

LEACHATE TREATMENT USING SUPERCRITICAL WATER

Leandro Ferreira-Pinto,¹ Andresa Carla Feihmann,^{2,4} Célia Regina Granhen Tavares,¹ Jane Selia dos Reis Coimbra,^{3,4} Marleny D. A. Saldaña,⁴ Diogenes R. L. Vedoy⁶ and Lúcio Cardozo-Filho^{1,4,5*}

1. Department of Chemical Engineering, Universidade Estadual de Maringá, 87020-900, Maringá – PR, Brazil

2. Department of Food Engineering, Universidade Estadual de Maringá, 87020-900, Maringá – PR, Brazil

3. Department of Food Technology, Universidade Federal de Viçosa, 36570-000, Viçosa – MG, Brazil

4. Department of Agricultural, Food and Nutritional Science, University of Alberta, T6G 2P5, Edmonton, AB, Canada

5. Agronomy Department, Centro Universitário da Fundação de Ensino Octávio Bastos (UNIFEOB), Av. Dr. Otávio Bastos, 2439, 13874-149, São João da Boa Vista – SP, Brazil

6. Department of Chemical and Materials Engineering, University of Alberta, T6G 2M9, Edmonton, AB, Canada

This work reports new experimental data for the oxidation degradation of landfill leachate using supercritical water treatment (ScWO) without addition of any oxidants. The treatment reduced significantly the original concentration of pollutant compounds in the liquid waste. The parameters used to evaluate the efficiency of the treatment (and leachate degradation) were chemical oxygen demand (COD), total organic carbon (TOC), turbidity, colour, and absorbance. The experiments were conducted using a continuous flow reactor built in Inconel 625. The degradation oxidation reactions were carried out using temperature between 350 and 600 °C (for COD initial concentrations of 1580 mg · L⁻¹) and between 450 and 700 °C (for COD initial concentrations of 2000 mg · L⁻¹), pressures of 15 and 22.5 MPa, feed streams of 6 and 12 g · min⁻¹, and reaction operation time of 40 min. Increasing pressure improved degradation of organic pollutant compounds, whereas the increase of the feed flow rate did not show any positive effect on the performance of the treatment. However, the most important factor on the degradation of leachate was temperature; increasing temperature from 350 to 600 °C reduced COD level in 31.3 and 34.4 % for 15 and 22.5 MPa, respectively. Hydrogen was the gas produced in the highest amount for all the experimental conditions studied. The results suggested that supercritical water is a promising technique to treat leachate and consequently reduce its pollutant capacity. Thus, the data presented here can be used as a basis for future studies.

Keywords: leachate, wastewater, ScWO, degradation

INTRODUCTION

The leachate produced after the degradation of waste disposed of in landfills is a complex effluent containing high amounts of different environmental pollutant compounds, such as organic and inorganic matter, ammonia, heavy metals, chlorinated organic compounds, and inorganic salts,^[1] which can contaminate groundwater and surface water contributing to the soil pollution.

Leachate treatment using conventional biological processes, such as the aerobic (activated sludge, aerated lagoons, and biological filters) and the anaerobic (ponds)^[2,3] processes, is the usual form of waste handling in most landfills.

Physico-chemical techniques, such as coagulation-flocculation,^[4-6] precipitation-adsorption,^[3,7,8] chemical oxidation,^[9] and incineration are traditional techniques applied in the leachate treatment. However, the use of the isolated biological treatment cannot reach satisfactory efficiency in the degradation of the organic matter^[2,3] to support their discharge in soils and water. Therefore, such techniques should be used in combinations of two or more in the complete treatment of the effluent.^[10]

Additionally, the biological processing of leachate needs, in most cases, large areas to run with the disadvantage of generating large amounts of sludge. Thus, it is necessary to develop techniques that allow the treatment of leachate in small places at shorter processing times with reduced generation of sludge, and that generate effluents with final composition within the standard legislation for waste discharge.

Some studies reported the treatment of leachate by means of unconventional processes such as ozonation,^[11-14] Fenton reaction,^[14-17] catalytic photo-oxidation,^[13,18-20] and membrane processes.^[21-25]

Nevertheless, the complex nature of the leachate generated in landfills is an impeditive factor in applying the cited techniques for its handling.

Therefore, the leachate oxidation treatment using supercritical water oxidation (ScWO) appears as a highly promising technology due to the advantages of supercritical water for decontamination of wastewater containing organic matter.^[2]

Meanwhile, few studies on supercritical oxidation of landfill leachate are available in the literature. Gong and Duan^[11] reported the influence of supercritical oxidation in reducing the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) parameters. The authors obtained the BOD parameter reduction of approximately 97 % (initial concentration of BOD of 1200 mg · L⁻¹) under temperature and pressure ranges of 322 to 431 °C and 18 to 30 MPa, respectively. Under

* Author to whom correspondence may be addressed.

