Chemical Engineering Journal 331 (2018) 578–586

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Oxidative degradation of landfill leachate by catalysis of $CeMnO_x/TiO_2$ in supercritical water: Mechanism and kinetic study

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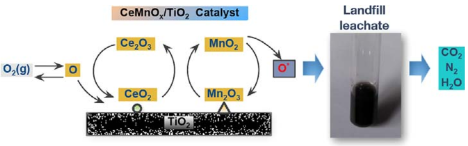
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Landfill leachate
Supercritical water oxidation
Kinetics
Co-oxidation
Catalyst

ABSTRACT

Landfill leachate is a typical refractory wastewater that contains high concentration of organic pollutants. In this work, we investigated the treatment of landfill leachate by supercritical water oxidation (SCWO) in a batch reactor. The effects of temperature (*T*, 450–600 °C), oxidation coefficient (OC, 1.2–3.4), reaction time (*t*, 60–600 s) and pH (4.13–8.05) on total organic carbon (TOC) removal efficiency (TRE,%) and ammonia nitrogen (NH_3-N) removal efficiency (NRE,%) were analyzed. TRE and NRE increased remarkably with increasing temperature and OC. At 3.4 OC and 600 °C, 92.5% TRE and 50.9% NRE were achieved after 600 s. A modified kinetic model on TRE and NRE considering the induction time was developed and accurately correlated the experimental results. A significant co-oxidation effect of methanol and landfill leachate in SCWO was detected. Furthermore, heterogeneous catalysts were added to SCWO of landfill leachate to improve the removal rate of organic contaminants. A series of composite catalysts ($CeMnO_x/TiO_2$) which consisted of the cerium, manganese and titanium oxides were prepared by impregnation method with varying Ce/Mn ratio. Compared with the SCWO of leachate without catalyst, the $CeMnO_x/TiO_2$ catalyst with Ce/Mn ratio of 1:2 exhibited high catalytic activity and stability. Additionally, a catalytic reaction mechanism was proposed. It was assumed that MnO_x is the active component and CeO_2 is the additive and oxygen supplier. The results obtained from this work suggest the SCWO with high-efficiency and stable catalyst could be a promising technology for landfill leachate treatment.

1. Introduction

Landfill leachate is generated from decomposing municipal solid waste (MSW) that seeps into surface, ground and rain water. A wide range of pollutants are present in landfill leachate, which includes dissolved organic matter, inorganic macrocomponents (e.g. ammonium, chloride, sulfate), heavy metals, and xenobiotic organic compounds [1]. For landfill leachate, biological treatment is most widely used for its reliability, simplicity and high cost-effectiveness. However, biological treatment will be hampered by the specific toxic substances (such as PAHs-polyaromatic hydrocarbons,

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http://dx.doi.org/10.1016/j.cej.2017.08.122
Received 25 June 2017; Received in revised form 26 August 2017; Accepted 28 August 2017

AOXs-adsorbable organic halogens, PCBs-polychlorinated biphenyls) and bio-refractory organics (such as humic substance or surfactants) [2]. For this reason, some additional processes are required besides biological treatment. Additionally, advanced oxidation processes (AOPs) have been reported to significantly enhance the biodegradability of mature landfill leachates, such as simple Fenton process, a combination of Fenton and ultraviolet (UV), TiO_2 photocatalysis, $S_2O_2^{8-}/Fe^{2+}$, ozonation and so on [3–6]. However, the common drawback of these techniques is the high treatment cost [7]. To reduce the treatment cost significantly, the best strategy seems to be the integration of biological processes and APOs [8].

Supercritical water oxidation (SCWO) is a green chemistry process that uses water exceeding the critical pressure and temperature of water (SCW, P_c = 22.12 MPa, T_c = 374.15 °C) to degrade organic pollutants into H_2O and CO_2. SCWO has been considered to be an extremely promising technology to treat organic wastewater and municipal sludge in recent decades [9]. Many refractory organics are decomposed with a conversion efficiency of greater than 99% in a few seconds during SCWO [10]. Furthermore, the low reaction temperature during SCWO mitigates the formation of secondary pollutants such as NO_x, SO_x, and dioxin [11]. Moreover, SCWO has been reported to be energetically self-sustaining for a reaction temperature of 650 °C when the heating value in feedstock exceeds 930 $kJ\cdot kg^{-1}$, and the excess energy can be recovered in the form of steam at even higher heating values [12,13].

The SCWO of landfill leachate has been previously investigated. Williams and Onwudili [14] first found that almost complete oxidation of the organic components in leachate is achieved under SCWO conditions in a batch autoclave reactor, although the high chloride in leachate led to the significant corrosion of reactor. Zou et al. [15] reported that the destruction efficiencies of chemical oxygen demand (COD) and NH_3-N in SCWO of leachate increased significantly with rising temperature and oxidant amount, with maximum values of 98.5% and 76.2% for COD and NH_3-N, respectively. Another interesting study of landfill leachate degradation using SCWO without any oxidants was reported by Ferreira-Pinto et al. [16]. They presented that up to 98% of pollutants were removed under optimum experimental conditions, indicating that SCWO is a promising technique to treat leachate. Moreover, Gong and Duan [17] presented a modified pseudo first-order rate model for oxidation of landfill leachate in a transpiring-wall SCWO reactor, taking into account the induction time effect. To increase the removal efficiency of refractory pollutant in mild reaction conditions, various catalysts have been examined in SCWO process. MnO_2 and Ni/Al_2O_3 are effective in SCWO of landfill leachate [18,19]. However, as a main shortcoming of MnO_2 catalyst, it is the formation of N_2O [18]. Although a removal efficiency of 98.2% in terms of total organic carbon (TOC) conversion was obtained, the total nitrogen (TN) removal achieved only about 57% in SCWO of landfill leachate over Ni/Al_2O_3 [19]. Generally, transition metal oxides such as manganese oxide, cerium oxide and titanium oxide are effective catalysts for SCWO of ammonia, organics and industrial wastewaters [20–23]. As well as high catalytic activity, MnO_2 and TiO_2 also have excellent hydrothermal stability, activity maintenance and resistance to metal leaching under SCWO conditions [21]. However, the Mn-Ce-Ti composite catalyst has not yet been applied to the SCWO of landfill leachate.

