Characteristics of Pollution from Waste Liquor of Poplar Pre-Conditioning Refiner Chemical Alkaline Peroxide Mechanical Pulping

Zong-zheng Yang,[a,*] Jie Zhang,[b] Meng-yao Zhang,[b] Ming-yue Wang,[b] and Jing-guo Cao [a,*]

The molecular weight distribution and composition of organic pollutants from chemi-mechanical pulping waste liquor was studied using ultra-filtration, Fourier transform infrared spectra, and gas chromatography-mass spectrometry. The concentration of dissolved chemical organic compounds was approximately 1.81×10^4 mg·L^{-1}. In addition, the wastewater had poor biodegradability. The chemical oxygen demand (COD) was primarily composed of small molecular organic pollutants, and the larger pollutants in the waste liquor were its primary source of color. The data indicated that there were chromophoric and auxochrome groups in the waste liquor. The waste liquor contained 38 types of organic pollutants, which were aromatic compounds, including phenols, ketones, alcohols, and fatty acids.

Keywords: Pre-conditioning refiner chemical alkaline peroxide mechanical pulping (P-RC APMP) effluent; Pulping waste liquor; Ultra-filtration; Fourier transform infrared spectroscopy; Chromatography

Contact information: a: Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin 300457, Tianjin, China; b: College of Marine and Environment, Tianjin University of Science and Technology, Tianjin 300457, Tianjin, China;
** Corresponding author: yzz320@tust.edu.cn; cjg@tust.edu.cn*

INTRODUCTION

The high pollution and energy consumption of the pulp and paper industry has led to a variety of problems, including water and raw material shortages. Poplar is a raw material most commonly used in the pulp and paper industry. This wood is characterized by its rapid growth, high cellulose content, high degree of whiteness, and easy softening. It has been widely used in the production of chemical and mechanical pulp (Hou *et al*. 2014).

Poplar chemi-mechanical pulping is a typically high-yield pulping process, which can be up to 95% efficient. The main pollutants in the wastewater are from lignin and its derivatives, fine cellulose, hemicellulose, polysaccharides, and other organic compounds that are dissolved during the pulping process. In addition, the waste liquor contains significant amounts of biological toxins, such as resin acid, phenol, toluene, and aldehyde (Chandra and Singh 2012), which causes considerable damage to the receiving waters (Zhang *et al*. 2012). Pulping waste liquid belongs to the organic waste liquid in high concentration. The organic waste liquid has a high concentration of organic matter that is produced and discharged as effluent. Therefore, the residual contaminant concentration is high, and the waste liquor does not reach a quality of water suitable for discharge to the environment after traditional processing techniques (Liu *et al*. 2011). However, the efficiency of the waste liquor treatment is related to the type of organic compounds. Therefore, distributing organic materials with different molecular weights in waste liquor

is useful for selecting a treatment process and studying the degradation mechanisms of organic compounds (Leiviska *et al*. 2009). Therefore, studying the pollution characteristics of pulping waste liquor is meaningful.

At present, conventional treatment methods for treatment of pulping wastewater include two sides: a physical-chemical method and a biological method (Hubbe *et al*. 2016). As the two methods both have some deficiencies, the two approaches are often employed in combination to deal with waste liquid in practical applications. In previous studies, modern analysis and testing techniques have been commonly employed to detect and identify toxic organic pollutants in waste water. The molecular weight distribution of the contaminants in alkaline-peroxide mechanical pulping (APMP) waste liquor and the composition of small organic pollutants were later examined using the ultra-filtration separation method (Liu and Hu 2007) and gas chromatography-mass spectrometry (GC-MS), respectively. The features of the pollution and the characteristic pollutants in the bleaching effluent of southern hardwood chemical pulp have been investigated using data obtained from infra-red (IR), ultraviolet (UV), and GC-MS (Lei *et al*. 2012). These technologies provide a foundation for the study of non-biodegradable pulping waste liquors. Because poplar pulping waste liquor has complex components, a bright color, and high chemical oxygen demand, research on the detection of its organic pollutants is less frequently reported.

The various molecular weight distributions of the contaminants and organic pollutants and the functional structure of pre-conditioning refiner chemical alkaline peroxide mechanical pulping (P-RC APMP) waste liquid were analyzed by ultra-filtration, Fourier transform infrared spectroscopy (FTIR), and GC-MS. The pollution characteristics of poplar APMP P-RC pulping waste liquor were analyzed, and the characteristics of pollutants and the difficult degradation of pollutants were identified. The present work attempts to identify the primary organic contaminants to provide a theoretical basis for treating contaminants and the biodegradation mechanisms of waste liquor from poplar P-RC APMP. In order to prepare for the subsequent use of pulping waste liquid as the acclimation function of the substrate to acclimate the functional microflora, making preparation by using the pulping waste liquid which has been treated by degradation of fungus to realize the resource utilization of the pulping waste liquid.

EXPERIMENTAL

Materials

Sample collection

Samples were collected during the preimpregnation process from poplar P-RC APMP in a paper factory in Yanzhou, Shandong.