E-mail address: lucio.cardozo@gmail.com

Can. J. Chem. Eng. 95:1442-1448, 2017

© 2017 Canadian Society for Chemical Engineering

DOI 10.1002/cjce.22818

Published online 16 March 2017 in Wiley Online Library

(wileyonlinelibrary.com).

these same conditions, the COD reduction was approximately 98 % (COD initial concentration of $1100 \text{ mg} \cdot \text{L}^{-1}$). However, these experiments were conducted with a large excess of oxidant, approximately $6.5 \text{ mol} \cdot \text{L}^{-1}$ of H_2O_2 (about 200 mL of oxidant per litre of leachate). Wang et al.^[2] obtained leachate COD reduction of 99.2 % at 500°C and 25 MPa in their supercritical oxidation experiments. Notwithstanding, the experiments were conducted under O_2 excess of 350 % relative to the initial concentration of oxygen dissolved in the leachate sample. Similarly, Zou et al.^[10] obtained COD reduction of 99 %, using approximately 300 % of O_2 excess (300 mL of H_2O_2 for each litre of leachate). Although these studies show satisfactory reduction of organic matter assessed in terms of COD, they were based on experiments performed under high excess of oxidants. In some cases, the excess approached 1/3 of the volume of leachate. However, experiments without the use of oxidants are not reported in the literature. Thus, to add information regarding the supercritical oxidation of leachates, in this work, the leachate oxidation reactions were carried out without any oxidants.

EXPERIMENTAL SECTION

Materials

The leachate used was donated by Objective Company[®] (Paraná, Brazil), which deals with the leachate generated in the landfill from Maringa city, PR, Brazil. All chemicals of analytical grade were used as received.

Apparatus and Experimental Procedure

Twenty litres (20 L) of raw leachate were used in the experiments. Each experiment ran for 40 min after the system had reached the

established pressure, temperature, and flow rate. The residence time varied between 7 and 163 s.

Figure 1 shows the homemade supercritical water apparatus, which consists of a reactor for continuous flow rate built in Inconel 625, a preheater, a condenser, and pipes made of stainless steel. The homemade supercritical water apparatus has been described in prior work.^[26] The apparatus specification is listed in Table 1. The leachate within the glass reservoir (1) was suctioned by a high pressure pump (Thar P50) (2), then conveyed through a 316 stainless steel tube ($L = 1.5 \text{ m}$, $\text{I.D.} = 3.175 \text{ mm}$) up to the valve V_1 (one-way valve). The leachate flowed to the preheater (3) ($L = 6 \text{ m}$, $\text{I.D.} = 3.175 \text{ mm}$) where it was heated at 50°C before it entered the reactor (4) ($L = 0.2 \text{ m}$, $\text{I.D.} = 13 \text{ mm}$). The heating of the reactor and the preheater was provided by two bipartite ovens (5), each of them equipped with two resistors in infrared ceramic (Corel, São Paulo-SP, Brazil) of 1000 W. The resistors were activated by control valves (Novus, Porto Alegre-RS Brazil) connected to type J thermocouples (accuracy $\pm 1.0^\circ\text{C}$) (T_1) contacting the preheater, (T_2) contacting the reactor, and (T_3) contacting the condenser. Outside of the glass reactor, the effluent filled a 316 stainless steel tube ($L = 2.5 \text{ m}$, $\text{I.D.} = 3.175 \text{ mm}$) for heat exchange with the external environment. The temperature was monitored by a type T thermocouple (accuracy $\pm 1.0^\circ\text{C}$, Novus, Porto Alegre-RS Brazil) (T_2). Then the resulting mixture filled the condenser (7) containing a coil of 316 stainless steel ($L = 2.5 \text{ m}$, $\text{I.D.} = 3.175 \text{ mm}$) for cooling at 10°C . The pressure was then adjusted in the back-pressure valve (V_2) and observed on the gauge (8). The separator (9) was used to separate the stream of gas from the liquid. The liquid phase was composed of water, unreacted leachate compounds, and other reaction products. The vapour phase consisted of the gaseous products of the reaction, mainly H_2 and CO_2 . All experimental conditions used to evaluate the leachate degradation by ScWO are listed in Table 2.

