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Characterization and Analysis of Acetaldehyde Wastewater by Molecular Weight Distribution, Hydrophilicity, and Chemical Composition

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Abstract: Acetaldehyde is a typical toxic substance of the petrochemical industry. Dissolved organic carbon (DOC) plays an important role in wastewater treatment. Therefore, the molecular weight, hydrophilicity, and chemical composition of DOC in acetaldehyde wastewater were evaluated. First, the molecular weight (MW) distribution was investigated; the results showed that acetaldehyde wastewater was mainly composed of components with a MW less than 1 kDa, and possessed higher proportion of protein-like substances that were dominant contributors to membrane fouling. Then, the distribution of hydrophobicity was evaluated; hydrophobic bases were reported to be slowly biodegradable fractions due to the high humic content. Finally, gas chromatography–mass spectrometry (GC-MS) was utilized to determine chemical composition, and 30 pollutants were detected. Aldehydes, hydrocarbons, ketones, alcohols, furans, phenols, and organic acids were the dominant pollutants. Most of them were moderately toxic compounds. The comprehensive characterization of acetaldehyde wastewater will contribute to control strategies and sustainable development.

Keywords: acetaldehyde wastewater; gas chromatograph–mass spectrometer; hydrophobicity; molecular weight

1. Introduction

Acetaldehyde is an important fine and specialty chemical intermediate, mainly used in the production of acetic acid and the synthesis of pyridine, pentaerythritol, and n-butanol [1,2]. Due to its broad range of applications in manufacturing and human life, wastewater from manufacturing processes is increasing every year. When acetaldehyde wastewater is directly discharged into biological treatment systems, it poses a threat to microorganisms. The receiving water can be polluted by acetaldehyde wastewater, the environment and humans will be severely affected [3–5]. Because acetaldehyde wastewater possesses complex water quality and toxicity to microorganisms, studies focusing on acetaldehyde wastewater have become increasingly more popular.

Current studies have placed more emphasis on the removal of pollutants in aldehyde wastewater. Physical or chemical methods and biochemical methods were applied to aldehyde wastewater treatments. For example, Wu [6] used a 5% ZSM-5-PDMS/Nylon membrane to deal with aldehyde mass concentration of 8%; the separation factor of acetaldehyde/water achieved was 35 and the permeation flux was 233.3 g·m⁻²·h⁻¹. Although pervaporation exhibited superior advantages in simplicity and recovery efficiency, it was



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). deficient in the economy. Biological methods are thought to be a more attractive strategy. Tian [7] proposed that hydrolytic acidification presented enormous potentiality in treating high-strength aldehyde wastewater for hydrolytic and acidifying bacteria showed superior performance in withstanding acetaldehyde. Tian [8] employed zero-valent iron-coupled hydrolytic acidification to pretreat chloroacetaldehyde wastewater, and the dechlorination ratio was found to increase by 20.23%. Many factors can influence removal effects, such as operation parameters, influent quantity, and the characteristics of typical pollutants. Among them, influent quality and pollutants characteristics are of vital significance to treatment process selection and operation. For example, Song investigated the performance of the micro aeration hydrolytic acidification process degrading wastewater from the manufacture of 2-butenal and the fluorescence characteristics of EPS. Moreover, the main refractory and toxic substances were determined with gas chromatography-mass spectrometry (GC-MS). They concluded that the micro aeration hydrolytic acidification process could be employed for the pretreatment of 2-butenal manufacture wastewater [9]. As it contains many types of high-strength organic matter, acetaldehyde wastewater has complicated character and varies over time. Until now, no comprehensive characterization of dissolved organic matter (DOM) has been performed on acetaldehyde wastewater. Therefore, the characterization and analysis of acetaldehyde wastewater are urgently required.

