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CHEMICAL
ENGINEERING
JOURNAL

Chemical Engineering Journal 200-202 (2012) 25–31

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Potassium persulfate promoted catalytic wet oxidation of fulvic acid as a model organic compound in landfill leachate with activated carbon

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HIGHLIGHTS

- A promising route for degradation of fulvic acid is reported.
- Fulvic acid and its COD are efficiently removed.
- Biodegradability of fulvic acid is greatly increased.
- Activated carbon exhibits good stability in the system.
- Radical mechanism is studied in detail.

ARTICLE INFO

Article history:
Received 15 January 2012
Received in revised form 9 May 2012
Accepted 9 June 2012
Available online 17 June 2012

Keywords:
Catalytic wet air oxidation
Active carbon
Potassium persulfate
Fulvic acid
Landfill leachate

ABSTRACT

Fulvic acid (FA) is known to be present at high concentration in leachates from “mature” and “old” landfills. In this work, the catalytic wet air oxidation (CWAO) of FA as a model of refractory organics of stabilized leachate was studied with activated carbon (AC) as catalyst and potassium persulfate ($K_2S_2O_8$) as promoter. The effect of temperature and the amount of AC and $K_2S_2O_8$ on the degradation of FA were investigated. Results revealed that FA could be efficiently degraded in the $K_2S_2O_8$/AC system. At 150 °C and 0.5 MPa oxygen pressure, almost complete FA conversion and 77.8% COD removal were achieved after 4 h of treatment. The biodegradability of BOD_5/COD ratio increased from 0.13 of raw FA solution to 0.95 after CWAO. AC exhibited good stability in the catalytic wet oxidation of FA. When AC was used for the fourth time, the FA conversion was still over 60%. Additionally, radical mechanism was studied and three radical scavengers (methanol, *tert*-butyl alcohol, sodium bromide) were used to determine the kind of major active species taking part in the degradation of FA. It was assumed that hydroxyl radical ($^{\cdot}OH$) and sulfate radical ($SO_4^{\cdot-}$) played a major role in the FA degradation.

1. Introduction

Landfilling continues to be the most attractive method to cope with the municipal solid waste [1–5]. The component of landfill leachate, well known for its high concentration of refractory organics and heavy metals [6], varies according to different landfill age (young, intermediate and stabilized). Fulvic acid (FA) is one of main refractory organics existing in the stabilized landfill leachate [7–11]. There are significant numbers of hydroxybenzene, ethylate, carboxyl and chromophore in FA [10]. Thus, when existing in water, FA can affect its sense and taste, and produce high value of Chemical Oxygen Demand (COD) in liquid [12]. Moreover, chemical reactions may occur between FA and disinfector of tap water to generate disinfection byproducts (DBPs) which were proved to be carcinogenic [13].

Since the landfill leachate could jeopardize the aquatic system directly or indirectly, it should be properly treated to remove the organics based on COD and Biochemical Oxygen Demand (BOD) before introduced into a sewage system [14,15]. Biological treatment is one of the most common ways for the treatment of landfill leachate [16]. However, biological processes are usually inefficient for the treatment of the refractory compounds (mainly humic substances) in landfill leachate [15]. As a consequence, alternative technologies have been developed to remove the refractory compounds as pretreatment or post-treatment stage. In the past decades, several methods have been developed to treat landfill leachate, such as physical adsorption [17,18], photochemistry [14,19], electrochemistry [20] and catalytic wet air oxidation (CWAO) [10,21].

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http://dx.doi.org/10.1016/j.cej.2012.06.029

CWAO process is the focus of numerous investigations in recent years. The positive performances of CWAO in degrading refractory organics in aquatic system demonstrates that it is an efficient degradation pathway where substances are chemically transformed into biodegradable substrates, harmless end products, or even carbon dioxide and water, comparing with simple adsorption method which is only a process of mass transfer [22,23]. Moreover, high treatment efficiency and low level of secondary pollution make the CWAO process attractive in treating high concentration and refractory organic wastewater [10,21,24–26]. Several CWAO systems have been used to treat landfill leachate, such as the $CuSO_4$ system [27] and Co/Bi system [28]. Activated carbon (AC) has been reported to be an effective catalyst for the CWAO of the organic pollutants [29,30]. In addition, the presence of promoters such as H_2O_2 [31] has resulted in higher oxidation efficiencies than those obtained in the simple AC-catalytic wet oxidation process at similar operating conditions. Persulfate ($S_2O_8^{2-}$) has been shown to be a powerful oxidant capable of generating sulfate radical that might initiate the radical chain reaction [32,33]. $K_2S_2O_8$/AC system has been used to degrade the azo dye Acid Orange 7 very recently [34]. In the present work, we use $K_2S_2O_8$ as the promoter to aid the AC-catalyzed WAO degradation of FA which is commonly present in landfill leachate. The aim of our study is to show that $K_2S_2O_8$ can promote the AC-catalyzed oxidation of FA at moderate reaction conditions.