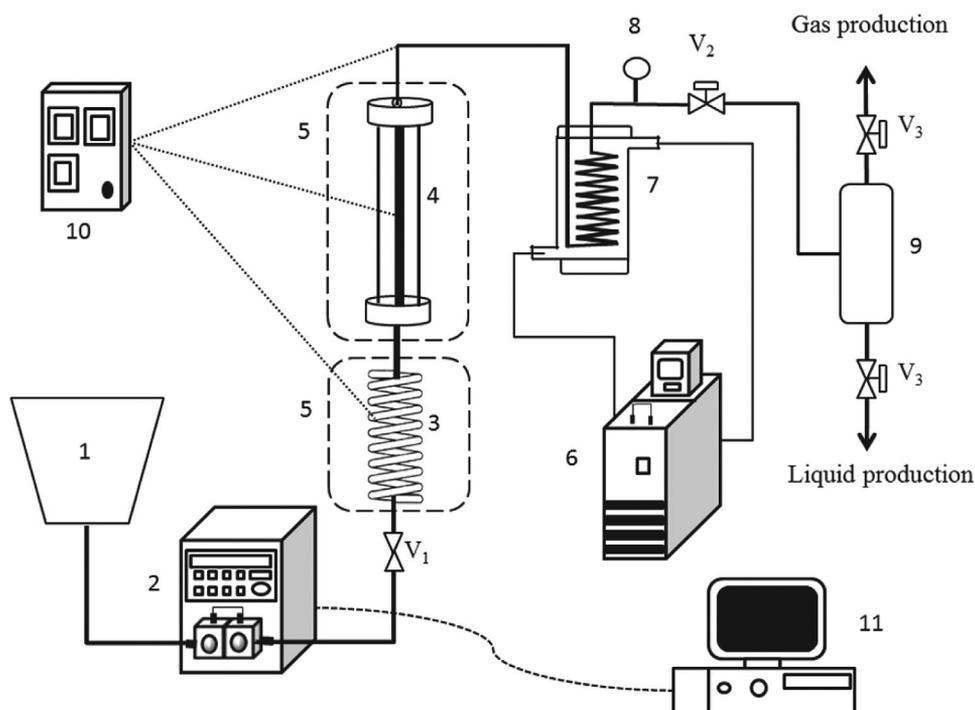


Figure 1. Scheme of the supercritical water oxidation apparatus. (1) Reservoir for the feed; (2) high pressure pump; (3) preheater; (4) reactor; (5) oven; (6) thermostatic bath; (7) condenser; (8) manometer; (9) phase separator; (10) temperature controller; (11) computer indicator; (V1) one-way valve; (V2) back-pressure regulator valve; (V3) valve.

Part	Material	Internal diameter (m)	External diameter (m)	Length (m)
Condenser	Stainless steel 316	3.175×10^{-3}	6.35×10^{-3}	2.5
Oven for the reactor	Stainless steel plate 304 coated internally with rock wool	0.1	0.3	0.3
Oven for the preheater	Stainless steel plate 304 coated internally with rock wool	0.1	0.3	0.4
Phase separator	Stainless steel 316	0.045	0.07	0.16
Preheater	Stainless steel 316	3.175×10^{-3}	6.35×10^{-3}	6.0
Reactor	Inconel 625	0.013	0.04	0.2

Chemical Analysis

Data of total organic carbon (TOC) were determined using a carbon analyzer equipment (Shimadzu, Total Organic Carbon Analyzer, TOC-L CPH/CPN, Kyoto, Japan) following APHA et al.^[27] The TOC results were calculated considering the difference between the concentrations of total carbon and inorganic carbon. The samples were filtered using a membrane filter (0.45 μm) and then acidified to pH 2. The chemical oxygen demand was determined by colourimetric method according to APHA et al.^[27] The samples were digested using a COD-Hach reactor. All measurements of COD, evaluation of colour at 455 nm, studies of turbidity, and evaluation of absorbance at 254 nm were performed in a spectrophotometer Hach DR/2010 (Hach, Colorado, USA) using the appropriate software for each parameter and the respective analytical curves. It should be emphasized that the absorbance at 254 nm was used as the indicator parameter for the degradation of humic and fulvic derived substances. The pH was measured using digital pH equipment (Digimed DM-2, Brazil). The composition of the gas produced during the leachate degradation was determined by gas chromatography methodology, whose essential description can be found in prior work.^[26] All chemical analyses were carried out in triplicate. Analytical

curves were constructed for each type of colourimetric analysis. All fluid leachate samples were collected and stored at 4 °C for posterior analysis.

Efficiency of Reduction and Residence Time Calculations

The percentual reduction of TOC, COD, colour, turbidity, and absorbance (at 254 nm) of humic and fulvic acids were calculated by subtracting the inlet minus outlet values and dividing the result by the initial value.

The residence time (τ) was calculated by Equation (1), according to van Bennekom et al.:^[28]

$$\tau = \frac{V_r \cdot \rho_{T,P}}{\phi_{m,STP}} \quad (1)$$

where V_r is the reactor volume, $\rho_{T,P}$ is the water density at temperature and pressure of the process, and $\phi_{m,STP}$ is the feed flow rate at standard conditions for temperature and pressure. For all residence time calculations the feed was assumed to consist only of pure water once the initial concentrations of other compounds were very low.

EXPERIMENTAL RESULTS

Two leachate samples were collected on different days at the Maringá municipal sewage treatment facility. The initial concentrations of chemical oxygen demand for these leachate samples were 1580 $\text{mg} \cdot \text{L}^{-1}$ (sample 1) and 2000 $\text{mg} \cdot \text{L}^{-1}$ (sample 2), according to Table 2.

Close to the temperature and pressure region where water behaves like a supercritical fluid, small increase of temperature can promote the precipitation of leachate inorganic salts which causes serious operational problems.^[29] For example, the deposition of these salts into the reactor walls decreases the efficiency of the degradation reaction and prevents the free circulation of the leachate inside the reactor. To test if this problem can be prevented by the use of higher pressures, we performed our experiments at two different pressures (15 and 22.5 MPa) which are near and above the supercritical pressure of water.