Methods

Sample preparation

The waste liquor was filtered with a pore size of 0.45 μm before the trials.

Molecular weight distribution of the pollutants in the pulping waste liquor

Ultra-filtration is a mature technology in membrane separation technology, and its separation mechanism is considered as a physical screening process. The UF membrane

is an organic membrane that allows the passage of water, inorganic salts, and small molecules. In this study, the molecular weight distribution of pollutants in waste liquid was investigated by using the MSC cup ultrafiltration device produced by American Millipore company. The ultra-filtration (UF) membrane was made from polyethersulfone (PES). According to the manufacturer (Millipore, Boston, MA, USA), the membranes exhibited cut-off values of 5 kDa, 10 kDa, and 25 kDa. The characteristics of the different filters and membranes are shown in Table 1. The membranes were pre-treated by soaking in ethanol for 1 h or washing with 0.3% NaOH and 100 mL of ultrapure water. The filtration device was manufactured by Millipore and operated in the batch mode.

The waste liquor was poured into the filtration equipment and magnetically stirred. After regulating the pressure of the pump, the water filtration equipment was stored at 25 °C, and the samples were collected for measuring the pH, turbidity, chromaticity, and conductivity to determine the amount of chemical oxygen demand (COD), soluble solids, ethanol, and soluble organic matter. Each experiment was repeated in triplicate.

Table 1. Specifications of the Separation Membranes

Membrane	Material	Cut-off value
UF 25000	PES	> 25 kDa
UF 10000	PES	> 10 kDa
UF 5000	PES	> 5 kDa

Fourier transform infrared (FTIR) spectrometry

Exactly 50 mL of the pulping waste liquor, previously evaporated, concentrated, and dried, was collected. Approximately 15 mg of the powder was used to make the sample according to the potassium bromide tableting technique. A Vector 22 FTIR spectrometer (Bruker, Karlsruhe, Germany) was used to measure the transmittance at wave numbers from 4000 cm^{-1} to 400 cm^{-1} and a resolution of 4 cm^{-1}.

Gas chromatography analysis

First, the pulping waste liquor was extracted using methylene chloride and diethyl ether. Second, the organic phase was extracted using quantitative ethyl acetate after being dried in a vacuum dryer. Finally, the extracted samples were analyzed using an MS4000 GC-MS (Varian/Agilent, Santa Clara, CA, USA) (Lei *et al*. 2012a).

Determining the pulping waste liquor quality index

The dissolved oxygen concentration (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD), chromaticity, amount of total soluble solids, amount of soluble organic matter, turbidity, pH, conductivity, amount of ammonia nitrogen, total phosphorus, total phosphate, and reducing sugar content were measured using a published method (SEPA 2002).

The metal ion concentration was measured using an inductively coupled plasma mass spectrometer (ICP-MS, Stage vacuum interface technology, Houk and Fassel, Iowa, USA). Acid-soluble lignin content was measured at 205 nm (GB 10337 2008). The SiO_2 content was investigated using the weight method (Zhou and Zhang 1992). The extracted hemicellulose was measured using ethanol precipitation (Bian *et al*. 2010).

RESULTS AND DISCUSSION

Characteristics of the Pre-Conditioning Refiner Chemical Alkaline Peroxide Mechanical Pulping Waste Liquor

Table 2 shows the water quality indicators of the P-RC APMP waste liquor. The pH was 6.38, resulting from organic acid dissolved during the pre-impregnation process (Xiao and Feng 2012). The concentration of dissolved organic compounds was high, and the COD was 18108.1 mg·L^{-1}. In addition, the value of BOD5/COD was 0.17, indicating poor biodegradability of the waste liquor. This may have been attributed to the following reasons. First, the soluble substances in the wood, such as alkali extract, chitosan, and furfural acids or other organic matter, were dissolved during the dipping process. Secondly, a small amount of debris fell into the waste liquor when the wood was crushed and torn during the extrusion process. Finally, the mechanical action may have caused lignin and drug residue to be drawn into the waste liquor, leading to a higher COD concentration and a higher total amount of solids (Liu and Hu 2007; Cai *et al*. 2010). The hemicellulose content of 11.6 g·L^{-1} was attributed to contamination after extraction and contained inorganic salts or organic matter with a low molecular weight (Liu and Hu 2007).