2. Materials and methods

2.1. Materials

FA was purchased from Shijiazhuang Lemandou Chemicals Co., Ltd. (China). A granular AC commercialized by Tianjin Kermel Chemical Reagent Co. (China) was used (particle size ranged from 40 to 60 mesh). $K_2S_2O_8$ and all other chemicals were purchased from Tianjin Kermel Chemical Reagent Co. (China). All the chemical reagents were of analytical grade and used without further purification. Distilled water was used throughout the experiments.

2.2. Experiments

The catalytic oxidation of FA aqueous solution was carried out in a 50 mL of Teflon-lined stainless steel autoclave equipped with a magnetic stirrer. The reaction temperature was measured using a thermocouple and controlled by a PID regulator. 0.4 g L^{-1} FA solution (20 mL) and certain amounts of AC and $K_2S_2O_8$ were added to the autoclave, the autoclave was then closed and charged with pure oxygen to 0.5 MPa and then heated to the desired temperature. The stirring speed was set at 550 rpm. After reaction (heating time included), the autoclave was cooled to room temperature with a water bath. Carefully depressurized and sampled for further analysis. The adsorption experiments were also performed in the autoclave under the same experimental conditions but replacing oxygen by pure nitrogen. For this purpose, 1 MPa nitrogen was charged into the autoclave and deflated slowly to drive out the air for three times and then 0.5 MPa nitrogen was charged into the autoclave.

2.3. Analysis methods

The concentration of FA was determined using UV–visible spectrophotometer (Shimadzu UV-2550, Japan) at the maximum absorbance wavelength of FA. COD was determined by a standard dichromate reflux method [35]. BOD_5 test was performed according to the Water quality-determination of Biochemical Oxygen Demand after 5 days (BOD_5) for dilution and seeding method (Standard Method HJ 505-2009, China). The biodegradability index was estimated from following equation:

$$\text{Biodegradability index} = \frac{BOD_5}{COD} \quad (1)$$

The AC before and after CWAO were washed by deionized water for three times to remove dust and dried at 105 °C to a constant weight to get rid of the moisture and other volatile impurities for further use. The surface functional groups of samples were determined by Fourier transform infrared (FTIR) spectroscopy (Nicolet Avatar 370, Nicolet Instrument Corp., USA) with the scanning range from 4000 cm^{-1} to 400 cm^{-1}. KBr pellets containing 1% of activated carbon samples approximate 12.5 mm in diameter and 1 mm in thickness were prepared in a manual hydraulic press at 10 ton and dried for 24 h at 105 °C before the spectra were recorded. The BET area, pore volume and micropore size of AC were measured by N_2 adsorption and desorption isotherms at 77 K with an accelerated surface area and porosimetry system (ASAP 2020) (Micromeritics Instrument Corp., USA). Before gas adsorption measurements, AC was degassed at 300 °C in vacuum condition for 2 h. N_2 adsorption and desorption isotherm was measured over a relative pressure (P/P_0) from 10^{-7} to 1. The BET surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) equation. The *t*-plot method was used to calculate the micropore area (S_{Micro}). Single point adsorption total pore volume (V_{Total}) was calculated by single point method at $P/P_0 = 0.98$. *T*-plot micropore volume (V_{Micro}) was calculated by *t*-plot methods. The average pore diameter (D_{Ave}) was determined by Barrett–Joyner–Halenda (BJH) method. The pH_{pzc} (point of zero charge) of AC was determined by a drift method described elsewhere [36], using a pH meter (Model 6309 POT, JENCO, USA).

3. Result and discussion

3.1. Preliminary experiments

Non-catalytic wet oxidation of FA (0.4 g L^{-1}) was carried out at 150 °C and 0.5 MPa oxygen pressure for 4 h. The result showed that 26.0% FA and 25.7% COD were removed. Upon using 0.5 g L^{-1} AC as the catalyst, FA and COD removal increased to 73.7% and 38.4% respectively. When 0.54 g L^{-1} $K_2S_2O_8$ was added to the AC system, FA and COD removal further increased to almost 100% and 65.3% respectively after 4 h of reaction. In consideration of these promising results, further studies were taken. The results of the only $K_2S_2O_8$ system, the only AC system and the $K_2S_2O_8$/AC combined system are shown in Fig. 1. It can be observed from Fig. 1 that $K_2S_2O_8$/AC system can degrade FA more efficiently, comparing with the other two systems. For instance, after 1 h reaction, FA and COD removal reached 94.8% and 58.4% respectively in $K_2S_2O_8$/AC system, while the FA and COD removal efficiency obtained in the only $K_2S_2O_8$ system were 85.6% and 49.2%, and in the only AC system were 47.5% and 43.6% respectively. On the other hand, the FA degradation process with reaction time in $K_2S_2O_8$/AC system can also be observed from Fig. 1. It can be seen that the degradation of FA is rapid. For example, within only 2 h of reaction time, FA and COD removal reached 96.9% and 63.5% respectively. When the reaction time was increased to 4 h, FA was almost completely degraded and the COD removal reached 77.8%. While further prolonging the reaction time to 8 h, the COD removal only ascended by 6.3% reaching 84.1%.

