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2,4,6-Trichlorophenol-promoted catalytic wet oxidation of humic substances and stabilized landfill leachate

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HIGHLIGHTS

• TCP could promote the degradation of FA with NaNO2 as catalyst.

• The mechanisms of the CWCO of FA and TCP were proposed.

• The CWCO was effective for degrading humic substances and landfill leachate.

• FA, HA and landfill leachate could be further removed by biological treatment.

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ABSTRACT

Humic substances, including humic acid (HA) and fulvic acid (FA), are the major components of the refractory organics existing in the stabilized landfill leachate. In this study, the NaNO₂-catalyzed wet co-oxidation (CWCO) of FA and 2,4,6-trichlorophenol (TCP) using TCP as the promoter was investigated. Compared with the NaNO₂-catalyzed wet air oxidation (CWAO) of FA under the same conditions, the presence of TCP in the reaction system efficiently promoted the degradation of FA. For example, when the CWCO of FA and TCP was carried out at 150 °C and 0.5 MPa for 4 h, the color completely turned to colorless and 61.8% of chemical oxygen demand (COD) was removed, while the color of FA without addition of TCP remained yellow–brown and 19.3% of COD was removed after the CWAO process. The biodegradability (BOD₅/COD ratio) was significantly improved from 0.10 to 0.39. Moreover, the radical scavengers (tert-butyl alcohol and sodium bromide) were used to study the radical mechanism and the results showed that hydroxyl radicals were primarily responsible for the destruction of FA and TCP as well as the mixture of landfill leachate and TCP.

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1. Introduction

Landfill leachate coming from the decomposition of waste materials and rainwater percolation through the waste layers is heavily polluted wastewater that contains large numbers of high concentration of organic and inorganic contaminants including organic compounds, ammonia–nitrogen, inorganic salts and heavy metals [1–4]. Therefore, landfill leachate needs to be sufficiently treated to meet the standards for discharge in receiving waters [3,5]. Conventional biological methods, e.g., the activated sludge process, have been widely used to treat landfill leachate because of its reliability, simplicity and high cost-effectiveness [5,6]. However, the major presence of large molecular refractory organic compounds such as humic acid (HA) and fulvic acid (FA) make the biological treatment often ineffective for the stabilized landfill leachate [5–8]. An attractive approach is to combine a pretreatment step with a sewage treatment plant [9].

Advanced oxidation processes, such as wet air oxidation (WAO) [10–12], Fenton oxidation [13,14], photocatalytic oxidation [15,16], and O_3 oxidation [17,18], were efficient pretreatment steps to improve the biodegradability of landfill leachate. WAO are suitable for treating medium–high-concentration wastewaters and utilize molecular oxygen or air as an oxidant, the most economically attractive and environmentally friendly oxidizing agent, thus WAO has been the subjects of considerable studies [19]. WAO is





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usually conducted at high temperature (220-320 °C) and high pressure (2–20 MPa) [20,21]. To reduce the temperature and pressure while maintaining high removal efficiency, an appropriate homogeneous or heterogeneous catalyst is often used [10,12,22]. Besides, another very attractive approach is the co-oxidation technology that employs some substances as promoters to increase the degradation of other recalcitrant substances. For example, when the co-oxidation of nitrobenzene and phenol was carried out at 200 °C and 1.0 MPa oxygen partial pressure for 3 h, the removal efficiency of nitrobenzene reaches 36%, while it is 3% in single oxidation experiment under the same conditions [23]. The degradation of thiocyanate is significantly enhanced when it is simultaneously oxidized together with phenol under the same conditions [24]. Highly efficient destruction of refractory 2,4,6-trichlorophenol (TCP) can significantly increase the degradation of p-nitrophenol (PNP) in NaNO₂-catalyzed wet air oxidation system [25,26]. The addition of gallic acid can aid the catalytic destruction of azo dye Acid Orange 7 with FeSO₄ as catalyst [27], and the incorporation of tetrahydrofuran can obviously improve the decomposition of decabromodiphenyl ether [28].

