



## Landfill leachate treatment by subcritical water oxidation with potassium permanganate in a batch reactor

## Tratamiento de lixiviados por oxidación subcrítica con permanganato de potasio en reactor batch

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### Abstract

**Introduction:** the treatment of landfill leachate by oxidation in subcritical water using potassium permanganate as oxidant was studied in a batch reactor.

**Objective:** to evaluate the effect of temperature, reaction time, and oxidant excess on the chemical oxygen demand (COD) conversion in the process.

**Methodology:** a temperature range of 300–350 °C, reaction time of 20–40 min, and oxidant excess from 0% (stoichiometric) to 25% were considered, using a factorial design 2<sup>3</sup>. Pressure was kept constant at 2500 psi (17.3 MPa). COD was measured in the liquid phase, and the effect of the factors on conversion was determined through ANOVA analysis.

**Results:** all runs yielded a yellowish liquid and a brown sludge that was difficult to resuspend. ANOVA results indicated that temperature was the only significant factor, with no relevant interactions. High COD conversions were obtained at 350 °C, 20 min, and stoichiometric oxidant. Total nitrogen, analyzed in selected samples, showed conversions above 90% at temperatures lower than those required in supercritical water oxidation (>500 °C) to achieve similar values. Total volatile solids analysis revealed that the sludge consisted of both organic and inorganic substances, possibly resulting from coagulation and adsorption by the manganese oxide byproduct.

**Conclusions:** the high conversions obtained, together with less stringent conditions than those required for supercritical water oxidation, represent an opportunity for the development of an efficient treatment for leachates, taking into account the management of the sludge generated.

**Keywords:** leachate treatment, subcritical water oxidation, KMnO<sub>4</sub>, COD, SCWO

### Resumen

**Introducción:** se estudió el tratamiento de lixiviado de vertedero por oxidación en agua subcrítica utilizando permanganato de potasio como oxidante en un reactor por lotes.

**Objetivo:** evaluar el efecto de la temperatura, el tiempo de reacción y el exceso de oxidante sobre la conversión de la demanda química de oxígeno (DQO) en el proceso.

**Metodología:** se consideró un rango de temperatura de 300–350 °C, tiempo de reacción de 20 a 40 min y exceso de oxidante desde 0% (estequiométrico) hasta 25%, empleando un diseño factorial 2<sup>3</sup>. La presión se mantuvo constante en 2500 psi (17,3 MPa). Se midió la DQO de la fase líquida y el efecto de los factores en la conversión mediante análisis ANOVA.

**Resultados:** todas las corridas mostraron un líquido amarillento y un lodo marrón de difícil resuspensión. El análisis ANOVA indicó que la temperatura fue el único factor significativo, sin interacciones relevantes. Se lograron altas conversiones de DQO a 350 °C, 20 min y oxidante estequiométrico. El nitrógeno total, analizado en muestras seleccionadas, presentó conversiones mayores al 90% a temperaturas inferiores a las requeridas en oxidación supercrítica (>500 °C) para obtener cifras similares. Los sólidos volátiles totales mostraron que el lodo estaba compuesto por sustancias orgánicas e inorgánicas, posiblemente resultado de coagulación y adsorción por el subproducto óxido de manganeso.

**Conclusiones:** las altas conversiones obtenidas y las condiciones menos exigentes que en oxidación supercrítica representan una oportunidad para desarrollar un tratamiento eficiente de lixiviados, considerando el manejo del lodo generado.