Table 2. Primary Wastewater Quality Indicators of Waste Liquor from Poplar Pre-Conditioning Refiner Chemical Alkaline Peroxide Mechanical Pulping

Parameter	Result	Parameter	Result
pH	6.38	PO_4^{3-}-P/mg·L^{-1}	62.18
COD/mg·L^{-1}	1.81×10^4	SS/mg·L^{-1}	7.30×10^3
BOD_5/mg·L^{-1}	3.04×10^3	Color/C.U	679
BOD_5/COD	0.17	Turbidity/NTU	509
Total solid/mg·L^{-1}	1.80×10^4	(Cr^{3+}/Cr^{6+})/mg·L^{-1}	5.98×10^{-4}
Inorganics/mg·L^{-1}	6.00×10^3	Cu^{2+}/mg·L^{-1}	4.78×10^{-5}
SiO_2/mg·L^{-1}	350	Zn^{2+}/mg·L^{-1}	1.54×10^{-6}
Reducing sugar/mg·L^{-1}	1.76×10^3	Cd^{2+}/mg·L^{-1}	4.7×10^{-3}
Total sugar/mg·L^{-1}	3.24×10^3	Pb^{2+}/mg·L^{-1}	3.73×10^{-4}
Acid-soluble lignin/mg·L^{-1}	1.74×10^3	K^+/mg·L^{-1}	677
Hemicellulose/mg·L^{-1}	1.16×10^4	Mg^{2+}/mg·L^{-1}	792.4
NH_3-N/mg·L^{-1}	77.59	Ca^{2+}/mg·L^{-1}	184.7
TP/mg·L^{-1}	73.93	(Fe^{3+}/Fe^{2+})/mg·L^{-1}	14.5

COD, chemical oxygen demand; BOD, biochemical oxygen demand; TP, total phosphorus; SS, suspended solid

In addition, the waste liquor was dark brown, and its chromaticity was 679 CU, indicating a large quantity of chromophoric and auxochrome groups. These groups usually are dissolved during the prepregnation dissolution and alkali extraction processes of lignin (Garg *et al*. 2005; Leiviskä *et al*. 2008; Lei *et al*. 2010). Furthermore, inorganic

elements, such as nitrogen, phosphorus, and metal ions (K^+ and Mg^{2+}) were found in the waste liquor.

Molecular Weight Distribution of Pollutants in the Pre-Conditioning Refiner Chemical Alkaline Peroxide Mechanical Pulping Waste Liquor

In this experiment, ultra-filtration of pollutants in the waste of poplar P-RC APMP was carried out by ultrafiltration membrane with molecular weight of 5 kDa, 10 kDa, and 25 kDa, respectively. And the change of pollutants in waste liquid before and after ultrafiltration was measured. The results are shown in Table 3.

Table 3. Quality Parameters of Filtrate after Ultra-filtration

Parameter	pH	COD ($mg \cdot L^{-1}$)	Total soluble solid ($mg \cdot L^{-1}$)	Dissolved organics ($mg \cdot L^{-1}$)	Turbidity (NTU)	Color (C.U)	Conductivity ($uS \cdot cm^{-1}$)
Pulping waste liquor	6.38	1.89×10^4	1.80×10^4	1.20×10^4	509	679	7.93
25 kDa	8.03	1.71×10^4	1.19×10^4	6.49×10^3	7.43	390	7.18
10 kDa	7.75	1.60×10^4	1.12×10^4	6.05×10^3	3.15	308	7.68
5 kDa	7.78	1.35×10^4	9.89×10^3	5.50×10^3	2.79	140	7.52

COD, chemical oxygen demand

Table 3 shows that the COD concentration, chromaticity, turbidity, total amount of soluble solids, and total amount of soluble organic matter decreased with decreasing membrane pore size (filter), relative to the molecular mass. However, the small components were the primary pollutants, and the 5 kDa fraction included a COD content of 1.35×10^4 $mg \cdot L^{-1}$. Compared to the original acidic waste liquor, the filtrate was alkaline after the high molecular weight (> 25 kDa) filter was applied, and the pH of other filtrates were neutral within the medium molecular weight range (< 10 kDa). There was no noticeable change in the conductivity, indicating that the salt content of the waste liquor was unaffected by ultra-filtration. The total dissolved solids exhibited no obvious variations, which was consistent with the change in the conductivity.

Table 4 shows the concentrations of the COD and total soluble solids and the color of different fractions of the waste liquor, measured using chemical methods.

Table 4. Contribution of Compositions with Different Molecular on Effluent Characteristics

Parameter	COD ($mg \cdot L^{-1}$)	COD proportion of total COD (%)	Total soluble solids ($mg \cdot L^{-1}$)	Total soluble solids proportion of the total in pulping waste liquor (%)	Color (CU)	Color proportion of the total color (%)
> 25 kDa	1.82×10^3	9.63	6.13×10^3	34.06	289	42.56
10 to 25 kDa	1.13×10^3	5.97	6.50×10^2	3.61	82	12.08
5 to 10 kDa	2.50×10^3	13.21	1.34×10^3	7.44	168	24.74
5 kDa	1.35×10^4	71.18	9.88×10^3	54.89	140	20.62

(COD: Chemical Oxygen Demand)

The low-mass organic pollutants in the pulping waste liquor were the primary components of the COD; however, the pollutants with larger molecular weights were the main source of its chromaticity (Table 4). This result was attributed to the lignin molecules that were broken during the extraction process or the fiber fines and hemicelluloses that were degraded during the impregnation process. As a result, new chromophoric groups, auxochrome groups, and colored matter were produced (Xie and Zhan 2001). Therefore, the 25 kDa fraction of the waste liquor accounted for 42.6% of the waste liquor's chromaticity, 9.6% of the total COD, and 34.1% of the total soluble solids.