In considering that the degradation of TCP with NaNO₂/O₂ can bring PNP to be remarkably removed, and TCP is a priority pollutant existing in landfill leachate [29–32], so we try to find a co-oxidation solution to simultaneously remove the refractory organic pollutants and TCP in landfill leachate exploiting the NaNO₂-catalyzed wet co-oxidation (CWCO) process. Consequently, the current study investigates the effectiveness of the TCP-promoted catalytic wet oxidation of humic substances and the stabilized landfill leachate.

2. Material and methods

2.1. Materials

FA (70% purity) was purchased from Shijiazhuang Lemandou Chemicals Co., Ltd. (China). TCP (98% purity) was purchased from Sigma–Aldrich Co. LLC. (America). HA (50–60% purity) was purchased from Acros Organics (Belgium). All other chemical reagents were of analytical grade and were used without further purification. Water was prepared with a Mili-Q water purification system (Millipore, Milford, MA, USA) throughout all the experiments. The pH values were adjusted by the addition of diluted aqueous solution of HCl or NaOH.

2.2. Landfill leachate

The stabilized landfill leachate was collected from the sanitary landfill site of Heimifeng (Changsha, China), which has been in operation since 2003. Raw leachate was collected on April 13, 2013 and placed in 20 L sealed plastic buckets. The sample was immediately transported to the laboratory, characterized, and then stored at 4 °C to minimize the biological and chemical reactions. The physico-chemical analysis was carried out within two days. The physico-chemical parameters of the examined leachate sample are presented in Table 1.

2.3. Catalytic wet co-oxidation

The CWCO of FA and TCP was carried out in a 50 mL Teflonlined stainless steel autoclave equipped with a magnetic stirrer. The reaction temperature was measured using a thermocouple and controlled by a PID regulator. Then the solution of FA (10 mL, 400 mg/L), TCP (10 mL, 1 mM) and NaNO₂ (10 μ L, 1 M) were added to the autoclave, thus, the initial concentrations of FA and TCP changed to 200 mg/L, and 0.5 mM (98.7 mg/L),

Table	1
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Characteristics of landfill leachate.

Parameters	Landfill leachate
COD (mg/L)	1888
$BOD_5 (mg/L)$	143
BOD ₅ /COD	0.08
$N-NH_4^+$ (mg/L)	2100
$N-NO_3(mg/L)$	266
TOC (mg/L)	803
Conductivity (mS/cm)	21.2
рН	8.4

respectively, and the molar ratio of TCP/NaNO₂ was 1:1 [25,26]. 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 500 rpm to ensure vigorous mixing. After reaction (heating time included), the autoclave was cooled to room temperature in a water bath, carefully depressurized, and sampled for further analysis. The co-oxidation experiments of HA or landfill leachate with TCP were similar as described above.

2.4. Analysis method

FA concentration in the mixture was measured with a UV-2550 spectrophotometer (Shimadzu Co., Japan) at 335 nm where the absorbance of TCP was almost zero and the absorbance difference between FA and TCP was the maximum. For generating calibration curve, FA concentrations in the mixture of FA and TCP were set at 10, 25, 50, 100, 200 and 300 mg/L, respectively, and TCP concentration was kept at 0.5 mM. These six solutions were measured with a spectrophotometer to generate a six-point calibration curve. The linear regression coefficient (R^2) of the standard curve is 1.0. Total organic carbon (TOC) analysis was performed using a Shimadzu TOC-V_{CPH} analyzer (Shimadzu Co., Japan). The pH value was measured with a PHSJ-5 pH meter (Rex Co., China). COD was determined by a standard dichromate reflux method [33]. BOD₅ test was performed according to the Water quality-Determination of biochemical oxygen demand after 5 days (BOD₅) for dilution and seeding method (Standard Method HJ 505-2009, China). N-NH₄ was determined according to the Water quality-Determination of ammonia nitrogen for Nessler's reagent spectrophotometry (Standard Method HJ 535-2009, China), and N-NO₃⁻ was determined according to the Water quality-Determination of nitrate nitrogen for ultraviolet spectrophotometry (Standard Method HJ 346-2007, China). The biodegradability index was estimated from the following equation:

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

The characteristics of the various synthetic wastewater samples containing FA, HA, (FA + TCP) and (HA + TCP) are given in Table 2.