The distribution of molecular weight (MW) and hydrophobicity are the basic properties and essentially representative indicators in wastewater quality analysis [10,11]; the distribution of hydrophobicity and MW were reported to be closely related to biodegradability and membrane fouling potential, etc. [12–14]. For example, Fan applied polyvinylidene fluoride (PVDF) membranes to samples isolated from surface waters to explore interactions between fouling potential and hydrophilic matter. The results showed that the order of membrane fouling potential was hydrophilic neutral (HIN) > hydrophobic acid (HOA) > hydrophilic matter (HIM) [15]. Park investigated spectroscopic and chromatographic changes in dissolved organic matter of influent and treated sewage for a wastewater biological treatment plant. The conclusion was that fractions with lower MW could be easily degraded, and that higher MW fractions were more biologically recalcitrant [16]. Samples with the various distributions of MW and hydrophobicity exhibited different optical signals. The interaction among MW, hydrophobicity and optical signals was helpful for the in-depth analysis of wastewater. For instance, ultraviolet (UV) and specific ultraviolet absorbance (SUVA) were instructive measurements for aromaticity [17]. The UV and SUVA can also be indicators of MW as higher MW fractions containing aromatics possessed higher MW. And rew [18] found that A^2O and A/O treatment process elevated wastewater aromaticity, and simultaneously increased the MW of dissolved organic matter (DOM) in municipal wastewater. The trend was in agreement with MBR; fractions with a higher MW had a higher SUVA than fractions with a lower MW [19]. However, textile dyeing wastewater followed the opposite pattern [20]. The differences may be attributed to the wastewater source. There is also a correlation between fluorescence properties and hydrophobicity. For example, hydrophobic fractions (HOS) were found to possess aromatic structure by three-dimensional excitation and emission matrix (3D EEM) fluorescence spectroscopy [21]. More humics were found in HOA and hydrophobic neutral (HON), and aromatic proteins were found in hydrophobic bases (HOB) more frequently [22,23]. The characterization of aromaticity and fluorescence properties cannot satisfy the requirement for wastewater quality analysis. More analysis techniques, such as GC-MS, have been applied for precise quantitative analysis [24,25].

The main objective of this study was to supply the research and treatment of acetaldehyde wastewater with an in-depth characterization. First, resin grading and multistage ultrafiltration were used to separate acetaldehyde wastewater into corresponding fractions, then the fractions were characterized using UV–Vis and 3D EEM spectroscopy to investigate the composition features. Further, GC-MS was utilized to qualitatively determine the dominant organic contaminant in acetaldehyde wastewater. The results of this study will provide some fundamental information about which classes of DOM in acetaldehyde wastewater should be removed to ensure the smooth operation of impending treatments.

2. Materials and Methods

2.1. Wastewater Collection and Storage

The water samples were taken from the drainage of an acetaldehyde production unit of a petrochemical enterprise in northeast China. The basic indicators were measured immediately after sampling. The remaining samples were stored at 4 °C in a refrigerator to ensure the accuracy of subsequent analyses.

2.2. Conventional Characterizations

The water sample was acidic (pH \approx 3.3) with COD of 3886.5 mg/L, BOD of 1943.1 mg/L, and DOC of 1305.6 mg/L. It shall be biodegradable due to the high B/C ratio (0.5).

All samples were filtered through 0.45 mm cellulose acetate membrane before analysis. A DRB200 COD digester (HACH, Loveland, CO, USA) and BOD TrakTM II BOD analyzer (HACH, Loveland, CO, USA) were used for COD detection and BOD₅ detection, respectively. The referenced analytical method was the Hach Company test program. pH was determined with a pH meter (METTLER TOLEDO FE20). DOC was determined by a TOC analyzer (TOC-VCPH, Shimazu, Japan).

2.3. Organic Carbon Analysis

The UV absorption spectra of samples were measured using a UV-1700 spectrophotometer (SHIMADZU, Kyoto, Japan) coupled with a 1 cm path length quartz cuvette. Analysis conditions were as follows: the scanning wavelength ranged from 190 nm to 400 nm; the scanning speed is medium automatic scanning; slit width was 5.0 nm; and sampling interval was 0.2 nm.

