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Determination of urine-derived odorous compounds in a source separation sanitation system

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ABSTRACT

Source separation sanitation systems have attracted more and more attention recently. However, separate urine collection and treatment could induce odor issues, especially in large scale application. In order to avoid such issues, it is necessary to monitor the odor related compounds that might be generated during urine storage. This study investigated the odorous compounds that emitted from source-separated human urine under different hydrolysis conditions. Batch experiments were conducted to investigate the effect of temperature, stale/fresh urine ratio and urine dilution on odor emissions. It was found that ammonia, dimethyl disulfide, allyl methyl sulfide and 4-heptanone were the main odorous compounds generated from human urine, with headspace concentrations hundreds of times higher than their respective odor thresholds. Furthermore, the high temperature accelerated urine hydrolysis and liquid–gas mass transfer, resulting a remarkable increase of odor emissions from the urine solution. The addition of stale urine enhanced urine hydrolysis and expedited odor emissions. On the contrary, diluted urine emitted less odorous compounds ascribed to reduced concentrations of odorant precursors. In addition, this study quantified the odor emissions and revealed the constraints of urine source separation in real-world applications. To address the odor issue, several control strategies are recommended for odor mitigation or elimination from an engineering perspective.

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Introduction

In recent years, the concept of source separation system has attracted increasing attention due to the improvement in the wastewater management practice (e.g., water conservation, biogas production, and nutrient recovery) (Bracken et al., 2007). The key to a source separation system is the use of urine diverting toilet, which can effectively separate the human excreta into yellow water (urine) and brown water (feces). The source-separated urine can be utilized in agriculture after

sufficient storage, or nutrient (NPK) recovery by engaging different urine treatment processes (Maurer et al., 2006; Larsen et al., 2009; Zhang et al., 2014).

Unlike the conventional wastewater treatment plants (WWTP), source separation-based facilities are designed to deal with wastewater streams with distinct physicochemical characteristics and potentially confront with more severe odor issues. Odor emissions have been investigated in WWTP, animal farms, food-processing plants, etc. (Easter et al., 2005; Kleeborg et al., 2005; Van Groenestijn and Kraakman, 2005).

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68 However, there is limited information on odor emissions
 69 derived from urine source separation systems. The odorous
 70 compounds present in urine could be influenced by gender,
 71 age, diet, physiological and hormonal status, and use of drugs
 72 (Edman and Brooks, 1983; Guernion et al., 2001). Some studies
 73 were conducted to identify the odorous substances that could
 74 serve as potential indicators for diseases or specific metabolic
 75 syndromes (Bolodeoku and Donaldson, 1996). Hiroshi et al.
 76 (2001) determined the malodorous substances derived from
 77 human excreta (feces and urine) using thermal-desorption
 78 cold-trap and gas chromatography-mass spectrometry.
 79 Their results showed that fatty acids were the main
 80 malodor-causing substances, and other odorous compounds
 81 included sulfur-containing compounds (hydrogen sulfide and
 82 methyl mercaptan) and nitrogen-containing compounds
 83 (ammonia, pyridine, pyrrole, indole, skatole and trimethyl-
 84 amine). It is important to recognize that odor could be an
 85 important issue of source separation systems because odor-
 86 related complaints could change the public acceptance of those
 87 systems.

88 Based on the source separation concept, systematic investi-
 89 gations on urine management were conducted in our previous
 90 studies. Urine hydrolysis was studied in open systems showing
 91 that hydrolysis process could be accomplished in 2 days at high
 92 temperature (35°C) by adding 20% stale urine (Zhang et al., 2013).
 93 In that study, it was also proven that electrical conductivity
 94 could serve as an ideal indicator for urine hydrolysis monitor-
 95 ing. Further studies indicated that phosphorus recovery from
 96 the hydrolyzed urine could be achieved through induced
 97 struvite precipitation using seawater as magnesium source,
 98 while nitrogen harvesting was accomplished by air stripping
 99 and subsequent acid adsorption (Liu et al., 2013, 2014).
 100 Afterwards, hydroponic system was applied to further polish
 101 the urine effluent in order to meet the discharge standards
 102 (Yang et al., 2015). Despite of the very promising results, the
 103 urine treatment systems were subjected to odor emissions
 104 which could obstruct real-world applications. The emitted
 105 compounds were generally non hazardous to human health,
 106 but unpleasant conditions were formed in the open treatment
 107 lines, especially when high temperatures were applied. It is
 108 therefore necessary to determine the odor emissions from
 109 source-separated urine in order to develop effective odor control
 110 strategies.