To gain a better insight into the CWAO process, the kinetics of FA wet oxidation under different reaction conditions were investigated at 0.5 MPa oxygen pressure. According to Refs. [34,37], it was possible to approximate the expression to pseudo-first order (Eq. (2)):

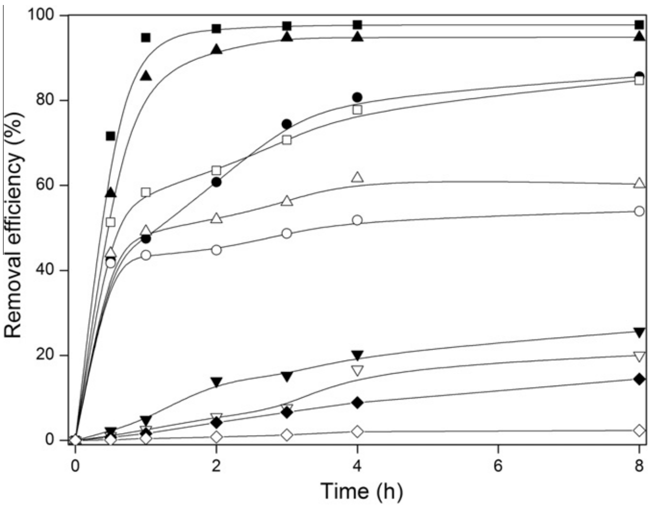

Fig. 1. FA removal by (■) $K_2S_2O_8$/AC, (▲) only $K_2S_2O_8$, (●) only AC, (▼) only heated for 4 h and (♦) AC ads; COD removal by (□) $K_2S_2O_8$/AC, (△) only $K_2S_2O_8$, (○) only AC, (▽) only heated for 4 h and (◇) AC ads.

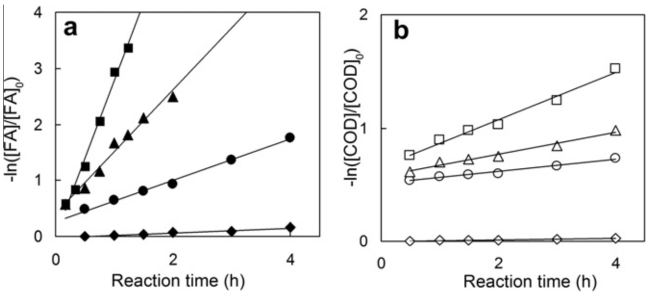

Fig. 2. Pseudo-first-order kinetics plots for FA catalytic wet oxidation. (a) FA removal by (■) $K_2S_2O_8$/AC, (▲) only $K_2S_2O_8$, (●) only AC and (♦) AC ads; (b) COD removal by (□) $K_2S_2O_8$/AC, (△) only $K_2S_2O_8$, (○) only AC and (◇) AC ads.

Table 1
Pseudo-first-order kinetic constants and correlation coefficients in FA catalytic wet oxidation.

Conditions	k'_{FA} (h^{-1})	R^2	k'_{COD} (h^{-1})	R^2
$K_2S_2O_8$/AC	2.7749	0.99	0.2077	0.99
$K_2S_2O_8$ only	1.1055	0.98	0.0957	0.98
AC only	0.3681	0.99	0.0530	0.97
N_2 experiments	0.0201	0.98	0.0053	0.97

$$-\ln\frac{[FA]}{[FA]_0} = k'_{FA}t \text{ or } -\ln\frac{[COD]}{[COD]_0} = k'_{COD}t \quad (2)$$

Fig. 2 shows the experimental data obey to the pseudo-first-order kinetic model for all the runs ($R^2 > 0.96$). The rate constants are listed in Table 1. It can be observed that both k'_{FA} and k'_{COD} in the $K_2S_2O_8$/AC system are higher than that of the $K_2S_2O_8$ or AC only system. It can be inferred that $K_2S_2O_8$ and AC have a synergistic effect on FA degradation in the $K_2S_2O_8$/AC combined system.

