



Release of volatile organic compounds during bio-drying of municipal solid waste

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Abstract

Three treatments were tested to investigate the release concentrations of volatile organic compounds (VOCs) during the bio-drying of municipal solid waste (MSW) by the aerobic and combined hydrolytic-aerobic processes. Results showed that VOCs were largely released in the first 4 days of bio-drying and the dominant components were: dimethyl disulfide, dimethyl sulfide, benzene, 2-butanone, limonene and methylene chloride. Thus, the combined hydrolytic-aerobic process was suggested for MSW bio-drying due to fewer aeration quantities in this phase when compared with the aerobic process, and the treatment strategies should base on the key properties of these prominent components. Malodorous sulfur compounds and terpenes were mainly released in the early phase of bio-drying, whereas, two peaks of release concentrations appeared for aromatics and ketones during bio-drying. Notably, for the combined hydrolytic-aerobic processes there were also high concentrations of released aromatics in the shift from hydrolytic to aerobic stages. High concentrations of released chlorinateds were observed in the later phase. For the VOCs produced during MSW bio-drying, i.e., malodorous sulfur compounds, terpenes and chlorinateds, their release concentrations were mainly determined by production rates; for the VOCs presented initially in MSW, such as aromatics, their transfer and transport in MSW mainly determined the release concentrations.

Key words: bio-drying; municipal solid waste; odors; release concentration; volatile organic compounds

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Introduction

Bio-drying is regarded as a good solution to reducing water content of municipal solid waste (MSW), favorable for energy recovery and mechanical separation before resource recovery (Adani et al., 2002; Choi et al., 2001; Rada et al., 2007). The aerobic process has been focused on to remove water mainly in the form of vapor by adequate aeration and high temperature resulting from organics degradation (Sugni et al., 2005). Nowadays, a combined hydrolytic-aerobic process, supplementing a hydrolytic stage prior to aerobic degradation, has been proposed (Bezama et al., 2007; Zhang et al., 2008). Volatile organic compounds (VOCs), such as malodorous sulfur compounds, aromatics, chlorinateds, terpenes and ketones, will also be released during bio-drying, being one of the main problems for application.

Many previous studies have reported VOCs and/or odors released from aerobic composting of different substrates (MSW, biowaste, fruits, food wastes, mixed papers, and yard wastes) in various scales (Das et al., 2000; Eitzer, 1995; Pierucci et al., 2005; USEPA, 2003; Wang and Wu, 2008). Staley et al. (2006) have also compared

the release of non-methane organic compounds during the decomposition of residential refuses and yard wastes under aerobic and anaerobic conditions. The microbial metabolism for the bio-drying process is similar to that for the composting process. However, the former mainly aims at water removal, while the latter focuses on bio-stabilization and maturity of composted materials (Zhang et al., 2009). Thus, the operating strategy, such as aeration, is different. This will influence the production, degradation, adsorption, dissolution, and retention in MSW free air space (FAS) for VOCs. Therefore, their release is also different between bio-drying and composting. Nevertheless, little information is available on the VOCs released during MSW bio-drying. Especially, regarding the combined bio-drying process, the environmental conditions and microbial metabolism are different in the hydrolytic stage and the shift between the hydrolytic and aerobic stages, when compared with the aerobic process. These will result in the differences in VOC release between combined bio-drying process and aerobic process. Until now, there are few publications that reported the release of VOCs during bio-drying by combined hydrolytic-aerobic process.

In this study, we investigated the release concentrations of VOCs during MSW bio-drying by combined

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hydrolytic-aerobic and aerobic processes, using the method of adsorption-gas chromatography (GC)-mass spectrometry (MS).

1 Materials and methods

1.1 Characteristics of the MSW feedstock

The MSW was sampled from a residential area in Shanghai, China. The initial water content was 68% (W/W, in wet weight). The MSW comprised 64% of food waste, 20% of paper and 7.5% of plastic as well as 8.5% of others.

1.2 Experimental treatments

Three bio-drying treatments were performed in this study, i.e., one aerobic process and two combined processes. The aerobic process was operated with an aeration procedure of 7 min run/23 min stop and the fed MSW were manually turned every 2 days. The combined processes were separated into the hydrolytic stage and aerobic stage. During the hydrolytic stage (0–4 day), the combined process 1 was operated without forced aeration, while the combined process 2 was operated with an aeration procedure of 10 min run/230 min stop. During the aerobic stage (5–16 days), the aeration and turning procedures for both combined processes were the same as those for the aerobic process. Experiment was performed in laboratory columns, as described below, and conducted for 16 days. After mixing adequately, 28 kg of the above-mentioned raw MSW was loaded into each column with a density of approximate 255 kg/m³. During the whole experiment, the aeration rate was fixed at 0.056 m³ per kg wet MSW per hour, according to the highest water removal rate at this aeration rate obtained in preliminary experiment.