2.4. 3D EEM Fluorescence Spectroscopy Analysis

Before the 3D EEM fluorescence spectroscopy (F-7000 FL, Hitachi, Tokyo, Japan) test, samples were diluted for measurement. The operation was conducted under 3D scanning mode at a scanning speed of 12,000 nm/min, the sampling interval was 5 nm, and excitation (EX) and emission (EM) scan areas were 200–450 nm and 200–550 nm, respectively.

2.5. Ultrafiltration Membrane Filtration

The samples were adjusted to neutral and prefiltered to ensure smooth progress of the subsequent ultrafiltration. The filtrate was then added to a built-in magnetic stirring agitated ultrafiltration cup with a volume of 400 mL. The ultrafiltration (UF) was then completed using high purity N₂ (99.999%) of less than 0.1 MPa as the driving force. The samples were filtered through an intercept with MW of 100 kDa, 30 kDa, 10 kDa, 5 kDa, and 3 kDa ultrafiltration membrane in parallel. Finally, filtrate at five MW levels was collected for analysis and testing.

2.6. Resin Fractionation

Nonionic Amberlite XAD-8 resins were used to isolate DOM into HIM, HOA, hydrophobic bases HOB and HON. The resins were soaked in 40 mL ultrapure water to remove visible impurities, and then were cleaned with 40 mL ethanol for 24 h and then rinsed with ultrapure water. Then, 20 mL (wet volume) cleaned XAD-8 resin was packed into a glass column and rinsed with 40 mL 0.1 mol/L NaOH, 0.1 mol/L HCl, and ultrapure water until the DOC of the effluent was less than 2 mg/L.

Fractionation was conducted concerning the method established by Leenhee [26]. One liter of neutral prefiltered sample was pumped through the XAD-8 resin column at a rate of 10 mL/min. The effluent was defined as fraction-1. The HOB was backwash eluted with 200 mL of 0.1 mol/L HCl followed by 100 mL of ultrapure water. Fraction-1 was adjusted to pH 2 with HCl and recycled through the XAD-8 column at the rate of 10 mL/min. The

portion that passed through the resin column was denoted the HIM. HOA was desorbed by backflush elution with 200 mL of 0.1 mol/L NaOH followed by 100 mL of ultrapure water. Then HON fraction was obtained by XAD-8 resin elution with methanol. After fractionation, each fraction volume was adjusted to one liter.

2.7. Liquid–Liquid Extraction/GC-MS (LLE-GC-MS)

Before GC-MS determination, 10 mL dichloromethane (HPLC-grade) was used to extract a sample of 100 mL three times under acidic (pH \approx 2) and alkaline (pH \approx 12) conditions for 2 min, respectively. The six extracted phases were mixed and anhydrous sodium sulfate was used to dehydrate the mixture. Then, the mixture was dried under nitrogen atmosphere at 25 °C. Dichloromethane (1.0 mL) was applied to dissolve the residue, and 1 µL of mixture was injected into 7890/5975 GC-MS system (Agilent, Santa Clara, CA, USA) coupled with an HP-5MS capillary column (60 m \times 0.25 mm i.d.). The injector temperature was maintained at 260 °C. The temperature program was operated at 40 °C for 2 min, raised at 8 °C/min to 300 °C, and kept at 300 °C for 3 min. The solvent delay time was 20 s. Agilent MSD Chemstation E.02.00.493 software was used to operate the system.

2.8. Purge and Trap-GC/MS

A sample of 5 mL was injected into a purge and capture sampler, and the purge gas flow rate was set at 40 mL/min. The purge time was 11 min; purge temperature was room temperature; dry purge lasted for 1 min; pre-desorption temperature was 180 °C; flow rate was 300 mL/min. The baking was conducted at 220 °C with a flow rate of 400 mL/min, and the process lasted for 10 min. The sample was injected by purge and capture procedure. The sample was separated by chromatography and then detected by mass spectrometry.

