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Combined processes of ozonation and supercritical water oxidation for landfill leachate degradation

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ABSTRACT

Leachate is a highly variable, heterogeneous and recalcitrant wastewater generated in landfills which may contain high concentrations of many organic and inorganic compounds, hampering the application of a single technique in its treatment. Therefore, this paper assessed leachate degradation through supercritical water oxidation (ScWO) as well as combined processes of ozonation and supercritical water oxidation (O_3/ScWO and ScWO/O_3), a yet innovative combination. Ozonation was carried out at different reaction times (30–120 min). ScWO was developed at 600 °C, 23 MPa, and spatial time (τ) from 29 to 52 s. A combination of ozonation (30 min) and supercritical water oxidation process (O_3-30'/ScWO) was the most efficient technique for the degradation of the leachate assessed. These conditions enabled to remove high values of apparent and true color (92% and 97%, respectively), biochemical oxygen demand ($BOD_{5,20}$) (95%), chemical oxygen demand (COD) (92%), total organic carbon (TOC) (79%), nitrite (78%), nitrate (84%), total (96%), dissolved (96%) and suspended (94%) solids. In addition, the combined process presented significant decrease in electric conductivity (EC) (68%) and less leachate turbidity removal (43%). Except for ammonia and nitrite, all parameters of the leachate treated by O_3-30'/ScWO met the specifications of Brazilian legislation (CONAMA Resolutions No. 357/2005 and No. 430/2011) for the disposal of wastewater in water bodies. Besides, both processes are considered to be clean technologies. This shows the great possibility of applying the O_3/ScWO combination to landfills leachates.

1. Introduction

The disposal of solid residues in landfills results in the formation of a wastewater known as leachate (Amaral-Silva et al., 2016). It is formed from water percolation through the layers of the discarded residues by dissolving and transporting organic and inorganic compounds inherent to the residues themselves or resulting from its decomposition (Molino et al., 2017).

The landfill leachate is considered refractory and has high complexity and variability. Its composition commonly presents varied organic and inorganic compounds, such as humic substances, ammonia and other nitrogen compounds, chlorine compounds, inorganic salts, toxic metals, and xenobiotic compounds (Kjeldsen et al., 2002; Li et al., 2009; Ye et al., 2017).

If discharged without treatment, leachate can cause soil, surface and underground water contamination, in addition to directly or indirectly affecting human health and the ecosystem (Deng and Englehardt, 2006; Tizaoui et al., 2007), implying the necessity of a proper treatment.

Many techniques have been used to treat landfill leachates, such as biological (Müller et al., 2015; Sun et al., 2015), physicochemical (coagulation/flocculation) (Tatsi et al., 2003; Verma and Kumar, 2016), adsorption (Foul et al., 2009), membrane separation (Piatkiewicz et al., 2001), chemical precipitation (Kim et al., 2007; Li and Zhao, 2003), surface gasification (Molino et al., 2017), among others. However, advanced oxidation processes (AOPs) have been approached in recent studies, such as ozonation (O_3) (Amaral-Silva et al., 2016; Jung et al., 2017) and supercritical water oxidation (ScWO) (Civan et al., 2015; Weijin and Xuejun, 2010), because of the low biodegradability of the landfill leachate and the importance of a treatment free of secondary residues.

AOPs aim at improving the biodegradability and treatability of landfill leachates and can be used as techniques either pre or post-treatment (Wu et al., 2004). Ozonation has been highlighted

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among AOPs due to the high oxidizing capacity of the ozone gas (O_3) (Amr and Aziz, 2012; Imai et al., 1998). O_3 is very reactive and selective for organic pollutants such as polyaromatic hydrocarbons, phenolic compounds, humic substances, among others (Cortez et al., 2010; Gonçalves, 2003; Hoigné, 1998).

This is a process capable of decomposing large and recalcitrant molecules into molecules of lower complexity and molecular weight, with a higher biodegradability than its precursor (Ghazi et al., 2014; Imai et al., 1998), either by direct ozone action on pollutants or indirect oxidation via hydroxyl radicals (OH) (Kurniawan et al., 2006; Rodrigues-Silva et al., 2014). Furthermore, O_3 is able to promote the water and wastewaters disinfection as well as reduction of color and organic matter (Chaturapruek et al., 2005; Ghazi et al., 2014).

Many studies have applied O_3 in the treatment of landfill leachates. Wu et al. (2004) by using a leachate with pH 8.1, mass flow of 40 mg O_3 min^{-1}, and reaction time of 30 min, obtained removal rates of 15% of total organic carbon (TOC) and approximately 90% of color. Tizaoui et al. (2007) were able to remove 27% of chemical oxygen demand (COD) and 87% of color by operating at pH 8.7, flow of 16 mg O_3 L^{-1}, and reaction time of 60 min. Amaral-Silva et al. (2016) reached removal rates of 34% and 95% of COD and color, respectively, by operating at pH 9.0, after 180 min of reaction and flow of 10 mg O_3 min^{-1}.

