



Research Article

The utilization of lathe waste as a catalyst for the treatment of landfill leachate in supercritical water conditions

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ABSTRACT

In this study, the treatment of landfill leachate in supercritical water conditions with and without catalyst use was investigated. A real waste, namely lathe waste, was used as the catalyst. The experiments were made at a constant 25 MPa pressure, at four reaction temperatures in the range of 450-600°C and four reaction times between 60 and 150 s. Through the experiments, the impacts of reaction temperature, reaction time and the use of lathe waste catalyst on landfill leachate treatment were investigated. The efficiency of the treatment was evaluated in terms of liquid reaction products' total organic carbon (TOC) and total nitrogen (TN) conversions. As a result, it was seen that elevated reaction temperatures and long residence times favored TOC conversions. On the contrary, greater TN reductions were encountered at lower reaction temperatures. The use of lathe waste was observed to promote the treatment efficiency for all experimental runs. The highest TOC conversion was seen at 600°C and 150 s conditions, which was 57.2% for the noncatalytic treatment. The employment of lathe waste improved this value to 66.9%. As for TN, the highest conversion was encountered at 450°C and at a reaction time of 150 s. At the foresaid reaction conditions, using lathe waste as the catalyst provided 41.9% reduction in the TN content of landfill leachate.

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INTRODUCTION

The incremental urban, industrial and economic growth in today's world have caused a prominent rise in the quantity of municipal solid waste (MSW) generation. The annual global MSW generation is speculated to reach 3.4 billion tons by 2050 [1-3]. In many countries, the commonly employed method for MSW disposal is sanitary landfilling. This is mainly because of its economic feasibility and convenience when compared with other methods

employed for the same purpose, such as composting and incineration [4,5]. Nevertheless, despite the global preference of sanitary landfilling, the generation of landfill leachate during the process is a major drawback.

Landfill leachate is the liquid effluent generated due to the rainfall percolation in the landfill, groundwater infiltration, inherent water content of the wastes and biochemical reactions taking place in the wastes [2,6]. Landfill leachate is reported to be produced in a landfill even after 50

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years after its enclosure [3]. It is a very hazardous wastewater with a composition generally affected by the age of the landfill, how the landfill was designed and operated, the waste composition and meteorological conditions [7,8]. Consequently, it can be considered as a wastewater with a complex structure. Landfill leachate is generally described by its high content of volatile fatty acids, heavy metals, polycyclic aromatic hydrocarbons, humic and fulvic substances, chlorinated organics, phenolic compounds, soluble salts and ammonia nitrogen. Most of these compounds are known to be toxic, and even carcinogenic [9-11]. Chen et al. [2] mentioned the toxicity report of 56 samples of landfill leachate, 32 of which may cause cancer, 21 of which may result in genetic damages and 10 of which may cause birth defects. Thus, landfill leachate is a great concern, as it may cause irrevocable harm to the terrestrial and aquatic environments without proper treatment.

Many methods have been explored up to date, in order to achieve an efficient treatment of landfill leachate. These methods generally involve biological processes and physico-chemical processes. The biological treatment methods that are commonly used are aerobic and anaerobic stabilization ponds, activated sludge process, upflow anaerobic sludge blanket reactor, membrane bioreactor and moving bed biofilm reactor [1,3]. Although these biological treatment methods offer a simple operation with low cost, the presence of refractory compounds and concentrated heavy metals cause difficulties. Besides, biological treatment methods are reported to be less efficient during landfill leachate treatment, in which leachate is generated in landfill sites with an age greater than 10 years [2,6]. Physico-chemical methods, on the other hand, involve chemical precipitation, adsorption, coagulation and flocculation, membrane processes (reverse osmosis, ultrafiltration, microfiltration, nanofiltration) and advanced oxidation processes (Fenton process, photocatalysis, ozonation, electrocatalysis, persulfate oxidation). Majority of these physico-chemical methods are not suitable for the treatment of landfill leachate that arise from landfills aged less than 5 years with high content of organics [12]. Moreover, membrane processes have issues regarding high operation costs and membrane fouling [2]. Though most of the advanced oxidation processes are more efficient in the degradation of refractory compounds, they require the addition of chemicals. This necessity results in the generation of large quantities of sludge, which is a significant drawback, as it needs further treatment [13].

Regarding the aforementioned reasons, nowadays research on landfill leachate treatment focuses on green technologies that prevent sludge formation and lessen the amount of chemical use. Processes taking place at supercritical water conditions are prominent examples of these green treatment methods. Above its critical point of 374°C and 22.1 MPa, water has very unique properties such as a high diffusivity, low density, low viscosity and it offers excellent transfer properties. Consequently, mass transfer

limitations can be prohibited, leading to increased reaction rates. When compared with water at ambient conditions, supercritical water has a much smaller dielectric constant. Thus under supercritical conditions, water becomes a non-polar solvent being completely miscible with molecular oxygen and organic substances. Therefore, because of the elimination of mass transfer limitations, the organic substances are efficiently destroyed in a very short amount of time. While an entirely homogeneous phase is provided for organic substances, the solubilities of inorganic salts decrease owing to the high polarity of ions [4,14-16].

Because of the foresaid properties of supercritical water, treatment in supercritical water conditions can be considered as an outstanding thermochemical treatment technology applied to organic wastes and wastewaters. It does not require the addition of toxic chemicals to the process. Furthermore, additional processing or drying of the wastewater prior to treatment is not required [17]. However unfortunately, the use of supercritical water for landfill leachate treatment is investigated in only a limited amount of studies. These studies investigated landfill leachate treatment with the use of an oxidant source [16,18,19], without the use of an oxidant source [15,19] and with the employment of a catalyst [4,14,18,20], which are summarized in Table 1.