3. Results and discussion

3.1. Preliminary experiments

The WAO of single FA (200 mg/L) was carried out at 150 °C and 0.5 MPa of O_2 for 4 h, and the result showed that only 12.2% TOC

Table 2	
Characterisations of the various synthetic wastewater samples.	

Sample	рН	COD (mg/L)	TOC (mg/L)	BOD ₅ (mg/L)
FA	5.6	322.7	63.2	0.11
FA + TCP	5.2	242.5	100.1	0.11
HA	7.0	200.9	106.0	0.08
HA + TCP	5.9	141.2	87.0	0.01

removal was obtained. When 0.5 mM NaNO₂ was incorporated into the reaction system, there was no obvious improvement in TOC removal and the color of the reaction mixture remained vellow-brown under the same experimental conditions. These results clearly showed that the catalytic activity of NaNO₂ was not high enough to thoroughly destroy FA. However, NaNO₂ exhibits the high catalytic capacity to activate molecular oxygen to destroy TCP [25]. For example, when NaNO₂-catalyzed wet oxidation of TCP (0.5 mM) was performed at 150 °C and 0.5 MPa of O₂ for 4 h, and TCP concentration was measured using a spectrophotometer at 293 nm which was the maximum absorption wavelength of TCP, the results showed that the TCP and TOC removal were 97.4% and 69.2%, respectively. In view of the above results, 0.5 mM TCP was added to the CWAO system of FA (200 mg/L) with 0.5 mM NaNO₂ as catalyst, after 4 h of reaction at 150 °C and 0.5 MPa of O₂, the color of the reaction mixture turned from initial vellow-brown to colorless and the TOC removal reached to 62.1%. We postulate that the TOC removal of TCP is still 69.2% (the CWAO result of TCP under the same experiment conditions) in the co-oxidation system, so the TOC removal of FA was about 60.4% according to the calculation results. These results demonstrated that the addition of TCP promoted the reduction of FA.

The absorption spectra of the mixture of FA and TCP before and after the CWCO process are shown in Fig. 1. The characteristic absorption peak of the mixture at approximately 286 nm disappeared without obvious absorption band emerging after the CWCO process. Concomitantly, the color of the reaction solution changed from the initial yellow–brown to colorless. This indicated that the chromophoric structures of FA and TCP were completely destroyed. These results also indicated the addition of TCP promoted the destruction of FA.

Encouraged by these promising results, the optimal operating conditions for CWCO of FA and TCP were systematically investigated with respect to reaction temperature, TCP concentration, NaNO₂ concentration, oxygen pressure and initial pH.

3.2. Effect of temperature

To evaluate the influence of temperature, the CWCO of FA and TCP were performed at 90, 110, 130 and 150 °C, respectively (Fig. 2). Fig. 2a shows the effect of temperature on the absorbance of the mixture solution. These results indicated that the absorbance of all the mixture solutions among the studied temperatures firstly increased and then decreased. And this could be confirmed by the change of the colour of the reaction solution. For example,



Fig. 1. Spectra of FA solution (0.4 g/L), mixture of FA and TCP before CWCO, TCP solution (1 mM) and mixture of FA and TCP after CWCO. Experimental conditions: $C_{\text{FA}} = 200 \text{ mg/L}; \quad C_{\text{TCP}} = 0.5 \text{ mM}; \quad C_{\text{NaNO2}} = 0.5 \text{ mM}; \quad T = 150 \text{ °C}; \quad P_{\text{O2}} = 0.5 \text{ MPa}; \text{ time } = 4 \text{ h}; \text{ pH} = 5.$

when reaction temperature was 150 °C, the color of the reaction solution turned from original yellow–brown to pink, then to slight yellow, and finally to colorless with reaction time increasing from 1 h to 4 h [25,26]. These results implied that the colored intermediate products might be formed when reaction time was not more than 1 h, and then be further oxidized to colorless substances with the reaction time prolonging to 4 h.