The components of the 10 to 25 kDa fraction of the waste liquor accounted for 6.0% of the COD, 0.65% of the total soluble solids, and 12.1% of the chromaticity. The components of the 5 to 10 kDa fraction accounted for 13.2% of the COD, 1.3% of the total soluble solids, and 24.7% of the chromaticity of the waste liquid. The 5 kDa fraction of the waste liquid accounted for 70% of the COD and 20% of the residual chromaticity that had not been removed by ultrafiltration. The small compounds were a mixture of the degradation products of lignin, hemicellulose, wood extract, and fines (Liu *et al*. 2011).

Consequently, the COD, chromaticity, and total amount of soluble solids insufficiently described the pollution characteristics of the pulping waste liquid. Modern large-scale instruments can detect the compositions and concentrations of pollutants and perform quantitative and qualitative analyses, especially for toxic pollutants (Liu and Hu 2007).

Fourier Transform Infrared Spectra Analysis

Fourier transform infrared spectroscopy is a simple, non-destructive, fast, highly sensitive, and pollution-free process (Durig *et al*. 2008). Molecular groups and chemical groups in pulping waste liquor were detected using FTIR spectroscopy (Fig. 1 and Table 5).

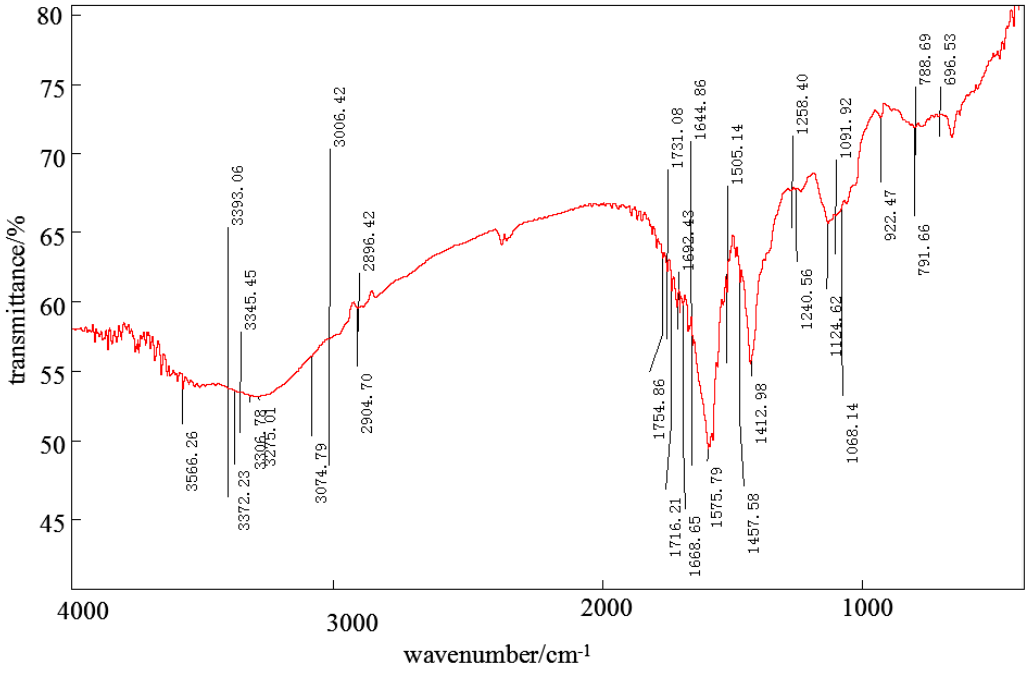

Fig. 1. Fourier transform infrared spectrum of poplar wood after P-RC APMP

Table 5. Analysis of the Infrared Spectrum

Peak	Wavenumber (cm^{-1})	Source of Absorbance
1	3200 to 3645	O-H stretch
2	3074.79, 3006.42	Aromatic C-H stretch
3	2904.7	Olefin CH_2 symmetric stretch
4	2896.42	Alkene C-H stretch
3	1754.86, 1731.08, 1716.21, 1692.43	Carbonyl stretch
4	1668.65, 1644.86	Olefin C=C stretch
5	1575.79, 1505.14, 1457.58, 1412.98	Alkene C-C stretch
6	1258.4, 1240.56	Aromatic ether C-O-C stretch
7	1124.62, 1091.92	Saturated fat ether C-O-C stretch
8	1068.14	Linear C-C stretch
9	922.47	O-H out-of-plane bending
10	791.66, 788.69, 696.53	Aromatic ring C-H out-of-plane bending

