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餐厨垃圾生物处理过程中VOCs的产生与控制研究进展

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摘要 餐厨垃圾生物处理包括好氧堆肥、厌氧消化及卫生填埋等方式, 在处理过程中产生的大量挥发性有机物(VOCs)造成二次污染, 对环境和人体健康均造成危害。为促进对餐厨垃圾生物处理过程中VOCs的控制, 对其产生机理、排放特征及控制方法方面进行综述。已有研究表明: 餐厨垃圾生物处理过程产生VOCs可达100种以上。好氧堆肥、厌氧消化、卫生填埋可产生总VOC量分别为57.40-12 736.72 mg/kg、25.98-29.19 mg/m³和106.20-1 103.70 mg/m³, 且VOCs组成成分复杂, 种类与气体量受处理季节、处理时间、处理技术等因素影响较大。当前的VOCs控制技术包括吸附净化、生物净化、热力燃烧等。吸附净化装置简单、成本低但热稳定性差、吸附容量较小; 热力燃烧适用于厌氧消化产生的小气体量VOCs, 但存在着能耗高、局限性大等缺点。相较于其他控制方法, 生物净化具有适用范围广、能耗低、二次污染小、去除效率高等优点, 可作为餐厨垃圾生物处理过程中VOCs的主要控制方法。提出未来将餐厨垃圾生物处理过程VOCs产生的微生物机理研究, 优化控制技术参数, 提高总体去除效率作为重点研究与技术突破方向。(图2表2参76)

关键词 餐厨垃圾; 挥发性有机物(VOCs); 堆肥; 厌氧消化; 卫生填埋

Review of the generation of volatile organic compounds during the bio-treatment process of food waste

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Abstract Food waste can produce a large number of secondary pollutants such as volatile organic compounds (VOCs) during the bio-treatment process that includes aerobic composting, anaerobic fermentation, and landfill, which harm the environment and human health. In this review, the mechanism, emission characteristics, and control methods of VOCs in the food waste bio-treatment process were summarized, which could benefit research of the generation mechanism and control methods of VOCs. The results showed that there were more than 100 types of VOCs produced by food waste. The concentration of VOCs produced by aerobic composting, anaerobic fermentation, and sanitary landfill was 57.40–12 736.72 mg/kg, 25.98–29.19 mg/m³, and 106.2–1 103.7 mg/m³, respectively. The components of VOCs released from food waste are complex and are greatly influenced by treatment time, season, technology, and other factors. Current control technologies of VOCs include adsorption purification, biological purification, and thermal combustion. Adsorption purification is simple and inexpensive; however, it has poor thermal stability and small adsorption capacity. Thermal combustion is suitable for VOCs of small gas volume from anaerobic digestion; however, it has the disadvantages of high energy consumption and large limitations. Compared with other control methods, biological purification has the advantages of a wide application range, low energy consumption, low secondary pollution, and high removal efficiency. This can be used as the main control method of VOCs in the bio-treatment process of food waste. The key research and technological breakthroughs for the future include determining the microbial mechanism of VOCs in the bio-treatment of food waste, optimizing the control parameters, and improving the overall removal efficiency.

Keywords food waste; volatile organic compounds (VOCs); composting; anaerobic fermentation; landfill

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餐厨垃圾是指居民生活之外的食品加工、餐饮服务、单位供餐等活动中产生的厨余垃圾和废弃食用油脂等。所称厨余垃圾,是指食物残余和食品加工废料;废弃食用油脂则是指不可再食用的动植物油脂和各类油水混合物^[1]。随着经济的快速发展与人民物质水平的提升,我国餐饮业呈现平均21%的年行业增速^[2],餐厨垃圾也随之增加,可占到城市生活垃圾的30%-50%^[3]。截至2018年末,我国的城镇化率已达到59.58%,城镇居民人数达8.3亿^[4]。若按城镇居民餐厨垃圾人均日产量0.15 kg^[5]计算,全国年均餐厨垃圾产生量超过4 500万t。餐厨垃圾由于富含蛋白质及有机质,具有很大的饲料^[6]、肥料^[7]、沼气能源的开发利用潜力^[8];但其含水率高,富含有机物、油和盐,且成分季节性影响大^[9]。如不合理处置,其高含水率会导致渗滤液污染地表与地下水,严重危害水体;其高含量有机物^[10]导致餐厨垃圾易腐烂发臭而污染环境。餐厨垃圾的处理现已成为固体废物资源化研究热点之一。生物处理技术因其处理成本低、易于实现和推广等特点被广泛运用于餐厨垃圾的处理过程中^[11],主要包括好氧堆肥、厌氧消化和卫生填埋等生物处理方式^[12-15]。