1.3 Experimental equipment

Made of organic glasses, each column was 1200 mm height and 400 mm internal diameter. The outer wall of column was wrapped by 100 mm-thick hollow cotton for thermal insulation. A 100 mm-high layer, filled with round stones (about 5 mm diameter), was placed at the bottom of column for leachate drainage and air distribution. Above the stones, there was a perforated baffle (2 mm mesh) to support the waste and to facilitate aeration. Two layers of straw and cotton were placed above the waste to avoid heat loss and vapor condensation. A sealed cover with an air outlet was placed on the top of column. There was an air inlet at the bottom of column. A whirlpool pump (XGB-8, Penghu Co., China), a gas-flow meter (LZB-10, Shanghai Instrument Co., China) and an active carbon tube were used for aeration. All the connecting tubes were Teflon-made.

1.4 Experimental monitoring

The experiment was monitored daily to get data of temperature and oxygen (O₂) concentration in each column. Temperature was monitored by a thermometer (WMY-01C, Huachen Co., China) with sensors located at the top, middle and bottom points along the longitudinal axis of

the column, and the average value was reported. The O₂ concentration was measured with an O₂ sensor (CYS-1, Xuelian Co., China), which was placed at the same point with the middle thermometer.

1.5 Sampling and analytical methods

The headspace air of column was taken through the Tenax cartridge by sampling pumps (72-31-230, Simon Co., USA) to draw air at a rate of 50 mL/min in an aeration circle (30 min). The VOCs in the input air were detected at the same time. Then, the target gases in the sampling tube were desorbed by a thermal desorber (Turbo Matrix ATD, PerkinElmer Co., USA) and injected into GC (HP-5MS, Trace GC Ultra, Finnigan, Thermo Electron Co., USA) with helium with an inlet pressure of 146 kPa and detected with MS (Trace DSQ, Thermo Electron Co., USA). The cartridges in stainless steel tube (E043 TA 20-35, Supelco, PerkinElmer Co., USA) were precleaned by thermal desorption to ensure that no traces of VOCs would be detected by a GC/MS.

Every 4 days when the fed materials were turned, about 300 g of waste samples were collected. The water content was measured at 70°C to a constant weight. The volatile solid content was determined by loss on combustion at 550°C after 6 hr.

2 Results

2.1 Water contents and organics degradation rates by bio-drying

The extent of organics degradation (EX) is calculated by Eq. (1).

$$EX = \frac{WM_0 \times (100\% - CW_0) - WM_t \times (100\% - CW_t)}{WM_0 \times (100\% - CW_0) \times VS_0} \times 100\% \quad (1)$$

where, WM₀ (kg) and WM_t (kg) are the wet weight of MSW in the column at time 0 and *t*; CW₀ (%) and CW_t (%) are water content of the MSW at time 0 and *t*, respectively; VS₀ (%) is the volatile solid of the initial MSW.

The water contents of bio-dried products were 54.6%, 50.6% and 52.7% for the combined process 1, the combined process 2 and the aerobic process respectively, reduced from the initial of 68.0%. After bio-drying, the aerobic process had the highest extent of the organics degradation (44.5%), followed by the combined process 2 (28.5%) and the combined process 1 (27.6%). Correspondingly, the water removal rates for combined process 1, combined process 2 and aerobic process were 57.4%, 64.0% and 68.1%, respectively. The ratios of leachate generation to water evaporation were 0.05, 0.09 and 0.00 for combined process 1, combined process 2 and aerobic process, respectively.

2.2 Release of total VOCs during bio-drying

Total VOCs could be defined as the summation of each component of released VOCs. Figure 1 presents the release concentrations of total VOCs during bio-drying. In the first 4 days, high release concentrations of total VOCs were observed for the combined processes and aerobic

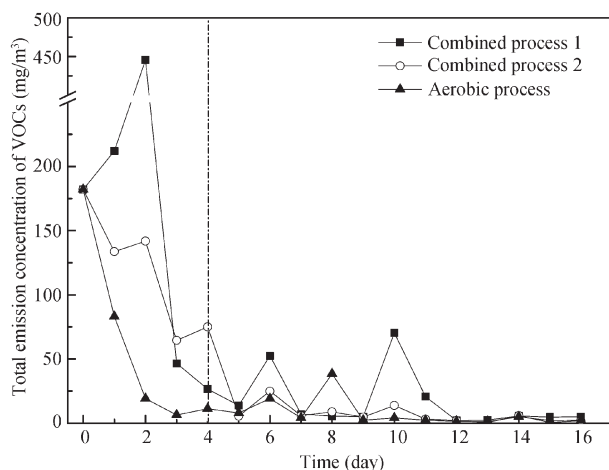


Fig. 1 Concentration of total released VOCs during bio-drying.

process. And the combined processes had much higher concentrations of total VOCs than the aerobic process. From day 5 on, the concentrations for the combined process 2 and the aerobic process decreased and remained at a low level without a significant difference. Nevertheless, the combined process 1 still had a much high concentration. After day 12, only a few VOCs could be detected for three treatments.

