Analysis of Effluent Characteristics of Bio-treated Pulping Wastewater (BTPW) during Ozonation

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The effluent of a pulp mill was subjected to a biological treatment followed by ozonation to study the potential biodegradability improvement of recalcitrant compounds. Characteristics of the bio-treated pulp wastewater (BTPW) before and after the ozonation process were analysed by Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, gel permeation chromatography, and gas chromatography, which detected the variations in the organic compounds in the effluents. Results showed that the ozonation treatment has the potential to turn some refractory compounds into biodegradable compounds and therefore increase the biodegradability of the BTPW. The increased biodegradability was accomplished because ozonation affects the structure of the refractory compounds and degrades the macromolecular organic matter into micromolecular organic matter. Furthermore, it is proposed that the degradation of macromolecular organic matter happens fast and therefore there are structural changes, since smaller molecules are formed. Then, these smaller molecules degrade over a longer period.

Keywords: Bio-treated pulping effluent; Ozonation; Biodegradability enhancement; Recalcitrant compounds

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INTRODUCTION

Complex pulping processes that require a large addition of chemicals result in highly polluted wastewater, and this makes treatment of this wastewater crucial (Toczyłowska-Mamińska 2017). However, the refractory compounds, such as lignin and its derivatives, contained in wastewater are difficult to remove effectively by the biological treatment (Lucas *et al.* 2012). Therefore, having to comply with the rigorous wastewater discharge standard for the pulp and paper industry in China (GB 3544-2008 2008) or in other countries is difficult, and further treatment must be adopted to treat the biological effluent to allow wastewater to be reused or meet discharge standards (Sarkar *et al.* 2017).

Presently, advanced oxidation processes (AOPs) have been adopted extensively as a tertiary treatment option to treat biologically treated pulping wastewater. For example, Fenton oxidation (Jamil *et al.* 2011), electron Fenton processes (Guvenc *et al.* 2017), Fenton-like heterogeneous catalysts (Zhou *et al.* 2015), ultraviolet-assisted oxidation processes (Hermosilla *et al.* 2012), and ozonation (Fontanier *et al.* 2006) can be used to remove recalcitrant organic matter. Even though these studies all claim that AOPs are adequate for treating secondary effluent for discharge or reuse, ozonation has been found to be the most promising process with various advantages (Biglari *et al.* 2017). For instance, ozone is more aggressive in destroying the structure of refractory organic pollutants than other oxidizing agents such as H_2O_2 and ClO_2, and ozonation is a well established, robust technology (Prieto-Rodríguez *et al.* 2013). To a large extent, ozonation is a promising method for treating biological effluent, not only because of the high efficiency in lowering the COD, but also because the treatment is able to turn refractory compounds into biodegradable compounds, which means this treatment has the ability to improve the biodegradability of the wastewater (Merayo *et al.* 2013).

Despite several studies being focused on biodegradability and studying the effects of combining a biological treatment with ozonation (Gupta *et al.* 2010), more study is needed regarding changes in the effluent characteristics caused by the ozonation treatment, which is the primary goal of this paper. In this study, ultraviolet-visible (UV-VIS) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, gel permeation chromatography (GPC), and gas chromatography (GC) were used to analyze the effluent characteristics to evaluate the effect of the ozonation treatment.

EXPERIMENTAL

Materials

The wastewater used in the experiments was the effluent of a pulp mill located in Guangdong Province, Southern China after the biological treatment. The wastewater samples were stored at 4 °C for around 90 days until they were used. The COD_{Cr} and BOD_5 of the BTPW were 380 mg/L ± 10 mg/L and 55 mg/L, respectively, while the color was 320 ± 30 and the pH was 7.5 ± 0.5.

Methods

Ozonation

The ozonation system is shown in Fig. 1. The system used in this study is similar to what was used in the previous study by the authors (Zhang *et al.* 2017). A 500-mL sample of BTPW was adjusted to the desired pH with 25% H_2SO_4 and 10% NaOH solutions, and then was poured into a 1-L flask. Oxygen gas with a purity of 99.5% was supplied by an oxygen cylinder and transported into the ozone generator (Model CH-ZTW2, Chuanghuan Ozone Electrical Equipment Co. Ltd., Guangzhou, China) with a reducing valve and gas flow meter (1-L/min flow rate).