3. Results and Discussions

3.1. The MW Size Distribution of Acetaldehyde Wastewater

3.1.1. DOC Distributions Based on MW

The DOC distribution of each fraction is shown in Figure 1. In general, the DOC content of fractions increased as MW decreased. In particular, fractions with MW below 1 kDa reached 1075.2 \pm 25.6 mg/L, accounting for 82% of the total dissolved organic carbon. The organic content of components with molecular weight ranging from 1 kDa to 3 kDa and 30 kDa to 100 kDa was slightly lower than that of the previously mentioned MW ranges; their DOC was 97.8 ± 9.8 mg/L and 58.2 ± 2.7 mg/L, accounting for 8 and 4% of the total dissolved organic carbon, respectively. The remaining molecular weight ranges (3~5 kDa, $5 \sim 10$ kDa, $10 \sim 30$ kDa, and > 100 kDa) contained less organics, with DOC of 27.9 ± 2.4 mg/L, 11.4 ± 1.1 mg/L, 8.4 ± 0.9 mg/L, and 26.7 ± 3.3 mg/L, respectively. Organic matter with molecular weight above 100 kDa only accounted for 2% of the total organic carbon content. Particle size distribution of DOM significantly depends on the type of wastewater [27]. Most dissolved organics possess lower MW in acetaldehyde wastewater, which was in agreement with industrial wastewater and municipal wastewater MW distribution [28]. Compared with higher MW fractions, the low MW fractions are more biodegradable [26]. Thus, it can be inferred that acetaldehyde wastewater is easily biodegradable, which is consistent with the relatively high B/C of acetaldehyde wastewater.

In conclusion, the selection of acetaldehyde wastewater treatment should focus on the removal of small molecular organic matter; it is recommended to apply biological methods to treat acetaldehyde wastewater.

3.1.2. UV Distributions Based on MW

The UV distributions are shown in Figure 2, there were similar trends in the UV absorption spectrum between different molecular weight intervals, indicating that the conjugate characteristics of organic compounds in different molecular weight intervals were almost the same. The strong absorption peak at 220~290 nm was attributed to carbon–

carbon double bonds and benzene rings. The absorbance value wavelengths greater than 300 nm gradually decreased and tended to zero, indicating that the wastewater did not contain organic compounds with polybenzene rings. The SUVA₂₅₄ of components showed a narrow distribution that varied from 0.14 to 0.16 $L \cdot mg^{-1} \cdot m^{-1}$. According to Edzwald's [17] theory, when the SUVA₂₅₄ is less than 3 $L \cdot mg^{-1} \cdot m^{-1}$, it means that the dissolved organic matter in wastewater has relatively lower MW and a high degree of biochemical properties. This conclusion was consistent with the biodegradability and MW distributions of samples.



Figure 1. DOC contents of various MW fractions in acetaldehyde wastewater.



Figure 2. The ultraviolet absorption spectrum of different MW fractions.

In summary, the focus of pollutant removal in acetaldehyde wastewater should be lower MW organics with carbon–carbon double bonds and benzene rings.

3.1.3. 3D Fluorescence Distributions Based on MW

The fluorescence properties of fractions with different MW were shown in Figure 3. The results showed that the shape of the spectra was roughly similar, but the location of Flu 1 was gradually red-shifted as the MW increased. Since the existence of carbonyl, hydroxyl, alkoxyl, and carboxyl constituents are responsible for the redshift [29,30]. It can be inferred that acetaldehyde wastewater contains organics with the above substituent groups possessing relatively higher MW. Fractions with MW below 1 kDa exhibited the highest overall fluorescence intensity, it was thought to be the main contributor to the fluorescence intensity of acetaldehyde wastewater.