**Palabras clave:** tratamiento de lixiviados, oxidación en agua subcrítica, KMnO<sub>4</sub>, DQO, SCWO.

### How to cite?

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Spanish version



### Why was this study conducted?

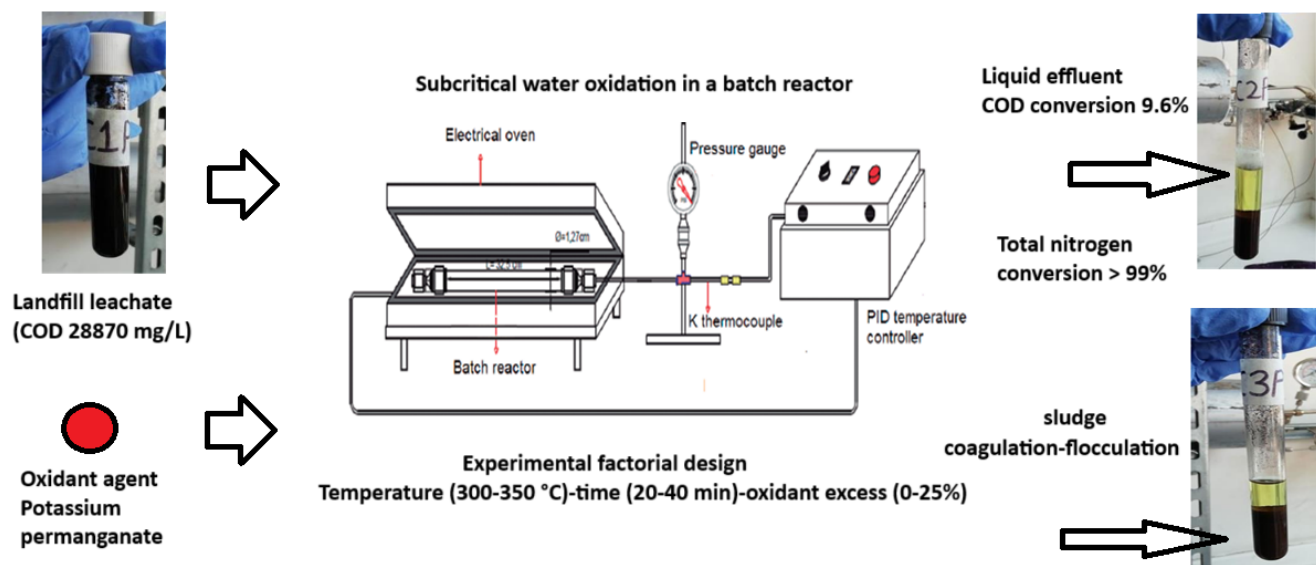
Landfill leachate efficient treatment remains a challenge in scientific literature. Though supercritical water oxidation has been proven to effectively destroy the organic matter in leachate, harsh reaction conditions limit its potential application. Milder reaction conditions could be achieved at subcritical water conditions if a stronger oxidant were used. Therefore, in our study we intended to assess how effective the oxidation of landfill leachates was in subcritical water media with potassium permanganate as oxidant.

### What were the most relevant findings?

Through an experimental design methodology, it was assessed the effect of temperature, oxidant excess and time in the destruction of organic matter measured as chemical oxygen demand conversion. Reaction temperature conditions were identified through the analysis of variance, in which chemical oxygen demand was shown to be effectively reduced in the reactor effluent. In addition, it was shown an interesting effect of coagulation-flocculation of organic matter in the produced sludge, which was attributed to the decomposition of potassium permanganate. It was also shown an effective reduction of total nitrogen in selected samples.

### What do these findings contribute?

The results indicate the proposed process of subcritical water oxidation with potassium permanganate of landfill leachate could be further assessed as a potential alternative to conventional and combined physic chemical treatment processes. The proposed reaction conditions are milder than those used in supercritical water oxidation while achieving similar results in regard to chemical oxygen demand removal.



## Introduction

Landfill leachate efficient treatment remains a major challenge for wastewater treatment practitioners, in spite of the fact that no other wastewater has received as much dedicated research efforts through emerging as well as conventional treatment methods. This highly complex wastewater is characterized not only by its high chemical oxygen demand, but also by the presence of heavy metals, recalcitrant organic substances, perfluoro alkylated substances (PFAS), microplastics, pharmaceuticals and personal care products (1), which results in no single method of wastewater treatment up to the task of accomplishing the required high discharge criteria (2). A combined approach involving physical, chemical, and biological processes is the predominant method for treating landfill leachate, though high costs and secondary pollution still remain as predominant issues (3). Recent literature reviews give a detailed account of different advancements reported in the application of conventional and emerging physic-chemical processes. For example, Siddiqi et al. (2) critically reviewed the limitations and strengths of biological, physicochemical and advanced oxidation processes for leachate treatment and pointed out the limitations of the biological and physicochemical processes related to heavy metals and ammonia, as well as the high cost involved in advanced oxidation processes. Alternatively, Guo et al. (4) reviewed the application of electrocoagulation and electro oxidation for effective leachate treatment and discussed the limitations that remain associated with electrode materials and duration as well as the large amount of sludge that can be formed. More recently, Mishra et al. (5) reviewed the hybrid anaerobic and aerobic treatment and identified limitations related to the large surface area, high hydraulic retention times, membrane fouling as well as high energy consumption that still need to be further assessed.

