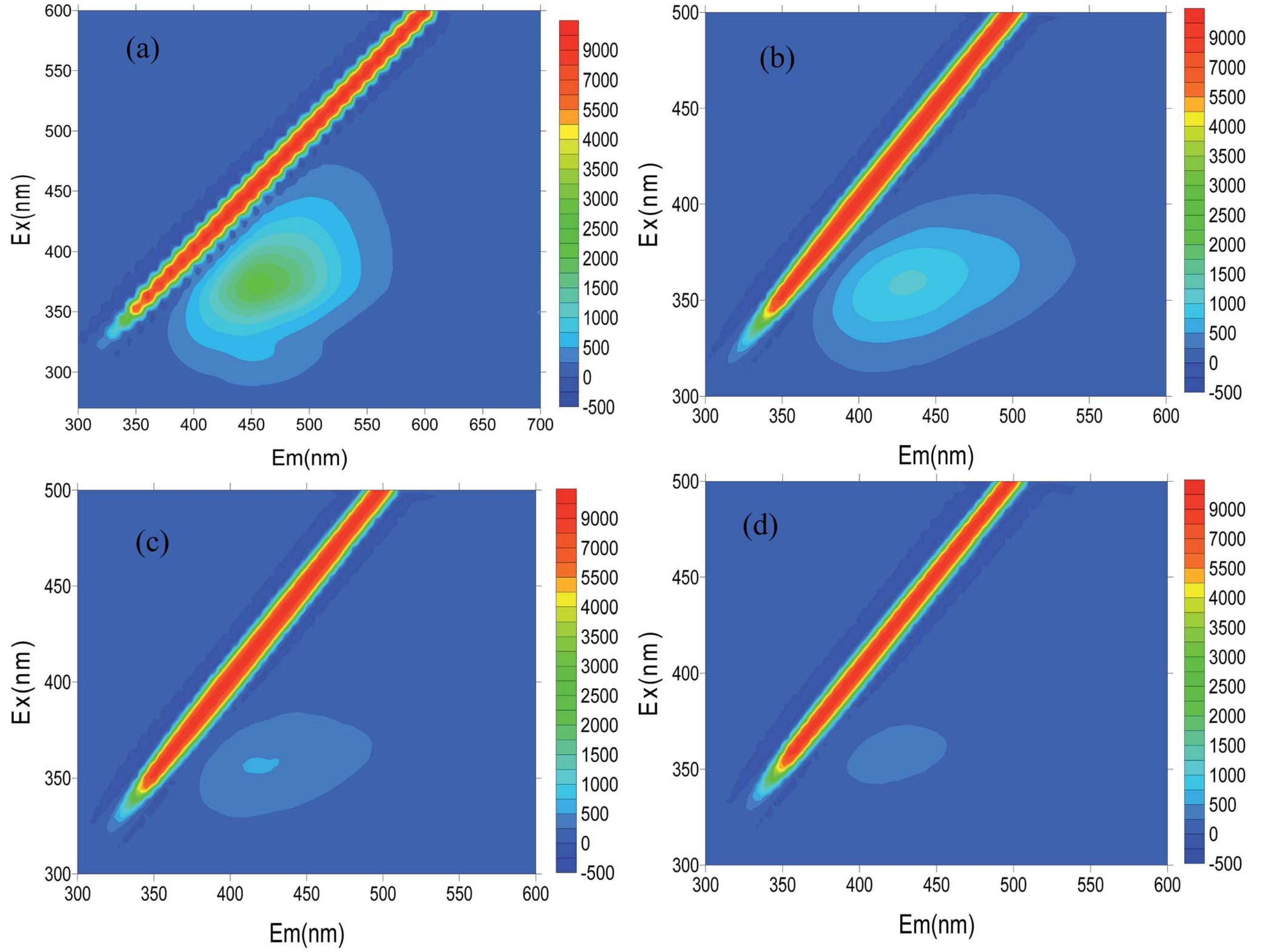

Fig. 8 3D-EEM fluorescence spectra of (a) raw landfill leachate (peak Ex. 375 nm/Em. 455 nm), (b) leachate treated with 0.2 mol L^{-1} persulfate (peak Ex. 360 nm/Em. 435 nm), (c) leachate treated with 0.5 mol L^{-1} persulfate (peak Ex. 355 nm/Em. 425 nm) and (d) leachate treated with 1.0 mol L^{-1} persulfate (peak Ex. 360 nm/Em. 420 nm).