As it can be seen from the scarcity of the studies mentioned in Table 1, there is still very limited information regarding landfill leachate treatment when supercritical water conditions are employed. Thus, aiming to make a contribution to the inadequate amount of knowledge on this topic, the treatment of landfill leachate in supercritical water conditions was investigated in this study. The experiments, which were comprised of two main parts, were conducted at a constant 25 MPa pressure; while the influence of four reaction temperatures (450, 500, 550, 600°C) and four residence times (60, 90, 120, 150 s) were selected to study. In the first part, the supercritical water treatment of landfill leachate was performed without any oxygen source nor catalyst use. In the second part, the experiments were made by using lathe waste as a catalyst. The lathe waste was obtained from a local lathe shop and characterization studies unveiled that it contained iron nickel and chromium compounds. Through the experiments, the effects of catalyst use, reaction temperature and time on the TOC and TN conversions of landfill leachate were investigated.

MATERIALS AND METHODS

Landfill Leachate

Landfill leachate used during the experiments was obtained from the landfill site of Samsun Municipality, which is located in Samsun province of Turkey. Throughout the experiments, it was used after being filtered roughly and without any dilution.

Table 1. The summary of literature studies made on landfill leachate treatment in supercritical water conditions.

Operation Conditions	Oxidant Use	Catalyst Use	Results	Reference
T = 400 – 600°C t = 30 – 150 s P = 25 MPa	1:1 – 1:3 O ₂ as oxidant per required O ₂	Ni/Al ₂ O ₃	TOC removal: 11% – 98.2% TN removal: 49% – 57% Optimum: 600°C, 150 s, 1:1 O ₂ as oxidant per required O ₂	[4]
T = 500 – 650°C t = 0 – 30 min P = 22.5 – 26 MPa	-	KOH, K ₂ CO ₃ , MnO ₂ and KMnO ₄	COD removal: 72.2% – 94.6% NH ₃ -N removal: 0.5% – 51.0% Optimum: 650°C, 60 s, KOH catalyst	[14]
T = 400 – 600°C t = 15 – 60 s P = 22.5 MPa	-	-	COD removal: 8% – 57% Optimum: 600°C, 60 s, 22.5 MPa	[15]
T = 250 – 500°C t = 2 – 18 min P = 10 – 35 MPa	DOD = 0.2 – 2.3	-	COD removal: 55% – 98% TOC Removal: 45% – 95% Optimum: 375°C, 7 min, 22.5 MPa, 2 DOD	[16]
T = 450 – 600°C t = 60 – 600 s P = 10 – 35 MPa	OC = 1.2 – 3.4	CeMnO _x /TiO ₂	TOC removal: 7.6% – 92.5% NH ₃ -N removal: -15.9% – 50.9% Optimum: 600°C, 3.4 OC, Ce/Mn = 1:2	[18]
T = 200 – 600°C t = 300 – 1200 s P = 23 – 29 MPa	OC = 1.2 – 3.4	-	TOC removal: -16.9% – 85.5% Optimum: 500°C, 600 s, 25 MPa, 0.2 OC	[19]
T = 600 and 700°C t = 300 – 1200 s P = 23 MPa	-	Clinoptilolite	TOC removal: 68% – 87% COD removal: 58% – 82% NH ₃ -N removal: -8.3% – 90%	[20]

Characterization of the Raw and Treated Landfill Leachate

The characteristics of raw landfill leachate that was used in the experiments are given in Table 2. In this study, landfill leachate treatment efficiency was measured in terms of the reductions in its TOC and TN contents. TOC and TN, along with inorganic carbon (IC) and total carbon (TC) measurements were made by a TOC-TN analyzer. The TOC-TN analyzer (Hach-Lange IL 550; Hach Company, Colorado, USA) was operated by using a highly sensitive multi-channel infrared detector, which used the combustion catalytic oxidation method. For providing precise data, the samples were analyzed in triplicate and the average values were given in the results. The chemical oxygen demand and biochemical oxygen demand (BOD₅) of the landfill leachate were measured according to the standard methods [21].

Lathe Waste as the Catalyst

The lathe waste used in the experiments for the catalytic treatment of landfill leachate in supercritical water conditions was obtained from a local lathe shop. It was loaded inside the reactor as it was obtained, without any modification. The external appearance of the lathe waste is presented in Figure 1a.

Characterization of the Catalyst

The surface morphology of lathe waste was investigated through the employment of a CamScan Apollo 300 field-emission scanning electron microscope (SEM) at 15 kV (CamScan, Oxford, UK). The detector of the apparatus was a back scattering electron (BEI) and the magnification was selected as 5000. The SEM morphological images of the two different regions of the lathe waste catalyst are given in Figure 1b and Figure 1c. The images show the heterogeneous layered structures present on the catalyst. The images

Table 2. The characteristics of the raw landfill leachate used in the experiments.

Parameter	Value
TOC (mg/L)	2535
COD (mg/L)	4750
TN (mg/L)	1375
IC (mg/L)	1585
TC (mg/L)	4120
BOD ₅ (mg/L)	2821
pH	9.52