然而,餐厨垃圾生物处理过程中会有100种以上挥发性有机化合物(VOCs)产生并扩散,其中包含烃类、酮类、酯类、醇类、醛类、萜烯类和有机硫化物等^[16]。作为一种危害人体的主要大气污染物,VOCs一直备受关注^[17]。大多数VOCs由于嗅觉阈值较低^[18]且具有较大毒性^[19],对居民生活与健康造成巨大影响与危害;同时,VOCs氧化可促进次生有机气溶胶(SOA)的形成,而次生有机气溶胶是细颗粒物(PM_{2.5})的主要成分^[20],因此餐厨垃圾生物处理过程中大量VOCs的产生也可能对大气环境造成危害。本文通过综述近年来餐厨垃圾生物处理过程中产生VOCs的机理、排放特征及控制方法,为其机理深入研究与高效去除提供思路。

1 餐厨垃圾生物处理过程中VOCs产生机理与特征

1.1 餐厨垃圾好氧堆肥过程中VOCs产生机理及特征

生物源VOCs占总VOCs排放量的90%,其中有很大一部分是好氧堆肥过程中微生物分解有机物贡献的^[21]。好氧堆肥是餐厨垃圾生物处理的有效途径之一,这一过程利用好氧微生物分泌的胞外酶^[22]将餐厨垃圾分解,会产生包括醇、烃类化合物、萜类、酯、硫化物、醚等在内的VOCs^[23-24]。该过程产生的总挥发性有机物(TVOCs)最高浓度可达12 736.72 mg/kg^[25],占初始碳的0.31%,高于CH₄的产生量(约占初始碳的0.2%)^[26]。

在餐厨垃圾好氧堆肥过程中,VOCs主要来自于其由于通气不充足而产生的厌氧过程^[27],见图1^[23, 28-33]。氧气充足时,垃圾中有机成分如蛋白质在好氧细菌作用下产生NH₃^[34];氧气不足时,厌氧细菌将有机物分解为不彻底的氧化产物如醇、醛、酮、酯等^[35]。其中,硫氨基酸厌氧降解产生含硫有机物如硫醇、硫醚、硫酚类等^[28-29];氨基酸脱羧产生胺类等^[36];芳香族污染物则直接从餐厨垃圾中挥发^[37]。

餐厨垃圾好氧堆肥过程产生的VOCs种类及含量与堆肥龄期、堆肥季节、堆肥处理的操作条件等方面因素有关。堆肥龄期是影响餐厨垃圾好氧堆肥过程VOCs产生的重要因素。Kumar等研究发现好氧堆肥前期VOCs的排放速率比后期高出5倍^[38];Eitzer等调查了8个城市好氧堆肥设施的VOCs排放

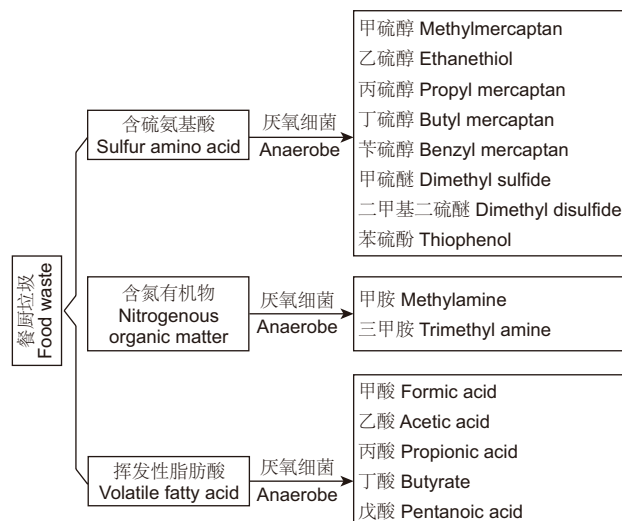


图1 餐厨垃圾好氧堆肥过程中VOCs排放^[23, 28-33]