The application of wet air oxidation (WAO) and supercritical water oxidation (SCWO) for treating landfill leachate was recently reviewed (1). WAO takes place at temperatures between 150-320 °C, pressures around 15 MPa in the presence of air or pure oxygen. Yet, no complete organic matter mineralization can be achieved by WAO and it was concluded this process could be a complementary method for leachate treatment. Alternatively, SCWO, which takes place at temperatures above 450 °C, pressures above 22 MPa and hydrogen peroxide as oxidant in high excess, has been shown to achieve high efficiencies as COD or TOC destruction with residence times requiring a few minutes. In spite of the high removal efficiencies, this process still struggles with the difficulties that arise from working at extremely harsh conditions and the cost of high-pressure equipment. Therefore, it was concluded that optimization strategies that can reduce the cost of the process are essential for sustainable implementation (1).

An alternative for increasing WAO COD destruction and removal efficiency while avoiding the high temperatures required in SCWO is the use of a catalyst or a stronger oxidant agent. Potassium permanganate ( $\text{KMnO}_4$ ) is a strong oxidant that has advantages related to its high efficiency, low toxicity and price, easy handling and stability. Advanced oxidation based on  $\text{KMnO}_4$  has been broadly employed for dealing with a wide spectrum of contaminants as recently reviewed in detail by Wang et al. (6). However, its use in subcritical or supercritical water oxidation has been scarcely addressed. Chang et al. (7) reported the SCWO of acetic acid with potassium permanganate at 400 °C and found high destruction efficiencies as well as a superior performance of  $\text{KMnO}_4$  in

comparison to hydrogen peroxide and oxygen as alternative oxidants. The higher efficiency of  $\text{KMnO}_4$  in comparison to hydrogen peroxide could lead to a reduction in the temperature required for SCWO processes, making it possible to work at subcritical water conditions as a means to improve process feasibility. Therefore, in this work we report on the landfill leachate treatment by subcritical water oxidation with  $\text{KMnO}_4$  as oxidant agent to assess the organic matter destruction efficiency in terms of chemical oxygen demand (COD) conversion. By contrasting the experimental results with experimental conditions reported for SCWO of leachates, insights on the feasibility of its potential application for dealing with high strength wastewaters are discussed.

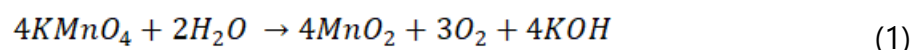
## Materials and methods

### Landfill leachate

A sample of landfill leachate was taken from a sanitary landfill which serves the city of Villavicencio (Colombia), in the wastewater treatment plant affluent sampling port. As recommended for posterior analysis of organic matter dissolved in water, chlorohydric acid solution was added to lower the pH to 2 to preserve the sample. The sampling bottle was protected from sunlight and atmospheric oxygen. To avoid further degradation of organic matter before use, the sample was maintained in a freezer until the moment of use.

### Chemicals

Solid potassium permanganate (Merck reagent grade) was used for the experiments. The corresponding weight of  $\text{KMnO}_4$  to be added for oxidation experiments was calculated according to the reaction scheme in Eq (1) as suggested in literature (7) and the stoichiometric amount of oxygen needed for complete oxidation as established by the chemical oxygen demand.

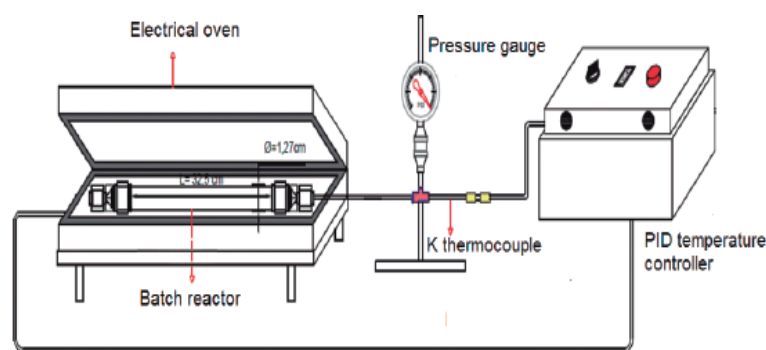


Accordingly, 4 moles of  $\text{KMnO}_4$  produce 3 moles of oxygen and the mass of  $\text{KMnO}_4$  required for providing the stoichiometric amount of oxygen for complete oxidation is equal to the estimated raw leachate COD.