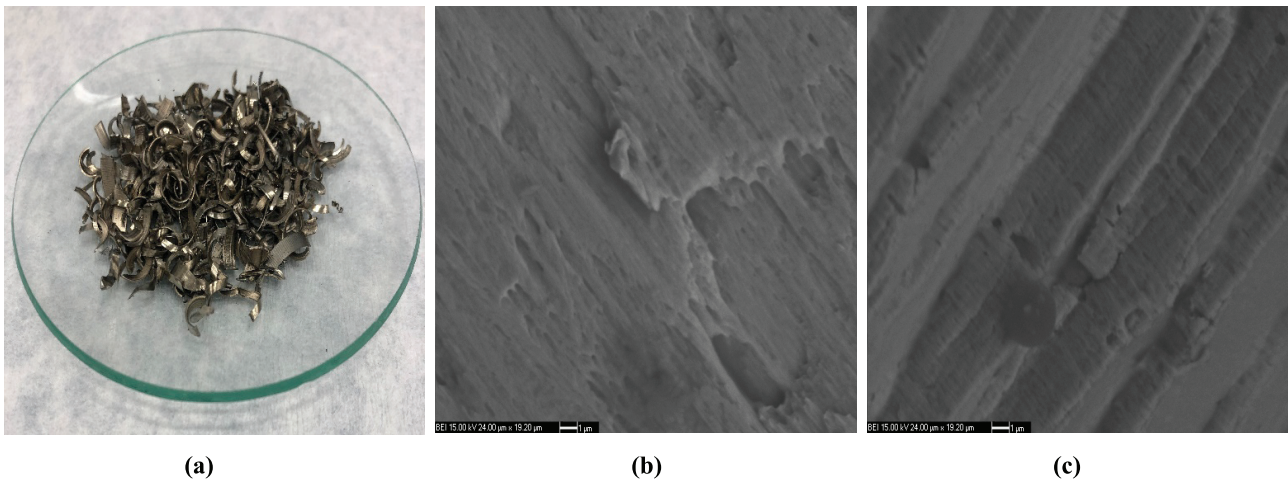


Figure 1. a) The lathe waste catalyst used in the experiments b) SEM morphological image of the catalyst from Region 1 c) SEM morphological image of the catalyst from Region 2.

also demonstrate the rod-like structures along with some round and agglomerated formations.

Further characterization of the lathe waste was established through a PANalytical Xpert Pro (PANalytical B.V., Almelo, The Netherlands) X-ray diffraction (XRD) equipment, by using the generator settings of 40 mA and 45 kV. In the X-ray diffraction analysis Cu-K α radiation ($\lambda = 1.53$

cm⁻¹) was used and 40-150° is selected for the 2 θ range. Accordingly, the XRD pattern and characteristic peaks of the phases for the lathe waste are given in Figure 2.

Regarding Figure 2, the lathe waste consists of three phases, containing elements of iron, chromium and nickel. The major phase has an XRD score of 81, with a powder diffraction file (pdf) number of 00-047-1405. This indicates

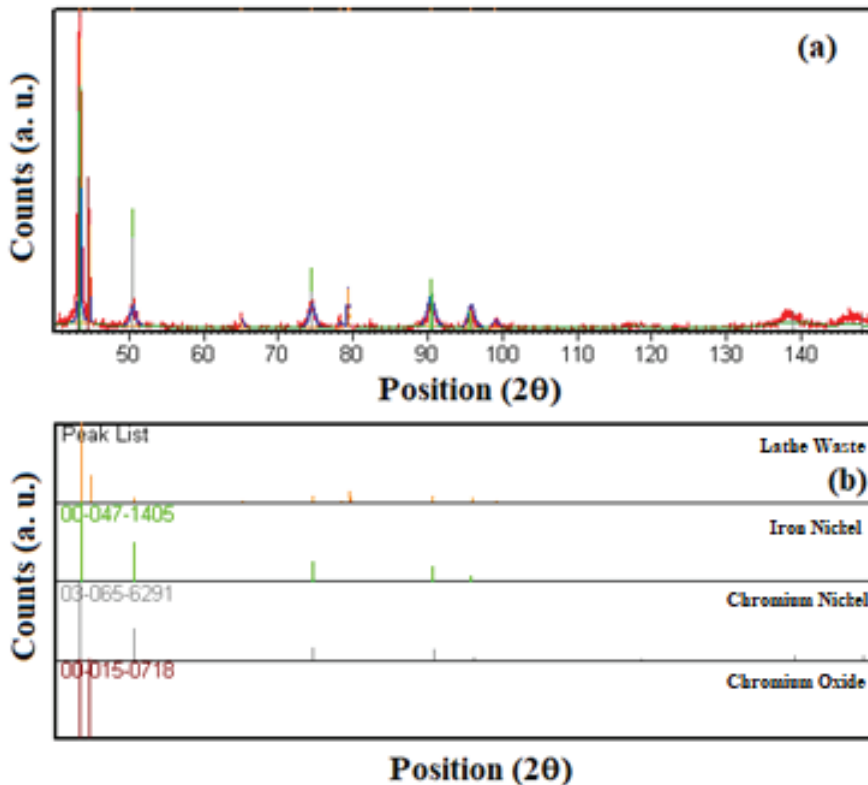


Figure 2. Lathe waste catalyst's a) XRD pattern, b) Phases' characteristic XRD peaks.

Table 3. Crystallographic data of lathe waste catalyst.

Crystallographic Parameter	Iron Nickel (Major Phase)	Chromium Nickel (Minor Phase 1)	Chromium Oxide (Minor Phase 2)
Powder diffraction file number	00-047-1405	03-065-6291	00-015-0718
Chemical formula	Fe _{0.64} Ni _{0.36}	Cr ₂ Ni ₃	Cr ₂ O ₃
Crystal system	Cubic	Cubic	Tetragonal
a (Å)	3.5922	3.5790	9.4800
b (Å)	3.5922	3.5790	9.4800
c (Å)	3.5922	3.5790	5.1600
Alpha (°)	90.0000	90.0000	90.0000
Beta (°)	90.0000	90.0000	90.0000
Gamma (°)	90.0000	90.0000	90.0000

that the major phase of the lathe waste has a molecular formula of Fe_{0.64}Ni_{0.36}, namely iron nickel. The XRD score indicates the similarity of the analyzed material to the theoretical compound. In other words, when all the peak locations and peak intensities (%) completely match with the reference card, the XRD score of the analyzed material is 100 [22]. Hence, the minor phases of the lathe waste catalyst have XRD scores of 69 and 65, with pdf numbers of 03-065-6291 and 00-015-0718. The corresponding molecular formulas are Cr₂Ni₃ (chromium nickel) and Cr₂O₃ (chromium oxide), respectively. Consequently, the phases present in the lathe waste were found to be iron nickel, chromium nickel and chromium oxide. The crystallographic data of these phases are presented in Table 3.

