



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 NaNO_2 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 NaNO_2 -catalyzed wet co-oxidation (CWCO) of FA and 2,4,6-trichlorophenol (TCP) using TCP as the promoter was investigated. Compared with the NaNO_2 -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 (BOD_5/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. Furthermore, this co-oxidation system was also effective for degrading the mixture of HA 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

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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

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 Teflon-lined 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 μL, 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
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
pH	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:

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

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 O₂ for 4 h, and the result showed that only 12.2% TOC

Table 2
Characterisations of the various synthetic wastewater samples.

Sample	pH	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

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