The composition of released VOCs during bio-drying is indicated in Fig. 2. The dominant compounds varied in different treatments and phases. In the first 4 days, malodorous sulfur compounds, aromatics, ketones and terpenes dominated for three treatments. Moreover, the combined process 1 had the highest share of malodorous sulfur compounds (about 58%), whereas the aerobic process had the highest proportion of aromatics (about 52%). From day 5 to day 12, the major components of released VOCs were malodorous sulfur compounds, ketones and terpenes. In the last 4 days, malodorous sulfur compounds and chlorinateds were the dominant ones.

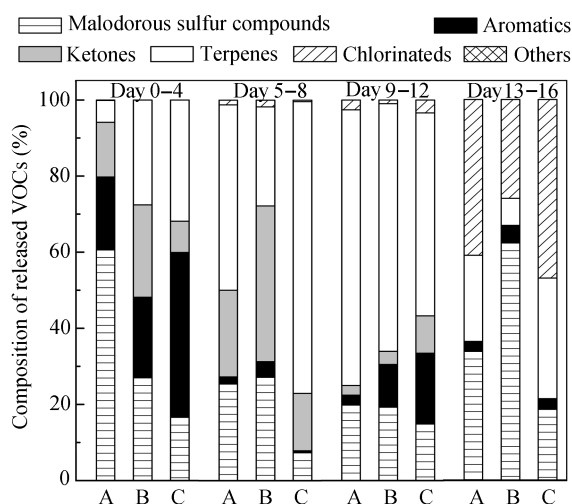


Fig. 2 Composition of released volatile organic compounds (VOCs) during bio-drying (based on the total amount). A: combined process 1; B: combined process 2; C: aerobic process.

2.3 Release of malodorous sulfur compounds during bio-drying

Malodorous sulfur compounds are the main cause of odor production (Millner et al., 2000; Pierucci et al., 2005; USEPA, 2003). The concentrations of released malodorous sulfur compounds during bio-drying are presented in Table 1. In the first 4 days, dimethyl disulfide was the major component with a share over 80% in the released malodorous sulfur compounds. Dimethyl sulfide (about 8%), allyl methyl sulfide (about 3%) and methyl 2-propopenyl sulfide (approximately 2%) were also important components among the released malodorous sulfur compounds. Other components, such as dimethyl trisulfide, diallyl methyl disulfide, allyl sulfide and 1-(methylthio)-propane were also detected with a quite minor ratio. From day 5 on when the combined processes were also in the aerobic conditions, the released malodorous sulfur compounds were almost dimethyl disulfide, over 99%.

In the first 4 days, the combined process 1 had the highest concentrations, followed by the combined process 2 and aerobic process. The peak concentrations of released dimethyl disulfide were 413.9 mg/m³ for the combined process 1, 54.3 mg/m³ for the combined process 2, and 15.4 mg/m³ for the aerobic process. Thus, the dimethyl disulfide concentration was 82800, 30860 and 3080 times above the odor threshold concentration (5 µg/m³) (Haug, 1993) for the combined process 1, combined process 2 and aerobic process, respectively. The peak concentrations of released dimethyl sulfide were 5170, 2026 and 855 times higher than the odor threshold concentration (3 µg/m³) (Haug, 1993) for the combined process 1, the combined process 2 and the aerobic process, respectively. From day 5 to day 8, only dimethyl disulfide and dimethyl trisulfide could be detected with relatively low concentrations and furthermore their concentrations followed a decreasing order of the combined process 1 > combined process 2 > aerobic process. The peak concentration of released dimethyl disulfide was still 2378, 799 and 504 times higher than the odor threshold for the combined process 1, combined process 2 and aerobic process, respectively. From day 8 on, a decreased concentration of release dimethyl disulfide was observed, where the peak concentrations were 484, 820 and 155 times higher than the odor threshold for combined process 1, combined process 2 and aerobic process.