More attention has been paid to co-oxidation process in SCWO, where the oxidation of labile, reactive species (such as methanol and ethanol) accelerates the decomposition rate of refractory, stable species (e.g. NH_3, acetic acid, phenol) [24]. For example, Ploeger et al. [25] found adding ethanol increased the conversion of NH_3 undergoing SCWO from 20% to 65%, and co-oxidation enhancement primarily occurred during the first 2 s of reaction time. Suzugaki et al. [26] also presented that the conversion of NH_3 to N_2O increased by approximately fourfold in the presence of methanol, in comparison to that without methanol. Furthermore, Zhang et al. [24] suggested that methanol accelerates the decomposition of acetic acid and phenol because methanol oxidizes rapidly and generates reactive intermediates $HOO^{\cdot}$ and $OH^{\cdot}$ at shorter reaction time. Generally, the stabilized landfill leachate is rich in ammonia (3000–5000 $mg\cdot L^{-1}$) [27], which is stable and refractory in SCWO environments [18]. It is suggested that co-oxidation with reactive species seemed to be a promising method to degrade refractory compounds in landfill leachate. To our knowledge, however, there are no published reports regarding co-oxidation between landfill leachate and any other reactive species in SCWO.

In this paper, firstly, we studied the effects of temperature, oxidation coefficient, reaction time and pH value of feed on SCWO of landfill leachate, and formulated a modified kinetics on the removal efficiencies of TOC and NH_3-N considering the induction time. Subsequently, the co-oxidation effect of methanol and landfill leachate was firstly investigated, due to the high oxidation reactivity of methanol in SCWO [26]. We also prepared a composite catalyst ($CeMnO_x/TiO_2$) which consisted of the cerium, manganese and titanium oxides, and examined the activity and stability of the synthesized catalyst in leachate SCWO. Finally, a possible catalytic mechanism was proposed, wherein titanium, manganese and cerium oxides are assumed to be the carrier, active constituent and auxiliary, respectively.

2. Materials and methods

2.1. Materials

Leachate was collected from a landfill site in Xi'an city, Shaanxi province, whose characteristics are shown in Table 1. 30 wt% H_2O_2 solution and methanol served as the oxidant and co-oxidation component, respectively. Furthermore, H_2SO_4 and NaOH were applied to adjust the pH values of leachate. As the precursors, $Ce(NO_3)_2\cdot 6H_2O$, 50 wt% $Mn(NO_3)_2$ solution and $TiCl_4$ were purchased from Tianjin Fuchen Chemical Regent Factory. All chemicals were of analytical reagent grade.

2.2. Catalyst synthesis process

$CeMnO_x/TiO_2$ composite catalyst was prepared as follows: first, pure $TiCl_4$ was added into purified water in a ice-water bath. A TiO_2 pellucid aqueous solution was obtained after ultrasonic wave for 30 min and aging for 12 h. Subsequently, ammonia hydroxide was added into the TiO_2 pellucid aqueous solution until the pH reached 7.00, then a TiO_2 emulsion was obtained. Subsequently, the TiO_2 emulsion was divided into six equal parts before adding precursors. Under strong agitation, $Ce(NO_3)_2\cdot 6H_2O$ and 50 wt% $Mn(NO_3)_2$ solution was added into TiO_2 emulsion by varying Ce/Mn molar ratio (3:0, 2:1, 1.5:1.5, 1:2 and 0:3) and the (Ce + Mn)/Ti molar ratio was specified as 1:10 for all catalysts. After vibration for 24 h under 30 °C, the resulting mixture residue was filtered, washed with ultrapure water, dried in air at 120 °C for 12 h, and lastly calcined in a muffle furnace at 650 °C for 4 h. The catalysts were grinded and sieved to a 200 mesh size range for later use. Additionally, self-made TiO_2 catalyst was also prepared in the absence of $Ce(NO_3)_2\cdot 6H_2O$ and $Mn(NO_3)_2$. All samples were labeled by Ce/Mn molar ratio as follows C0M0, C3M0, C2M1, C1.5M1.5, C1M2 and C0M3, respectively. Here, C0M0 stands for the TiO_2 catalyst with no Ce and Mn.

Table 1
Characteristics of landfill leachate.

COD/$mg\cdot L^{-1}$	NH_3-N/$mg\cdot L^{-1}$	TN/$mg\cdot L^{-1}$	TOC/$mg\cdot L^{-1}$	Conductivity/$us\cdot cm^{-1}$	pH
35000 ± 330	2484.4 ± 54.4	3100 ± 81.7	12347.2 ± 376	8050 ± 175.2	6.56 ± 0.02