### Experimental equipment and procedure

An experimental lab scale set-up comprised by a reactor and a clamp-type high temperature oven was used in the study. The reactor was built from Swagelok high pressure tubing  $\frac{1}{2}$ " (1.27 cm) OD and screw-caps. The temperature in the oven is controlled by a PID controller and a K type thermocouple inserted directly in the reactor as shown in Figure 1. In a typical experimental run the volume of raw leachate sample to be oxidized is estimated by means of the water density from steam tabs at reaction temperature and pressure which guarantee subcritical water conditions, and the total volume of the reactor. Leachate volume sample and solid potassium permanganate crystals are added to the batch reactor, the screw-caps are tightened and the reactor is inserted in

the clamp-type electrical resistance oven, previously preheated at the desired temperature. Heating time to the desired reaction temperature for each run was between 10-15 min, and the reactor was left in the oven for a specific period of time from this point according to the experimental design. Upon completion of reaction time, the reactor was removed from the oven and the reaction stopped by means of tap water, then the reactor caps were unscrewed and the effluent collected in sample tubes.

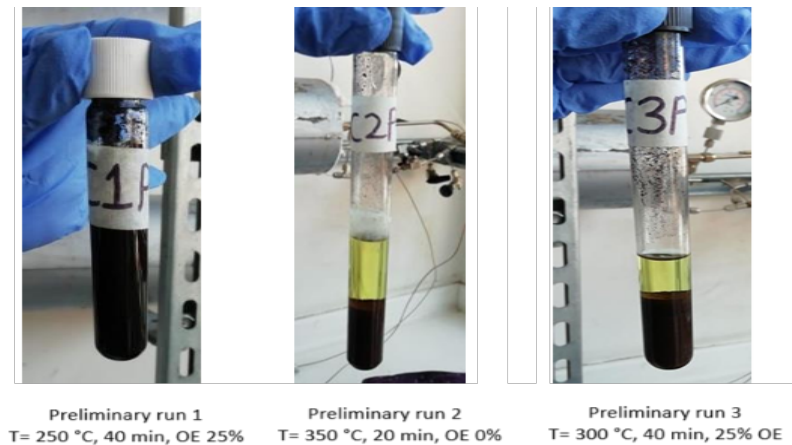


**Figure 1.** High pressure batch reactor equipment

**Source:** The authors.

## Experimental section

Three preliminary runs were carried out at temperatures of 250-350 °C, times from 20-40 min and oxidant excess from stoichiometric to 25 % excess, based on the measured COD for the raw leachate in order to qualitatively assess the effluent characteristics. As shown in Figure 2, the collected effluent for preliminary run 1 at 250 °C was similar in appearance to the crude leachate, whereas preliminary runs 2 and 3 at 300-350 °C showed a clear yellowish liquid phase and a bottom brown sludge. Accordingly, a  $2^3$  factorial experimental design with the factors temperature (A), reaction time (B) and oxidant excess (C) was selected with low (-1) and high (+1) levels of 300 and 350 °C, 20 and 40 min and stoichiometric (0%) to 25 % excess, respectively, whereas pressure was kept constant in all runs at 2500 psi (17.23 MPa), which is high enough to keep water as a pressurized liquid at the defined temperatures in the experimental design. In addition, two runs in the central point corresponding to a temperature of 325 °C, time of 30 min and excess 12.5% were carried out for a total of 10 runs, which leaves only one degree of freedom (DF) for error estimation. To overcome this limitation, three order interaction ABC, which is not expected to be significant, was removed from the model to add an additional DF to error. The term for the center point was also removed from the model, which adds one DF to error estimation for a total of 3 DF for error estimation. Statistical analysis was performed by means of the statistical software Minitab®. The model quality of fit was determined by the coefficient of determination R-squared ( $R^2$ ) and residual standard deviation.