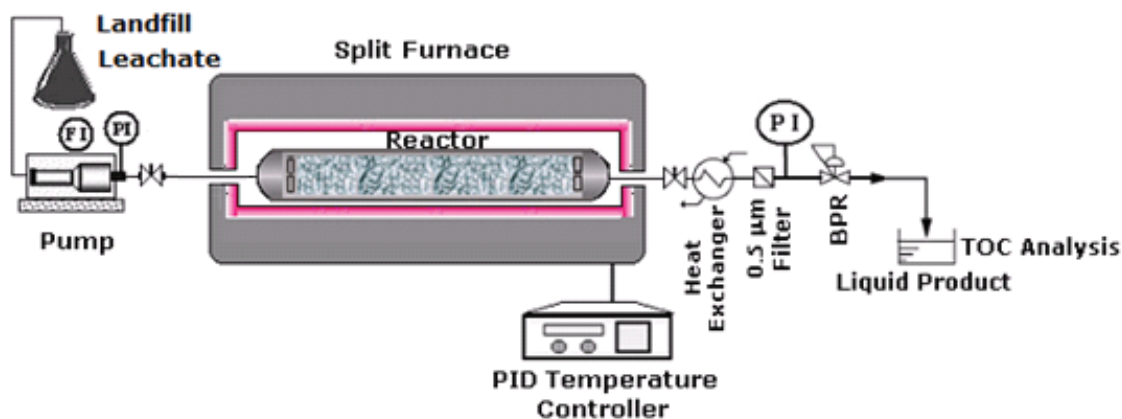
Experimental Method

Experiments regarding the treatment of landfill leachate in supercritical water were made in the system, which is schematically demonstrated in Figure 3. All of the wetted parts of the experimental setup were comprised of 316 SS. The packed bed reactor (PBR) was placed in a split furnace (Protherm) that was PID-controlled, which kept the

reaction temperature with $\pm 1^\circ\text{C}$ precision. The reaction pressure was kept constant at 25 ± 0.1 MPa, by using a back pressure regulator (GO Regulator Inc.). The residence time of landfill leachate inside the PBR, on the other hand, was determined with respect to Equation 1 stated below:

$$\tau = \frac{V_{\text{reactor}}}{F} \times \frac{\rho_{\text{SC}}(T,P)}{\rho_L} \quad (1)$$

In Equation 1, t stand for the residence times in the reactor, which were chosen as 60, 90, 120 and 150 s for each designated reaction temperature. r_{SC} and r_L are the fluid densities at the reaction conditions and under the feed conditions, respectively. Taking into account that the reaction media at each experiment involved dilute mixtures of leachate components in water, the aforementioned fluid densities inside the reactor and in the feed were assumed to be those of pure water [23]. During the treatment studies without the catalyst, the reactor had a volume of 25.13 mL. For the catalytic treatment experiments on the other hand, 25 g of lathe waste was loaded in the reactor, which yielded a void volume of 11.38 mL. Therefore, for the void volume

**Figure 3.** The experimental setup for the catalytic treatment of landfill leachate in supercritical water.

of the PBR, stated as V_{reactor} in the equation above, the fore-said values were used. In this regard, based on the reaction conditions and the appointed residence times, the total volumetric flow rates of the feed streams (F) were between 0.36 mL/min and 1.83 mL/min for the catalytic treatment experiments, and between 0.80 mL/min and 4.04 mL/min for the noncatalytic treatment experiments in supercritical water, respectively.

Once the operation conditions were determined, landfill leachate was pumped to the reactor by using a high pressure pump (Autoclave Engineers). At the reactor's exit, the effluent was immediately passed through a heat exchanger. After the rapid cooling, it was then brought to atmospheric pressure by the back pressure regulator. At the final step, the effluent was taken to a gas-liquid separator, from which the liquid samples were collected and subjected to their TOC and TN analyses.

RESULTS AND DISCUSSION

The Effect of Temperature on the Treatment of Landfill Leachate

Figure 4 presents the effects of reaction temperature and reaction time on the TOC conversions during the treatment of landfill leachate without any catalyst use (Figure 4a) and with lathe waste used as the catalyst (Figure 4b). From the figures, it is clear that the reaction temperature had a prominent impact on the enhancement of landfill leachate treatment efficiency. Considering the noncatalytic experiments first, for a reaction time of 60 s, the TOC conversion increased from 36.7% to 46.2% as the reaction

temperature increased from 450°C to 600°C. For the longest reaction time employed, which was 150 s, the TOC conversion increased from 46.0% to 57.2% for the same temperature interval. The highest treatment efficiency, i.e. TOC conversion was encountered during the experiment performed at 600°C and 150 s. At these conditions, the liquid effluent had a TOC value of 1084.8 mg/L, which corresponded to a 57.2% TOC reduction. A similar tendency was also observed during the experiments conducted by using lathe waste as the catalyst. At 450°C, the TOC conversions were between 39.4% and 51.6%. These values were in the range of 40.3% and 59.8% at 500°C, 57.2% and 66.0% at 550°C, 63.4% and 66.9% at 600°C, respectively. Likewise the noncatalytic experiments, the highest treatment efficiency was observed during the 600°C and 150 s run. The liquid product had a TOC value of 839.1 mg/L and a 66.9% TOC conversion was encountered. These results signify the increase in the organic content degradation of landfill leachate at elevated temperatures.

Similar findings were also reported in literature studies regarding the temperature effect on the landfill leachate treatment efficiency. Chen et al. [14] investigated the treatment of landfill leachate between 500°C and 650°C, for a reaction time of 20 minutes. The authors reported that as the temperature increased from 500 to 650°C, COD removal rates improved from 72.2% to 79.3%. It was also stated that higher reaction temperatures were beneficial in order to obtain greater carbon gasification efficiencies and COD removal rates. Gong et al. [18] performed the SCWO of landfill leachate in a batch reactor. At a reaction time of 600 s, as the temperature increased from 450 to 600°C, the