Fig. 2b displays the effect of temperature on the TOC removal of the mixture of (FA + TCP). Obviously, with the reaction temperature increasing, the TOC removal increased correspondingly. For example, the TOC removals were only 11.1% and 12.8% after 8 h of reaction when reaction temperatures were 90 and 110 °C, respectively. Raising reaction temperature to 130 °C, the TOC removal increased to 24.3% after 4 h of reaction. Further increasing reaction temperature to 150 °C, 62.1% TOC removal was obtained after 4 h of reaction. However, at 150 °C of reaction temperature, further prolonging the reaction time to 8 h did not lead to obvious enhancement in TOC removal.

From the above results we can conclude that higher temperatures are favorable for the CWCO of FA and TCP. However, from the practical point of view, higher temperatures lead to higher operating costs and more severe corrosion problems. Thus, the reaction temperature and time were respectively set at 150 °C and 4 h for the consequent optimization of experimental conditions.

3.3. Effect of TCP concentration

Fig. 3 reveals the effect of TCP concentration on the TOC removal of the mixture of (FA + TCP). It can be seen from Fig. 3 that as TCP concentration in the mixture increases, the TOC removal



Fig. 2. Effect of reaction temperature on the absorbance (a) and TOC removal (b). Experimental conditions: $C_{FA} = 0.2 \text{ g/L}$; $C_{TCP} = 0.5 \text{ mM}$; $C_{NaNO2} = 0.5 \text{ mM}$; $P_{O2} = 0.5 \text{ MPa}$; pH = 5.

increases. For example, the TOC removals were 31.6%, 38.6%, 48.7% and 62.1% when TCP concentrations were 0.05, 0.125, 0.25 and 0.5 mM, respectively, whereas the TOC removal of FA was only 14.6% without addition of TCP under the same experimental conditions. The remarkable results indicate that the addition of TCP could efficiently promote the degradation of FA. In addition, from the proposed degradation mechanism for the CWCO of FA and TCP (Section 3.9.) we can conclude that the increase of TCP concentration leads to the production of more high-concentration peroxynitrous acid (ONOOH), which might act as the most important active species for the degradation of TCP and FA. Based on the above results, we consider 0.5 mM as better TCP concentration in the present co-oxidation system.

3.4. Effect of NaNO₂ concentration

Fig. 4 shows the influence of NaNO₂ concentration on the TOC removal of the mixture of (FA + TCP). It was noteworthy that when low-concentration of NaNO₂ (0.05 mM) was added to the mixture, the TOC removal reached to 43.4%. When NaNO₂ concentration was increased to 0.5 mM, 62.1% TOC removal was obtained. The results indicate that increasing NaNO₂ concentration is beneficial to the degradation of the mixture of (FA + TCP). However, when NaNO₂ concentration was higher than 0.5 mM, there was no obvious improvement in the TOC removal. It can be seen from Eq. (4), the stoichiometric ratio of NaNO₂ to TCP is 1:1, so 0.5 mM NaNO₂ was sufficient for the complete reaction of TCP when the concentration of TCP was fixed at 0.5 mM. The above results indicate that 0.5 mM might be ideal NaNO₂ concentration in the present co-oxidation system.