In the case of leachate sample 1 (COD of 1580 $\text{mg} \cdot \text{L}^{-1}$), the degradation via supercritical water oxidation was performed using 400 to 600 °C, 15 and 22.5 MPa, 6 $\text{g} \cdot \text{min}^{-1}$, and 40 min of reaction time. It should be emphasized that all experiments at 15 MPa pressure were performed to check the influence of pressure on the leachate degradation. Table 3 shows all the experimental conditions used during treatment of sample 1 as well as COD reduction which is commonly used to evaluate the degradation of organic pollutants present in leachate and

COD initial concentration ($\text{mg} \cdot \text{L}^{-1}$)	Flow rate ($\text{g} \cdot \text{min}^{-1}$)	Pressure (MPa)	Temperature (°C)	Physico-chemical parameters evaluated	
1580	6	15	350	COD	
			400		
			500		
		600			
		350			
		400			
	22.5	6	22.5	500	COD TOC Colour Turbidity Absorbance
				600	
				450	
		12	22.5	500	
				575	
				650	
2000	12	22.5	700	COD TOC Colour Turbidity Absorbance	
			450		
			500		
2000	12	22.5	575	COD TOC Colour Turbidity Absorbance	
			650		
			700		

Table 3. COD reduction for leachate degradation* at different pressures

Feed flow rate (g · min ⁻¹)	Temperature (°C)**	15 MPa			22.5 MPa		
		Residence time (s)	COD concentration (mg · L ⁻¹)	COD reduction (%)	Residence time (s)	COD concentration (mg · L ⁻¹)	COD reduction (%)
6	25	–	1580.0	–	–	1580.0	–
	350	23	731.3 ± 2.8	53.5 ± 2.0	163	561 ± 24.0	63.0 ± 1.0
	400	17	787.8 ± 33.0	48.1 ± 2.1	34	517.5 ± 26.0	65.6 ± 2.0
	500	13	610.7 ± 20.0	60.1 ± 1.2	21	227 ± 35.0	83.4 ± 2.0
	600	11	218.0 ± 22.0	84.8 ± 1.4	17	39.0 ± 2.3	97.40 ± 2.0

*Operational conditions (flow rate: 6 g · min⁻¹, COD initial concentration of leachate: 1580 mg · L⁻¹); **u(T) = 1.0 °C.

therefore indicates the overall efficiency of the treatment. Figure 2 shows the influence of pressure and temperature on the leachate degradation and the effect of increasing temperature on the COD parameter. Increasing temperature (from 350 to 600 °C) promoted the highest decrease on COD reduction values (31.3 and 34.4 %, respectively) for both pressures tested (15 and 22.5 MPa, respectively), suggesting that temperature is the most important factor on the degradation of leachate. On the other hand, increasing pressure (from 15 to 22.5 MPa at 600 °C) resulted in a more modest improvement on COD reduction (12.6 %); whereas the feed flow rate did not affect the treatment of leachate.

The highest COD reduction of 97 % occurred at the highest values of pressure and temperature, 600 °C and 22.5 MPa.

Table 4 shows the degradation results for sample 2 (COD of 2000 mg · L⁻¹). Two flow rates were used to evaluate the effect of residence time on the leachate degradation. In this case, temperatures above 600 °C were used to study the treatment efficiency in degrading leachate.

The efficiency of different treatments on removing pollutant compounds was evaluated using colour, turbidity, absorbance at 254 nm (indicating degradation of humic and fulvic compounds), TOC, and COD as a function of temperature and feed flow rate (Figures 3 to 7).

Figure 3 shows that the colour reduction was close to 100 % for both feed flow rates at 22.5 MPa, decreasing from 10 980 to 200 mg · L⁻¹ Pt-CO (Platinum-Cobalt Scale). The results indicate that residence time does not significantly affect the degradation of

organic compounds (such as humic and fulvic acids, which are associated with colour^[30]), especially at temperatures higher than 500 °C.

Figure 4 presents the turbidity and turbidity reduction as a function of temperature and feed flow rate. Similar to colour reduction, increasing temperature decreases turbidity regardless of the flow rate used, suggesting leachate degradation. The highest leachate turbidity reduction (around 95 %) is reached around 500 °C, and no significant decrease in turbidity is observed after this point.

Figure 5 indicates that the degradation of humic and fulvic acids occurs along the entire temperature interval tested. The leachate degradation (indicated by reduction in absorbance at 254 nm) began at 450 °C, reached approximately 90 % at 500 °C, and was nearly 100 % at 700 °C. The feed flow rates did not affect the 254 nm absorbance reduction of leachate compounds.

Figure 6 shows that the leachate reduction of total organic carbon (TOC) profile was similar to the profiles of colour, turbidity, and absorbance (254 nm) of compounds as a function of temperature and feed flow rate. The TOC reduction of leachate reached values between 70 % and 98 %. Apparently, at temperatures above 500 °C the leachate TOC reduction increased. The behaviour of the leachate TOC reduction was not affected by changes in feed flow rates.