ACs are normally used as adsorbents because of their large porosity and surface area, so it is necessary to evaluate the FA adsorption capacity of AC. AC adsorption experiments (as shown in Fig. 1 for AC ads) were performed using N_2 instead of O_2 [38]. Both FA and COD removal obtained under inert atmosphere (N_2) were rather low. For example, only 8.9% FA removal and 2.3% COD removal were obtained after 4 h adsorption. The rate constants of FA and COD removal were only 0.0201 h^{-1} and 0.0053 h^{-1} respectively (Table 1). The results revealed that (a) FA was thermally stable at 150 °C and (b) the contribution of adsorption to FA and COD removal was negligible.

In view of above desirable results, we then systematically investigated and optimized the reaction conditions (the use amount of $K_2S_2O_8$ and AC, temperature).

3.2. Effect of amount of $K_2S_2O_8$ and AC

The effect of $K_2S_2O_8$ and AC amount on the degradation of FA was then investigated respectively.

Firstly, the influence of $K_2S_2O_8$ amount on COD removal of FA was investigated with the dosage of AC fixed at 0.5 g L^{-1} (150 °C, 4 h). Results are shown in Fig. 3. It can be observed that more than 92% FA was removed for all the runs. Meanwhile, the COD removal increased rapidly with the $K_2S_2O_8$ dosage within a certain range, and the increased tendency become relatively flat afterward. For example, when 0.14 g L^{-1} $K_2S_2O_8$ was added into the system, only 54.0% COD removal was observed. While $K_2S_2O_8$ dosage reached 0.81 g L^{-1}, 68.8% of COD removal was observed. But when $K_2S_2O_8$ dosage was further increased to 1.62 g L^{-1}, the COD removal extent only increased 3.0%, achieving 71.8%. That might because that the excessive amount of $S_2O_8^{2-}$ reacted with $SO_4^{\cdot-}$ to form SO_4^{2-} [34,39]. The results indicated that 0.81 g L^{-1} was the optimum amount for $K_2S_2O_8$ in the present degradation system for FA.

Experiments were then carried out to investigate the impact of AC amount on the degradation of FA. The amount of $K_2S_2O_8$ was fixed at 0.81 g L^{-1}. Efficient FA removal (>92%) can also be obtained by all the runs (Fig. 3). Fig. 3 also shows the effect of AC dosage on COD removal. When AC dosage was 0.13 g L^{-1}, the COD removal efficiency was merely 56.8%. But when 0.75 g L^{-1} AC was added into the system, the COD removal efficiency reached up to 72.2%. However, as the dosage further increased to 1.0 g L^{-1}, COD removal almost did not change. The results indicated that the AC amount of 0.75 g L^{-1} was sufficient amount in the present CWAO system for FA degradation.

To discuss the influence of the total amounts change of catalyst ($K_2S_2O_8$ + AC) on the degradation of FA, further investigation was performed. With the mass ratio of $K_2S_2O_8$ to AC setting at 1.08–1, the total amounts of ($K_2S_2O_8$ + AC) were set at (0.14 g L^{-1} + 0.13 g L^{-1}), (0.27 g L^{-1} + 0.25 g L^{-1}), (0.54 g L^{-1} + 0.50 g L^{-1}), (0.81 g L^{-1} + 0.75 g L^{-1}) and (1.08 g L^{-1} + 1.00 g L^{-1}) respectively. Accordingly, FA removal were 88.2%, 94.1%, 95.5%, 97.8% and

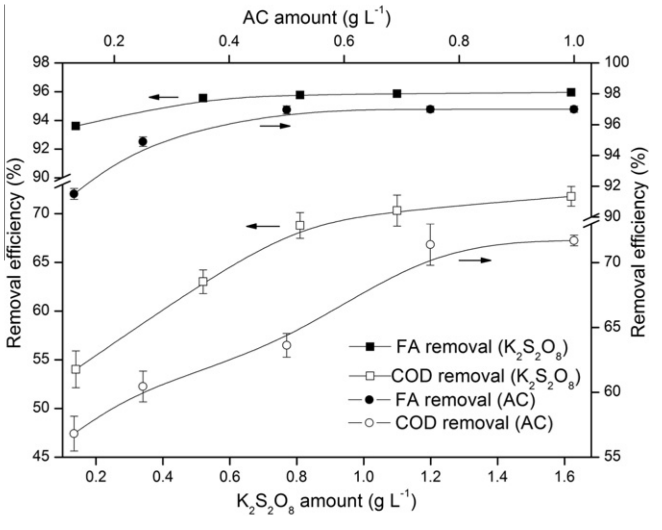

Fig. 3. Effect of AC and $K_2S_2O_8$ amount on FA and COD removal.