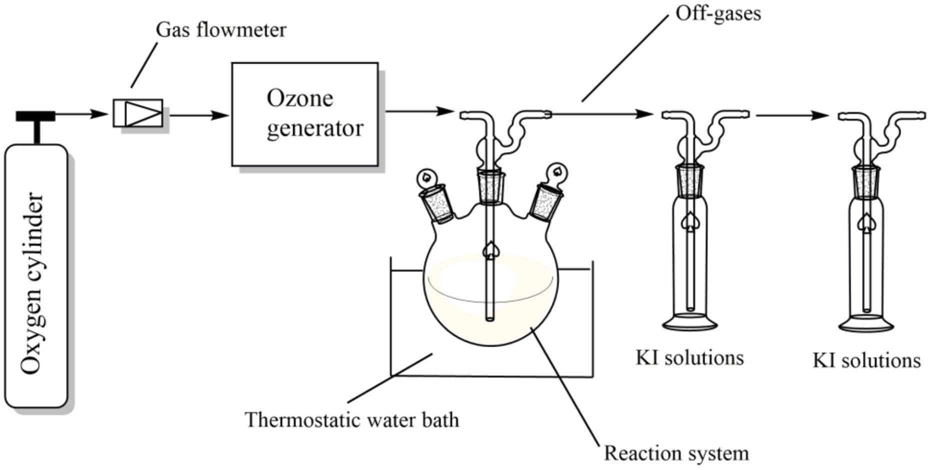

Fig. 1. Scheme of the ozonation system

Then, the ozone generated in the ozone generator was transported into the reaction system through a porous gas diffuser situated at the bottom of the flask. The diameter of the gas diffuser was 15 mm, the length was 20 mm, and the pore diameter ranged from 80 µm to 100 µm. The flask was placed in a thermostatic water bath kept at the desired temperature during the ozonation process. After ozonation, the wastewater was taken for analysis and the off-gas of the reaction system was absorbed by a 2% KI solution.

Analytical methods

A Hach UV-VIS spectrophotometer (DR6000, Loveland, CO, USA) and BRUKER FT-IR spectrometer (TENSOR 27, Karlsruhe, Germany) were used to analyse the molecular structure of the compounds in the water samples. An Agilent gel permeation chromatograph (Pledge Mixed-D, Santa Clara, CA, USA) was employed for analyzing the molecular weight distribution of the effluent, and an Agilent gas chromatograph (6890N) was used to analyze the composition of the effluent. The biodegradability was calculated according to the COD and BOD values. The COD and BOD_5 were measured according to a standard method (APHA 2000) with a Hach spectrophotometer (DR2800) and Hach BOD detector (BOD Trak II), respectively.

RESULTS AND DISCUSSION

Effect of Ozonation on Biodegradability

In an earlier paper (Zhang *et al.* 2017), the authors studied the effect of ozonation on the BOD_5 and BOD/COD ratio of BTPW in detail, under conditions of initial pH value 11, initial COD_{Cr} 386.61 mg/L, temperature 25 °C, and ozone concentration of 24.83 mg/L. The results are shown in Fig. 2.