Figure 7 represents the profile of leachate chemical oxygen demand (COD) reduction as a function of the temperature and feed flow rates. Similar to the other parameters studied, the higher the temperature of operation, the higher the value of leachate COD reduction. The lowest feed flow rate and higher temperature favoured the leachate COD reduction which reached more than 90 % at temperatures above 600 °C.

The landfill leachate is produced from the decomposition of carbonaceous materials which also generates methane, carbon dioxide, and a complex mixture of organic acids, aldehydes, alcohols, and simple sugars. Thus, we evaluated the potential of converting leachate into different gases for energy use purposes.

The capacity of gasification of the leachate was measured in terms of mole fractions of hydrogen, dioxide carbon, methane, and monoxide carbon gases. Table 5 shows that the hydrogen was the most abundant gas produced under the operational conditions studied, suggesting that the production of hydrogen gas from the leachate would be feasible. Carbon monoxide was not detected in the gas streams.

Figure 8 shows the quantity of gases produced during the leachate gasification. The lowest feed flow rate (6 g · min⁻¹) seems to favour the production of hydrogen, which reached approximately 90 % at temperatures higher than 575 °C.

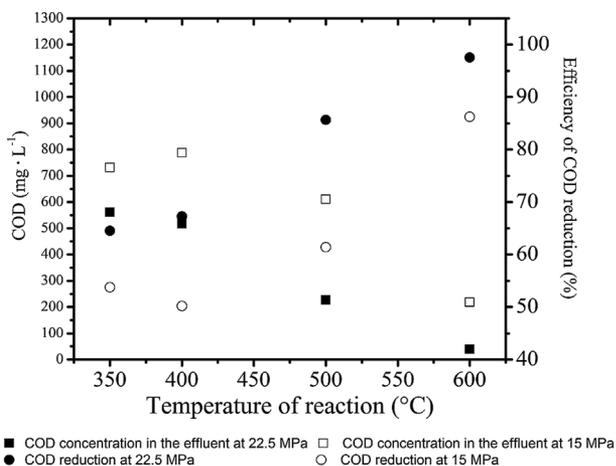


Figure 2. Leachate COD reduction as a function of temperature at 15.0 and 22.5 MPa and 1580.0 mg · mL⁻¹.

Table 4. Experimental results for physico-chemical parameters after supercritical water oxidation of leachate at 25 MPa*

Feed flow rate (g · min ⁻¹)	Temperature (°C)**	Residence time (s)	Colour (mg · L ⁻¹ Pt-CO)		Absorbance (254 nm)		Turbidity (NTU)		TOC (mg · L ⁻¹)		COD (mg · L ⁻¹)	
			Reduction	(%)	Reduction	(%)	Reduction	(%)	Reduction	(%)	Reduction	(%)
	25		10 980	–	59.0	–	1600.0	–	1270.0	–	1918.0	–
6	450	25	620 ± 27	94 ± 0.2	3.2 ± 0.3	94 ± 0.5	186.0 ± 2.0	88 ± 0.1	342.4 ± 8.0	72 ± 0.6	694.5 ± 72.0	60 ± 4.0
	500	21	190 ± 13	98 ± 0.1	2.6 ± 0.2	95 ± 0.3	57.0 ± 1.0	96 ± 0.1	205.9 ± 4.0	84 ± 0.3	679.8 ± 14.0	64 ± 0.7
	575	17	235 ± 4	99 ± 0.1	2.0 ± 0.3	96 ± 0.5	52.0 ± 1.6	97 ± 0.1	230.9 ± 12.0	81 ± 1.0	431.8 ± 21.0	76 ± 1.0
	650	15	180 ± 15	98 ± 0.1	1.1 ± 0.1	98 ± 0.1	70.0 ± 0.4	96 ± 0.1	142.0 ± 0.3	89 ± 0.02	154.8 ± 14.0	91 ± 0.7
	700	14	210 ± 7	98 ± 0.1	0.6 ± 0.1	99 ± 0.1	98.5 ± 2.1	94 ± 0.1	30.6 ± 3.0	97 ± 0.2	22.2 ± 7.0	99 ± 0.4
12	25		10 980	–	59.0	–	1600.0	–	1270.0	–	1918.0	–
	450	12	935 ± 53	91 ± 0.5	3.7 ± 0.7	92.5 ± 1.0	252.5 ± 2.0	84 ± 0.1	368.8 ± 9.0	70 ± 0.7	1059.2 ± 53.0	42 ± 3.0
	500	10	390 ± 21	96 ± 0.2	2.8 ± 0.7	94.1 ± 1.0	120.5 ± 0.7	92 ± 0.1	324.4 ± 0.6	74 ± 0.1	857.7 ± 39.0	53 ± 2.0
	575	9	140 ± 17	99 ± 0.1	2.5 ± 0.3	95.3 ± 0.5	32.7 ± 5.0	98 ± 0.3	247.0 ± 1.0	80 ± 0.1	511.0 ± 30.0	72 ± 2.0
	650	8	305 ± 33	97 ± 0.3	2.1 ± 0.5	95.6 ± 0.8	143.5 ± 0.9	91 ± 0.1	153.9 ± 4.0	88 ± 0.3	170.2 ± 22.0	90 ± 1.0
	700	7	235 ± 9	98 ± 0.1	1.5 ± 0.1	97.3 ± 0.1	87.0 ± 2.0	94 ± 0.1	145.9 ± 7.0	88 ± 0.5	171.2 ± 11.0	90 ± 1.0

*Operational conditions (25 MPa, COD initial concentration of leachate: 2000 mg · L⁻¹); **u(T) = 1.0 °C.