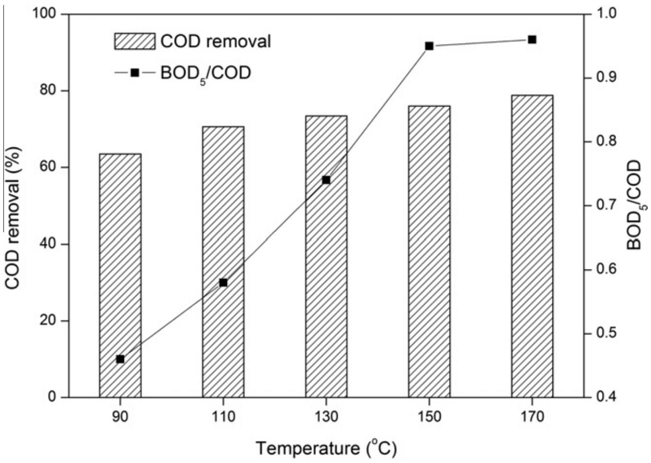

Fig. 4. Effect of temperature on COD removal and biodegradability index change.

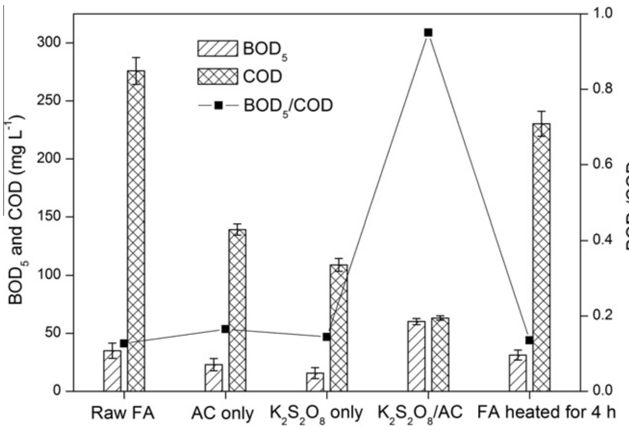

Fig. 5. Biodegradability change after degradation of FA.

97.3%, and the COD removal efficiency were 54.5%, 60.2%, 62.8%, 72.1% and 71.8% respectively. Therefore, (0.81 g L^{-1} $K_2S_2O_8$ + 0.75 g L^{-1} AC) was selected to be the optimum amount of ($K_2S_2O_8$ + AC).

3.3. Effect of temperature

In CWAO process, it is important to optimize the running temperature, because it can influence the practical applicability of a CWAO process. Fig. 4 shows the effect of temperature on the removal of FA, with the amount of AC and $K_2S_2O_8$ fixed at 0.75 g L^{-1} and 0.81 g L^{-1} respectively. After heated for 4 h, COD removal were 63.5%, 70.6%, 73.4%, 76.0% and 78.8% at 90, 110, 130, 150 and 170 °C respectively. Although COD removal have not a significant increase with temperature, the BOD_5 test results revealed that higher temperature was favorable for the increase of biodegradability of FA. For instance (Fig. 4), the biodegradability indexes of 90, 110, 130, 150, 170 °C were 0.46, 0.58, 0.74, 0.95 and 0.96 respectively. It has been reported that the biodegradability index (Eq. (1)) is a reliable parameter to evaluate whether an aqua is harmful to environment and livings or not [40]. Considering the biodegradability of FA, 150 °C was considered to be an ideal temperature for FA degradation in the present CWAO system.

3.4. Biodegradability change after degradation of FA

As mentioned above, the biodegradability of FA could be significantly improved by the $K_2S_2O_8$/AC system at 150 °C. To further study the biodegradability change after CWAO, the biodegradability indexes of four control groups ($K_2S_2O_8$ only, AC only, raw FA and FA heated for 4 h) were determined under the optimum conditions.

Fig. 5 shows that the biodegradability indexes of raw FA, FA heated, AC only and $K_2S_2O_8$ only for 4 h are 0.13, 0.14, 0.17 and 0.15 respectively, while the index reaches 0.95 after treated by the $K_2S_2O_8$/AC combined system. It can be observed that the biodegradability indexes of FA after treated only using AC or $K_2S_2O_8$ were both low, while the index obtained from the combined system was significantly increased. The results indicate the enhancement of biodegradability of FA come from the synergistic effect of AC and $K_2S_2O_8$. On the other hand, it has been reported that when the biodegradability index was under 0.2, an aqua should be seen as toxic water, and 0.4 was the required value for an effective treatment by biochemical technique [41]. It can be inferred that the $K_2S_2O_8$/AC combined system can ameliorate FA from relatively hazardous liquid to safer one. Although complete COD removal was not achieved (Fig. 1), the degradation products were easily biodegraded. Result indicated that the present system might be used as the pretreatment approach for the biological treatment of landfill leachate.