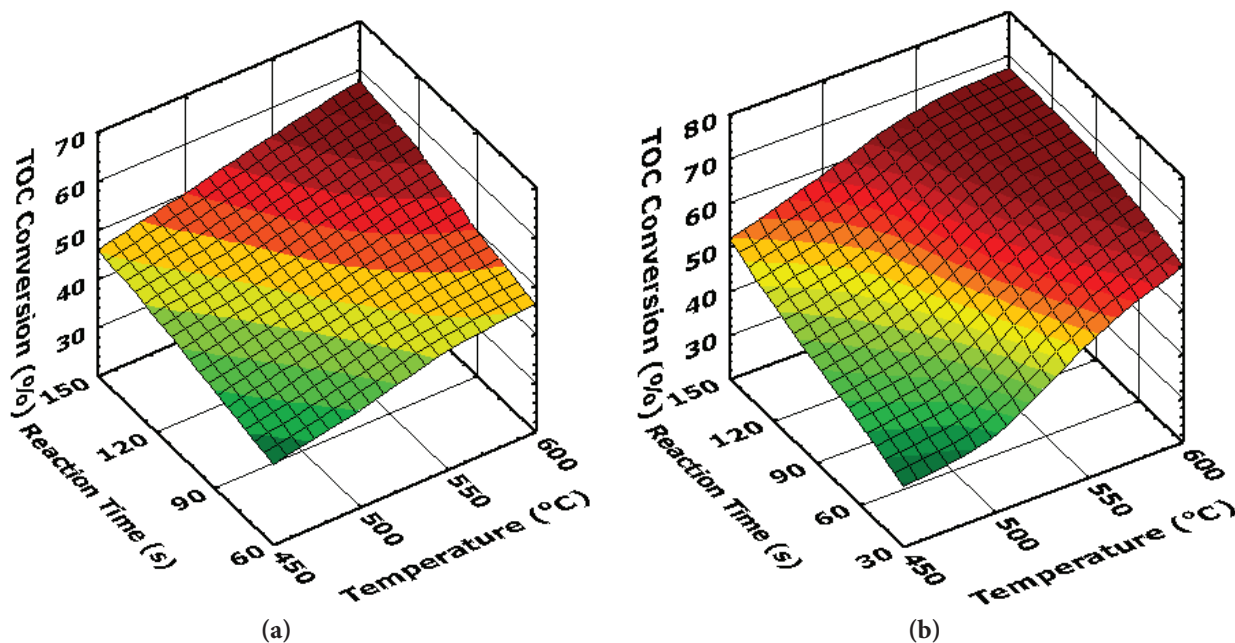


Figure 4. The effects of reaction temperature and time on the TOC conversions of a) noncatalytic treatment experiments and b) catalytic treatment experiments with lathe waste.

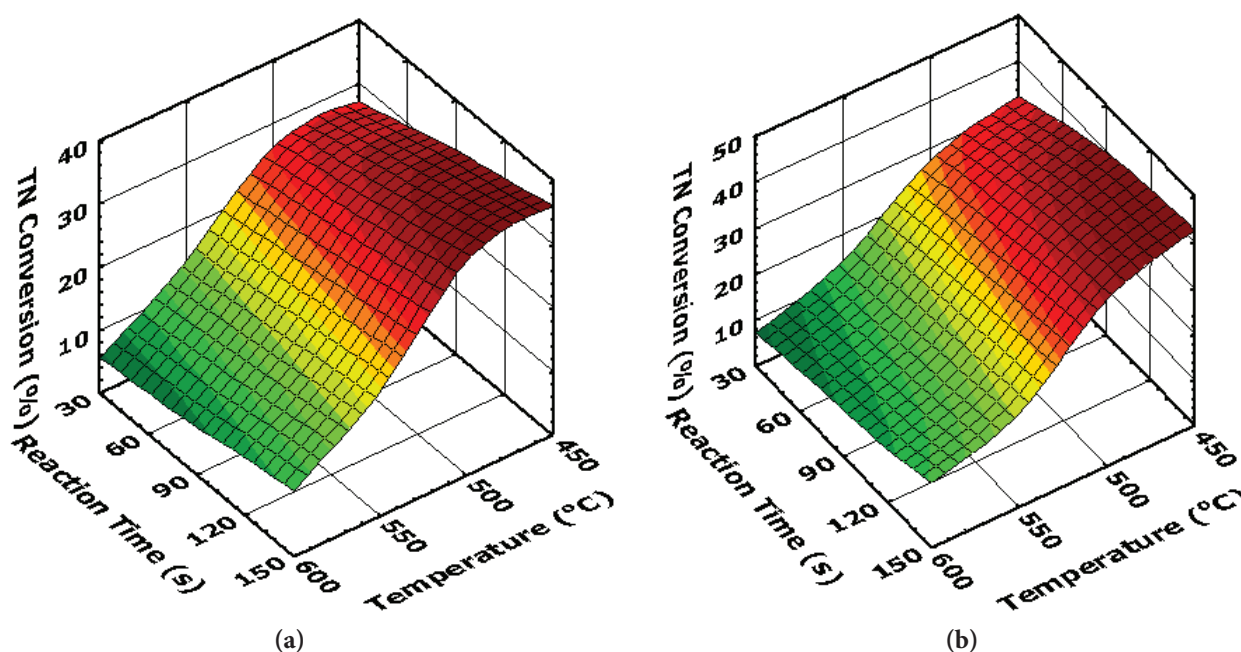


Figure 5. The effects of reaction temperature and time on the TN conversions of a) noncatalytic treatment experiments and b) catalytic treatment experiments with lathe waste.

TOC removal efficiencies increased from 7.6% to 87.2%. Even though oxidative treatment was performed and longer reaction times were employed in the foresaid study, the experimental results obtained in the present study showed a higher TOC conversion at 450°C, which was in the range of 36.7% and 46.0% for the reaction times employed (60–150 s). Scandelai et al. [20] investigated landfill leachate treatment in supercritical water and reported that as the temperature increased from 600 to 700°C, TOC removal also increased from 68% to 85%. Though the foresaid study has proximate residence times to the present one, the TOC conversion obtained at 600°C is about 10% higher, mainly due to the employment of SCWO process with a different reactor system. Civan et al. [4] reported that the TOC removal improved with temperature and that the highest temperature employed in their study, 600°C, yielded the highest TOC conversion. In another study, similar results were found and it was concluded that the organics in landfill leachate were remarkably degraded at higher reaction temperatures [19].