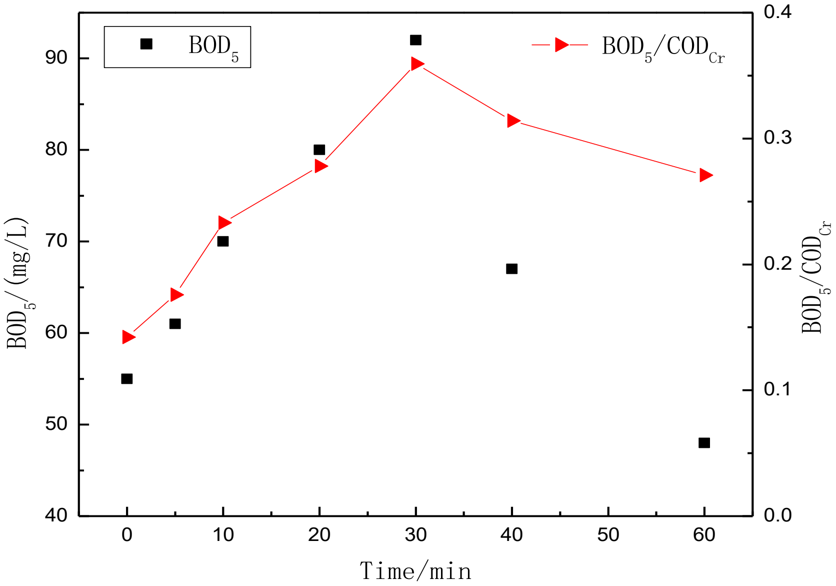

Fig. 2. Variation of COD_{Cr}, BOD_5, and BOD/COD ratio of BTPW during ozonation

Generally, the BOD_5 value first increased and then decreased, while COD_{Cr} decreased during the ozonation process. Therefore, the BOD/COD ratio first increased and then decreased during the 60-min ozonation process. The BOD/COD ratio before ozonation was less than 0.15, which means a poor biodegradability. After ozonation for 10 min, the BOD/COD ratio increased by 64%. The maximum BOD/COD ratio achieved was 0.36 when the ozonation time increased to 30 min, which means a 153% increase. Eventually, with the ozonation time being increased to 60 min, the BOD/COD ratio increased by 90% in comparison with the ratio at 0 min. Therefore, the biodegradability of the BTPW could be effectively enhanced by the ozonation treatment.

The great increment of BOD/COD ratio from 0 min to 30 min can be attributed to the quick degradation of macromolecular organic matter in the wastewater into low molecular mass organic matter during this period, which caused the dramatic increase of BOD but decrease of COD_{Cr}. However, during the subsequent 30 minutes, the structural changes of smaller molecules began to be the dominant reaction of the treatment. Thus, despite that the COD_{Cr} was still decreasing, the BOD was decreasing in a higher velocity, which therefore led to the tendency of firstly rising and then falling of BOD/COD ratio as well as the maximum ratio at 30 minutes during the ozonation treatment.

Effect of the Ozonation Treatment on the BTPW

UV-VIS analysis

The UV-VIS spectra of the wastewater for the various ozonation treatment times are shown in Fig. 3. There were four distinct absorption bands in the wastewater before ozonation treatment, which were at 195 nm to 200 nm, 210 nm to 215 nm, 223 nm, and 225 nm. The UV absorption peaks of the effluent changed noticeably during the ozonation treatment. After ozonation for 60 min, the absorption peak of the wastewater at 195 nm to 200 nm was reduced, which indicated that the structure of the most absorbed material changed during the ozonation treatment. Meanwhile, the peaks at 254 nm and 280 nm of the wastewater were reduced by 87.4% and 91.5%, respectively. The UV absorbances at 254 nm and 280 nm were mainly caused by the soluble aromatic derivatives and lignin-derived compounds commonly found in pulp-mill effluent, and these reductions indicated that removal or structural change of the aromatic compounds and lignin-derived substances in the BTPW occurred during the ozonation treatment. The UV spectra of the wastewater were blue-shifted, which may have been related to the structural changes of the compounds during the ozonation treatment, such as large molecules of aromatic aldehydes and ketones becoming small molecules of aliphatic aldehydes and ketones.

The ratio of the UV absorbances at 253 nm and 203 nm (A_{253}/A_{203}) can reflect the degree of substitution and types of substituents on the aromatic rings (Nishijima and Speitel Jr. 2004). When the substituents on the aromatic ring are mainly fatty chains, the A_{253}/A_{203} ratio is generally low. When the structure of the substituents is complex and the contents of carbonyls, carboxyls, hydroxyls, and esters are higher, the A_{253}/A_{203} value is relatively higher. With an increase in the ozone treatment time, the A_{253}/A_{203} value gradually decreased. Eventually when the ozonation time was increased to 60 min, the A_{253}/A_{203} value decreased by 68.6%, which indicated that the substituents on the aromatic ring of the refractory substances in the wastewater had become mainly aliphatic chains. Thus, the molecular structure became relatively simple as the aromatization degree was low. The organic substances content was greatly reduced, and the composition was simpler after the treatment. These observations strongly suggested that the ozonation treatment can improve the biodegradability of the BTPW by changing the structure of the refractory organic compounds to make them biodegradable.