2.4 Release of aromatics during bio-drying

The concentrations of released aromatics during bio-drying are presented in Table 2. From day 0 to day 4, benzene dominated in released aromatics for three treatments (over 80%), whereas others had a minor proportion, including toluene, ethyl benzene, *p*-xylene, styrene, *o*-xylene, 1-methylethyl-benzene, 1-methyl-3-(1-methylethyl)-benzene, and 2-ethenyl-1,4-dimethyl-benzene. Additionally, neither *o*-xylene nor 1-methylethyl-benzene could be detected under the hydrolytic conditions. From day 5 to day 16, the major components of aromatics were benzene, *p*-xylene and

Table 1 Release concentrations for the malodorous sulfur compounds during bio-drying (mg/m³)

Compounds		Day 0	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Day 11	Day 12	Day 13	Day 14	Day 15	Day 16
Dimethyl sulfide	A	ND	14.48	5.34	3.86	4.42	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	ND	5.68	5.76	3.43	0.06	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	ND	2.40	0.42	0.50	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Allyl methyl sulfide	A	ND	7.94	2.13	0.22	0.14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	ND	2.38	1.09	0.13	0.11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	ND	1.09	0.57	1.26	0.05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Methylthio-propane	A	ND	0.18	0.17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dimethyl disulfide	A	3.13	36.84	413.88	31.84	21.76	11.91	3.65	4.21	0.08	2.41	1.70	13.91	1.49	2.06	1.08	1.24	1.76
	B	3.13	52.31	15.10	54.35	15.24	3.43	2.32	2.48	4.03	1.86	0.57	0.59	1.61	0.16	4.09	0.35	0.91
	C	3.13	15.44	14.00	0.71	9.61	0.69	2.54	1.72	0.19	0.48	0.02	0.55	0.46	0.79	0.58	0.26	0.31
Methyl 2-propenyl disulfide	A	0.09	2.34	3.85	0.05	0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	0.09	0.08	0.15	2.03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	0.09	0.77	0.03	0.07	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dimethyl trisulfide	A	0.01	0.04	0.10	0.05	0.06	0.05	0.06	0.01	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	0.01	0.08	0.07	0.06	0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	0.01	ND	0.03	0.03	0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Diallyl disulfide	A	ND	0.28	0.05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	ND	0.01	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Malodorous sulfur compounds	A	3.23	62.10	425.53	36.02	26.43	12.05	3.71	4.22	0.08	2.41	1.70	13.91	1.49	2.06	1.08	1.24	1.76
	B	3.23	60.53	22.17	59.99	15.46	3.43	2.32	2.48	4.03	1.86	0.57	0.59	1.61	0.16	4.09	0.35	0.91
	C	3.23	19.70	15.05	2.57	9.69	0.69	2.54	1.72	0.19	0.48	0.02	0.55	0.46	0.79	0.58	0.26	0.31

A: combined process 1; B: combined process 2; C: aerobic process; ND: not detected.

Table 2 Release concentrations for aromatics during bio-drying (mg/m³)

Compounds		Day 0	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Day 11	Day 12	Day 13	Day 14	Day 15	Day 16
Benzene	A	116.11	52.38	0.66	0.60	0.15	1.15	ND	ND	0.11	0.22	0.22	ND	0.02	0.01	0.01	ND	ND
	B	116.11	1.35	1.96	1.69	0.26	1.09	ND	ND	0.22	0.27	0.24	0.03	0.05	0.02	ND	0.03	0.01
	C	116.11	0.88	2.56	3.71	0.36	0.01	0.01	ND	0.02	0.13	0.17	0.05	0.03	0.01	0.01	0.01	ND
Toluene	A	0.96	0.74	0.11	ND	ND	ND	ND	ND	ND	0.11	ND	0.01	0.05	0.00	0.02	0.01	ND
	B	0.96	0.14	0.06	ND	0.04	ND	ND	ND	ND	0.14	ND	0.01	0.05	0.00	ND	ND	ND
	C	0.96	0.34	0.34	0.02	0.01	ND	ND	ND	ND	0.03	ND	0.03	0.02	0.01	ND	ND	ND
Ethylbenzene	A	0.73	0.02	ND	ND	ND	0.02	ND	ND	ND	0.08	0.12	0.08	ND	0.00	ND	ND	ND
	B	0.73	0.12	ND	ND	ND	0.01	ND	ND	0.01	0.14	0.02	0.02	0.01	0.00	ND	ND	ND
	C	0.73	0.23	0.01	ND	0.06	0.01	ND	ND	ND	0.03	0.02	0.01	0.01	0.01	ND	ND	ND
<i>p</i> -Xylene	A	0.94	0.01	ND	ND	ND	0.10	ND	ND	0.01	0.47	0.35	0.37	0.04	0.01	0.04	0.03	0.01
	B	0.94	0.01	0.01	ND	ND	0.45	ND	ND	ND	0.48	0.31	0.38	0.04	0.04	0.00	0.01	0.02
	C	0.94	0.29	0.24	ND	ND	0.02	ND	0.16	0.19	0.25	0.15	0.37	0.05	0.07	0.01	0.01	0.01
Styrene	A	0.32	0.10	0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND
	B	0.32	ND	0.10	0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND
	C	0.32	0.14	0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND
<i>o</i> -Xylene	A	0.36	0.00	ND	ND	ND	ND	ND	0.05	0.20	0.09	0.10	0.08	0.13	0.09	0.09	0.09	0.02
	B	0.36	0.00	ND	ND	ND	ND	ND	0.05	0.22	0.11	0.09	0.10	0.11	0.08	0.07	0.01	0.01
	C	0.36	0.24	0.11	0.02	0.06	ND	ND	ND	0.05	0.08	0.15	0.11	0.06	0.05	0.03	0.03	ND
1-Methyl ethylbenzene	A	0.18	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	0.18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	0.18	ND	0.10	ND	0.01	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Methyl-3-(1-methylethyl)-benzene	A	0.22	0.04	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	0.22	0.00	0.42	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	0.22	0.05	0.78	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Ethenyl-1,4-dimethylbenzene	A	ND	ND	0.26	ND	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	ND	ND	0.42	ND	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	ND	ND	ND	0.02	0.33	ND	0.08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aromatics	A	119.83	53.29	1.30	0.61	0.15	1.29	ND	ND	0.17	1.07	0.78	0.56	0.19	0.15	0.16	0.13	0.04
	B	119.83	1.62	2.96	1.73	0.32	1.58	0.01	ND	0.28	1.25	0.68	0.54	0.24	0.16	0.09	0.12	0.05
	C	119.83	2.18	4.18	3.77	0.83	0.02	0.12	ND	0.23	0.45	0.59	0.35	0.49	0.13	0.11	0.05	0.01