111 The main purpose of this study was to determine, both
 112 qualitatively and quantitatively, the odorous substances in
 113 the headspace of urine storage tank during the hydrolysis
 114 process. The effects of temperature, dilution, stale/fresh urine
 115 ratio on the odorous emissions were investigated as well. The
 116 findings from this study could provide a useful reference for
 117 the odor control, while several methods are proposed to
 118 mitigate or eliminate odorous emissions.

120 1. Materials and methods

121 1.1. Chemicals

122 All reagents used in this study were of analytical grade. Six
 123 odorant standards including dimethyl disulfide (DMDS), allyl
 124 methyl sulfide (AMS), 4-heptanone, allyl methyl disulfide

(AMDS), methyl propyl disulfide (MPDS), and menthol were 125
 provided by Sigma-Aldrich (Singapore) with high purity (98%). 126

127 1.2. Batch experiments

128 Fresh urine was collected from 25 healthy adults and stored in a 128
 sterile plastic tank. Batch experiments were carried out in glass 129
 carboys (5 L) to monitor the urine hydrolysis process and 130
 determine the odorous emissions under different conditions, 131
 including two temperatures (23, 35°C), three dilution factors (no 132
 dilution, 1:2, 1:5) and fresh/stale urine ratio (4:1). Each carboy 133
 was loaded with 1 L of urine solution. The urine-loaded carboys 134
 were then capped with a liquid sampling port and two gas 135
 sampling outlets as well as one gas inlet. 136

137 1.3. Chemical analysis of urine samples

138 The ammonium concentration in urine samples was measured 138
 using a DR 2800 spectrophotometer based on the salicylate 139
 method (Hach, USA). The pH-value was measured with a D-54 140
 pH meter (Horiba, Japan). The volatile fatty acids (VFA) in urine 141
 samples were determined by gas chromatography (Agilent 142
 Technologies 7890A, USA) equipped with a flame ionization 143
 detector and a DB-FFAP capillary column (30 m × 0.32 mm 144
 i.d. × 0.50 μm film thickness, J&W Scientific, Agilent). The 145
 collected urine samples were first filtered through 0.45 μm 146
 cellulose acetate membrane filters and the injection volume was 147
 1 μL. At least two parallel replicates were engaged throughout 148
 the study for quality assurance. 149

150 1.4. Odor quantification analysis

151 Odorous gas sample was actively collected from the carboy 151
 headspace using two digital air sampling pumps (GilAir Plus, 152
 USA) operated at a flow rate of 100 mL/min. A total volume of 153
 1 L gas sample was aspirated and passed through a stainless 154
 steel sampling tube packed with 130 mg Tenax TA adsorbent 155
 (Perkin Elmer, USA). 156

157 Gas analysis was then carried out with a thermal desorber 157
 (TD-100, Markes International, Llantrisant, UK) followed by 158
 gas chromatography-mass spectrometry (TD-GC/MS) (7890A/ 159
 5975C, Agilent). A two-stage desorption process was applied 160
 to desorb the target compounds from the Tenax TA sorbents. 161
 The desorption temperature was set at 280°C for 10 min, and 162
 then at 320°C for 5 min. The flow rate of carrier gas (N₂) was 163
 held at 100 mL/min and the cold trap temperature was kept at 164
 0°C. The split ratios for sample injection were adjusted 165
 between 1:10 and 1:200 according to the concentrations of 166
 target compounds collected in the sampling tubes. The oven 167
 temperature program was 40°C hold for 10 min, ramping to 168
 250°C at 10°C/min and held for 5 min. A DB-5 ms capillary 169
 column (30 m × 0.25 μm i.d., thickness 0.25 mm) was used 170
 to effectively separate the target compounds with a helium 171
 flow rate of 1.2 mL/min. The MS was operated in electronic 172
 ionization (EI mode) and scan mode. The target compounds 173
 were quantified with external calibration curve established 174
 over a range of standard concentrations: 22, 44, 110, 220 175
 and 440 mg/L. 2 μL of standard solution was injected into 176
 the Tenax TA sorbent with 100 mL/min carrier gas (N₂) for 177
 5 min. 178

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