3.5. Effect of oxygen pressure

Fig. 5 shows the effect of oxygen pressure on the TOC removal of the mixture of (FA + TCP). Six experiments were conducted with oxygen pressures increasing from 0.1 to 0.5 MPa. The results showed that the TOC removal increased with oxygen pressure increasing. This might be because high dissolved oxygen concentration in the liquid phase is beneficial to the oxidation of pollutants. It can be seen from Eq. (4) that O_2^- can be generated in the reaction between O_2 dissolved in the liquid phase and sodium trichlorophenolate, which then reacts with NO to generate powerful oxidizing ONOO⁻, leading to enhanced removal of TOC. So with the concentration of dissolved oxygen increasing, the concentration of ONOO⁻ increases correspondingly. According to the Henry's law, the concentration of oxygen dissolved in the liquid phase is



Fig. 3. Effect of TCP concentration on the TOC removal. Experimental conditions: $C_{FA} = 200 \text{ mg/L}$; $C_{NaNO2} = 0.5 \text{ mM}$; $T = 150 \degree$ C; $P_{O2} = 0.5 \text{ MPa}$; time = 4 h; pH = 5.



Fig. 4. Effect of NaNO₂ concentration on the TOC removal. Experimental conditions: $C_{FA} = 200 \text{ mg/L}$; $C_{TCP} = 0.5 \text{ mM}$; $T = 150 ^{\circ}\text{C}$; $P_{O2} = 0.5 \text{ MPa}$; time = 4 h; pH = 5.



Fig. 5. Effect of oxygen pressure on the TOC removal. Experimental conditions: $C_{FA} = 200 \text{ mg/L}$; $C_{TCP} = 0.5 \text{ mM}$; $C_{NaNO2} = 0.5 \text{ mM}$; T = 150 °C; time = 4 h; pH = 5.

proportional to the partial pressure of oxygen in the gas phase [21]. Therefore, an increase in the oxygen pressure in the gas phase could promote the CWCO of FA and TCP. Therefore, the oxygen pressure of 0.5 MPa was considered to be sufficient in the present system.

3.6. Effect of initial pH

Fig. 6 shows the effect of initial pH value of the mixture solution on the TOC removal of (FA + TCP). When initial pH values of the mixture solutions were 3 and 5, FA and TCP could be efficiently degraded. For example, when the CWCO of FA and TCP was conducted at pH 5, 62.1% TOC removal was achieved. However, when the initial pH values of the mixture solutions was basic, the TOC removal decreased to 36.2% at pH 7, 36.3% at pH 9, and 29.8% at pH 11, respectively. According to the proposed degradation mechanism in Section 3.9, when the initial pH value of the mixture solution was neutral or basic, TCP mainly existed in the form of anion in the solution and minor amounts of HNO₂ were yielded from TCP and NaNO₂, therefore the TOC removal was not high at solution pH higher than 7.

In addition, the changes of pH value of the reaction solution with reaction time were investigated. The results showed that the final pH of a reaction solution with initial pH 11 decreased to 6.0, 3.6, 3.5 and 3.5 for 1 h, 2 h, 3 h and 4 h, respectively. And the final pH value of a reaction solution with initial pH 9 decreased to 3.5, 3.4, 3.3 and 3.2 for 1 h, 2 h, 3 h and 4 h, respectively. It was worth mentioning that the final pH values of all the reaction



Fig. 6. Effect of pH on the TOC removal. Experimental conditions: $C_{FA} = 200 \text{ mg/L}$; $C_{TCP} = 0.5 \text{ mM}$; $C_{NaNO2} = 0.5 \text{ mM}$; T = 150 °C; $P_{O2} = 0.5 \text{ MPa}$; time = 4 h.

solutions were around 3 no matter whether the initial pH values of the reaction solutions were acid or not [22]. The reason for the reduction of pH may be that small molecular organic acids such as acetic acid, formic acid, pyruvic acid and succinic acid formed after the CWCO of FA and TCP [22,25].