3.5. Characteristics of AC before and after CWAO

To understand the mechanisms involved in the present system, analysis of characteristic of the AC before and after CWAO is indispensable. Nitrogen adsorption and desorption is a standard method to determine the porosity of carbonaceous materials [42]. The branches of AC before and after reaction are presented in Fig. 6, with the lower branches of each sample depicting the isotherm of nitrogen adsorption and the upper desorption. According to the BDDT (Brunauer–Deming–Deming–Teller) classification, a type I with somewhat type IV character nitrogen isotherm can be observed in Fig. 6 from both the original and used AC. A sharp rise at low relative pressure and a hysteresis loop can be observed in the figure of both the samples. The former was due to the micropore filling and the latter was associated with capillary condensation of mesoporous solids [43], indicating that there were micropores as well as mesoporous structures in both the ACs. Moreover, it can be observed from the figure that the adsorption branches have a sharp rise at saturation vapor pressure while the desorption branches are steep at the middling relative pressure (typical B-type hysteresis loop) of both the samples. This observation revealed that the pore type of both the ACs pertained to the parallel slit-shaped pore [42],

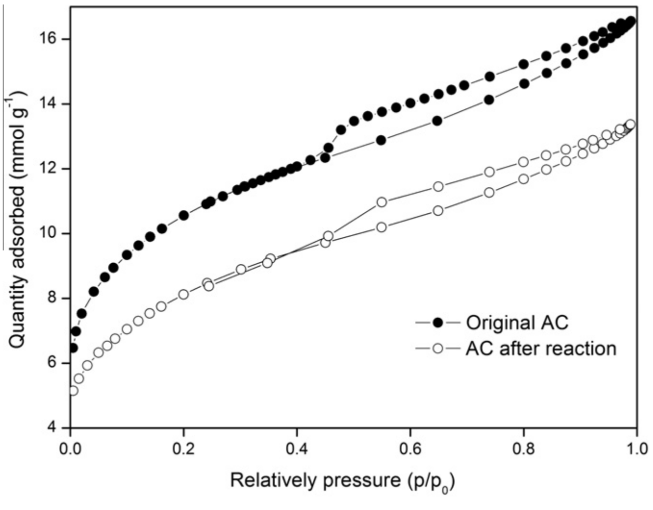

Fig. 6. N_2 adsorption and desorption isotherms of the ACs.

Table 2
Characteristics of the porous structure of AC before and after CWAO.

AC samples	S_{BET} ($m^2\ g^{-1}$)	S_{Micro} ($m^2\ g^{-1}$)	V_{Total} ($cm^3\ g^{-1}$)	V_{Micro} ($cm^3\ g^{-1}$)	D_{Ave} (nm)	pH_{pzc}
Original AC	838	228	0.57	0.10	4.50	6.7
AC after CWAO	652	98	0.46	0.04	4.39	5.1

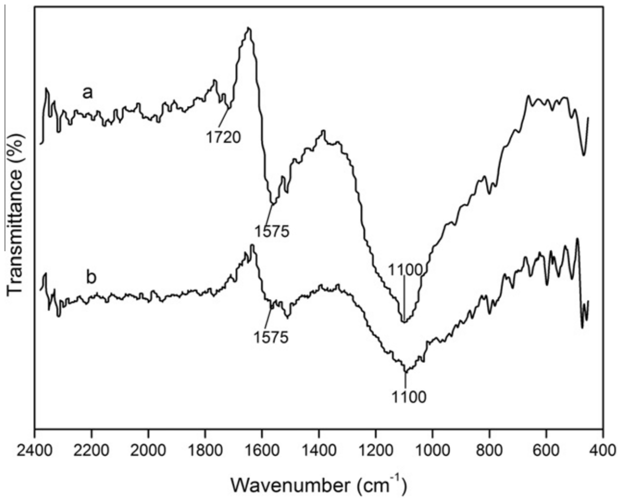

Fig. 7. FTIR spectra of (a) AC after CWAO and (b) original AC.

indicating that the CWAO process did not change the main type of pores of AC. The pore size distribution of the AC calculated by the BJH method illustrated that the average pore diameter (D_{Ave}) of AC before and after CWAO estimated to be 4.50 nm and 4.39 nm respectively (Table 2).

Table 2 also shows other structural parameters calculated from nitrogen isotherms. It can be observed that the surface area and microporous volume of AC after CWAO decreases. For instance, after 4 h reaction, S_{BET} of AC altered from 838 $m^2\ g^{-1}$ to 652 $m^2\ g^{-1}$ and V_{Micro} decreased from 0.10 $cm^3\ g^{-1}$ to 0.04 $cm^3\ g^{-1}$. Lower BET surface area and microporous volume might have a negative influence on the removal of FA [44]. The reconfiguration of AC structure might result from the fact that the disadvantageous intermediate products of FA degradation gradually occupied the active area of AC surface and diminished the microporous volume of AC [34,39].