Figure 1 shows the spectroscopic profiles for wavenumbers in the region from 4000 to 400 cm^{-1}. Hydroxyl groups were present between 3200 and 3645 cm^{-1}, as shown in Table 5, because of the stretching vibrations of OH from hydrone, phenol, or alcohol (Lei *et al*. 2012a). There were two absorption peaks at 3074.79 and 3006.42 cm^{-1}, which were attributed to the stretching of aromatic hydrocarbons (Andreas 2007). This result reflected the presence of numerous aromatic compounds in the pulping waste liquor. The bands at 2904.7 cm^{-1} and 2896.42 cm^{-1} were attributed to the stretching of olefin CH_2 and alkane C-H, respectively. The bands at 1754.86, 1731.08, 1716.21, and 1692.43 cm^{-1} were attributed to the stretching vibrations of C=O from a carbonyl group, ester carbonyl group, or aldehyde group. The bands at 1668.65 cm^{-1} and 1644.86 cm^{-1} were attributed the stretching of olefin C=C. The absorption spectra of the C-C bonds in aromatic rings exhibited peaks at approximately 1575.79, 1505.14, 1457.58, and 1412.98 cm^{-1}. In addition, peaks were centered at approximately 1258.4 to 1091.92 cm^{-1}, 1068.14 cm^{-1}, and 922.47 cm^{-1} for C-O-C, C-C, and O-H groups, respectively. Furthermore, the peaks at approximately 791.66 cm^{-1}, 788.69 cm^{-1}, and 696.53 cm^{-1} were assigned to the surface stretching of C-H bonds from the aromatic rings. The chromaticity of pulping waste liquid increased with carbonyl and hydroxyl groups, benzene rings, among others. In particular, carbonyl groups combined with benzene rings, forming conjugated double bonds, increased the chromaticity (Chen *et al*. 2007). In addition, hydroxyl groups were present as auxochrome groups in the waste liquor (Lei *et al*. 2012a).

In sum, the organic matter in the pulping waste liquor was resolved, generating hydroxyl groups, carbonyl groups, benzene rings, double bonds, carboxyl groups, esters, *etc*. Therefore, organic pollutants, such as aromatic compounds, alkanes, aldehydes, ketones, and esters (Lei *et al*. 2012a), were the primary components of the COD.

Characterization of the Organic Fraction of the Poplar Pre-Conditioning Refiner Chemical Alkaline Peroxide Mechanical Pulping Waste Liquor

To confirm the primary pollutants and the distribution of organic pollutants in the waste liquor, experiments were performed using GC-MS. The ion chromatography of the organic matter, after liquid-liquid extraction using methylene chloride and ethyl ether, is shown in Fig. 2.

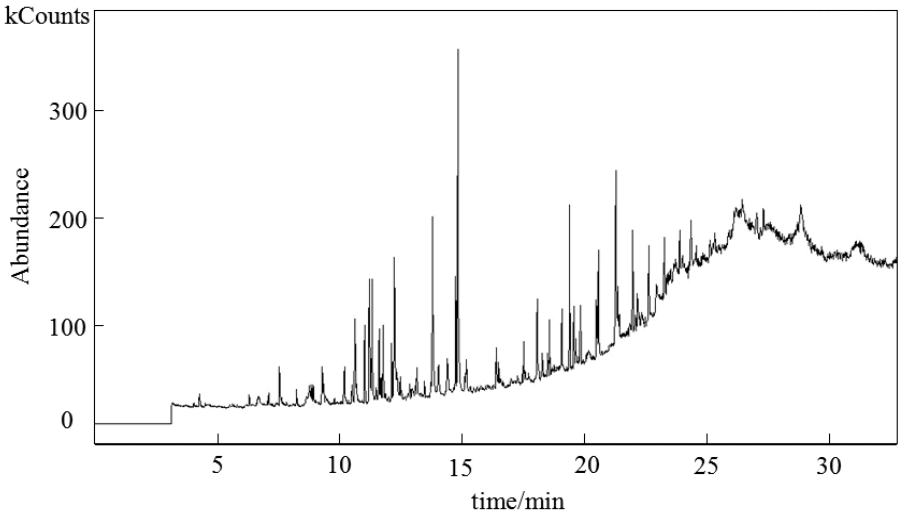

Fig. 2. Gas chromatography-mass spectrometry analysis of the poplar pre-conditioning refiner chemical alkaline peroxide mechanical pulping effluent

Target compounds were identified by matching their mass spectra with spectra obtained from the National Institute of Standards and Technology (NIST) library. Because of the lack of standard references for the different types of organic matter, the content of organic pollutants in water samples were expressed relative to the content determined by the GC-MS processing system. The results are shown in Table 6.