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

concentration was 0.01, 0.1, 0.2, 0.5, and 1.0 mol L^{-1} respectively. As shown in Fig. 3, the removal rate of the COD increases as the persulfate concentration increases. The maximum removal rate of 66.2% was achieved at a persulfate concentration of 0.5 mol L^{-1}. When the persulfate concentration was further raised to 1.0 mol L^{-1}, the COD removal efficiency was not significantly improved. Basically, the COD removal efficiency increases as the concentration of $Na_2S_2O_8$ increases.[26] However, the detailed mechanisms of sulfate radical attack on the leachate organic matter are not well understood. The pathways of organic degradation are difficult to determine.[7] Meanwhile, the lesser Fe(II)-GAC catalyst (1 g per 100 mL) limits the activation of high concentration persulfate, resulting in the decrease of the COD removal efficiency.

3.3 Influence of ferrous concentration

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

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

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

Integrated, the two equations become:

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

It can be seen from eqn (1.6) that excessive Fe^{2+} will reduce the utilization of the sulfate free radicals. Therefore controlling the ferric dosage is very important in the persulfate oxidation process. In this study, we maintained a fixed amount of catalyst (1 g per 100 mL) in the heterogeneous persulfate oxidation experiments. So the amount of immobilized Fe(II) on the GAC determined the ferric dosage. Before Fe(II)-GAC was calcined in the tube furnace, GAC was immersed in 50 mL of ferrous solution with concentrations of 0.05, 0.1, 0.2, 0.5 and 1.0 mol L^{-1} under ultrasonic treatment (100 W, 20 kHz, 25 °C). These catalysts calcined at 550 °C were sent for ICP analysis and the iron content in the catalysts (w/w, %) is listed in Table 3. Obviously, a high ferrous concentration caused more immobilization of Fe(II) on the GAC. The highest iron content in Fe(II)-GAC reached 3.98% when the ferrous concentration was 1.0 mol L^{-1}. Fig. 4 shows the COD removal with different ferrous concentrations. Similar to previous research, the change of the COD removal efficiency was not a linear increase with the Fe^{2+} dosage. When the Fe^{2+} dosage was moderate, 127 mg L^{-1} ($Fe^{2+}/S_2O_8^{2-}$ = 254 mg mol^{-1}), the removal rate of the COD was highest (66.8%). The results demonstrated that Fe^{2+} has a great influence on the persulfate for generating the sulfate free radicals, with too much or too little Fe^{2+} negatively affecting for the production of 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 the initial pH on the removal of the COD by Fe(II)-GAC activated persulfate oxidation at room temperature is shown in 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 the following equations, specifically, the persulfate is activated effectively by Fe(II) and generates more sulfate radicals under acidic conditions.[11]

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_4^- \quad (1.7)$$

$$HS_2O_4^- \rightarrow SO_4^{-\bullet} + SO_4^{2-} + H^+ \quad (1.8)$$

The $SO_4^{-\bullet}$ formed can rapidly attack any oxidizable agents including any organic contaminants.[28] But too many H^+ will inhibit the formation of the sulfate radicals (eqn (1.8)). Also, the presence of $SO_4^{-\bullet}$ in an aqueous solution can result in radical interconversion reactions to produce hydroxyl radicals ($^\bullet OH$, $E_0 = 2.8$ V) in accordance with eqn (1.9) and (1.10).[28,29] That is why the removal COD also remains at a high level under the alkaline conditions (pH = 11).

$$\text{All pHs: } SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + {}^\bullet OH + H^+ \quad (1.9)$$

$$\text{Alkaline pH: } SO_4^{-\bullet} + OH^- \rightarrow SO_4^{2-} + {}^\bullet OH \quad (1.10)$$