Fig. 1 VOCs release from food waste composting^[23, 28-33]

量,发现大多数VOCs是在初始堆肥阶段排放的,最大排放量是后期浓度的1.5-2倍^[31];研究发现堆肥初期VOCs的产生量很大,其浓度可超过14 000 mg/m³^[33]。Komilis等发现餐厨垃圾好氧堆肥过程中VOCs的排放随着各个阶段表现出不同的特征:在堆肥初期(3-6 d)具有最高的醇类排放量(12.95 mg m⁻² min⁻¹),占VOCs排放量的85%,其次为酸、酯类,生物烃和醛类;在堆肥后期(14-21 d)不含醇类VOCs排放量(1.37 ± 0.10 mg m⁻² min⁻¹)几乎是堆肥初期(2.28 ± 0.87 mg m⁻² min⁻¹)的一半,醇类排放降低至总排放量的66%(2.62 ± 0.05 mg m⁻² min⁻¹)^[32](图2)。堆肥初期,餐厨垃圾堆体处于中温状态,微生物种类丰富且代谢旺盛,堆体有机物降解速度快,VOCs排放浓度较高;当堆肥龄期到达中后期时,堆体进入高温状态,微生物活性下降,腐殖质趋于稳定,VOCs排放量较前期大幅降低。因此,堆肥初期是控制VOCs排放的关键。

餐厨垃圾好氧堆肥季节的不同对产生VOCs的种类与含量会产生影响。通过检测全年餐厨垃圾好氧消化处理系统VOCs排放情况分析发现,除醇类外,醛类(5%-21%, m/m)和萜烯类(2%-20%, m/m)在10月份是VOCs排放的主要组分,而萜类(7%-20%, m/m)、有机硫类(5%-16%, m/m)和烷类(5%-11%, m/m)在1月份占显著比例,说明VOCs排放量的变化与季节变化有关^[16]。这也许受不同季节人们饮食结构(例如植物或肉类含量)调整的影响。

另外,好氧堆肥处理的操作条件(通风、温度等)也是影响VOCs排放的重要因素之一^[39]。适当增加通风量可减少83%的VOCs排放^[40-41]。但同时,过量曝气会大幅度提高含氮化合物的释放^[42],而曝气不足^[43-44]可能会产生较多含硫化物,均增加VOCs的排放量。温度也是影响好氧堆肥过程VOCs释放的重要因素,高温消化产生的挥发性脂肪酸类(VFA)VOCs量远高于中温过程^[45]。因此,在餐厨垃圾好氧堆肥过程中通过优化好氧堆肥工艺参数(如含氧量、温度等),保持良好的运行条件,可以有效降低VOCs排放量。当然,即使在最佳条件下有一些特定种类VOCs仍然会在好氧堆肥过程中产生^[46]。