According to the theory proposed by Chen [29], the spectrum is divided into five regions: region I ($Ex/Em = 200 \sim 250 \text{ nm}/280 \sim 330 \text{ nm}$) indicates tryptophan, tyrosine, phenylalanine and other aromatic proteins. Region II ($Ex/Em = 200 \sim 250 \text{ nm}/330 \sim 380 \text{ nm}$)

indicates an aromatic protein. Region III (Ex/Em = $200 \sim 250 \text{ nm}/380 \sim 550 \text{ nm}$) indicates a fulvic acid-like substance. Region IV (Ex/Em = $250 \sim 280 \text{ nm}/280 \sim 380 \text{ nm}$) indicates a solubility-like microbial metabolite. Region V (Ex/Em = $>250 \text{ nm}/380 \sim 550 \text{ nm}$) indicates humic acid like substance. Two predominant peaks were identified in all the EEM spectra (Flu1 Ex/Em near 240/375 nm; Flu 2, Ex/Em near 320/400 nm). Flu1 and Flu 2 were assigned to aromatic protein-like (I) and humic acid-like substances, respectively. Flu 3 was a unique peak of fractions with MW less than 1 kDa, located at Ex/Em near 280/360 nm. It was thought to be related to solubility-like microbial metabolite. For further exploration of fluorescence properties, fluorescence regional integration (FRI) was employed for quantititave analysis of the fractions.



Figure 3. Three-dimensional fluorescence spectra of different compositions with MW of (**a**) 1 KDa, (**b**) 3 KDa, (**c**) 5 KDa, (**d**) 10 KDa, (**e**) 30 KDa, (**f**) 100 KDa.

To perform FRI analysis, the first step is to normalize the integrated volume of the EEM spectrum to the relative area, and then the normalized percent fluorescence response (P) is calculated as a ratio of normalized volumes in each region to the total volumes. The profiles of FRI in each fraction are shown in Figure 4. P_p is defined as the sum of protein-like regions (Regions I, II, and IV) and P_h is defined as the sum of humic- and fulvic-like regions (Regions III and VI).



Figure 4. FRI distribution of the five defined regions with various MW (Region I represents tryptophan, tyrosine, phenylalanine, and other aromatic proteins. Region II represents an aromatic protein. Region III represents fulvic acid-like substances. Region IV represents solubility-like microbial metabolite. Region V represents a humic acid-like substance.).

As MW increased, P_p decreased in the following order of 62.2, 51.8, 51.4, 39.6, 44.8% and 46.2%, respectively. It is generally accepted that protein-like substances are more biodegradable, but also preferentially attach to membrane surfaces, resulting in fouling [31–34]. Acetaldehyde wastewater is mainly composed of protein-likes substance with low MW, so it is recommended to apply biological methods to treat acetaldehyde wastewater; previous studies have reported employing membrane bioreactors (MBRs) for aldehydes-containing wastewater [35–37]. With the application of MBR technology, protein-like substances with lower MW will be removed.

3.2. The Hydrophobicity Distribution of Acetaldehyde Wastewater

3.2.1. DOC Distributions Based on Hydrophobicity

After the adsorption and separation of acetaldehyde wastewater by Xad-8 macroporous adsorption resin, samples were divided into HOA, HOB, HIM, and HON. The DOC distribution of each component was shown in Figure 5. According to Figure 5, the DOC of HIM in acetaldehyde wastewater was the highest, at 576.6 \pm 31.6 mg/L, accounting for 44% of the total DOC. HOB and HOA follow HIM, accounting for 23 and 30% of total DOC, respectively. HON has the lowest soluble organic carbon content of 42.8 \pm 17.7 mg/L.

In summary, the organic matter in acetaldehyde wastewater was mainly hydrophilic substances, while the hydrophobic organic matter was mainly composed of acidic and alkaline substances. The hydrophobicity distribution of DOM in acetaldehyde wastewater was similar to Wang's [26]. An increment in HOB content may be attributed to the lower pH of acetaldehyde wastewater, which causes the generation of hydrophobic fractions [38].