**Figure 2.** Qualitative assessment of preliminary runs

**Source:** The authors.

### Analytical methods

Effluent samples consisted of a clear yellowish liquid phase and a precipitated sludge. Efficiency of the oxidation reaction was followed by means of chemical oxygen demand (COD) and total nitrogen (TN), measured for the clear yellowish liquid phase, whereas sludge formed was collected by means of a filter paper to further analyze total solids and total volatile solids in selected samples. COD measurement was carried out according to the standardized Hach spectrophotometric method 5310D. Total organically and inorganically bound nitrogen in crude leachate and selected samples was measured according to standardized method Hach TNb 220. A spectrophotometer was used and blanks were prepared with distilled and deionized water. The test consisted of pouring the contents of the ampuls of reagents for each method to a sample or blank, then digested in thermo reactor followed by measuring concentration in the Hach instrument. COD conversion was estimated according to Eq. (2)

$$X_{COD} = 1 - \frac{COD}{COD_0} \quad (2)$$

Where COD is the chemical oxygen demand measured in the effluent yellowish liquid phase and  $COD_0$  is the raw leachate chemical oxygen demand.

Total nitrogen conversion was estimated in selected samples according to Eq. (3)

$$X_{TN} = 1 - \frac{TN}{TN_0} \quad (3)$$

Where TN is the effluent total nitrogen measured in the effluent yellowish liquid phase and  $TN_0$  is the raw leachate total nitrogen.

Water in a collected sludge sample was first dried by placing it in a crucible at 103-105 °C for four hours. After this time the crucible was placed in a desiccator and the initial weight (IW) was estimated by subtracting the previously measured weight of the crucible. Total fixed solids were estimated by heating the crucible with the known solids weight at 550 °C for 2 hours. Total volatile solids is the portion of the sample weight lost during this period, which can be essentially



considered organic matter, and fixed solids corresponding to the mass left in the crucible can be considered inorganic substances such as manganese oxide, salts and metals present in the raw leachate.

## Results and discussion

Undiluted raw leachate organic matter composition was determined by means of the chemical oxygen demand (COD) and total nitrogen (TN), measured in triplicate with mean values 28870 ( $\pm$  456) mg/L and 2400 ( $\pm$ 97) mg/L, respectively, whereas the effluent COD and TN for selected samples after each experiment were the result of a single measurement. As was observed in the preliminary runs, all of the collected samples showed a clear yellowish liquid and a brown sludge. The yellow color in effluent samples was also reported by Chang (7) in the supercritical water oxidation of acetic acid with potassium permanganate, and was attributed to the result of a mixture of different manganese ions or from reactor corrosion products. Table 1 summarizes the experimental conditions for each run, the volume of raw leachate sample in ml added to the reactor and the corresponding weight of solid potassium permanganate required according to the oxidant excess (OE) used, effluent COD of the yellowish liquid phase and COD conversion.

As can be observed in Table 1, lowest measured COD conversion was 66.9% in run 6 (300 °C, 40 min, stoichiometric), whereas the highest conversion was 97.6% in run 8 (350 °C, 40 min, 25 %) and conversions higher than 90% were obtained for all the runs with temperature of 350 °C. The ANOVA results are shown in Table 2.

Table 1. Summary of experimental conditions, effluent COD concentration and COD conversion

Run order	Temp (°C)	Time(min)	OE (%)	Volume(mL)	KMnO <sub>4</sub> (g)	COD effluent (mg/L)	<i>X<sub>COD</sub></i>
							(%)
1	350	20	0	13.1	2.5	1335	95.4
2	300	20	25	16.3	3.9	4380	84.8
3	350	40	0	13.1	2.5	1890	93.5
4	350	20	25	13.1	3.1	1060	96.3
5	325	30	12.5	15.1	3.2	5130	82.2
6	300	40	0	16.5	3.1	9550	66.9
7	300	40	25	16.5	3.9	6180	78.6
8	350	40	25	13.1	3.1	700	97.6
9	325	30	12.5	15.2	3.2	2540	91.2
10	300	20	0	16.5	3.1	6210	78.5