3.7. Biodegradability index

Biodegradability index is a good indicator determining whether organic matters can be degraded by microorganism efficiently or not. To further study the biodegradability change of the mixture of (FA + TCP) after the CWCO process, the biodegradability indexes of eight control groups (raw FA, FA after WAO, FA after CWAO, raw TCP, TCP after WAO, TCP after CWAO, raw mixture of FA and TCP and mixture of FA and TCP after WAO) were determined under the optimum conditions ($C_{FA} = 200 \text{ mg/L}$; $C_{TCP} = 0.5 \text{ mM}$; $C_{\text{NaNO2}} = 0.5 \text{ mM}$; T = 150 °C; $P_{\text{O2}} = 0.5 \text{ MPa}$; time = 4 h; pH = 5), and the results are shown in Fig. 7. Compared with the biodegradability indexes of raw FA (0.11), FA after WAO (0.11), FA after CWAO (0.09), raw TCP (0.01), TCP after WAO (0.18), TCP after CWAO (0.84), raw mixture of FA and TCP (0.10) and mixture of FA and TCP after WAO (0.09), the biodegradability index of the mixture of (FA + TCP) after the CWCO process reached to 0.39. It can be seen that the biodegradability indexes of FA after CWAO with NaNO₂ or WAO with TCP were both low, while the index obtained from the CWCO system in the presence of NaNO₂ and TCP significantly increased. The results demonstrated the enhancement



Fig. 7. BOD₅, COD and biodegradability indexes of different samples. Experimental conditions: $C_{FA} = 200 \text{ mg/L}$; $C_{TCP} = 0.5 \text{ mM}$; $C_{NaNO2} = 0.5 \text{ mM}$; T = 150 °C; $P_{O2} = 0.5 \text{ MPa}$; time = 4 h; pH = 5.

of biodegradability of FA came from the synergistic effect of $NaNO_2$ and TCP. On the other hand, it has been reported that when the biodegradability index is higher than 0.4, wastewater can be considered completely biodegradable [14]. Therefore, the present CWCO process was able to ameliorate FA from refractory substance to biodegradable substance. Although complete COD removal was not achieved, the degradation products were easily biodegraded.

3.8. Reaction kinetics

To gain a better insight into the CWCO process, the reaction kinetics of mixture of FA and TCP were investigated in the temperature range of 120–150 °C, at 0.5 MPa of O₂. According to Refs. [22,34], it was possible to approximate the expression to pseudofirst order, given by the following equation (Eq. (2)):

$$-\ln\frac{[COD]}{[COD]_0} = k'_{COD}t \tag{2}$$

$$\ln k'_{COD} = \ln A - \frac{Ea}{RT}$$
(3)

Fig. 8a shows the experimental data obey to the pseudo-firstorder kinetic model for all the runs ($R^2 > 0.96$, except 150 °C for 6 h). When the CWCO of FA and TCP was conducted at 150 °C for 4 h, most organic compounds were removed ($R^2 = 0.97$). Even when the reaction time was prolonged to 6 h, there was a little increase in COD removal. As can be seen form Fig. 8b that k'_{COD} under different temperatures follows the Arrhenius equation (Eq. (3)), the activation energy, Ea can be calculated by performing a linear fit of ln k'_{COD} versus 1/*T*, as shown in Fig. 8b. The activation energy for the degradation of the mixture of FA and TCP was found to be 40.3 kJ/mol ($R^2 = 0.95$).



Fig. 8. Pseudo-first-order kinetics plots (a) and Arrhenius plot (b) for CWCO of FA and TCP. Experimental conditions: $C_{FA} = 200 \text{ mg/L}$; $C_{TCP} = 0.5 \text{ mM}$; $C_{NaNO2} = 0.5 \text{ mM}$; $P_{O2} = 0.5 \text{ MPa}$; pH = 5.