An interesting phenomenon is encountered when the change in TN conversions is observed, as presented in Figure 5. Figure 5a shows the TN conversions for noncatalytic treatment experiments and Figure 5b shows the TN conversions for the lathe waste catalytic treatment experiments at supercritical water conditions, for the designated reaction temperatures and times. Accordingly, for all of the experiments, it was observed that TN conversion was inversely proportional to the reaction temperature. For the treatment studies performed without the catalyst, TN conversion was in the range of 6.9% and 10.6% at 600°C.

These values improved to 29.1% to 35.7% at 450°C, the lowest reaction temperature employed. The use of lathe waste resulted in likewise outcomes. TN conversions were in the range of 9.2% and 15.2% at 600°C, 13.8% and 17.5% at 550°C, 32.5% and 39.3% at 500°C, 35.6% and 41.9% at 450°C. At 450°C and 150 s, the TN content of the liquid effluent was 798.9 mg/L, which corresponded to the highest TN removal of 41.9%.

This inversely proportional relationship between TN conversion and temperature was mentioned in other literature studies as well. Gong et al. [19] studied the treatment of landfill leachate at 200–600°C, 600 s and 25 MPa. The authors stated that under all experimental conditions, TN and $\text{NH}_3\text{-N}$ concentrations were always greater than those of raw landfill leachate. The authors also indicated that since the concentration of $\text{NH}_3\text{-N}$ was consistently at the vicinity of the TN concentration, TN of the liquid effluent was approximately completely composed of $\text{NH}_3\text{-N}$. The increase in TN concentration was attributed to the dissolution of solid organics during the treatment of landfill leachate at supercritical water conditions with temperature. Several authors remarked that supercritical water could donate a proton for converting the nitrogen present in the organics to NH_3 with an increase in temperature [14,24,25]. Being a refractory compound resistant to degradation, and being even more stable than hydrocarbons in supercritical water media, ammonia was reported to be the main obstacle in the treatment processes [14,18,25]. Thus, additional measures such as oxidant and catalyst use were suggested [15,25].

The Effect of Reaction Time on the Treatment of Landfill Leachate

As it can be seen from Figure 4, increasing reaction time from 60 s to 150 s improved the treatment efficiency of landfill leachate for both noncatalytic and catalytic experiments. For landfill leachate treatment without any catalyst use, TOC conversion increased from 36.7% to 46.0% at 450°C, 39.4% to 49.9% at 500°C, 45.6% to 54.2% at 550°C and 36.7% to 57.2% at 600°C, respectively. When lathe waste was used as the catalyst, on the other hand, the highest TOC conversions were again observed at the highest reaction time of 150 s. The maximum TOC conversion was encountered at the experiment performed at 600°C and 150 s, which was 66.9%. Civan et al. [4] reported similar results regarding the impact of reaction time on landfill leachate treatment efficiency, stating that the TOC removal improved with increasing residence times. The maximum TOC removal, which was 84%, was obtained during the experiment performed at the highest temperature (600°C) and longest reaction time (150 s). At these experimental conditions of 600°C and 150 s, the noncatalytic treatment efficiency was 57.2% in the present study. The difference between these TOC conversion values can be attributed to hydrogen peroxide use as the oxygen source, and the employment of Ni/Al₂O₃ as the catalyst to promote the treatment efficiency in Civan et al.'s study [4]. In another investigation of landfill leachate treatment in supercritical water at 650°C, as the reaction time increased from 0 to 30 minutes, the COD conversion increased from 74.1% to 81.9% [14]. The authors suggested that the foresaid reaction time increase promoted the degradation of landfill leachate and thus, decreased the COD concentration. Gong et al. [19] also reported a significant improvement on the TOC removal efficiency of landfill leachate with reaction time, stating that increasing reaction time favored the degradation of the organics. Accordingly, during the experiments conducted at 500°C and 25 MPa, as the reaction time increased from 300 to 1200 s, the TOC removal efficiency was seen to increase from 6.4% to 48.2%.

Though not as distinct as in TOC conversion, increasing the reaction time was seen to favor the conversion of TN as well, as it can be seen from Figure 5. This impact was especially prominent at lower reaction temperatures. For noncatalytic treatment experiments, increasing the time from 60 s to 150 s increased the TN conversion from 29.1% to 35.7% at 450°C, 30.1% to 35.4% at 500°C, 13.9% to 17% at 550°C and 6.9% to 10.6% at 600°C. When lathe waste was used as the catalyst, increasing the time from 60 s to 150 s increased the TN conversion from 35.6% to 41.9% at 450°C, 32.5% to 39.3% at 500°C, 13.8% to 17.5% at 550°C and 9.2% to 15.2% at 600°C, respectively. Regarding their study on the treatment of landfill leachate in supercritical water conditions, Chen et al. [14] had similar results at 650°C, demonstrating an improvement in NH₃-N removal rates as the residence time increased from 0 to 30 minutes. On the other hand, in another study that was conducted at

500°C and 25 MPa, increasing the reaction time from 300 s to 1200 s was reported not to have any significant effect on the removal efficiency of NH₃-N. This was attributed to ammonia being a very stable refractory substance at supercritical water conditions [19]. In their article on the SCWO of landfill leachate by using Ni/Al₂O₃ as the catalyst, Civan et al. [4] also stated that increasing the reaction time from 30 to 150 s caused a slight increase in nitrogen removal. The authors stated that, for a reaction temperature of 400°C, the TN removal increased from 49% to 57% as the time increased from 30 s to 150 s. The higher TN conversions encountered in the aforementioned study is due to the use of an additional oxygen source to enhance treatment efficiency and the use of a lower reaction temperature than the present study.