1.2 餐厨垃圾厌氧消化过程中VOCs的产生及特征

厌氧消化处理是餐厨垃圾生物处理的主流方法之一^[47]。相较于堆肥与填埋,厌氧消化对运行空间与能量输入的要求更低,因此随着餐厨垃圾问题的凸显,厌氧消化处理技术

越来越受关注。目前我国80多个城市的餐厨垃圾资源化、无害化项目中近八成采用厌氧消化技术^[48]。餐厨垃圾厌氧消化是在无氧条件下,兼性或专性厌氧菌降解餐厨有机固废最终生成甲烷等气体的过程^[49]。餐厨垃圾厌氧消化过程可以分为4个阶段:第一阶段为水解阶段,消化细菌为获取能量,会将难溶复杂有机物水解为简单小分子有机物,水解过程中餐厨垃圾中复杂的有机高分子被分解为氨基酸、单糖和脂肪酸;第二阶段为酸化阶段,可溶性小分子物质在产酸菌如*Ruminococcus*^[50]的作用下变为丙酸、丁酸等VFAs、CO₂、H₂等^[51],如氨基酸经*Anaerospaera*和*Aminomonas*转化为醋酸盐、丙酸盐和氨^[50];第三阶段为产乙酸阶段,前阶段产生的小分子物质被进一步消化,产生乙酸、CO₂、H₂,这也是甲烷的必要来源;第四阶段为产甲烷阶段,在厌氧条件下甲烷菌如*Methanosarcina*^[52]将中间产物转化为甲烷、水和CO₂。甲烷菌对环境条件十分敏感,如过程控制不当,前阶段产生的中间产物如醇、醛、VFAs等将无法继续消化,这也是餐厨垃圾厌氧消化过程中VOCs的主要来源。

餐厨垃圾厌氧消化处理过程释放的VOCs,其中部分成分如有机硫、芳香烃、酯、烷烃、柠檬烯以及由鱼类及其他高蛋白食物降解产生的^[53]三甲胺等会散发恶臭。如餐厨垃圾厌氧消化释放出的VOCs浓度为25.98-29.19 mg/m³,其中1%为硫化物(如乙基硫)、15%为氮化合物(如三甲胺)、49%为芳香族化合物(如甲苯、萘)、2%为烷烃(如十四烷)、1%为酯(如邻苯二甲酸二丁酯)、4%为挥发性脂肪酸(如丁酸)、28%为其他化合物(例如癸醛、苯酚和柠檬烯)。其中萘(1 651 mg/m³)、柠檬烯(3 735 mg/m³)、二甲酰胺(2 404

mg/m³)、4-(对甲苯)-丁酸(1 581 mg/m³)、二十碳烷(504.9 mg/m³)、硫化乙酯(281.3 mg/m³)和邻苯二甲酸盐(157.7 mg/m³)的浓度最高^[54]。研究发现,厌氧消化过程中萜类化合物排放量在VOCs中占优势,过程中累计萜烯排放量相当于新鲜生物废物中实验测定的原始含量的104%^[23]。

1.3 餐厨垃圾填埋过程中VOCs的排放特征

餐厨垃圾填埋处理是指未分选或分选不完全的餐厨垃圾与其他生活垃圾共同进入垃圾填埋场填埋。由于其含水率、有机物含量高的特点,餐厨垃圾的直接填埋会造成生物质能源的浪费,其填埋后形成的渗滤液、臭气等也会以二次污染的形式危害水体与大气环境^[5]。

餐厨垃圾的填埋包含好氧和厌氧两种生物转化过程,因此产生的填埋气成分复杂,其中VOCs含量可达到填埋气的1%^[55],是填埋场恶臭气体的主要成分,且具有产生量大、持续时间长、影响范围广等特点^[56]。表1列举国内外部分垃圾填埋场排放的VOCs种类与成分,可以看出填埋过程中产生VOCs种类较多,可达34-140种,其主要成分为烷烃、烯烃、芳香族化合物、苯系物、酮类等。TVOCs浓度变化范围较大,为106.2-1 103.7 mg/m³^[57-58],最高可达到7 896 mg/m³^[59]。

餐厨垃圾填埋产生VOCs组成与含量受填埋季节、填埋时间、填埋技术等因素影响。北京市某填埋场夏季和冬季分别分离出98种和86种不同VOCs,且夏季VOCs含量大多高于冬季,表明夏季有机物消耗量增加且高温加速了有机物的降解,这两种因素可能导致夏冬两季VOCs组成与含量产生巨大差异^[61];上海秋季垃圾填埋场空气中VOCs种类多于春季,这可能与10月瓜果类垃圾量大、气温较春季高有关^[57]。另外,填