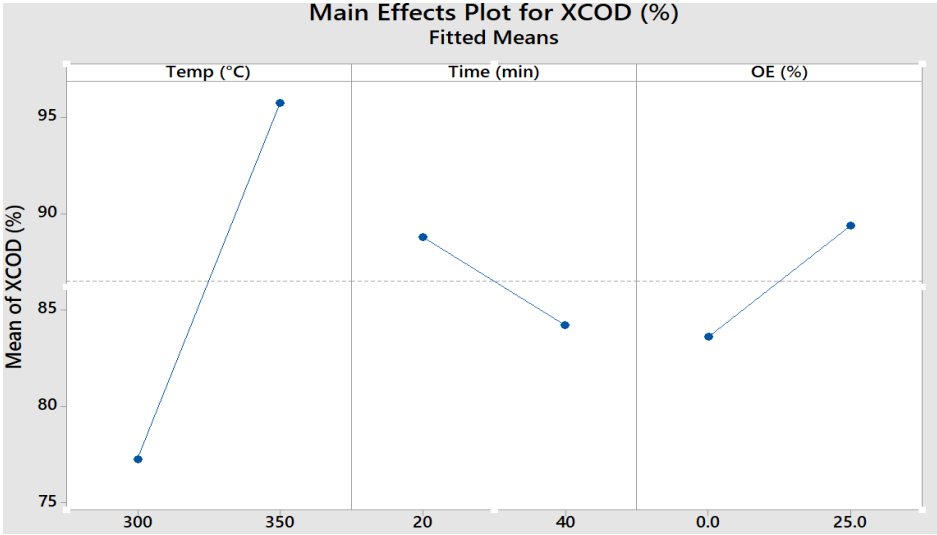
**Source:** The authors.

Table 2. ANOVA results

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	6	858.845	143.141	10.49	0.040
Linear	3	792.215	264.072	19.36	0.018
Temp (°C)	1	682.836	682.836	50.06	0.006
Time (min)	1	42.735	42.735	3.13	0.175
OE (%)	1	66.644	66.644	4.89	0.114
2-Way interactions	3	66.630	22.210	1.63	0.349
Temp(°C)*Time (min)	1	36.680	36.680	2.69	0.200
Temp(°C)*OE(%)	1	20.898	20.898	1.53	0.304
Time(min)*OE(%)	1	9.053	9.053	0.66	0.475
Error	3	40.924	13.641		
Lack of fit	2	0.693	0.347	0.01	0.991
Pure error	1	40.230	40.230		
Total	9	899.769			

Source: The authors.

As shown in Table 2, only the temperature factor is significant (P-value < 0.05) whereas time, OE or the second-order interactions AB, AC and BC were not significant (P-value >0.05), with a model regression coefficient (R<sup>2</sup>) of 95.45% and a standard deviation of 3.69. The factorial plots, which show the relationship between COD mean conversion and the main effects are shown in Figure 3.



Source: The authors.

Figure 3. Factorial plots for main effects Temperature (A), time (B) and OE (C)

As can be observed in Figure 3, a higher mean COD conversion was obtained for the runs which were carried out at the high level of temperature. Yet, time and OE were not significant in the ANOVA, which means similar results for COD mean conversions were obtained when working with low and high levels for these factors. Therefore, these results suggest high COD conversions can be obtained at 350 °C with the low levels of time (20 min) and OE (stoichiometric), as a result of the increased efficiency of potassium permanganate as oxidant in subcritical water when compared to



other oxidants. Indeed, Chang et al. (7) assessed the effect of different oxidants in the destruction of acetic acid by SCWO at 400 °C, density of 0.3 g/cm<sup>3</sup> and 6.5 min reaction time and reported KMnO<sub>4</sub> is more efficient than hydrogen peroxide, oxygen and air, with a COD destruction efficiency for KMnO<sub>4</sub> of 79% to 46 % with H<sub>2</sub>O<sub>2</sub>. Table 3 shows a comparison of reaction conditions for SCWO of leachates using hydrogen peroxide and a catalyst and the present work with potassium permanganate as oxidant and without a catalyst.