Table 6. Organic Pollutants in the Poplar Pre-Conditioning Refiner Chemical Alkaline Peroxide Mechanical Pulping Effluent According to Gas Chromatography-Mass Spectrometry

Peak	Residence Time (min)	Molecular formula	Compound	Peak area (% of total)
1	4.477	$C_7H_8O_2$	2-Methoxyphenol	0.60
2	7.311	$C_9H_{10}O_2$	4-Hydroxy-2-Methylacetophenone	0.41
3	7.744	$C_8H_{10}O_3$	2,6-Dimethoxyphenol	1.23
4	8.432	$C_8H_8O_3$	3-Hydroxy-4-methoxybenzaldehyde	0.46
5	9.049	$C_{10}H_{12}O_2$	trans-2-methoxy-4-propenylphenol	0.49
6	9.125	$C_{10}H_{14}O_2$	2-methoxy-4-propyl-Phenol	0.69
7	9.484	$C_{11}H_{14}O$	1-(2,4,6-trimethylphenyl)-ethanol	0.87
8	9.544	$C_{10}H_{10}O_2$	4-Hydroxybenzylideneacetone	0.34
9	9.994	$C_{10}H_{12}O_3$	3-Methoxy-4-hydroxypropiophenone	0.11
10	10.398	$C_{11}H_{16}O_2$	4-Hydroxy-3-tert-butylanisole	1.56
11	10.557	$C_{11}H_{16}O_2$	5,6,7,7a-Tetrahydro-4,4,7a-trimethyl-2(4H)-benzofuranone	0.11
12	10.690	$C_{10}H_{12}O_3$	4-Propoxybenzoic acid	0.89
13	10.829	$C_9H_{12}O_4$	3,4,5-Trimethoxyphenol	2.56
14	11.407	$C_9H_{10}O_4$	Homovanillic acid	5.33
15	11.525	$C_9H_{10}O_4$	3,4-Dimethoxy-5-hydroxybenzaldehyde	4.11
16	11.683	$C_{10}H_{12}O_3$	Coniferyl alcohol	0.56
17	11.809	$C_{12}H_{16}O_2$	1,2-Dimethoxy-4-(2-propenyl)benzene	2.24

Peak	Residence Time (min)	Molecular formula	Compound	Peak area (% of total)
18	11.883	$C_{11}H_{12}O_3$	3-(2-methoxy-5-methyl phenyl)acrylic acid	0.71
19	11.975	$C_{11}H_{14}O_3$	4-Allyl-2,6-dimethoxyphenol	2.47
20	12.209	$C_{10}H_{12}O_3$	3-Methoxy-4-hydroxybenzalacetone	0.2
21	12.322	$C_{10}H_{12}O_4$	4'-Hydroxy-3',5'-dimethoxyacetophenone	1.83
22	12.440	$C_{10}H_{12}O_3$	4-methoxy-2,6-dimethyl Benzoic acid	6.72
23	12.669	$C_{11}H_{14}O_4$	1-(2,4,6-Trihydroxy-3-methylphenyl)-1-butanone	0.56
24	13.065	$C_{11}H_{12}O_4$	3,4-Dimethoxycinnamic Acid	0.48
25	13.283	$C_{14}H_{10}O_2$	2,2'-Biphenyldicarbaldehyde	0.29
26	13.344	$C_{11}H_{12}O_4$	3,5-Dimethoxy-4-hydroxycinnamaldehyde	0.92
27	13.981	$C_{10}H_{12}O_5$	acid,4-hydroxy-3,5-dimethoxy-enzeneacetic	8.46
28	14.232	$C_{10}H_{10}O_5$	6-formyl-2,3-dimethoxy-Benzoic acid	1.77
29	14.586	$C_{16}H_{32}O_2$	Hexadecanoic acid	0.53
30	14.928	$C_{11}H_{12}O_4$	2,3-Dimethoxycinnamic acid	3.97
31	15.013	$C_{11}H_{14}O_4$	3-(2,5-Dimethoxyphenyl)propanoic acid	15.73
32	15.675	$C_{11}H_{14}O_5$	3,4,5-Trimethoxyphenylacetic acid	0.35
33	20.732	$C_{18}H_{38}$	Octadecane	11.19
34	21.440	$C_{20}H_{42}$	Eicosane	7.79
35	22.132	$C_{27}H_{56}$	Heptacosane	6.32
36	22.789	$C_{28}H_{58}$	Octacosane	3.89
37	24.522	$C_{27}H_{42}O$	Cholesta-3,5-Dien-7-One	2.2
38	25.307	$C_{29}H_{50}O$	Beta-Sitosterol	1.11

There were various organic pollutants in the P-RC APMP waste liquor (Fig. 2). The GC-MS data showed that the pulping waste liquor contained a large amount of organic compounds, primarily phenols, ketenes, alcohols, organic acids, among others (Table 6), which was consistent with the groups represented by the FTIR absorption peaks.

Lignin contains phenylpropane, which was connected by C-C and C-O bonds and exhibits numerous functional groups, including phenolic hydroxyl, methoxy, carboxyl, and carbonyl groups. Lignin was available for hydroxymethylation, carboxylation, and alkylation because the chemical bonds were broken during the chemical and extrusion processes (Lei *et al*. 2012b). Therefore, the compounds, guaiacol, lilac, alcohol, coniferyl alcohol and vanillin, were found in the waste liquor (Table 5).