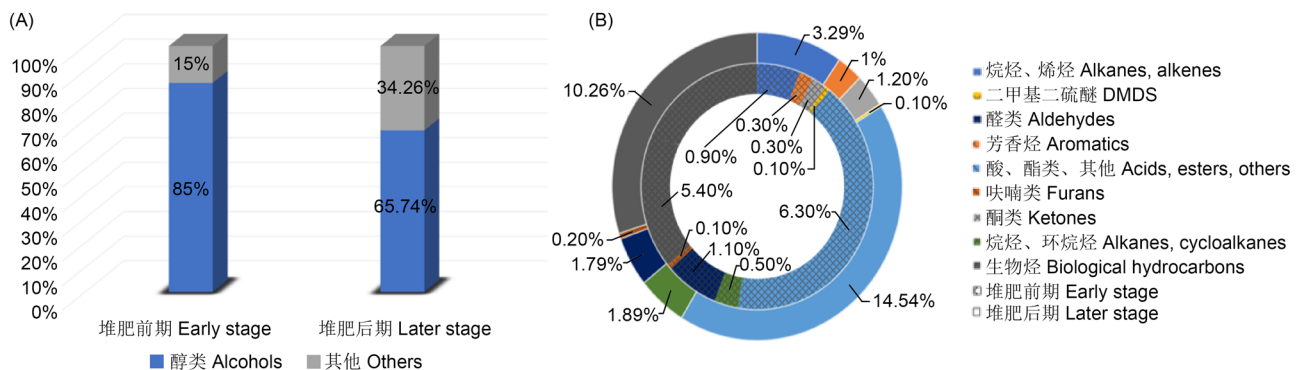


图2 不同堆肥阶段醇类与非醇类VOCs组分组成(A)以及非醇类VOCs组分组成(B)^[32]。

Fig. 2 Composition of alcoholic and non-alcoholic VOCs (A), and composition of non-alcoholic VOCs (B) in different composting stages.

表1 部分垃圾填埋场VOCs种类及成分

Table 1 Types and compositions of VOCs in some landfills

采样地点 Sampling site	VOCs种类 VOCs type	主要成分 Main component	参考文献 Reference
北京市安定生活垃圾填埋场 Anding waste sanitary landfill in Beijing, China	48	烷烃、烯烃、芳香烃、环烷烃、萜类、酯类、醛酮类、卤代烃、醇类、硫化物、含氮化合物 Alkanes, alkenes, aromatic hydrocarbons, cycloalkanes, terpenes, esters, aldehydes and ketones, halogenated hydrocarbons, alcohols, sulfides, nitrogen-containing compounds	[55]
上海市老港垃圾填埋场 Laogang waste sanitary landfill in Shanghai, China	34	卤代脂肪烃、单环芳烃、醛酮、丙烯、丙酮、正己烷、苯系物等 Halogenated aliphatic hydrocarbons, monocyclic aromatic hydrocarbons, aldehydes and ketones, propylene, acetone, <i>n</i> -hexane, benzene series, etc.	[57]
广州市大田山垃圾填埋场 Datianshan landfill in Guangzhou, China	64	氯代烃类、苯系物、氯代苯类、萘等 Chlorinated hydrocarbons, benzene series, chlorinated benzenes, naphthalene, etc.	[60]
英国某垃圾填埋场 Landfill in England	140	烷烃、芳香烃、萜类、醇类、酮类、卤代化合物 Alkanes, aromatic hydrocarbons, terpenes, alcohols, ketones, halogenated compounds	[59]

埋时间也是影响VOCs特征的重要因素,随着填埋龄的增加,填埋场VOCs浓度呈现先增加后降低的趋势,填埋时间为5-7年时VOCs浓度达到最大值^[62];采用不同卫生填埋技术也会导致VOCs浓度出现规律性变化,相较于土覆盖处理技术,采用膜覆盖技术的填埋过程释放的VOCs有大幅度减少^[61]。因此,应针对气象特点及填埋情况,采取HDPE膜覆盖、渗滤液加盖等卫生填埋技术,加强夏秋季填埋场管理,实现VOCs排放控制。