The FTIR spectra of AC before and after degradation are shown in Fig. 7. The obtained FTIR spectra revealed that the AC after CWAO not only contained more bands but also had higher band intensity than that of the original AC, indicating that the surface of AC experienced chemical changes during the CWAO process. In the spectrum of the AC after reaction, there is a band at 1720 cm^{-1} that can be assigned to C=O stretching vibration from ketones, aldehydes and carboxyl groups [45], which is absent in the spectrum of the original AC. A band at 1575 cm^{-1} can be observed in both the AC before and after reaction, but the CWAO process increased the intensity of the band. It was assigned to aromatic C=C stretching vibrations augmented by the presence of coupled carbonyl groups [45,46]. In the range of 1000–1450 cm^{-1}, a broad band can be observed from both the samples, with the AC after reaction being characteristic of higher band intensity. This band might be caused by the presence of various forms of oxygen surface groups such as —OH groups, carboxyl structures and thermally stable carboxyl-carbonate structures [45].

The results of pH_{pzc} analysis of AC before and after reaction (Table 2) indicated that the presence of $S_2O_8^{2-}$ acidified the original AC after CWAO (pH_{pzc} decreased from 6.7 to 5.1).

The formation of oxygen-containing functional groups such as —OH groups and carboxyl structures on the surface of AC and the acidity increase of AC would contribute to the formation of free radicals to improve the degradation of FA [36,39,44], while the disadvantageous reconfiguration of AC surface might decrease the removal efficiency of FA to some extent [34].

3.6. Degradation mechanism

In advanced oxidation processes, the formation of ·OH or $SO_4^{\cdot-}$ free radicals has been verified to lead to a high target substrates removal efficiency [38,47–50]. In the present system, AC might have a catalytic effect on ·OH generation in the CWAO process [51,52]. Meanwhile, it was possible that the persulfate decomposed when it was added into the AC catalyzed CWAO system (Eq. (3)), and then released the sulfate radical with the help of oxygen-containing functional groups on the surface of AC (Eqs. 4 and 5) [39]. Both $SO_4^{\cdot-}$ and ·OH possibly took part in the destruction of FA.

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{\cdot-} \tag{3}$$

$$\text{AC surface—OOH} + S_2O_8^{2-} \rightarrow SO_4^{\cdot-} + \text{AC surface—OO}^{\cdot} + HSO_4^- \tag{4}$$

$$\text{AC surface—OH} + S_2O_8^{2-} \rightarrow SO_4^{\cdot-} + \text{AC surface—O}^{\cdot} + HSO_4^- \tag{5}$$

The radical scavenger experiment is often used to confirm the existence of assumed radicals [34,47]. To find the evidence of the generation of aforementioned free radicals in the present system, CWAO experiments were conducted under the optimum conditions in the presence of ·OH and $SO_4^{\cdot-}$ scavengers (methanol: MA; *tert*-butyl alcohol: TBA; bromide: in the form of NaBr) [34,47]. The molar ratio of scavengers to persulfate was 500–1 [53,54]. The reaction rate constants ($R^2 > 0.94$) of CWAO in the presence of TBA, MA and NaBr were 1.1556, 0.0841 and 0.077 h^{-1}, respectively. Results indicated that FA removal was obviously inhibited by both organic (MA and TBA) and inorganic (NaBr) scavengers (Fig. 8). The stronger decrease in k'_{FA} values in the Br^- ($k_{Br^-/HO^\cdot} = 2.0 \times 10^9 - 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$, $k_{Br^-/SO_4^{\cdot-}} = 3.5 \times 10^9\ M^{-1}\ s^{-1}$) added CWAO system as compared to the less effective ·OH and $SO_4^{\cdot-}$ scavenger MA ($k_{HO\cdot/MA} = 1.2 \times 10^9 - 2.8 \times 10^9\ M^{-1}\ s^{-1}$, $k_{SO_4^{\cdot-}/MA} = 1.6 \times 10^7 - 7.7 \times 10^7 M^{-1}\ s^{-1}$) and TBA ($k_{HO\cdot/TBA} = 3.8 \times 10^8 - 7.6 \times 10^8\ M^{-1}\ s^{-1}$, $k_{SO_4^{\cdot-}/TBA} = 4 \times 10^5 - 9.1 \times 10^5\ M^{-1}\ s^{-1}$) [55,56] suggested that ·OH and $SO_4^{\cdot-}$ radicals played a major role in the degradation of FA [47]. Moreover, at ambient temperature, the reaction rate of MA with ·OH is close to that with $SO_4^{\cdot-}$, but the reaction rate of TBA with ·OH is approximately 1000 times greater than that with $SO_4^{\cdot-}$. Therefore, it can be inferred that the generation of ·OH and $SO_4^{\cdot-}$ in the present CWAO system can be authenticated by comparing the inhibiting effect of different scavengers [53,54,57]. After 4 h reaction, FA removal decreased from 94.8% to 63.1% with the presence of TBA in the $K_2S_2O_8$/AC system. It could be inferred that ·OH was generated in the present system. When MA was present, FA removal decreased to 44.1%. Comparing the results of TBA and MA experiments, it can be concluded that the $SO_4^{\cdot-}$ radical was generated in the CWAO system (Fig. 8). The results also suggested that ·OH and $SO_4^{\cdot-}$ radicals were the primary active species formed in the $K_2S_2O_8$/AC system [53].