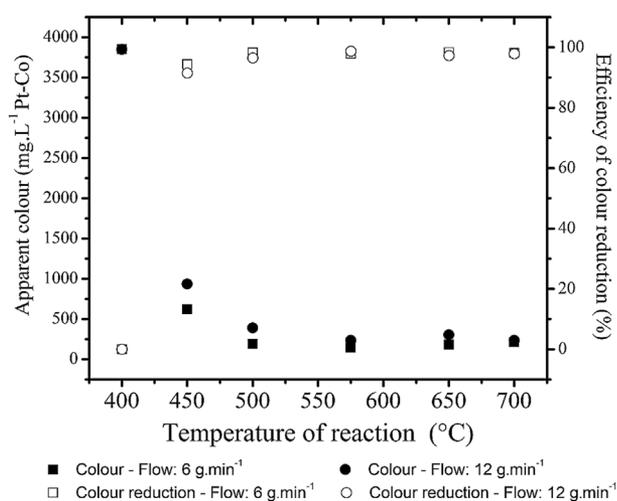


Figure 3. Leachate colour reduction as a function of temperature at flow rates of 6 and 12 g · min⁻¹ and 22.5 MPa.

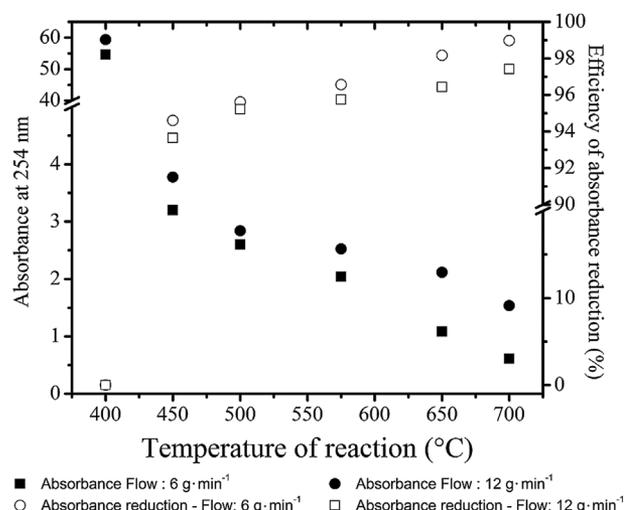


Figure 5. Leachate absorbance reduction as a function of temperature at flow rates of 6 and 12 g · min⁻¹ and 22.5 MPa.

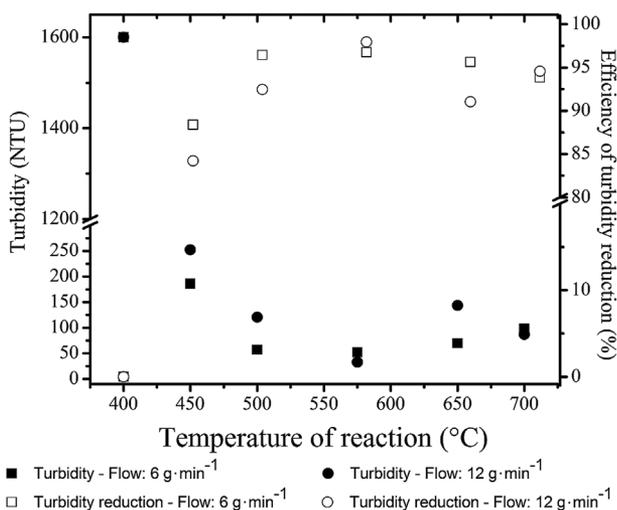


Figure 4. Leachate turbidity reduction as a function of temperature at flow rates of 6 and 12 g · min⁻¹ and 22.5 MPa.

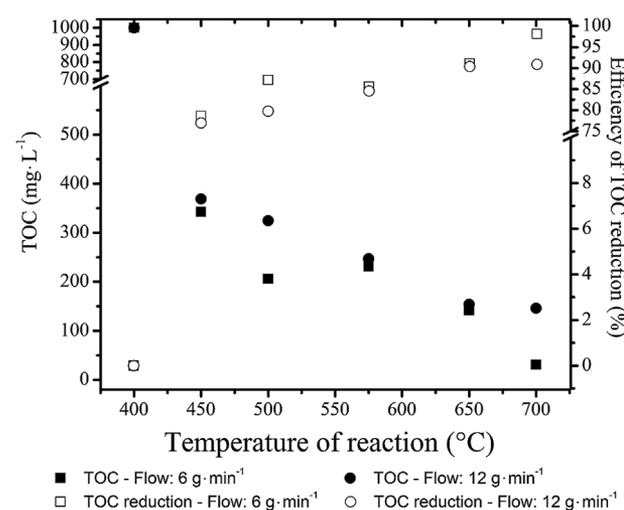


Figure 6. Leachate total organic carbon (TOC) reduction as a function of temperature at flow rates of 6 and 12 g · min⁻¹ and 22.5 MPa.