2 餐厨垃圾生物处理过程中VOCs控制

餐厨垃圾生物处理过程中VOCs的控制主要分为原位控制与污染物治理两方面。在原位控制方面,好氧堆肥法可以通过辅料添加、通气散热等方式对二甲基硫(DMS)、二甲基二硫醚(DMDS)、正己烷、丁酸等^[63]部分恶臭VOCs的产生进行抑制,可减少排放49.6%以上^[64-65];厌氧发酵法可以通过提升设施密闭性实现VOCs释放量的降低;填埋技术则可以通过结合不同填埋季节、填埋时间、填埋技术下VOCs的产生特征实现源头管理。

餐厨垃圾生物处理过程中VOCs的控制包括物理法、化学法和生物法(表2)。吸附净化是控制低浓度VOCs的主要物理方法之一,可用于好氧堆肥、厌氧消化和填埋处理3种餐厨垃圾生物处理过程中,具有操作简单、工艺流程较短的优点,但其吸附容量较小、热稳定性差且存在二次污染危险。如活性炭通过改性吸附可实现甲苯77%以上的吸附效率^[66];燃烧法作为化学法适用于处理污染物浓度高、气体量小的VOCs,操作简便,能将碳氢化合物彻底氧化降解,去除率可达99.99%以上^[67],但处理负荷有限会造成二次污染且无法进行溶剂回收,投资与运行费用高昂,有机物浓度不高时的能耗较

大,适用于餐厨垃圾厌氧发酵产生低浓度VOCs的集中处理;包括生物滴滤和生物过滤法在内的生物净化法利用生物填料上的微生物将VOCs降解为无害或低害类物质^[68],具有适用范围广、去除效率高、无二次污染等优点,具有较好的使用前景,是餐厨垃圾好氧堆肥和填埋处理过程VOCs主要控制方法,但目前还不完全成熟,存在易堵塞、高效微生物驯化困难等问题。活性土壤降解法可去除超过57%的氯代烃以及74%的氯乙烯^[69],生物膜过滤器可对苯系物进行去除,甲苯去除率超过90.2%^[70]。实验发现,通过改变填料组成、填料层高度等工艺参数,可使生物滤池对VOCs去除率达到98.38%^[71]。通过驯化生物滴滤池微生物,如利用*Bacillus firmus*可对500-3 000 mg/m³的二甲苯实现100%降解^[72]。与其他方法比较,生物净化法更清洁高效,应用前景广阔。因此,在餐厨垃圾生物处理过程产生的VOCs控制上,应一方面结合不同处理方式产生VOCs的特点进行原位控制,另一方面不断优化生物净化法,实现VOCs总体高效去除。

3 结论及展望

在餐厨垃圾产生量激增的今天,餐厨垃圾的生物处理对其减量化和资源化具有重要意义,但其处理过程中产生的VOCs造成的二次污染不可小视。好氧堆肥可产生TVOCs 57.4-12 736.72 mg/kg;厌氧消化可产生VOCs 25.98-29.19 mg/m³;填埋可产生VOCs 106.2-1 103.7 mg/m³。餐厨垃圾好氧堆肥由于通风不足产生的厌氧过程是VOCs释放的主要原因;厌氧处理虽为封闭状态,但也会有少量VOCs释放;填埋过程由于包含好氧和厌氧两段生物处理过程,其VOCs释放的种类与含量较大,且伴随着占地面积大等问题已逐渐被好氧堆肥与厌氧消化两种生物处理方式取代。相较于其他处理方