3.2.2. UV₂₅₄ Distributions Based on Hydrophobicity

The UV absorption spectra of each component in acetaldehyde wastewater is shown in Figure 6. It can be seen that the UV absorption spectra of HOA, HOB, and HIM varied similarly (HON's UV absorption spectrum was ignored due to the reaction of eluent and acetaldehyde wastewater). The ultraviolet absorbance of HOB at 225 nm was higher than that of other components, indicating that most of the conjugated double bonds in the wastewater were attributed to hydrophobic alkaline substances. The spectral curve of HOA at the wavelength of 310–340 nm was higher than that of other components, indicating that benzene macromolecular organics alkaline were attributed to hydrophobic acid.



Figure 5. DOC contents of various hydrophilic fractions in acetaldehyde wastewater.



Figure 6. The ultraviolet absorption spectrum of the various hydrophilic fractions.

HOA and HOB contained a large amount of unsaturated structuralized aromatic compounds, and their UV₂₅₄ reached 0.84 and 0.75, respectively, accounting for 45% and 40% of the total UV₂₅₄. HIM and HON processed a lower content of unsaturated structured aromatic compounds, accounting for 14 and 1% of the total UV₂₅₄, respectively. (UV₂₅₄ of HON was determined as the difference between the measured UV₂₅₄ and the sum of identified fractions.)

The spectral slope S_R (the ratio of the logarithmic slope of absorption coefficients in the wavelength ranges of 275–295 nm and 350–400 nm) is often used to indicate the molecular weight change of DOM, which is inversely proportional to MW [39]. The S_R of HIM, HOB, and HOA was 1.7165, 0.8238, and 0.7702, respectively. It could be inferred the order of MW ranked as HOA > HOB > HIM. The conclusion was consistent with Yan's [40] conclusion that the lower content of hydrophilic corresponded to low MW components. Since the degradation of acetaldehyde wastewater is focused on lower MW fractions, the removal of HIM should also be taken seriously.

As is shown in Figure 7, the 3D EEM spectra of three fractions and the original sample were different from each other. Three fluorescence peaks were identified in HOB (Flu 1 Ex/Em near 230/375 nm; Flu 2 Ex/Em near 330/375 nm; Flu 3 Ex/Em near 290/330 nm); Flu 1 and Flu 2 were also detected in HIM, and the fluorescence peak intensity of HOB was much higher than that of HIM. Two fluorescence peaks were identified in HOA (Flu 4 Ex/Em near 220/355 nm; Flu 5 Ex/Em near 270/315 nm). A weak fluorescence peak was detected in the raw water, which was located at Ex/Em near 320/425 nm. All the fractions contained fluorescence peaks that did not exist in the original water sample. One possible reason may be that HON or impurities introduced by the grading operation contained substances that covered fluorescence; another speculation is the interaction between the components caused fluorescence quenching.



Figure 7. Three-dimensional fluorescence spectra of (a) origin sample, (b) HOA, (c) HOB, (d) HIM.

The profiles of FRI in each fraction are shown in Figure 8; the order of humic content was HOB > HOA > HIM, with relative content of 25.5, 15.7, and 15.3%, respectively. Humic was thought to be biological recalcitrant. It can be inferred that the biological recalcitrant substance in acetaldehyde wastewater was HOB. Therefore, tertiary treatment should focus on the removal of HOB. On the contrary, HIM contains a higher content of proteinaceous substances, which may cause membrane fouling [34]. The conclusion was consistent with previous research that the hydrophilic fraction is more frequently considered as the major foulant of the membrane [41].



Figure 8. FRI distribution of the five defined regions with various hydrophobicities. Region I represents tryptophan, tyrosine, phenylalanine, and other aromatic proteins. Region II represents aromatic protein. Region III represents fulvic acid-like substance. Region IV represents solubility-like microbial metabolite. Region V represents humic acid-like substance.