The Effect of Lathe Waste as a Catalyst on the Treatment of Landfill Leachate

Figures 6 and 7 present the TOC and TN conversions that were obtained for all of the performed experiments, respectively. In both figures, the dark bars symbolize the results for the catalytic treatment experiments and the lighter bars symbolize those for the noncatalytic treatment experiments in supercritical water conditions. Considering Figure 6 firstly, the impact of lathe waste on the treatment efficiency can be clearly observed, especially at elevated reaction temperatures. For instance, the highest TOC conversions were encountered during the experiments conducted at 600°C and 150 s, for both catalytic and noncatalytic studies. At these reaction conditions, the maximum TOC conversion was 57.2% for the noncatalytic experiments; however, this value was increased to 66.9% when lathe waste was used as the catalyst. Thus, the use of lathe waste catalyst reflected an almost ten percent increase in the treatment efficiency. However, the enhancement of treatment efficiency by lathe waste was observed to be less prominent at lower reaction temperatures. At 450°C, lathe waste improved the TOC conversion from 36.7% to 39.4% for a reaction time of 60 s, and from 46.0% to 51.6% for a reaction time of 150 s. Nevertheless, for all reaction temperatures investigated, the impact of catalyst use was especially distinct at higher reaction times. For the highest reaction time, 150 s, the use of the catalyst enhanced the treatment efficiency from 57.2% to 66.9% at 600°C, from 54.2% to 66.0% at 550°C, from 49.9% to 59.8% at 500°C, and from 46.0% to 51.6% at 450°C respectively. Though there are very limited literature studies that focus on catalyst use during landfill leachate treatment in supercritical water, similar results were reported. Civan et al. [4] employed Ni/Al₂O₃ catalyst during their study on CT-SCW of landfill leachate. The authors stated that, for a residence time of 30 s, TOC removal that was in the range of 11-33% for the blank experiments performed without the catalyst improved to 35-68% when Ni/Al₂O₃ was used. In another study that investigated the use of alkali catalysts, which was carried out at 650°C and 20 minutes, it was reported that catalyst use improved COD reduction significantly [14]. This reduction in COD

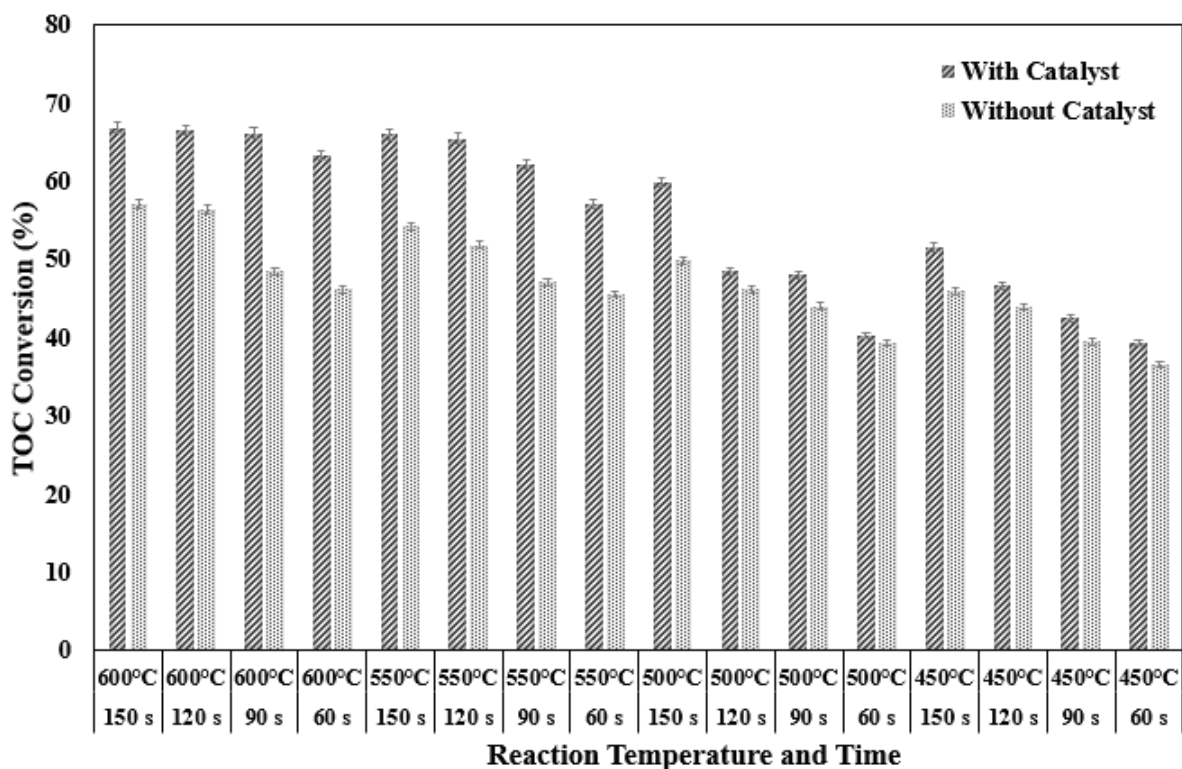


Figure 6. The comparison of TOC conversions with and without the use of lathe waste catalyst.