A: combined process 1; B: combined process 2; C: aerobic process; ND: not detected.

o-xylene for the combined processes and the aerobic process. Furthermore, there was a lower proportion of toluene, ethyl benzene and 2-ethenyl-1,4-dimethyl-benzene in this stage. No styrene, 1-methylethyl-benzene and 1-methyl-3-

(1-methylethyl)-benzene were detected.

In the first 4 days, all the combined processes and the aerobic process had high concentrations of released aromatics. Moreover, for the combined processes, in the

shift from the hydrolytic to aerobic stages (day 5), high concentrations of the released benzene, ethyl benzene, *p*-xylene and 2-ethenyl-1,4-dimethyl-benzene were still observed. Notably, for three treatments, benzene, toluene, ethyl benzene, *p*-xylene, and *o*-xylene were observed to be released again from day 8 on, and the peak of release concentrations appeared on day 9.

2.5 Release of ketones during bio-drying

The concentrations of released ketones during bio-drying are presented in Table 3. 2-Butanone was the dominant ketones for combined processes and aerobic process, with a share over 80%.

In the first 4 days, high concentrations of released ketones were observed, wherein the combined processes had a higher concentration than the aerobic process. After a low concentration period, high concentrations of ketones appeared again from day 6 to day 11, especially for 2-butanone. Then, almost no ketones could be detected for three treatments.

2.6 Release of terpenes during bio-drying

The concentrations of released terpenes during bio-drying are presented in Table 4. Limonene accounted for over 80% of terpenes for three treatments. In the first 10 days, the concentrations of terpenes remained at a high level for combined processes and aerobic process. From day 11 on, negligible terpenes could be detected.

2.7 Release of chlorinateds during bio-drying

The potential sources for chlorinateds in MSW were: aerosol, paint remover, dry cleaning agents, dyeing solvents, foam blowing agents, soaps and paints (Chiriac et al., 2007). The concentrations of released chlorinateds during bio-drying are shown in Table 5. Methylene chloride was the dominant chlorinateds for combined processes and aerobic process. And 1, 2-dichoro-ethane was also an important component for the combined process 2. During the whole process, the combined process 1 had the highest concentrations, followed by combined process 2 and aerobic process. Moreover, in the last 3 days, large amount of chlorinateds was released from MSW for three treatments.