3.7. Reuse of AC

Reuse efficiency of catalyst has a close connection with running cost in practical use. In order to investigate the reuse efficiency of AC, 0.81 g L^{-1} of $K_2S_2O_8$ and 0.75 g L^{-1} of AC were added into the

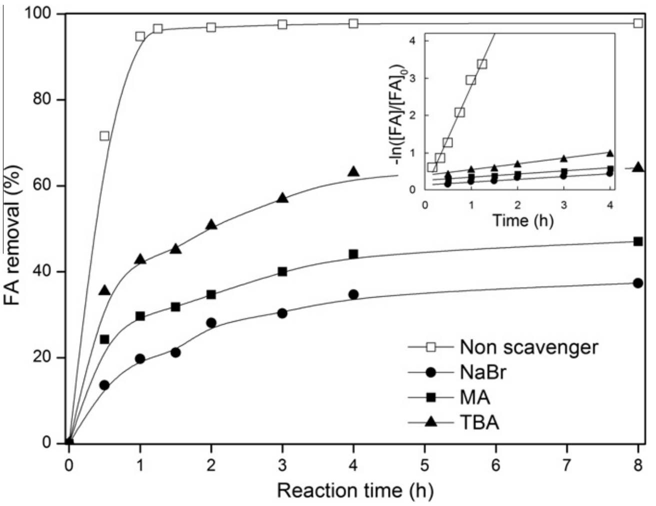

Fig. 8. Reactions of FA in the presence of different radical scavengers. The molar ratio of scavenger/persulfate = 500/1.

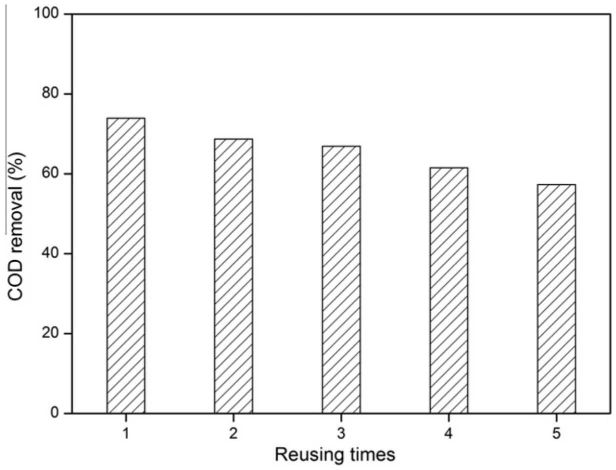

Fig. 9. Reuse of AC.

CWAO system to decompose FA under the optimum conditions. AC was separated and dried after reaction, and 0.81 g L^{-1} $K_2S_2O_8$ was added to repeat the aforementioned experiment. Fig. 9 shows that COD removal is more than 60% for the initial 4 times (73.9%, 68.7%, 66.9%, and 61.5%). However, the removal efficiency dropped to 57.3% when AC was used for the fifth time, implying that an extent of inactivation had happened to the catalyst. Disadvantageous reconfiguration of AC structure (verified by ASAP 2020 analysis in Section 3.5) was supposed to be the reason for the inactivation of AC.

4. Conclusions

In this study, $K_2S_2O_8$ promoted AC-catalyzed WAO system was used to treat FA which is commonly present in landfill leachate. This promising free radical promoted CWAO treatment system exhibited high efficiency in decomposing FA. FA almost totally degraded and 77.8% COD was removed (T = 150 °C; oxygen pressure = 0.5 MPa), with the dosage of AC and $K_2S_2O_8$ was 0.75 g L^{-1} and 0.81 g L^{-1} respectively. Furthermore, this CWAO method could significantly improve the biodegradability of FA. This study provides a desirable pretreatment approach for the biological treatment of landfill leachate.

Acknowledgements

The study was financially supported by the National Natural Science Foundation of China (51008121, 50978088, 51039001), the Environmental Protection Technology Research Program of Hunan (2007185), the Hunan Provincial Innovation Foundation for Postgraduate (CX2009B078, CX2010B157), the Hunan Key Scientific Research Project (2009FJ1010, 11JJ4041), the Hunan Provincial Natural Science Foundation of China (10JJ7005), the Program for New Century Excellent Talents in University (NCET-08-0181) and the Research Fund for the Doctoral Program of Higher Education of China (20100161110012).

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