In conclusion, HOB shall be the focus of tertiary treatment, and HIM shall be removed to eliminate membrane fouling.

3.3. Analysis of Organic Pollutants

To ascertain the dominant organic contaminant in acetaldehyde wastewater, GC-MS was used to determine organics qualitatively. As shown in Table 1, 30 compounds in acetaldehyde wastewater could be detected by this method. The toxicity level of the compounds was obtained by searching both the chemical toxicity database and toxicity grading standard. As shown in Table 1, there was one highly toxic compound, fourteen moderately toxic compounds, six mildly toxic compounds, and nine compounds with unknown toxicity in acetaldehyde wastewater. It can be seen that acetaldehyde wastewater exhibited moderate toxicity, and could therefore not be directly discharged into the microbial treatment system.

Aldehydes, acids, alkane, alcohols, and ketones comprised about 70, 4, 6, 17, and 4% of the acetaldehyde wastewater. Both aldehydes and alcohols were low-MW organics; this might explain why the acetaldehyde wastewater is mainly composed of fractions with MW below than 1 kDa. The large amounts of 5-methyl furfural, crotonaldehyde, acetic acid, chloroacetaldehyde, and 3-furaldehyde presented in acetaldehyde wastewater verified the existence of carboxyl and carbonyl groups, which account for the redshift in the fluorescence spectra. Most organics have hydrophilic groups, such as carboxyl and hydroxyl groups. This is consistent with the conclusion that acetaldehyde wastewater was mainly composed of HIM.

NO.	Rt (min)	Name	Possibility %	Molecular Weight	CAS	Structural Formula	Percentage %	Toxicity Grade ^a	Methods
1	5.785	Chloroacetald-ehyde	96	77.987	000107-20-0	cı=0	4.91	3	LLE-GC-MS
2	6.177	Acetic acid	86	60.021	000064-19-7	ОН	3.56	3	LLE-GC-MS
3	6.504	Trichloromethane	91	117.914	000067-66-3	CI CI	0.235	2	LLE-GC-MS
4	6.782	Dichloroacetaldehyde	97	111.948	000079-02-7	°≫CI	1.63	3	LLE-GC-MS
5	7.109	Crotonaldehyde	91	70.042	000123-73-9	0	4.97	3	LLE-GC-MS
6	7.219	2-Butenal	74	70.040	004170-30-3	0	0.318	3	LLE-GC-MS
7	7.335	2-Chloroethanol	78	80.003	000107-07-3	HO	1.94	3	LLE-GC-MS
8	7.808	Chloroacetone	80	92.003	000078-95-5	O CI	0.640	3	LLE-GC-MS
9	9.391	3-Penten-2-one	72	84.058	003102-33-8	~~~	0.253	U	LLE-GC-MS
10	9.556	Aldol	78	88.052	000107-89-1	HO	0.834	2	LLE-GC-MS
11	10.676	2,4-Pentanedione	64	100.052	000123-54-6	ů,	0.355	U	LLE-GC-MS
12	11.711	3-Furaldehyde	95	96.021	000498-60-2	5~0	10.2	3	LLE-GC-MS
13	12.090	3-Chloropropyne	53	73.992	000624-65-7	CI	4.56	3	LLE-GC-MS
14	12.430	Furfural	91	96.021	000098-01-1	o to	0.276	3	LLE-GC-MS
15	14.699	2-Chloromethyl-1,3-dioxolane	72	122.013	002568-30-1	o ⊂o ⊂i	0.405	U	LLE-GC-MS
16	14. 841	Ethanone, 1-(2-furanyl)-	86	110.037	001192-62-7	CH,	0.223	3	LLE-GC-MS
17	15.171	2-Acetylfuran	91	110.037	001192-62-7	\sim	0.193	4	LLE-GC-MS
18	15.311	5-Methyl furfural	91	110.037	000620-02-0	o	36.8	2	LLE-GC-MS

 Table 1. LLE-GC-MS qualitative results of acetaldehyde wastewater.