3 Discussion

The fate of VOCs in MSW during bio-drying is presented in Fig. 3. The release of VOCs was influenced by their inherited concentrations, production, degradation, adsorption, dissolution and retention in MSW. Wherein, the concentrations of inherited VOCs were related to MSW characteristics, and the production and degradation of VOCs were affected by microbial metabolisms and VOC properties. The adsorption of VOCs was influenced by VOC properties, solid properties, temperatures and aeration. As for the retention of VOCs in FAS, it was mainly related to environmental conditions in column,

Table 3 Release concentrations of ketones during bio-drying (mg/m³)

Compounds	Day 0	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Day 11	Day 12	Day 13	Day 14	Day 15	Day 16
Acetone	A	5.24	3.80	4.60	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	5.24	2.82	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	5.24	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01	ND	0.02	ND	ND	ND
2-Butanone	A	17.26	82.47	6.71	3.05	ND	ND	16.57	0.02	1.39	ND	1.16	1.30	0.01	ND	ND	ND
	B	17.26	68.34	37.24	ND	11.38	ND	17.22	ND	1.24	ND	0.83	ND	ND	ND	ND	ND
	C	17.26	ND	ND	ND	ND	6.98	2.42	ND	1.14	0.02	0.95	ND	ND	ND	ND	ND
2-Pentanone	A	2.22	5.69	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	2.22	ND	ND	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	C	2.22	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ketones	A	24.72	91.95	11.30	3.05	ND	ND	16.57	0.02	1.39	ND	1.16	1.30	0.01	ND	ND	ND
	B	24.72	71.16	37.24	ND	11.40	ND	17.22	ND	1.24	ND	0.83	ND	ND	ND	ND	ND
	C	24.72	ND	ND	ND	ND	6.98	2.42	ND	1.14	0.02	0.96	ND	0.02	ND	ND	ND

A: combined process 1; B: combined process 2; C: aerobic process; ND: not detected.

Table 4 Release concentrations of terpenes during bio-drying (mg/m³)

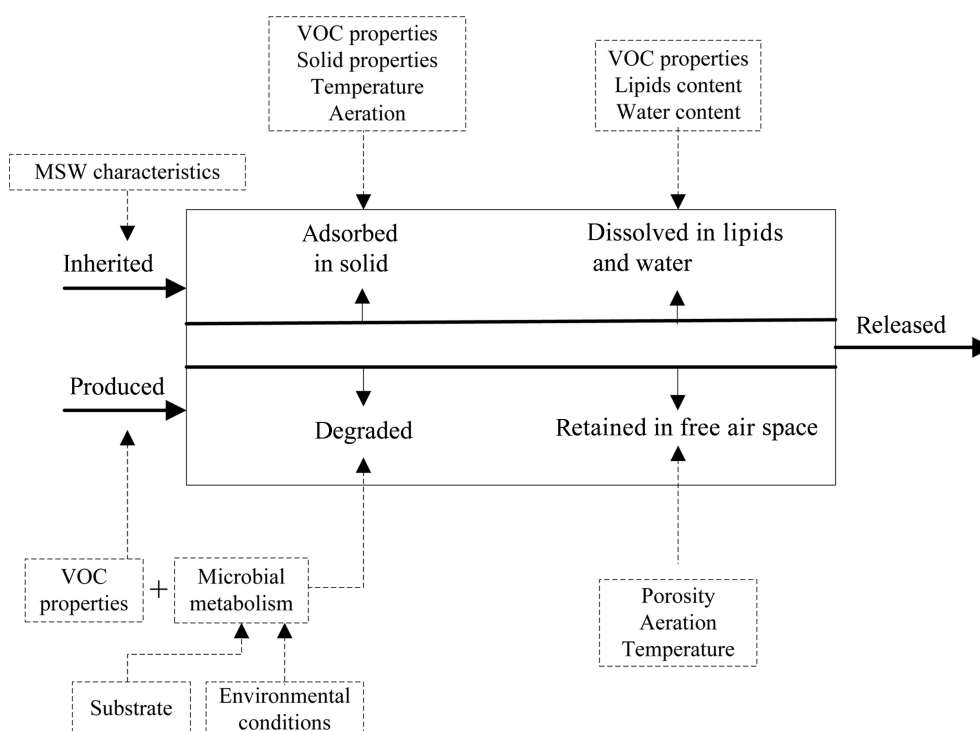
Compounds	Day 0	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Day 11	Day 12	Day 13	Day 14	Day 15	Day 16
Limonene	A	28.71	1.94	5.96	7.00	ND	0.01	29.17	2.73	3.34	1.47	43.02	1.47	0.08	0.11	2.33	0.11
	B	28.71	0.03	79.24	2.73	45.86	0.04	4.44	2.96	3.11	1.52	10.37	0.14	0.07	0.11	0.17	0.06
	C	28.71	61.19	ND	ND	ND	0.18	10.87	2.46	35.61	1.26	1.15	0.16	0.11	0.18	2.62	0.04
alpha-Pinene	A	5.62	0.20	0.19	ND	ND	ND	0.90	0.11	0.09	0.10	21.58	2.45	0.12	0.10	0.07	0.17
	B	5.62	0.21	0.16	0.07	1.84	ND	0.90	0.09	0.09	0.09	1.31	1.90	0.12	ND	0.03	0.06
	C	5.62	ND	ND	ND	ND	0.03	1.58	0.04	1.21	0.06	1.12	1.24	0.13	0.12	0.07	0.06
beta-Pinene	A	ND	2.59	ND	ND	ND	ND	2.00	0.03	0.03	0.02	0.96	0.03	0.00	0.00	ND	ND
	B	ND	0.09	0.07	0.02	0.11	ND	0.12	0.02	ND	0.04	0.06	0.02	0.03	0.00	ND	ND
	C	ND	ND	ND	ND	0.79	ND	1.53	ND	0.07	0.03	0.09	0.02	0.04	0.00	0.04	ND
Terpenes	A	34.33	4.73	6.16	7.00	ND	0.01	32.07	2.87	3.46	1.59	65.56	3.96	0.20	0.21	2.40	0.28
	B	34.33	0.34	79.47	2.82	47.81	0.04	5.46	3.07	3.19	1.66	11.74	2.05	0.21	0.11	0.20	0.12
	C	34.33	61.19	ND	ND	0.79	0.21	13.97	2.51	36.89	1.35	2.36	1.42	0.28	0.30	2.74	0.10

