



## 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.

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### 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<sub>5</sub>/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.

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### 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 disinfectant 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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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  $\text{CuSO}_4$  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  $\text{H}_2\text{O}_2$  [31] has resulted in higher oxidation efficiencies than those obtained in the simple AC-catalytic wet oxidation process at similar operating conditions. Persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) has been shown to be a powerful oxidant capable of generating sulfate radical that might initiate the radical chain reaction [32,33].  $\text{K}_2\text{S}_2\text{O}_8/\text{AC}$  system has been used to degrade the azo dye Acid Orange 7 very recently [34]. In the present work, we use  $\text{K}_2\text{S}_2\text{O}_8$  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  $\text{K}_2\text{S}_2\text{O}_8$  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).  $\text{K}_2\text{S}_2\text{O}_8$  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.  $0.4 \text{ g L}^{-1}$  FA solution (20 mL) and certain amounts of AC and  $\text{K}_2\text{S}_2\text{O}_8$  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].  $\text{BOD}_5$  test was performed according to the Water quality-determination of Biochemical Oxygen Demand after 5 days ( $\text{BOD}_5$ ) for dilution and seeding method

(Standard Method HJ 505-2009, China). The biodegradability index was estimated from following equation:

$$\text{Biodegradability index} = \frac{\text{BOD}_5}{\text{COD}} \quad (1)$$

The AC before and after CWAO were washed by deionized water for three times to remove dust and dried at  $105^\circ\text{C}$  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  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$ . 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  $105^\circ\text{C}$  before the spectra were recorded. The BET area, pore volume and micropore size of AC were measured by  $\text{N}_2$  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  $300^\circ\text{C}$  in vacuum condition for 2 h.  $\text{N}_2$  adsorption and desorption isotherm was measured over a relative pressure ( $P/P_0$ ) from  $10^{-7}$  to 1. The BET surface area ( $S_{\text{BET}}$ ) was calculated using the Brunauer–Emmett–Teller (BET) equation. The  $t$ -plot method was used to calculate the micropore area ( $S_{\text{Micro}}$ ). Single point adsorption total pore volume ( $V_{\text{Total}}$ ) was calculated by single point method at  $P/P_0 = 0.98$ .  $T$ -plot micropore volume ( $V_{\text{Micro}}$ ) was calculated by  $t$ -plot methods. The average pore diameter ( $D_{\text{Ave}}$ ) was determined by Barrett–Joyner–Halenda (BJH) method. The  $\text{pH}_{\text{pzc}}$  (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 ( $0.4 \text{ g L}^{-1}$ ) was carried out at  $150^\circ\text{C}$  and 0.5 MPa oxygen pressure for 4 h. The result showed that 26.0% FA and 25.7% COD were removed. Upon using  $0.5 \text{ g L}^{-1}$  AC as the catalyst, FA and COD removal increased to 73.7% and 38.4% respectively. When  $0.54 \text{ g L}^{-1}$   $\text{K}_2\text{S}_2\text{O}_8$  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  $\text{K}_2\text{S}_2\text{O}_8$  system, the only AC system and the  $\text{K}_2\text{S}_2\text{O}_8/\text{AC}$  combined system are shown in Fig. 1. It can be observed from Fig. 1 that  $\text{K}_2\text{S}_2\text{O}_8/\text{AC}$  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  $\text{K}_2\text{S}_2\text{O}_8/\text{AC}$  system, while the FA and COD removal efficiency obtained in the only  $\text{K}_2\text{S}_2\text{O}_8$  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  $\text{K}_2\text{S}_2\text{O}_8/\text{AC}$  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)):

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