Tabl	e 1	. Cont.
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NO.	Rt (min)	Name	Possibility %	Molecular Weight	CAS	Structural Formula	Percentage %	Toxicity Grade ^a	Methods
19	16.036	3,3-Dimethyl-2,4-pentanedione	72	128.084	003142-58-3	otto	0.474	U	LLE-GC-MS
20	17.285	2-Acetyl-5-methylfuran	86	124.052	001193-79-9	ofor	1.85	3	LLE-GC-MS
21	18.372	CIS-1,3-Dichloropropene	72	109.969	010061-01-5	CICI	0.299	3	LLE-GC-MS
22	19.476	2-Dichloromethyl-1,3-dioxolane	42	155.974	002612-35-3	⊂°≻– <ci< td=""><td>0.152</td><td>U</td><td>LLE-GC-MS</td></ci<>	0.152	U	LLE-GC-MS
23	20.405	1-Octanol	42	130.14	000111-87-5	HO	0.0737	2	LLE-GC-MS
24	21.276	3-Methyl-2-cyclohexen-1-one	47	110.073	001193-18-6	0	0.258	2	LLE-GC-MS
25	21.506	1-Chloromethyl-4- methylenecyclohexane	50	144.071	000823-83-6		0.663	U	LLE-GC-MS
26	23.299	5-chloro-2-methoxy-phenol	50	158.013	003743-23-5	но-С	0.368	U	LLE-GC-MS
27	25.231	5-chlorobenzene-1,3-diol	72	143.998	005278-23-1	HO O-CI	0.249	U	LLE-GC-MS
28	26.386	4-Chlorophenetole	38	156.034	000622-61-7	c-{}-0-	0.166	U	LLE-GC-MS
29	5. 072	Acetaldehyde	59	44.026	000075-07-0	~ ⁰	2.46	3	Purge and trap-GC/MS
30	5.276	Ethyl alcohol	80	46.042	000064-17-5	∕_ ^{OH}	3.33	2	Purge and trap-GC/MS

^a Toxicity grade-"U": unknown; "0": non-toxic, $LD_{50} > 15 \text{ g/kg}$; "1": actual non-toxicity, $5 \text{ g/kg} < LD_{50} < 15 \text{ g/kg}$; "2": low toxicity, $0.5 \text{ g/kg} < LD_{50} < 5 \text{ g/kg}$; "3": medium toxicity, $50 \text{ mg/kg} < LD_{50} < 500 \text{ mg/kg}$; "4": high toxicity, $LD_{50} < 50 \text{ mg/kg}$. The above toxicity data were all tested in rats.

4. Conclusions

To operate a wastewater treatment capable of removing undesirable pollutants from acetaldehyde wastewater in an energy-effective manner, the distribution of MW/hydrophobicity, optical characteristics, and chemical composition of acetaldehyde wastewater were analyzed. The concluding remarks and suggestions may be considered as follows:

- (i) Acetaldehyde wastewater is enriched with fractions of MW < 1kDa. It is therefore recommended to use a biological method to treat acetaldehyde wastewater, but if membrane-related technology is applied, to reuse it, protein-like substances should be removed in pretreatment.
- (ii) The treatment of acetaldehyde wastewater should focus on HIM and HOB, given their potential for membrane fouling and resistance to biodegradation of HOB.
- (iii) In acetaldehyde wastewater, 30 compounds were determined by GC-MS; 5-methyl furfural, 3-furaldehyde, chloroacetaldehyde, acetic acid, and acetaldehyde were dominant pollutants. Due to their high content and relatively strong toxicity, the process of acetaldehyde wastewater treatment should focus on their fates.

In conclusion, the comprehensive characterization of acetaldehyde wastewater will contribute to control strategies and sustainable development.

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