Table 3. Chemical oxygen demand (COD) and total nitrogen (TN) destruction efficiency in different SCWO experimental studies

<i>COD<sub>o</sub></i> (mg/L)	<i>TN<sub>o</sub></i> (mg/L)	T (°C)	P(MPa)	OE(%)	time(s)	<u>Catalyst</u>	<i>X<sub>COD</sub></i> (%)	<i>X<sub>TN</sub></i>	Ref
14210	1545	450	25	350	300	MnO <sub>2</sub>	99.5	98.4	(8)
		500	25	350	300	-	99.2	95.4	
4750	1375	600	25	180	150	Ni/Al <sub>2</sub> O <sub>3</sub>	98.2	57	(9)
34600	1615	500	28	300	120	fly ash	99.2	-	(10)
35000	2484	600	25	340	600	CeMnO <sub>x</sub> / TiO <sub>2</sub>	92.5	50.9	(11)
8700	2800	400	-	100	1800	-	98.2	60.2	(12)
		500	-	100	1800	-	86.6	92.2	
28870	2400	350	17.2	0%	1200	-	95.4	-	This work
		350	17.2	25%	2400	-	97.6	99.07	

Source: The authors.

As can be observed in Table 3, similar or even higher COD and TN destruction efficiencies are achieved working at 350 °C and potassium permanganate as oxidant when compared to SCWO studies carried out at higher temperatures, use of a catalyst and hydrogen peroxide excess over 100%. Organic nitrogen oxidation in SCWO has been shown to proceed by means of the formation of ammonia, which is considered an intermediary refractory byproduct whose transformation and further destruction have been noted as the rate limiting controlling step (8) and a big obstacle of the application for this technique (13,14). While high conversions for COD have been reported in several studies as indicated in Table 3, some studies have reported moderate conversions for TN even at temperatures of 600 °C and high OE, requiring even higher temperatures than those required for achieving high COD destruction efficiencies. For example, Marulanda et al. (12) reported as optimal operation conditions in the SCWO of leachates a temperature of 400 °C, 30 min and OE of 100%. Yet, at these conditions only 68 % of total nitrogen destruction was accomplished, requiring a temperature of 500 °C, 30 min and 100 % OE for a 92.2 %. Due to the potential environmental impact of nitrogen on eutrophication, efficient ammonia nitrogen destruction should be considered as equally important as COD destruction (14).



Total nitrogen was measured for selected runs 3, 8 and 9 and the total nitrogen conversion (TN) was calculated according to Eq (3) and the measured total nitrogen for the raw leachate (TN<sub>o</sub>) of 2400 mg/L. Total nitrogen conversion results are shown in Table 4. High figures for TN conversion were obtained for all the measured runs and the highest conversion was 99 % at 350 °C, 40 min and 25 OE, which was also the run with the highest COD conversion. As indicated in the table, a high nitrogen conversion was measured even at 325 °C, whereas the highest nitrogen conversion was obtained for run 8.

Table 4. Total nitrogen conversion

Run	T (°C), t(min), OE (%)	TN (mg/L N)	X <sub>TN</sub> (%)
3	350, 40, 0	104.7	95.64
8	350, 40, 25	22.4	99.07
9	325, 30, 12.5	186.8	92.22

**Source:** The authors.

The sludge that was formed could be partly the result of manganese oxide (MnO<sub>2</sub>), which is insoluble in water, and results from the decomposition of potassium permanganate upon heating (6), as well as potassium hydroxide formed according to Eq (1) (7). MnO<sub>2</sub> has been shown to be catalytically active in wet air oxidation studies. The generated MnO<sub>2</sub> in situ could not only catalyze KMnO<sub>4</sub> reaction, but also possesses adsorption, coagulation and oxidation capabilities (6). A similar effect of manganese dioxide adsorption formed during the oxidation of dye wastewaters with potassium permanganate was reported (15).

Accordingly, the collected sludge could be formed by insoluble manganese oxide, potassium hydroxide and coagulated/adsorbed organic matter which was not oxidized. Inorganic substances and organic matter in the sludge can be estimated by means of the total volatile solids (TVS) and total fixed solids. Total fixed solids were measured for the sludge in selected runs 1 and 4 which had the highest conversions according to the results in Table 5.