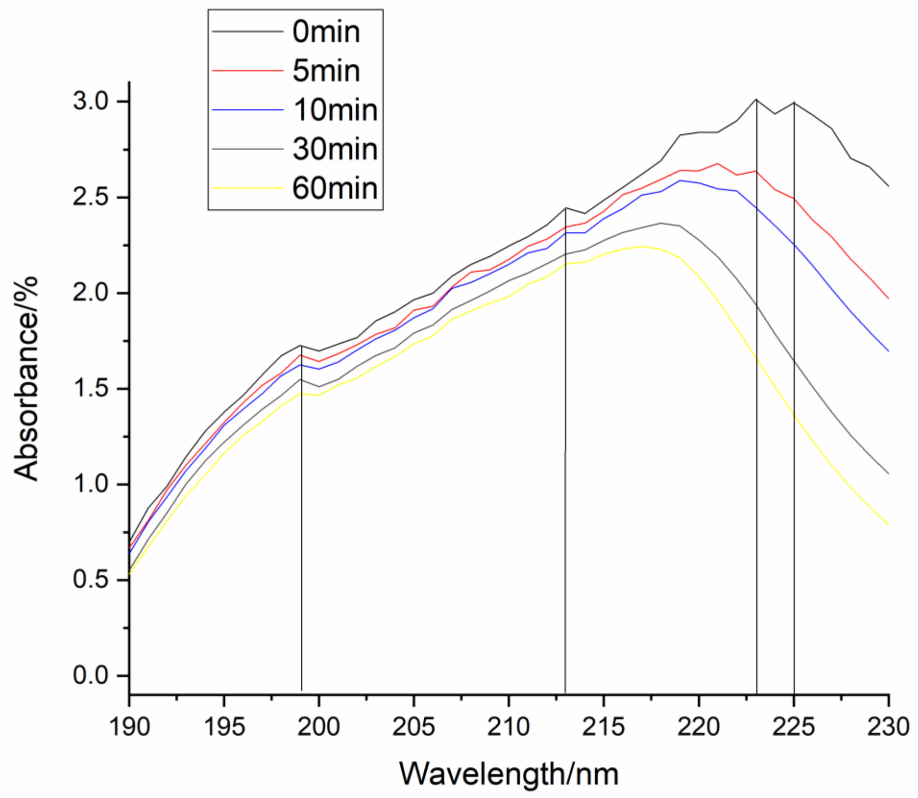

Fig. 3. UV-VIS spectra of the BTPW for various ozonation treatment times

FT-IR analysis

The FT-IR spectra of the BTPW for various ozonation treatment times is presented in Fig. 4. The band characteristics of the wastewater in the regions of 3400 cm^{-1} (H-bonded OH stretching of carboxyls, phenols, and alcohols), 1600 cm^{-1} to 1650 cm^{-1} (C=O stretching of COO-, ketonic C=O, and aromatic C=C conjugated with COO-), and 1400 cm^{-1} (aliphatic CH bending and COO asymmetric stretching) should be noted (Zaki and El-Gendy 2014).

For the BTPW sample before the ozonation treatment, the transmittance peaks at 1640.3 cm^{-1} and 3445.9 cm^{-1} represented C=O stretching and N-H bending, respectively, which suggested the possible presence of amide groups. The peaks at 1119.2 cm^{-1} and 618.7 cm^{-1} were related to the presence of inorganic sulfates. During the ozonation treatment, remarkable changes occurred. For instance, new peaks appeared at 1412.7 cm^{-1} at 5 min, 1411.2 cm^{-1} at 10 min, 1414.3 cm^{-1} at 30 min, and 1414.3 cm^{-1} at 60 min, which could all be attributed to O-H bending. New peaks also appeared at 1134.8 cm^{-1}, 1127.2 cm^{-1}, 1127.4 cm^{-1}, and 1132.3 cm^{-1} at 5 min, 10 min, 30 min, and 60 min respectively, which corresponded to C=O stretching and may have explained the increase in the BOD_5/COD_{Cr} ratio and BOD_5 during ozonation because compounds with these bonds, such as carboxylic acids, are very likely to be biodegradable. Thus, the FT-IR analysis results indicated that the improvement in the biodegradability can be partly attributed to the structural changes in the BTPW organic matter caused by the ozonation treatment, which are supposed to start at the very beginning of the treatment.