The results of the analysis showed that there was a large amount of alkane (29.19%). Three major EPA pollutants (Fang and Hu 1993) were found in the waste liquor: octadecane, eicosane, and octacosanol. Because phenolic hydroxyl groups of lignin are hydrophilic, lignin decomposes to phenolic compounds easily. Therefore, six types of phenolic compounds were detected in the pulping waste liquor, totaling 7.7%. Because of the oxidation of methyl and hydroxylmethyl groups in benzene rings and side chains, aldehyde, carboxylic acid, and their derivatives were created. As a result, there

were nine types of organic acids, including benzoic acid, benzene acetic acid, and cinnamic acid, totaling 43.17%. Moreover, 3-(2, 5-dimethyl phenyl) propionic acid, an unsaturated acid, was the most prevalent and reached 15.73% of the waste liquor. In addition, five types of aromatic aldehyde and nine types of ketone were detected, with relative contents of 7.55% and 9.76%, respectively. Finally, alcohols and ethers were found in the waste liquor; however, two types of priority control pollutants, diethyl phthalate and dibutyl phthalate, were not detected (Cox and Deshusses 1998). This was primarily related to the fact that lignin and its derivatives were broken down into low molecular weight organic compounds, while benzene rings and their side chains were fractured or combined to form phenols and organic acids after pharmaceutical impregnation with hydrogen peroxide. These results were consistent with the FTIR analysis.

According to the results of ultra-filtration, FTIR analysis, and GC-MS, low molecular weight organic compounds, especially aromatic compounds, such as carbonyl, carboxyl, and ether groups, were the primary pollutants in the pulping waste liquor. The higher content of aromatic compounds showed that these compounds were typical low-molecular-weight components of the pollution in pulping waste. These substances did not directly affect the chromaticity of the waste liquor; however, their biological (toxicity) effect on the biochemical treatment of waste liquor should be further studied.

CONCLUSIONS

1. Poplar APMP P-RC pulping waste liquor was acidic as the pH was 6.38. The concentration of dissolved organic compounds was high, and the COD was 18108.1 $mg \cdot L^{-1}$. Besides, the value of BOD5/COD was 0.17, which indicates the poor biodegradability of the waste liquor. The waste liquor was dark brown and chromaticity was 679 CU. In addition, inorganic elements, such as nitrogen, phosphorus, and metal ions (K^+ and Mg^{2+}) were found in the waste liquor.
2. The 5 kDa fraction of the waste liquor components indicated that 70% of the COD and 20% of the residual chromaticity of the waste liquor was not removed. The physical and chemical properties of the pollutants with molecular weights below 5 kDa require further study.
3. The organic pollutants in the pulping waste liquor were primarily benzene, hydroxyl, carboxyl, carbonyl, and conjugated double-bonding compounds, among others. The primary organic compounds were aromatic compounds, alkanes, ethers, esters, acids, *etc*. The primary chromophoric groups included carbonyl and double-bonded groups. The primary auxochrome groups included carboxyl, hydroxyl, and ether groups.
4. The GC-MS data showed that the pulping waste liquor contained a large amount of organic compounds such as primarily phenols, ketenes, alcohols, organic acids and so on. The results of the analysis showed that there was a large amount of alkane (29.19%). Three major EPA pollutants were found in the waste liquor: octadecane, eicosane, and octacosanol.

ACKNOWLEDGMENTS

The authors are grateful for financial support from the National Science and Technology Support Foundation of China (2011BAC11B04).

REFERENCES CITED

Andreas, B. (2007). "Infrared spectroscopy of proteins," *Biochimica et Biophysica Acta (BBA) – Bioenergetics* 1767(9), 1073-1101. DOI: 10.1016/j.bbabio.2007.06.004

Bian, J., Peng, F., Peng, P., Xu, F., and Sun, R. (2010). "Isolation and fractionation of hemicelluloses by graded ethanol precipitation from *Caragana korshinskii*," *Carbohydrate Research* 345(6), 802-809. DOI: 10.1016/j.carres.2010.01.014

Chandra, R., and Singh, R. (2012). "Decolourisation and detoxification of rayon grade pulp paper mill effluent by mixed bacterial culture isolated from pulp paper mill effluent polluted site," *Biochemical Engineering Journal* 61(15), 49-58. DOI: 10.1016/j.bej.2011.12.004

Cai, Q., Fu, F., and Shi, Y. (2010). "The effect of different P-RC APMP pulping process on effluent properties," *Paper Science & Technology* 29(2), 86-90. DOI: 10.3969/j.issn.1671-4571.2010.02.021

Chen, X., Huang, B., Gao, Y., and Dai, D. (2007). "On the more effective utilization of organic leftovers from paper pulp-preparation liquids," *Journal of Safety and Environment* 7(1), 107-111. DOI: 10.3969/j.issn.1009-6094.2007.01.032

Cox, H. H. J., and Deshusses, M. A. (1998). "Biological treatment of waste gas in biotrickling filters," *Current Opinion in Biotechnology* 9(3), 256-262. DOI: 10.1016/S0958-1669(98)80056-6

Durig, J. R., Pamela, T., Cohn, K. C., Durig, B. R., Zhou, X., Zheng, C., and El Defrawy, A. M. (2008). "Infrared and Raman spectra, conformational stability, structural parameters, *ab initio* calculations and vibrational assignments of aminodifluorophosphine," *Journal of Molecular Structure* 875(1-3), 406-418. DOI: 10.1016/j.molstruc.2007.04.045

Fang, L., and Hu, W. (1993). "Sieving principle, procedure and method for environmental priority pollutants," *Shanghai Environmental Sciences,* No.5, 1993, pp.37-39.