Table 5. Total volatile solids (TVs) in selected samples sludge

Run	T (°C), t(min), OE (%)	Weight (IW) 105 °C (g)	Weight (FW) 550°C (g)	TVs (g)	TVs/IW ratio
1	350, 20, 0	2.4147	1.0546	1.3601	0.56
4	350, 20, 25	2.9568	1.594	1.3628	0.46

**Source:** The authors.

As shown in Table 5, total volatile solids (TVs) to initial weight (IW) ratio as well as the final weight (FW) of the sample indicate the sludge is comprised by a fraction of organic matter, which is lost at 550 °C, and a fraction of mineral substances left in the crucible after calcination. These results suggest not only oxidation but also coagulation and adsorption of organic matter could potentially

take place. Both runs were carried out at 350 °C and 20 min and only differ in the oxidant excess used, and the results indicate TVs/IW ratio decreases with the increase in oxidant excess, which could be attributed to a higher availability of oxygen in the run with 25% OE to oxidize organic matter. Yet, this conclusion cannot be generalized since the results of the ANOVA showed the OE had no positive effect in the reduction of organic matter as COD.

The milder conditions of the subcritical water oxidation of leachates with  $\text{KMnO}_4$  than those required for SCWO with  $\text{H}_2\text{O}_2$ , as well as the potentially high TN conversions and organic matter coagulation and adsorption, could represent a new opportunity for the development of an efficient treatment of leachates. In this aspect, SCWO still struggles with the two biggest challenges for SCWO processes: corrosion and salt precipitation/accumulation (16). Salt precipitation is the result of the considerably reduced solubility exhibited by salts in supercritical water and can lead to clogging and plugging of the reactor (16). Corrosion in SCWO, a consequence of the aggressive nature of water at supercritical conditions, is most severe at temperatures around 400 °C presented before (preheater) and after (cool down heat exchanger) the reactor. Qian et al. (17) assessed the corrosion characteristics of Fe, Ni and Ti based alloys near the critical point of water, and reported that at 350 °C all materials tested exhibited a low corrosion rate (0.05 mm/yr) in comparison to 400 °C (0.4 mm/yr) and increase up to 1.4 mm/yr at 450 °C (17). While corrosion cannot be avoided, even at subcritical water conditions, it is considerably less than at SCWO conditions, which allows using 316L stainless steel in the reactor instead of costlier corrosion resistant alloys

Additional advantages come from the fact that potassium permanganate as oxidant can be directly added to the wastewater in a solid form, not requiring dilution water as is the case when using hydrogen peroxide. The ANOVA results also suggest that reaction conditions could be further improved by an additional reduction in the oxidant below the stoichiometric level (0%) and reaction time below 20 min, since optimal levels from the experimental design were those for the low levels of these factors. Wastewater treatment by subcritical water oxidation with potassium permanganate benefits from not only the increased efficiency of  $\text{KMnO}_4$  as oxidant but also the properties of water at subcritical conditions and the high temperature media to achieve high COD destruction efficiencies while avoiding operating conditions that could result in limitations such as is the case for SCWO.

## Conclusions

Leachate treatment by subcritical water oxidation using potassium permanganate as oxidant was studied in a batch reactor and the effect of factors temperature, time and oxidant excess was established by means of the analysis of variance. The results showed the temperature was the only significant factor, whereas the effect of time and oxidant excess or its interactions were not significant. As a result, high chemical oxygen demand conversions can be obtained at 350 °C, 20 min reaction time and stoichiometric oxidant. Total nitrogen was measured in selected samples and conversions higher than 90 % were measured in all the samples. The collected brown sludge was characterized according to the total volatile and fixed solids in selected samples, and the results showed the sludge was comprised by an organic volatile phase and a fixed mass of non-

volatile substances such as minerals and salts originally present in the leachate or formed from the decomposition of potassium permanganate. The studied process benefits from the high efficiency of potassium permanganate as oxidant agent as well as the properties of subcritical water as a high temperature reaction media to accomplish the treatment of leachates. In addition, the reported experimental conditions are less stringent than those used in SCWO, while avoiding the drawbacks that can be associated to excessive corrosion and salt precipitation.

#### Author contributions

Laura Moreno-Tamayo: Research, Writing-Original Draft

Paula Manrique-Andrade: Research, Writing-Original Draft, Resources.

Victor Marulanda-Cardona: Writing-Original Draft, Writing-Review & Editing.

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