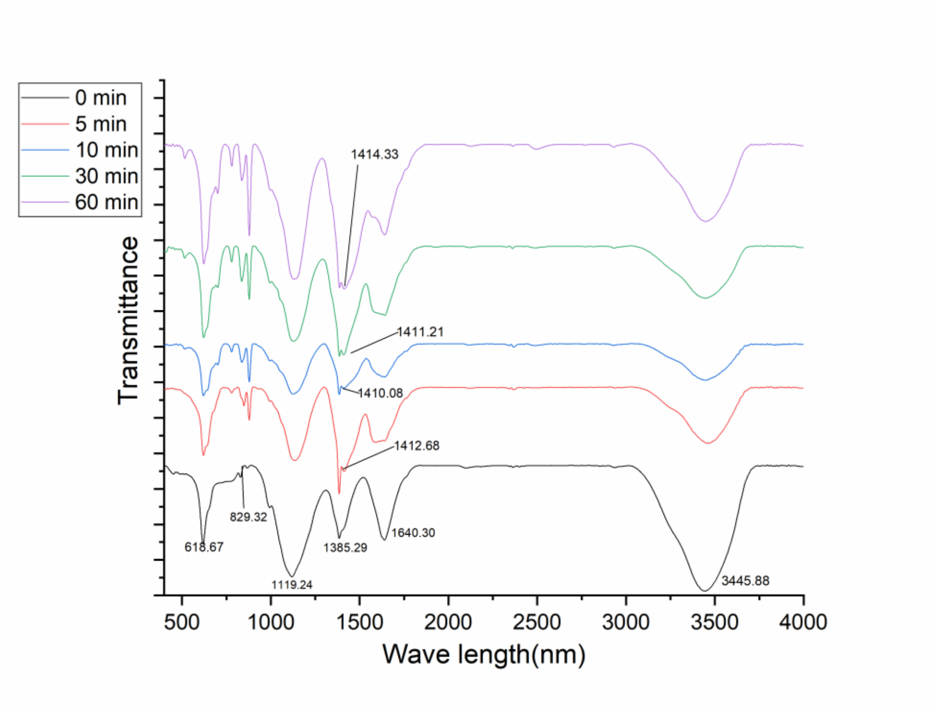

Fig. 4. FT-IR spectra of the BTPW for various ozonation treatment times

GPC

The GPC chromatograms of the BTPW for various ozonation treatment times are presented in Fig. 5. For the BTPW before the ozonation treatment, the peak was at the retention time of 16.2 min.

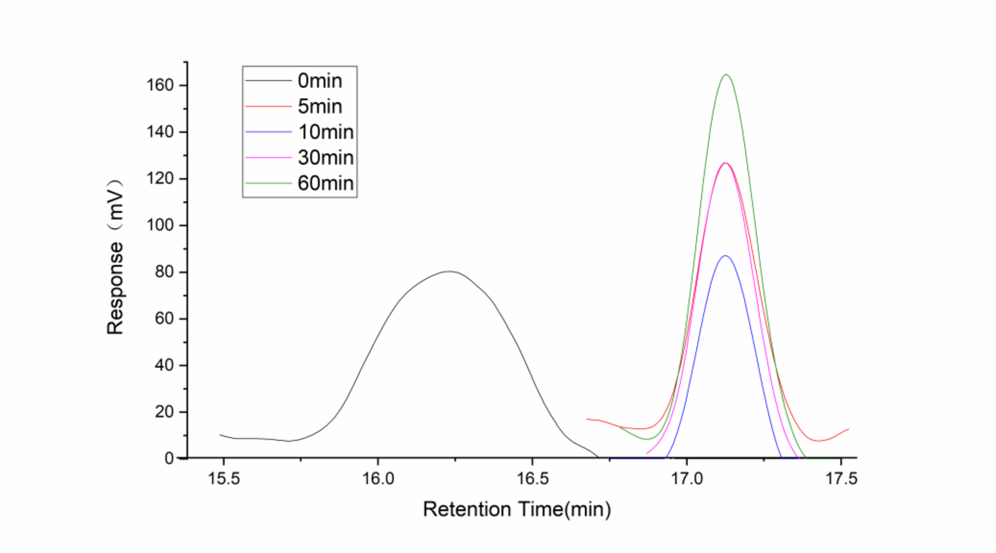

Fig. 5. GPC chromatograms of the BTPW for various ozonation treatment times

A remarkable change occurred at the beginning of the treatment, and then the corresponding retention time of the peak became 17.1 min after 5 min of the ozonation treatment, which suggested a decline in the molecular mass during the first 5 min of the ozonation treatment. During this time, a certain amount of macromolecular organic matter was degraded into micromolecular organic matter. With this degradation being dramatic, the consequence had a similar trend as that of the increase in the BOD_5 from 55 to 61 and the BOD_5/COD_{Cr} ratio from 0.142 to 0.176 during the first 5 min of the ozonation treatment, as the micromolecular organic matter was easier to biodegrade compared with the macromolecular organic matter. However, the retention time underwent almost no change during the next ozonation treatment, which indicated that the degradation of the macromolecular organic matter occurs mainly during the first several minutes of the ozonation treatment. With the FT-IR analysis results, the effect of the ozonation in the following minutes was mainly structural changes in the compounds.