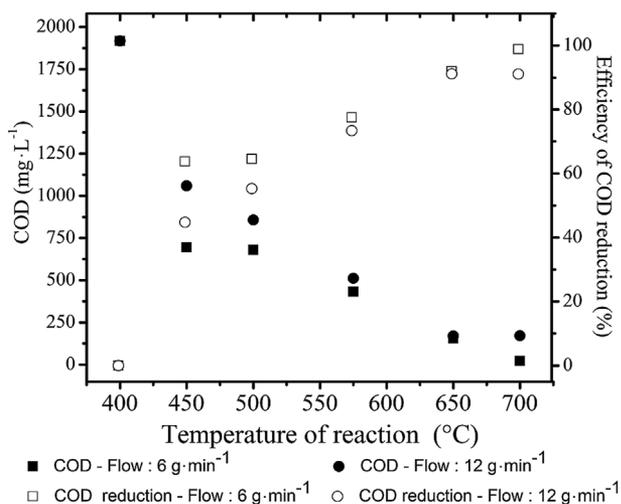


Figure 7. Leachate chemical oxygen demand (COD) reduction as a function of temperature at flow rates of 6 and 12 g · min⁻¹, 22.5 MPa, and 2000 mg · mL⁻¹.

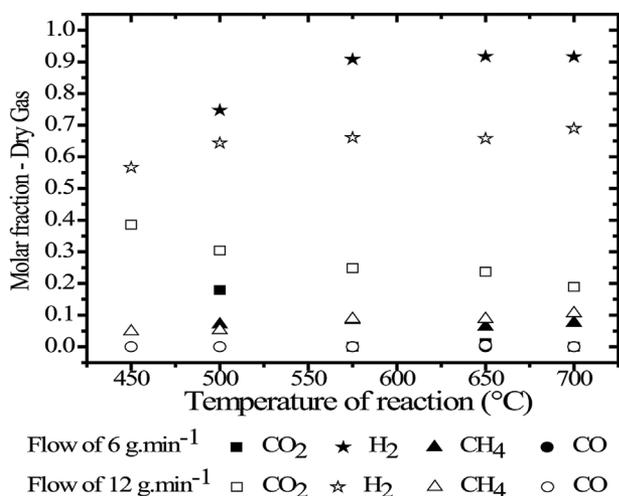


Figure 8. Effect of temperature on gas composition (molar fraction) at flow rates of 6 and 12 g · min⁻¹ and 22.5 MPa.

Table 5. Gas composition after supercritical water oxidation of leachate*

Feed flow rate (g · min ⁻¹)	Temperature (°C)**	Residence time (s)	Gas composition (mole fraction)			
			H ₂	CO ₂	CH ₄	CO
6	450	25	-	-	-	-
	500	21	0.75	0.18	0.07	-
	575	17	0.91	-	0.08	-
	650	15	0.92	0.01	0.06	-
	700	14	0.91	-	0.07	-
12	450	12	0.56	0.38	0.05	-
	500	10	0.64	0.30	0.05	-
	575	9	0.66	0.25	0.09	-
	650	8	0.65	0.24	0.09	-
	700	7	0.69	0.19	0.10	-

*Operational conditions (22.5 MPa, COD initial concentration of leachate: 2000 mg · L⁻¹); **u(T) = 1.0 °C.

REMARKS AND CONCLUSIONS

We used supercritical water oxidation (ScWO), without addition of any oxidants, to treat landfill leachate. COD, TOC, turbidity, colour, and absorbance at 254 nm were used to evaluate the degradation and reduction of polluting compounds present in leachate. The hydrogen produced was also measured to evaluate the feasibility of converting leachate into gas for energy use.

The results presented in this study indicated that supercritical water treatment can drastically reduce the polluting compounds present in landfill leachate, converting these pollutants into hydrogen for potential energy applications.

Higher temperature, pressure, and residence time as well as lower feed flow rate favoured the landfill leachate treatment. Hydrogen, methane, carbon monoxide, and carbon dioxide were the major gas products recovered from treated leachate.

Under the best experimental conditions, up to 98 % of pollutants were removed from the liquid effluents by the supercritical water oxidation, indicating that ScWO can be successfully used for the treatment of landfill effluents without assistance of oxidants.

The results presented in this work showed that higher temperatures and absence of oxidants can deliver degradation rates similar to the ones obtained with oxidants at lower temperatures. The reactivity of the water and its physical and chemical properties significantly increase near critical pressure and temperature above 600 °C. This higher reactivity can be explained by the changes in the water dielectric constant caused by the increase in the temperature for a pressure of 20 MPa.

ACKNOWLEDGEMENTS

The authors would like to thank CAPES, Fundação Araucária, and CNPq for the financial support of this work and for the scholarships of L. Ferreira-Pinto. We are also grateful to Natural Sciences and Engineering Research Council (NSERC, Canada).