Garg, A., Mishra, I. M., and Chand, S. (2005). "Thermochemical precipitation as a pretreatment step for the chemical oxygen demand and color removal from pulp and paper mill effluent," *Industrial & Engineering Chemistry Research* 44(7), 2016-2026. DOI: 10.1021/ie048990a

GB 10337 (2008). "Raw material and pulp – Determination of acid-soluble lignin," General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Beijing.

Hou, Q. X., Wang, Y., Liu, W., Liu, L. H., Xu, N. P., and Li, Y. (2014). "An application study of autohydrolysis pretreatment prior to poplar chemi-thermomechanical pulping," *Bioresource Technology* 169, 155-161. DOI: 10.1016/j.biortech.2014.06.091

Hubbe, M. A., Metts, J. R., Hermosilla, D., Blanco, M. A., Yerushalmi, L., Haghighat, F., Lindholm-Lehto, P., Khodaparast, Z., Kamali, M., and Elliott, A. (2016). "Wastewater treatment and reclamation: A review of pulp and paper industry

practices and opportunities," *BioResources* 11(3), 7953-8091. DOI: 10.15376/biores.11.3.Hubbe

Lei, L., Ma, L, and Li, Y. (2010). "Electrocoagulation treatment of chemithermo-mechanical pulp (CTMP) chemical pretreatment effluent," Conference paper published Jun 2010 in 2010 4th International Conference on Bioinformatics and Biomedical Engineering. DOI: org/10.1109/icbbe.2010.5517125

Lei, L., Li, Y., and Ma, L. (2012a). "Pollution feature and characteristic pollutants of bleaching effluent of southern hardwood chemical pulp," *Journal of Chemical Industry and Engineering (China)* 63(1), 244-250. DOI: 10.3969/j.issn.1005-0930.2012.03.004

Lei, L., Ma, L, and Li, Y. (2012b). "Eucalyptus chemimechanical pulp effluent treatment with composite electrolysis electrochemical method and mechanism analysis," *Journal of Basic Science and Engineering* 20(3), 377-385. DOI: 10.3969/j.issn.0438-1157.2012.01.034

Leiviskä, T., Nurmesniemi, H., Pöykiö, R., Rämö, J., Kuokkanen, T., and Pellinen, J. (2008). "Effect of biological wastewater treatment on the molecular weight distribution of soluble organic compounds and on the reduction of BOD, COD and P in pulp and paper mill effluent," *Water Research* 42(14), 3952-3960. DOI: 10.1016/j.watres.2008.06.016

Leiviska, T., Ramo, J., Nurmesniemi, H., Poykio, R., and Kuokkanen, T. (2009). "Size fractionation of wood extractive, lignin and trace elements in pulp and paper mill wastewater before and after biological treatment," *Water Research* 43(13), 3199-3206. DOI: 10.1016/j.watres.2009.04.051

Liu, T., He, Z., Hu, H., and Ni, Y. (2011). "Treatment of APMP pulping effluent based on aerobic fermentation with *Aspergillus niger* and post-coagulation/flocculation," *Bioresource Technology* 102(7), 4712-4717. DOI: 10.1016/j.biortech.2011.01.047

Liu, Y., and Hu, H. (2007). "The separation and application of the hemicellulose from the process paper pulping," in: *China Association for Science 137th Young Scientists Forum*, Tianjin, China, TS74, pp. 69-76.

State Environmental Protection Administration (SEPA) (2002). *Water and Wastewater Monitoring and Analysis Methods* (4th Ed.), China Environmental Science Press, Beijing, China.

Xiao, X., and Feng, W. (2012). "Studies occurrence regularity and origination cause of pollutants in poplar APMP process," *China Pulp & Paper Industry* 33(4), 49-53. DOI: 10.3969/j.issn.1007-9211.2012.04.012

Xie, L., and Zhan, H. (2001). *The Principle and Process of Pulping*, China Light Industry Press, Beijing.

Zhang, C., Chen, J. N., and Wen, Z. G. (2012). "Alternative policy assessment for water pollution control in China's pulp and paper industry," *Resources, Conservation and Recycling* 66, 15-26. DOI: 10.1016/j.resconrec.2012.06.004

Zhou, S., and Zhang, K. (1992). "Advance in research on the technique of treating waste pulping liquid in small-scale straw pulp mills in China," *Rural Eco-environment* No.1, pp. 40-41.

Article submitted: June 7, 2016; Peer review completed: August 20, 2016; Revised version received: October 15, 2016; Accepted: November 2, 2016; Published: November 22, 2016.
DOI: 10.15376/biores.12.1.457-468