GC

The GC chromatograms of the BTPW before and after the ozonation treatment are presented in Figs. 6 and 7, respectively, and the organic compounds detected in the BTPW before and after the ozonation treatment are summarized in Table 1. Except for some impurities that were not affected by the ozonation treatment, the changes to the main organic compounds in the BTPW before and after the ozonation treatment made it possible to explain the improvement in the biodegradability of the BTPW. Of all of the compounds that had a change in the occupancy rate, benzoic acid should be the first one to be noted, as it increased from 1.85% to 9.75%, which was an evident consequence of oxidation. Also, organic compounds, such as phthalic acid, isobutyl octyl ester, and 1H-indole-3-carboxylic acid,5-hydroxy- were generated because of oxidation during ozonation. This was supported by the FT-IR analysis, where it was found that ozonation could turn recalcitrant compounds into biodegradable compounds in the BTPW by affecting the structure of the refractory compounds. In contrast, the decrease and disappearance of some compounds in the BTPW during the ozonation treatment suggested the degradation of macromolecular organic matter. For instance, the large decrease in 6,6'-di-tert-butyl-2,2'-methylenedi-p-cresol from 10.36% to 1.98% and the disappearance of 1,2-bis(trimethylsilyl)benzene was evidence that the ozonation treatment improved the biodegradability by degrading the macromolecular organic matter into micromolecular organic matter.

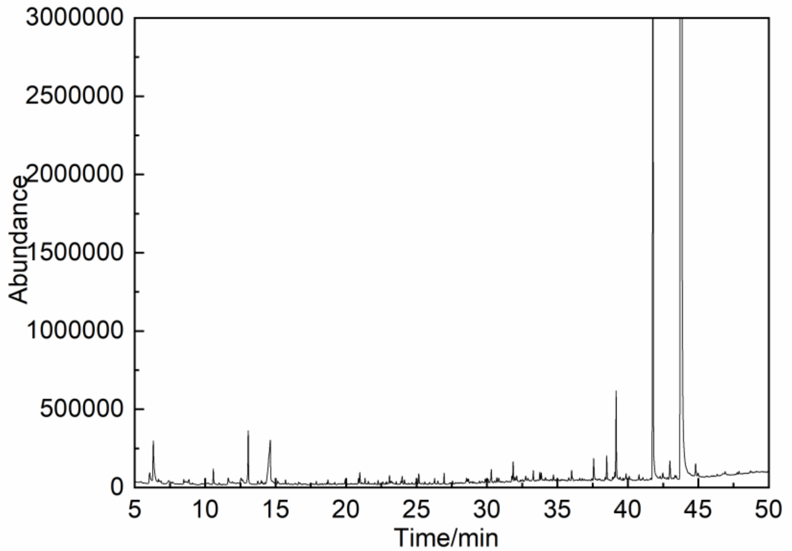

Fig. 6. GC chromatogram of the BTPW before the ozonation treatment

Table 1. List of Organic Compounds Identified by GC in the BTPW Before and After the Ozonation Treatment