REFERENCES

- [1] W. Gong, X. Duan, *Waste Manag.* **2000**, *30*, 2103.
- [2] S. Wang, Y. Guo, C. Chen, J. Zhang, Y. Gong, *Waste Manag.* **2011**, *31*, 2027.
- [3] B. Morawe, D. S. Ramteke, A. Vogelpohl, *Chemical Engineering and Processing: Process Intensification* **1995**, *34*, 299.
- [4] C. R. G. Tavares, C. T. Benatti, B. P. Dias Filho, *Appl. Biochem. Biotech.* **2002**, *98–100*, 935.
- [5] K. Pedroso, C. R. G. Tavares, R. C. Souza, P. R. Z. Dias, E. F. da Costa Jr., P. V. Viotti, *Revista de Engenharia e Tecnologia* **2001**, *3*, 45.
- [6] K. Pedroso, C. R. G. Tavares, V. Janeiro, T. L. Silva, P. Z. Dias, *Revista de Engenharia e Tecnologia* **2012**, *4*, 87.
- [7] A. Imai, K. Onuma, Y. Inamori, R. Sudo, *Environ. Technol.* **1998**, *19*, 213.
- [8] A. C. Silva, M. Dezotti, G. L. Sant'Anna, *Chemosphere* **2004**, *55*, 207.
- [9] D. W. Smith, F. Wang, *J. Environ. Eng. Sci.* **2003**, *2*, 413.
- [10] D. Zou, Y. Chi, C. Fu, J. Dong, F. Wang, M. Ni, *J. Hazard. Mater.* **2013**, *248–249*, 177.
- [11] N. Mokhtarani, A. Nasiri, H. Ganjidoust, S. Y. Yasrobi, *Ozone-Sci. Eng.* **2014**, *36*, 540.

- [12] H. Qin, H. Chen, X. Zhang, G. Yang, Y. Feng, *J. Chem. Technol. Biot.* **2014**, *89*, 1402.
- [13] A. Anfruns, J. Gabarró, R. Gonzalez-Olmos, S. Puig, M. D. Balaguer, J. Colprim, *J. Hazard. Mater.* **2013**, 258–259, 27.
- [14] S. S. Abu Amr, H. A. Aziz, *Waste Manag.* **2012**, *32*, 1693.
- [15] H. Zhang, C. P. Huang, *Chinese J. Chem. Eng.* **2002**, *10*, 128.
- [16] A. F. Cheibub, J. C. Campos, F. V. da Fonseca, *J. Environ. Sci. Heal. A* **2012**, *49*, 1718.
- [17] A. Amiri, M. R. Sabour, *Waste Manag.* **2014**, *34*, 2528.
- [18] P. Wang, G. Zeng, Y. Peng, F. Liu, C. Zhang, B. Huang, *Chem. Eng. J.* **2014**, *247*, 216.
- [19] R. Poblete, L. Prieto-Rodríguez, I. Oller, M. I. Maldonado, S. Malato, E. Otal, *Chemosphere* **2012**, *88*, 1090.
- [20] J. Sun, M. Song, J. Feng, Y. Pi, *Sci. Pollut. Res.* **2012**, *19*, 1536.
- [21] Y. Dong, Z. Wang, C. Zhu, Q. Wang, J. Tang, Z. Wu, *J. Membrane Sci.* **2014**, *471*, 192.
- [22] M. El-Fadel, J. Hashisho, *J. Air Waste Manage.* **2014**, *64*, 1073.
- [23] A. Kuusik, K. Pachel, A. Kuusik, E. Loigu, W. Z. Tang, *Environ. Technol.* **2014**, *35*, 2416.
- [24] G. Wang, Z. Fan, D. Wu, L. Qin, G. Zhang, C. Gao, *Desalination* **2014**, *349*, 136.
- [25] F. Ilhan, H. A. Kabuk, U. Kurt, Y. Avsar, H. Sari, M. T. Gonullu, *Chemical Engineering and Processing: Process Intensification* **2014**, *75*, 67.
- [26] L. Ferreira-Pinto, A. C. Feirhrmann, M. L. Corazza, N. R. C. Fernandes-Machado, J. S. R. Coimbra, M. D. A. Saldanã, L. Cardozo-Filho, *Int. J. Hydrogen Energ.* **2015**, *40*, 12162.
- [27] American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), *Standard Methods for the examination of Water and Wastewater*, 21st edition, Washington **2005**.
- [28] J. G. van Bennekom, R. H. Venderbosch, D. Assink, H. J. Heeres, *J. Supercrit. Fluid.* **2011**, *58*, 99.
- [29] G. Brunner, *J. Supercrit. Fluid.* **2009**, *47*, 373.
- [30] A. B. Castilho-Junior, R. L. Dalsasso, F. Rohers, *Revista Engenharia Sanitária* **2010**, *15*, 385.

Manuscript received May 14, 2016; revised manuscript received January 1, 2017; accepted for publication January 4, 2017.