A: combined process 1; B: combined process 2; C: aerobic process; ND: not detected.

Table 5 Release concentrations of chlorinateds during bio-drying (mg/m³)

Compounds		Day 0	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Day 11	Day 12	Day 13	Day 14	Day 15	Day 16
Methylene chloride	A	ND	ND	ND	ND	ND	0.36	ND	ND	0.45	0.05	ND	ND	0.06	ND	2.02	1.91	1.36
	B	ND	ND	ND	ND	ND	0.37	ND	0.34	0.06	ND	ND	0.05	0.06	ND	1.51	ND	0.74
	C	ND	ND	ND	ND	ND	0.00	0.05	0.06	0.07	0.06	0.07	ND	0.05	0.05	1.45	1.64	1.76
1,2-Dichoro- ethane	A	ND	ND	1.30	ND	ND	0.05	0.09	0.04	ND	0.09	1.27	1.00	0.09	ND	0.09	1.28	0.77
	B	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02	ND	ND	0.02	ND	ND	ND	0.02
	C	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02	ND	ND	0.04	ND	ND	ND	ND
1,3-Dichloro- benzene	A	ND	ND	0.11	ND	ND	ND	0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B	ND	ND	0.05	ND	0.03	0.02	ND	ND	ND	ND	0.03	ND	0.04	0.02	ND	ND	ND
	C	ND	ND	ND	ND	0.06	0.05	0.05	ND	0.03	ND	ND	0.03	0.08	ND	ND	ND	ND
Chlorinateds	A	ND	ND	1.41	ND	ND	0.41	0.11	0.04	0.45	0.14	1.27	1.00	0.15	ND	2.11	3.19	2.13
	B	ND	ND	0.05	ND	0.03	0.40	ND	0.34	0.06	0.02	0.03	0.06	0.12	0.02	1.51	ND	0.76
	C	ND	ND	ND	ND	0.06	0.05	0.10	0.06	0.10	0.08	0.07	0.03	0.17	0.05	1.45	1.64	1.76

A: combined 1; B: combined 2; C: aerobic; ND: not detected.

**Fig. 3** Fate of VOCs in municipal solid waste during bio-drying.

such as porosity, aeration, temperatures, and so on. And, the dissolution was affected by lipids and water contents and certain key properties of these VOCs, e.g., boiling point, vapor pressure, solubility and octanol-water partition coefficient. In addition, the aeration could not only bring VOCs out of waste but also dilute the concentration of released VOCs.

For the VOCs produced by microbial metabolisms during bio-drying, their release concentrations were mainly determined by their production rates which were further related to the corresponding substrate properties and concentrations in MSW as well as environmental conditions in column (Fig. 3). Malodorous sulfur compounds were mainly produced under anaerobic conditions or in the incomplete aerobic process (Pierucci et al., 2005). Moreover, the degradation of malodorous sulfur compounds was negligible due to low degradation rates (Ho et al., 2008; Smet et al., 1998). In the first 4 days of bio-drying, the combined processes had much lower O₂ concentrations

than the aerobic process due to lower aeration quantities in the hydrolytic stage (Fig. 4). Therefore, the combined processes had much higher concentrations of released malodorous sulfur compounds than the aerobic process. From day 5 on, malodorous sulfur compounds remained lower concentrations due to sufficient O₂ supply, nevertheless, they could be still detected since anaerobic zones existed in MSW, especially for the combined processes. As for terpenes, they could not only be produced by branches and deciduous tree leaf litters of plants, but also be emitted from the decomposition of fruits, vegetables and table-ready foods (Staley et al., 2006; Wang and Wu, 2008) during MSW bio-drying. Therefore, the concentrations of released terpenes remained at a higher level in the first 10 days, due to the intensive degradation of these substrates in MSW. After that, almost no terpenes could be detected attributed to the complete degradation of these substrates. In addition, chlorinateds would be released with the decomposition of chlorinated materials in MSW. These