Retention Time (min)	Compound	Proportion (%)		Matching (%)
		Before Ozonation	After Ozonation	
6.31	Ethane, 1,1,2,2-tetrachloro-	0.89	2.43	97
8.85	Cyclotetrasiloxane,octamethyl-	0.16	0.27	91
13.03	2Ethane, 2,2-dichloro-1,1,1-trifluoro-	0.67	1.17	81
14.53	Benzoic acid	1.85	9.75	95
23.08	Pentasiloxane, dodecamethyl-	0.1	0.51	75
26.95	Benzeneacetic acid, alpha,3,4-tris [(trimethylsilyl)oxy]-,trimethylsilyl ester	0.13	0.18	66
30.30	Cyclononasiloxane, octadecamethyl-	0.19	0.23	93
36.01	Benzeneacetic acid, alpha,3,4-tris[(trimethylsilyl)oxy]-,trimethylsilyl ester	0.14	0.18	67
37.58	1-Propene-1,2,3-tricarboxylic acid, tributyl ester	0.3	0.28	94
s39.17	Tributyl acetylcitrate	1.19	1.41	91
41.79	6,6’-Di-*tert*-butyl-2,2'-methylenedi-*p*-cresol	10.36	1.98	98
42.98	1,2-Benzenedicarboxylic acid, diisooctyl ester	0.28	0.34	85
6.06	Oxome-,methoxy-phenyl-	0.78	0	74
10.52	Propanenitrile,3-chloro-	0.2	0	68
11.64	1,2-Bis(trimethylsilyl)benzene	1.10	0	82
18.70	Cyclohexasiloxane,dodecamethyl-	0.1	0	90
19.95	2-(1,1-dimenthylethyl)-4-methyl	0.32	0	92
20.97	Benzene,1,4-diethoxy-	0.18	0	66
23.08	Ethanone,1-(3-hydroxyl-4-methoxyphenyl)-	0.1	0	75
23.98	Phenol,2,4-bis(1.1-dimethylethyl)	0.13	0	96
26.28	Hexadecane	0.09	0	98
28.55	Heptadecane	0.17	0	97
30.70	Octadecane	0.1	0	98
31.86	Phthalic acid,isobutyl undecylester	0.26	0	90
32.11	2H-1-Benzopyram,3,4-dihydro-	0.18	0	80
32.75	Decane,3,8-dimethyl-	0.12	0	94
33.28	7H-Dibenzo[b,g]carbazole,7-methyl	0.15	0	64
33.75	Dibutyl phthalate	0.21	0	94
34.71	Eicosane	0.07	0	98
38.49	Octacosyl acetate	0.35	0	93
39.87	4-(3-Aminobutyl)-2-methoxyphenol	0.13	0	87
6.81	1H-Indole-3-carboxylic acid, 5-hydroxy-	0	0.78	74
31.85	Phthalic acid, isobutyl octyl ester	0	0.44	90
33.28	Octasiloxane, 1,1,3,3,5,5,7,7,9,9, 11,11,13,13,15,15-hexadecamethyl-	0	0.20	57
38.49	1,1,1,5,7,7,7-Heptamethyl-3,3-bis(trimethylsiloxy) tetrasiloxane	0	0.35	68
44.82	13-Methyl-tetradecanoic acid, pyrrolidide	0	0.25	38

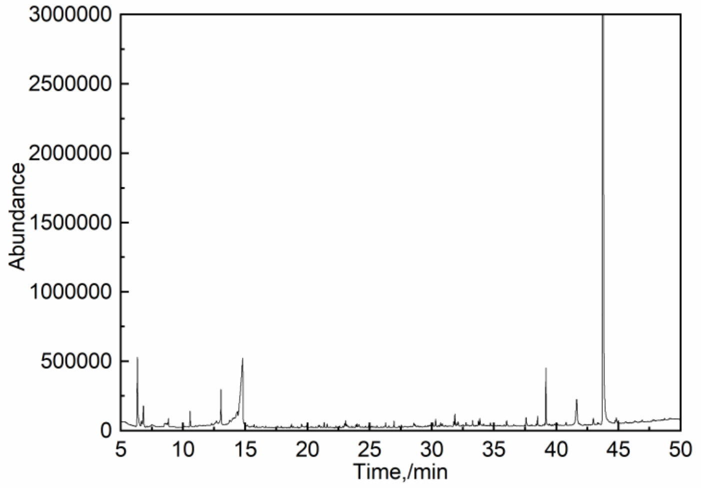

Fig. 7. GC chromatogram of the BTPW after the ozonation treatment

CONCLUSIONS

1. Because of the strong oxidizing ability of ozone, ozonation can turn recalcitrant compounds into biodegradable compounds in the BTPW by changing the structure of the refractory compounds and by degrading the macromolecular organic matter into micromolecular organic matter.
2. It was proposed that the degradation of macromolecular organic matter occurred mainly during the first several minutes of the ozonation process, and the structural changes were thought to occur over an hour. It was also suggested that both processes contributed to the improvement of the biodegradability.

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