3.9. Degradation mechanism

As for WAO, the reactions generally proceed according to a free-radical mechanism [22,35]. In addition, based on the proposed degradation mechanism for the CWCO of PNP and TCP [26], TCP is reacted with NaNO₂ to generate sodium trichlorophenolate and HNO₂ (Eq. (4)). The oxidation of sodium trichlorophenolate with dioxygen is to form O_2^- and trichlorophenol radical (Eq. (4)). HNO₂ decomposes into NO and NO₂ (Eq. (5)), then NO reacts extremely easily with O_2^- to generate ONOO⁻ (Eq. (6)). So we deduced that peroxynitrite (ONOO⁻) might be generated in the present CWCO system. At acid pH, ONOO⁻ is protonated rapidly to its conjugate acid, peroxynitrous acid (ONOOH) which was also a powerful oxidizing species (Eq. (7)). ONOOH was unstable and rapidly decomposes to highly reactive 'OH and 'NO₂ through homolytic reaction (Eq. (8)) [36–42].



 $2HNO_2 \rightarrow NO + NO_2 + H_2O \tag{5}$

 $ONOO^{-} \stackrel{\mathrm{H}^{+}}{\Longrightarrow} ONOOH$ (7)

$$ONOOH \rightarrow NO_2 + OH$$
 (8)

ONOOH might act as the most important active species for the degradation of TCP and FA. ONOOH oxidizes the pollutants resulting in generating degradation offspring and NO₂. While the NO₂ oxidized [Cl⁻], which is generated from the degradation of TCP, to chlorine species [Cl], itself was reduced to regenerate NO [25,26]. With the assistance of water, [Cl] is transformed to oxidized chlorine species [HClO], which decompose into active oxygen species and [Cl⁻].

In order to confirm the existence of hydroxyl radicals produced in the CWCO process, the radical scavengers (tert-butyl alcohol and sodium bromide) were used. The radical scavenger experiments were conducted under the optimum conditions, and the molar ratios of radical scavengers to TCP were both set at 500:1 [34]. The results showed that the presence of radical scavengers negatively affect the CWCO of FA and TCP. For example, when the mixture reacted with tert-butyl alcohol at 150 °C and 0.5 MPa of O_2 for 8 h, its absorbance measured at 335 nm increased from 0.041 to 0.442, and when it reacted with sodium bromide under the same experimental conditions, its absorbance increased from 0.041 to 0.619. Thus the results indicated that the highly reactive hydroxyl radicals (\cdot OH) were involved in the main degradation mechanisms of the CWCO of FA and TCP.

3.10. Degradation of HA and landfill leachate

The CWCO process was also applied to the oxidative degradation of HA. After reaction for 4 h at 150 °C and 0.5 MPa of O_2 , the COD removal of the mixture of HA and TCP could reach to 56.5% and the color turned from brownish black to colorless, concomitantly the biodegradability index increased from 0.05 to 0.50, indicating that the mixture was thoroughly biodegradable.

In view of the effective oxidation of FA and HA in the CWCO system, the CWCO process was further applied to the degradation of landfill leachate. Firstly, landfill leachate was diluted 10 times (DLL). Then the pH value of the mixture of DLL and TCP was adjusted to 5. When the CWCO of DLL and TCP was conducted at 150 °C and 0.5 MPa of O_2 for 4 h, the COD removal of the mixture of (DLL + TCP) reached to 56.7% and the color turned from yellow–brown to colorless. Furthermore, the biodegradability index of the mixture could also increase from 0.08 to 0.34. Therefore, the CWCO process could be chosen as an alternative pretreatment method to improve the biodegradability of landfill leachate.

4. Conclusions

The CWCO process efficiently oxidized the recalcitrant FA, HA and landfill leachate to CO_2 and biodegradable products with high conversion in the presence of TCP under mild conditions (150 °C, 0.5 MPa of O_2). Hydroxyl radicals had been determined to be dominant active spices generated in the CWCO system. The obtained results confirmed that the CWCO process was useful to improve the biodegradability of the stabilized landfill leachate up to a value compatible with further biological treatment.

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