表2 好氧堆肥过程中VOCs处理方法

Table 2 VOCs treatment in composting process

方法 Method	适用类型 Type	适用处理方式 Process	优点 Advantage	缺点 Disadvantage	去除效率 Removal efficiency	参考文献 Reference
吸附净化 Adsorption purification	浓度较低的VOCs或二次处理 Low concentration or secondary treatment	好氧堆肥 Aerobic composting 厌氧消化 Anaerobic digestion 填埋处理 Landfill	(1) 装置设备简单、工艺流程较短;(2) 有利于VOCs的资源化利用。 (1) Simple equipment and short process; (2) Conductive to the resource utilization of VOCs.	(1) 对于一些大分子有机物吸附性较大;(2) 在湿度较大时,吸附性会降低;(3) 可能会存在热稳定性差、易着火的安全隐患;(4) 活性炭再生或更换会提高成本。 (1) High adsorption for some macromolecular organic matter; (2) Adsorption decreasing under high humidity; (3) Relatively poor thermal stability and security risks of fire; (4) High costs for replacing activated carbon.	甲苯净化率达77%以上 Over 77% toluene purification rate	[66, 73, 74]
生物滴滤 Biotrickling	负荷较高、降解后生成酸性物质的VOCs High concentration VOCs	好氧堆肥 Aerobic composting 填埋处理 Landfill	(1) 对生长缓慢的微生物保留性好;(2) 负荷量大,缓冲能力强;(3) 高效。 (1) Better retention to slow growing microorganisms; (2) Large load and strong buffering ability; (3) High efficiency.	(1) 装置占地较大;(2) 若填料选择不当,会发生堵塞;(3) 操作复杂,运行成本较高。 (1) Large occupation; (2) Blockage if the filler is not properly selected; (3) Complexity in construction and operation, high operation cost.	95%左右 About 95%	[67, 74, 75]
生物过滤 Biological filtration	气量大、浓度较低的VOCs High concentration VOCs	好氧堆肥 Aerobic composting 填埋处理 Landfill	(1) 价格低廉;(2) 启动运行容易,操作简单;(3) 不产生二次污染。 (1) Low price; (2) Easy to run and operate; (3) No secondary pollution.	(1) 反应条件不易控制;(2) 易发生堵塞、气体短流、沟留;(3) 占地面积大,且对进气负荷变化适应过程较慢。 (1) Poor control of operation conditions; (2) Easy to cause blockage, short gas flow and ouch; (3) Large occupation and slow adaption to variation in gas concentration.	93%-96%	[74, 75]
燃烧法 Combustion	气体量小、污染物浓度高 Low gas content and high concentration of pollutants	厌氧消化 Anaerobic digestion	(1) 将碳氢化合物彻底氧化降解;(2) 操作简便。 (1) Completely oxidative degradation of hydrocarbons; (2) Easy to operate.	(1) 有机物浓度不高时,能耗较大;(2) 无法对VOCs成分进行回收利用;(3) 处理不好将造成污染。 (1) Large energy consumption for low concentration of pollutant; (2) Unable for VOCs recycling; (3) Pollution under invalid treatment.	99.99%以上 More than 99.99%	[67, 74, 76]

式,餐厨垃圾厌氧消化处理产生的VOCs总量上远小于堆肥与填埋,且更容易收集与处理。因此,在实现餐厨垃圾减量化和资源化的同时,应注重其无害化处理。从二次污染控制的角度上,厌氧消化工艺的优化应是餐厨垃圾生物处理今后的重点研究与应用方向。

我国餐厨垃圾成分复杂,含油、含水率较高,且受季节影响较大,其处理过程中产生的VOCs含量与组成呈季节波动,且受处理时间、处理温度以及操作条件等影响,物料变化较大。目前对餐厨垃圾生物处理过程VOCs产生的微生物机理尚

不清楚,未来可通过基因组学等分子技术解析餐厨垃圾在不同生物处理模式、不同时间、季节、操作条件下VOCs产生和变化机理,为实现VOCs的高效控制提供理论依据。

餐厨垃圾生物处理过程产生VOCs的控制主要有吸附净化、热力燃烧以及生物净化法。吸附净化与热力燃烧存在着热稳定差、能耗高、局限性较大等缺点。相较于其他方法,生物净化法作为餐厨垃圾生物处理过程中VOCs的主流控制技术清洁高效,前景广阔,未来可以通过工艺参数优化和功能微生物的选育等实现VOCs的高效去除。

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