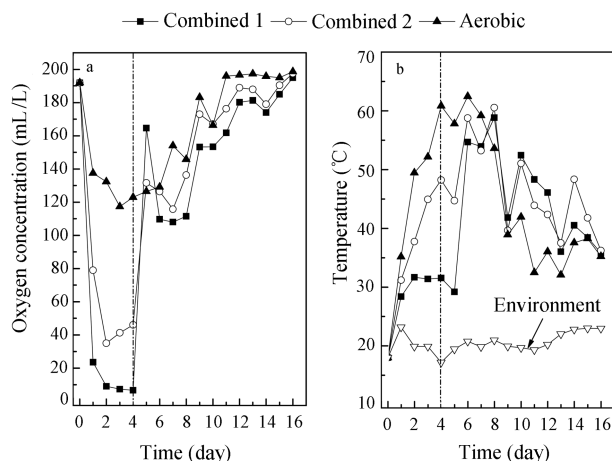


Fig. 4 Temporal evolution of the O₂ concentrations and the temperatures during bio-drying. (a) O₂ concentrations before aeration; (b) temperature.

chlorinated materials would start to be largely degraded in the latter half of bio-drying when the putrescible materials were degraded completely. Thus, higher concentrations of released chlorinated materials were observed in the later stage of bio-drying.

For the VOCs presented initially in MSW, their transfer and transport in MSW during bio-drying mainly determined the release concentrations. And the transfer and transport were influenced not only by temperatures, aeration and porosity, but also by the effective concentrations of VOCs. Besides retained VOCs in FAS, the effective concentrations were related to the degradation, desorption (from solids) and desolvation (out of water and lipids) of VOCs in MSW. Generally, two peak concentrations of released VOCs appeared during bio-drying. Aromatics were largely contained in foods, polymer packaging materials and papers in MSW and the biodegradation half-lives of aromatics were relatively long (Fleming-Jones and Smith, 2003; Staley et al., 2006; USEPA, 2003). The first peak was attributed to the release of inherited aromatics contained in MSW. The second peak appeared since organics degradation would decrease the adsorbed aromatics and the aromatics dissolved in water or lipids were released due to the reduction of water (36.5% for combined process 1, 45.3% for combined process 2 and 53.6% for aerobic process on day 8) and degradation of lipids (55.5% for combined 1, 56.6% for combined 2 and 71.3% for aerobic process on day 8). Furthermore, this might be associated with lignin degradation (USEPA, 2003), since the structure of these aromatics was similar to moieties found in the lignin polymer. Notably, for the combined processes, there was another peak concentration of released aromatics in the shift from hydrolytic to aerobic stages. The possible reasons were that the increased aeration would carry out these components remained in FAS of the columns due to lower temperatures and less aeration quantities in the hydrolytic stage.

The ketones were likely inherent existing in MSW (Staley et al., 2006). Also, they could be produced under anaerobic conditions or as intermediates of aerobic metabolism. In the first 4 days, high concentrations of

ketones were observed, attributed to the inherited ketones release and the production in the course of amylums degradation. Second peak concentration occurred as the lignocelluloses began to be degraded largely and the transfer and transport of ketones were promoted by relatively high temperatures and porosity enhancement. In the last 4 days, neglectable ketones could be detected since the improvement of aerobic conditions due to porosity enhancement mitigated the production of these intermediates. At the same time, they could be further degraded immediately as lower temperatures were unfavorable for the transfer and transport of ketones.

4 Conclusions

VOCs release concentrated in the first 4 days of bio-drying and the dominant materials were: dimethyl disulfide, dimethyl sulfide, benzene, 2-butanone, limonene and methylene chloride. Therefore, the combined process was suggested for MSW bio-drying due to fewer aeration quantities in the first 4 days and the treatment should base on these prominent VOCs. For the VOCs produced by microbial metabolisms during bio-drying, their release concentrations were mainly determined by their production rates. For the VOCs presented initially in MSW, the transfer and transport of inherited VOCs mainly determined the release concentrations and two peak concentrations of released VOCs appeared during bio-drying. Notably, for the combined processes there were also high concentrations of released aromatics in the shift from hydrolytic to aerobic stages.

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