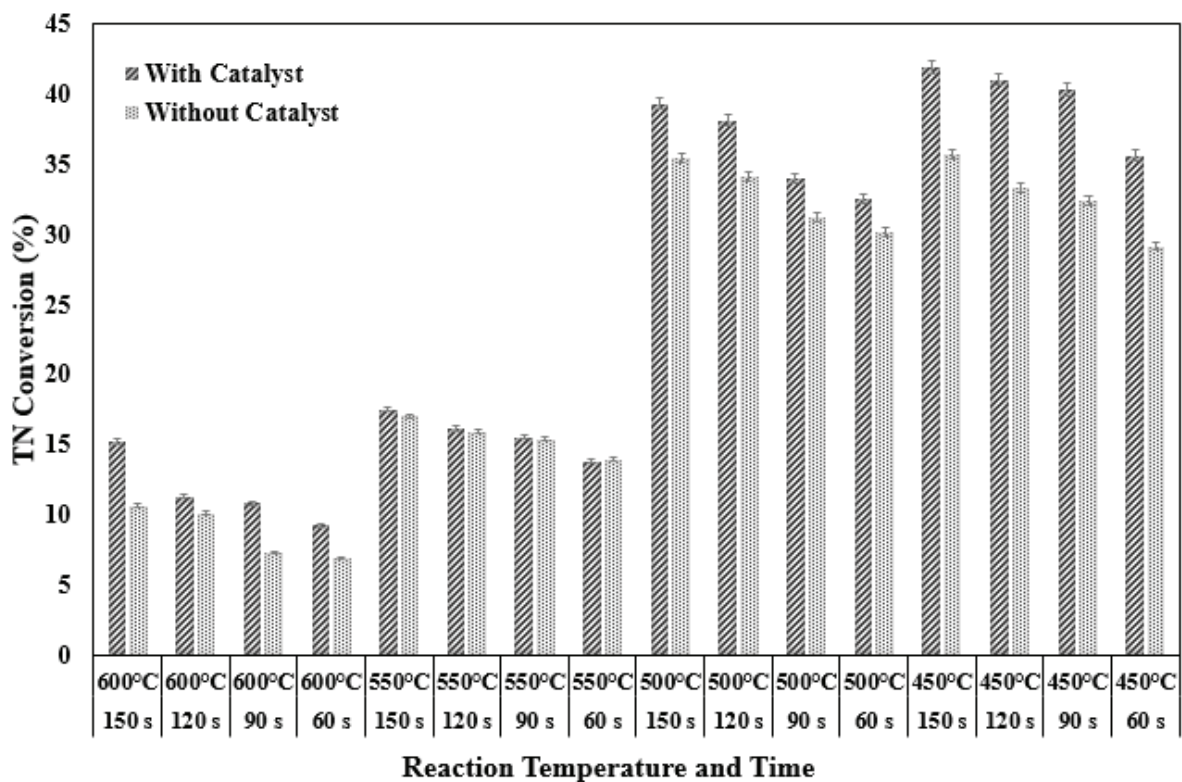


Figure 7. The comparison of TN conversions with and without the use of lathe waste catalyst.

was more emphasized when KOH and KMnO_4 catalysts were used. Gong et al. [18] used several composite catalysts ($\text{CeMnO}_x/\text{TiO}_2$) with different Ce/Mn ratios during the treatment of landfill leachate by SCWO. It was stated that Ce/Mn ratio of 1:2 highly improved the TOC removal efficiency. The last study that employed a catalyst, namely a zeolite, on the treatment of landfill leachate reported likewise results [20]. Accordingly, when compared with the noncatalytic experiments, the use of zeolite improved TOC removal from 68% to 73% at 600°C and from 85% to 87% at 700°C, respectively.

When considering the effect of lathe waste on TN removal (Figure 7), it can be seen that the catalyst promoted TN conversions especially at lower reaction temperatures. The highest TN removal, which was obtained at 450°C and 150 s was 35.7% for the noncatalytic treatment experiments. This value improved to 41.9% when lathe waste was used. For a 150 s of reaction time, lathe waste increased TN conversions from 35.4% to 39.3% at 500°C, from 17.0% to 17.5% at 550°C, and from 10.6% to 15.2% at 600°C, respectively. Considering elevated reaction temperatures, lower TN conversions were encountered. For noncatalytic treatment experiments performed at 600°C, TN conversions were in the range of 6.9–10.6%. The use of lathe waste catalyst enhanced TN reduction to the range of 9.2–15.2% at this temperature. Hence, the use of lathe waste catalyst, along with the employment of low reaction temperatures and high reaction times were found to improve TN conversions. In the literature, it was reported that the use of composite $\text{CeMnO}_x/\text{TiO}_2$ catalysts during the SCWO of landfill leachate improved the $\text{NH}_3\text{-N}$ removal efficiencies [18]. Chen et al. [14] reported that the use of alkali KOH catalyst increased $\text{NH}_3\text{-N}$ conversion. However, the authors informed that the use of K_2CO_3 , MnO_2 and KMnO_4 catalysts yielded lower $\text{NH}_3\text{-N}$ conversions when compared to the $\text{NH}_3\text{-N}$ conversion obtained without any catalyst.

CONCLUSION

In this study, the treatment of landfill leachate at supercritical water conditions was performed with and without catalyst use. To the best of our knowledge, there has not been a study made on literature regarding the utilization of a real waste as a catalyst, to promote the treatment efficiency of landfill leachate. Therefore, in the present study, the treatment of landfill leachate was made in supercritical water conditions by employing a real waste as a catalyst, for the first time in literature. Through the experiments, the effects of catalyst use, reaction temperature and time on the TOC and TN conversions of landfill leachate were investigated. The experiments demonstrated that the use of lathe waste as the catalyst increased landfill leachate treatment efficiency in terms of TOC and TN conversions. It was seen that increasing the reaction temperature and reaction time increased the TOC conversions for all experiments. Considering TN on the other hand, high reaction times and

low reaction temperatures were found to favor TN conversions. The TOC removals were in the range of 36.7% and 57.2% for noncatalytic landfill leachate treatment experiments. This range improved to 39.4% and 66.9% when lathe waste was employed as the catalyst. The maximum TOC removal (66.9%) was obtained during the catalytic treatment experiment that was conducted at 600°C and 150 s conditions. Lathe waste was also found to favor TN conversion, increasing the 6.9%–35.7% range obtained for noncatalytic runs to 9.2%–41.9% range. For a reaction temperature of 450°C and a reaction time of 150 s, lathe waste proved to remove 41.9% of the TN content of landfill leachate. Elevated reaction temperatures and long reaction times were seen to improve TOC removals, whereas low reaction temperatures and long reaction times were found to increase TN removals. Consequently, the use of lathe waste as a catalyst was seen to enhance landfill leachate treatment, with respect to both TOC and TN conversions.

NOMENCLATURE

BOD ₅	Biochemical oxygen demand
COD	Chemical oxygen demand
CT-SCW	Catalytic treatment in supercritical water
DOD	Dimensionless oxidant dose
IC	Inorganic carbon
MSW	Municipal solid waste
OC	Oxidation coefficient
PBR	Packed bed reactor
pdf	Power diffraction file
SCWO	Supercritical water oxidation
SEM	Scanning electron microscope
TC	Total carbon
TN	Total nitrogen
TOC	Total organic carbon
XRD	X-ray diffraction

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AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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