ScWO, in turn, has proved to be a potential treatment for the decontamination of wastewaters rich in organic matter (Wang et al., 2011), such as landfill leachates. The ScWO process occurs in conditions of temperature and pressure above the critical point of water, 374 °C and 22.1 MPa (221 bar) (Kritzer and Dinjus, 2001). Under these conditions, water behaves as a low-polarity solvent, enabling the full miscibility of organic compounds and molecular oxygen (Savage, 1999), forming a single phase between liquid and vapor (Voisin et al., 2017), reducing the limitations of mass transference and promoting high reaction rates (Bermejo and Cocero, 2006a). This procedure allows the oxidation of organic compounds to carbon dioxide and water in a short elapsed reaction time and yields close to 100% removal (Barner et al., 1992). Supercritical water has higher density and diffusivity as well as lower viscosity when compared with the water in its normal condition, besides presenting low solubility of inorganic salts, thus promoting their precipitation during the treatment (Akiya and Savage, 2002; Gloyna and Li, 1993).

Despite still being an incipient technique for the treatment of landfill leachates, studies encompassing this wastewater have presented good results regarding the degradation of organic matter, especially refractory. Weijin and Xuejun (2010) carried out the process at 430 °C, 30 MPa, using excess oxidant (hydrogen peroxide) in a transpiring-wall continuous reactor and obtained removal rates of 98% of BOD and 97% of COD. Zou et al. (2013) operated with a batch reactor in conditions of 500 °C, residence time of 2 min, 300% of excess oxygen, and 6 g of fly ashes (catalyst), having reached a removal of approximately 99% of COD. Without using any oxidant, Ferreira-Pinto et al. (2017) operated with a continuous reactor under conditions of 700 °C, 25 MPa, and mass flow of 6 g min^{-1}, with removal rates of color, turbidity, TOC, and COD of 98%, 98%, 97%, and 99%, respectively.

The efficiencies presented by the O_3 and ScWO processes individually, in previous studies, show the importance of these techniques for the wastewaters treatment, especially landfill leachates. In addition, both techniques are considered clean and environmentally friendly technologies, since they do not generate solid by-products (sludge). On the contrary, the ScWO can still form gases that can be used for the production of energy.

Facing the complex and recalcitrant composition of landfill leachates as well as the difficulty to treat this wastewater effectively, the goal of this paper is to innovatively investigate the efficiency of the supercritical water oxidation process (ScWO) and its combination with the ozonation process (O_3/ScWO and ScWO/O_3) regarding the degradation of leachate from the landfill of Maringá City, Paraná, Brazil by assessing ozone-leachate contact time.

2. Experimental section

2.1. Leachate sampling

Maringá landfill, Paraná, Brazil, has been operating since 2010 in an area of 290,400 m^2, where approximately 400 tons of residues are discharged on a daily basis. This landfill has been receiving solid residues of domestic origin, public cleaning services, non-hazardous industrial waste (sludge from domestic wastewater treatment plants), and residues from large generators – facilities which daily generate an amount above 100 L or 50 kg.

The leachate was collected at the landfill of Maringá/PR, encompassing four different points of the leachate storage tank, being characterized as integrated sample, according to Von Sperling (2014). This tank contains the leachates generated in active and inactive cells of residues of the landfill studied. After the collection, the leachate was characterized by determining its physicochemical parameters and following storage at 4 °C until the completion of all tests.

Because of the variability in its characteristics during storage as a consequence of natural biological degradation and long elapsed time of the experiments, the leachate underwent a characterization before each test. Therefore, a single leachate collection resulted in three samples of leachate with different physicochemical characteristics, named RL1, RL2 and RL3.

2.2. Physical-chemical characterization of leachate

The leachate characterization for both raw leachate samples (in nature) (RL1, RL2, and RL3) and after the treatments processes (O_3 and ScWO), was carried out by determining the physicochemical parameters of pH, electric conductivity (EC), apparent and true color, turbidity, chemical oxygen demand (COD), biochemical oxygen demand ($BOD_{5,20}$), total organic carbon (TOC), total solids (TS), total suspended solids (TSS), total dissolved solids (TDS) and nitrogen series: total ammoniacal nitrogen (NH_3-N), nitrite (NO_2-N), and nitrate (NO_3-N).

Values of pH and EC were measured through potentiometry using a digital pH meter (Digimed DM/20) and a multi-parameter gauge (Hanna HI4522), respectively, according to the methodologies recommended for the equipment. Concentrations of apparent and true color were obtained using a visible spectrophotometer (Hach DR-2010) through the platinum-cobalt method at 455 nm (Method 8025, Hach Company, 1996). Turbidity was measured using a portable turbidimeter (Digimed DM-TU) through the nephelometric method. COD concentration was measured in triplicate and through colorimetric testing (Method 5220 D, APHA, 1998) using a digestion block (Hach COD-Reactor 45600) at 150 °C and a visible spectrophotometer (Hach DR-2010) for absorbance readings at 600 nm. $BOD_{5,20}$ was obtained through respirometry (Method 5210 D, APHA, 1998) (Hach BODTrak™ II) and by subjecting the samples to five-day incubation at 20 ± 1 °C. The analysis of TOC was carried out in triplicate through high-temperature combustion method (Method 5310B, APHA, 1998) using an analyzer of total organic carbon (Shimadzu TOC-L CSH). TOC concentration was obtained from the difference between the concentration of total carbon (TC) and inorganic carbon (IC). Gravimetry (Methods 2540B, C and D, respectively, APHA, 1998) was applied to measure the set of solids (TS, TDS and TSS). Concentrations of NO_2-N and NO_3-N were obtained, respectively, through the methods of reduc-

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