pH plays a more complex role in the persulfate oxidation of contaminants.[28,30,31] In previous research, the highest COD removal in the 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] The reaction mechanisms of $SO_4^{-\bullet}$ and $HO^\bullet$ with organic compounds could be quite different. The reaction between $SO_4^{-\bullet}$ and organic compounds is primarily through electron transfer, H-atom abstraction and addition–elimination, whereas $HO^\bullet$ reacts with organic compounds preferentially *via* the addition of C═C double bonds and abstracting H from the C–H, N–H, or O–H bonds.[11,30] Therefore, pH affects the persulfate oxidation by altering the predominant oxidizing species in the solution, further bringing about different mechanisms for pollutant degradation. Furthermore, pH can also 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 the Fe(II)-GAC catalytic persulfate oxidation for mature landfill leachate treatment at pH 3, with an Fe^{2+} dosage of 127 mg L^{-1} ($Fe^{2+}/S_2O_8^{2-}$ = 254 mg mol^{-1}) and a persulfate concentration of 0.5 mol L^{-1} (*i.e.* $S_2O_8^{2-} : 12COD_0 = 1.08$). The COD removal rate achieved was 87.8% under optimal conditions. Compared with the heat-activated persulfate oxidation for landfill leachate treatment, the optimal COD removal rate 91% was higher than in this study at $S_2O_8^{2-} : 12COD_0 = 2$, 50 °C and pH 4,[7] but more persulfate was required and more energy consumption occurred in that process to achieve a similar performance. Under similar reaction conditions, the maximum removal rates of the COD were 66.0, 59.3 and 87.8% at a reaction time of 120 min for the Fe^{2+}/PS, PS/GAC and PS/Fe(II)-GAC systems, respectively (Fig. 6(a)). The high correlation coefficient (R^2) suggests that the COD degradation in all the catalytic systems could be well expressed by pseudo-first-order kinetics within the first 30 min (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 that of the Fe^{2+}/PS and PS/GAC systems. These results suggested that the Fe(II)-GAC catalyst combined the catalysis of Fe(II) and the adsorption of GAC and enhanced the persulfate oxidation of the landfill leachate.

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

The Fe(II)-GAC catalysts used were separated from solution by filtration and cleaned with ultrapure water. Then the catalysts were dried in a vacuum drying oven at 65 °C and calcined in a tube furnace at 550 °C under a N_2 atmosphere for 1 h. The catalysts were then reused in the persulfate oxidation of mature landfill leachate treatment. The recycling experimental results are presented in Fig. 7. As shown in Fig. 7, the catalytic performance of Fe(II)-GAC gradually declines with the number of times recycled. When the Fe(II)-GAC was reused three times, the COD removal rate dropped by almost half. But when the reused catalysts were put in a ferrous solution with ultrasonic treatment and calcined at 550 °C under a N_2 atmosphere to regenerate them, then the catalytic performance of Fe(II)-GAC could be recovered and the COD removal rate achieved a similar level to the fresh catalyst. The perfect renewable characteristics of Fe(II)-GAC exhibit its advantage in the heterogeneous persulfate oxidation. The detection result for iron ions before and after the persulfate oxidation showed that the amount of ferrous and ferric ions leached was considerably low (data not shown), which is similar to previous research.[12,21] It also proved that the persulfate was mainly heterogeneously activated by Fe(II)-GAC instead of the Fe^{2+} in the 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 analyse the dissolved organic matter (DOM) in the landfill leachate before and after persulfate oxidation. Fluorescence data were collected using scanning excitation wavelengths in the range from 300 to 700 nm in 5 nm steps, and detecting the emitted fluorescence in 5 nm 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 the shorter emission wavelengths (Table 4).[33,34]

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

3.8 Cost of Fe(II)-GAC catalyst method

According to the optimal conditions of the Fe(II)-GAC catalytic persulfate oxidation, 100 mL of landfill leachate treatment needs about 1 g of GAC, 11.9 g of persulfate, 2.78 g of $FeSO_4\cdot 7H_2O$, and 3 mL of H_2SO_4 as well as considering the energy consumption. Based on the price in China (GAC = 150 US$ per t, $FeSO_4\cdot 7H_2O$ = 65 US$ per t, persulfate = 130 US$ per t and H_2SO_4 = 90 US$ per t), the cost was estimated to about 82 US$ for 1000 gallons of leachate. Compared with the cost of the other AOP treatments, 50 US$ to 800 US$ per 1000 gallons,[4,37] it demonstrated that the 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 a heterogeneous persulfate catalyst to pretreat mature landfill leachate. The optimal experimental conditions for the Fe(II)-GAC catalytic persulfate oxidation were pH 3, Fe^{2+} dosage of 127 mg L^{-1} ($Fe^{2+}/S_2O_8^{2-}$ = 254 mg mol^{-1}) and persulfate concentration of 0.5 mol L^{-1} (*i.e.* $S_2O_8^{2-} : 12COD_0 = 1.08$), in which a maximum COD removal rate of 87.8% was achieved. The kinetics study demonstrated that the persulfate activation by Fe(II)-GAC was a rapid process and the COD removal in all the experiments reached the best value after about 30 minutes because the $SO_4^{-\bullet}$ formed can rapidly attack any oxidizable agents including organic contaminants. The catalytic performance of Fe(II)-GAC gradually declines with the number of times it is recycled and the COD removal rate dropped by approximately half after three times of reuse. The Fe(II)-GAC could be regenerated through calcination at 550 °C under a 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 the sulfate free radicals from the Fe(II)-GAC activated persulfate.

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