Application of Deodorant in Odor Control of Municipal Solid Waste

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Abstract. More than 70% of China's municipal solid waste is disposed by landfill, which has caused lots of environmental problems, among which odor pollution is one of the most serious problems. The stench from landfills can seriously affect the daily life of nearby residents and cause a variety of diseases. Due to its wide spread and significant influence, it usually causes mass incident, and lead to bad social impact. An economical and efficient deodorant was developed in this paper. The results showed that the deodorant developed in this paper could remove 47% of ammonia gas, 40% of isobutylene and 20% of other gases with 20 min. The apparent deodorization rate in this paper is relatively low, which may be caused by the small experimental container and the continuous production of odor, the actual deodorization rate should be more than 50%. Moreover, the overall deodorization rate of the deodorant developed in this paper is higher than that of the commercial deodorant, but the cost is only 60% of that of the commercial deodorant.

1. Introduction
With the rapid development of China's economy and the increase of urban population, the generation of urban garbage is also increasing, and the pressure on the environment is also increasing. At present, more than 70% of China's garbage is buried in landfills, which not only occupied vast expanses of limited land resources, but also causes potential harm to the environment [1].
After the disposal of household garbage to the landfill site, it will ferment and produce more than 50 kinds of malodorous mixed gases with complex components, mainly including hydrogen sulphide, ammonia gas, methyl mercaptan, dimethyl sulphide, dimethyl sulfate and carbon disulphide [2]. These bad odors enter the human body through the respiratory system, which is harmful to human body. They could stimulate people's sense of smell and makes people feel unhappy. Hydrogen sulphide is an acute, highly toxic substance, and inhaling small amounts of high concentrations can be deadly in a short period of time [3]. Ammonia gas is a gas with irritating smell under normal temperature, which can absorb moisture tissue in the skin, make its protein degenerate, and make tissue fat saponify, damage skin cell membrane structure, and destroy human immune system. Most other malodorous gases can lead to asphyxiation and weak anesthesia, causing acute poisoning [4].
At the beginning of the 20th century, European countries began to study the deodorization of garbage odor, and accumulated much experience in prevention and treatment of odor. Among them, Germany, the United States, the Netherlands and Japan have developed relatively advanced technologies [5]-[7]. By contrast, research on China's odor pollution began in the late 1980s and has focused on investigations, tests and environmental standards [8], [9]. In addition, because of the difference of the dietary structure between foreign countries and China, the component of municipal solid waste is also
different from each other. So the source and category of the odor has significant difference, so as the treatment technology of the odor. So far, we can see that there are mainly physical, chemical, and biological methods for the removal of odor from garbage at home and abroad. These methods of deodorization are essentially aimed at removing the odor by changing the phase and material structure of the odor [10].

Deodorant is an end-of-pipe treatment technology that combines several deodorization principles. Deodorant available REDOX reaction, the decomposition reaction, neutralization reaction, etc., to produce the fetid stench into odourless gas or directly to eliminate odor, or change the adsorption odor molecules stereo configuration, weaken the molecular association bond, decrease the stability of odor molecules, or to make it easy to react with other molecules. For example, hydrogen sulphide reacts with deodorant to form sulfuric acid ions and water, while ammonia can form nitrogen and water [8], [11], [12].

According to the investigation, most deodorants sold in the market are ecological deodorant, and the active principle is so-called plant extracts, like enzyme. However, the exact composition of these deodorant were unknown, and the deodorization efficiency is also not good enough. A new deodorant was developed and compared with the commercial deodorant used in a landfill in Xiamen city. By optimizing the formula of deodorant, to make the deodorant with high deodorizing efficiency and low cost, and provides a possible solution to effectively alleviate the odor pollution in landfill sites.

2. Materials and methods
2.1 Materials and instruments
Mercury iodide, acrylic acid, maleic acid, ferrous sulphate, methenamine, and acetaldehyde were purchased from Tianjin fuchen chemical reagent factory. Peppermint essence, Holly essence from Guangzhou sipu essence and perfume co. LTD. RAE 3000 VOC detector, PGM- 7340(ppb), RAE Systems, USA; Metrohm 883 Ion Chromatography, Swiss Metrohm co. LTD; 722 Visible spectrophotometer, Shanghai spectrophotometer co. LTD; 0.45μm, 0.22μm ultrafiltration membrane, Shanghai xinya purification device factory.

2.2 The preparation of deodorant
Based on literatures and the results of pre-experiment, the formula of the deodorant is as following: it contains 40ml wood vinegar, 20ml fungicide, 20ml mixed acids (3 ml of acrylic acid, maleic acid and boric acid combined with the ration of 1:1:1, neutralized by methenamine, and then diluted to 20ml), 10ml essence, 10ml ferrous sulfate (the ferrous sulfate solution was prepared in the concentration of 0.1mol/L and stored in a brown bottle), and 20ml ethylene glycol. This formula was named as Deodorant 1 (DO1). To improve the possible deodorization efficiency, we increased the amount of wood vinegar to 50ml, fungicide to 30ml and mixed acids to 30 ml, and the others are keep the same amount. This formula was named as Deodorant 2 (DO2). A total of 50 ml, 20 ml, 10 ml DO1 were took and diluted to 1 L, and the diluted deodorants were named as DO11, DO12 and DO13. The DO2 was diluted as DO1, and then the DO21, DO22 was obtained.

2.3 Experiment methods
A total of 5kg of waste at a depth of 30cm was taken from the landfill site and placed in a transparent glass box. The waste in it was fully reacted in the natural state until the concentration of emitted odor gas is relatively steady, and then the lid was put on to make it a relatively sealed environment. The initial concentration of malodorous gas in the box was detected as the initial concentration. The deodorant developed by this project and the commercial deodorant was sparged respectively, and then the air sample was taken in 5, 10, 20, and 30 min. The concentration differences of odor gas were calculated before and after the deodorant spraying, and the deodorizing effect of deodorant was evaluated. In the parallel group and the control group, the odor was not treated to assess the concentration and composition changes of the odor in the experiment box. The results indicated that the concentration of odor gas slightly increased within 1h, but the increasing of the concentration is not significant.
Six gases were selected as the representative substances of odor, including ammonia gas, isobutylene, hydrogen sulphide, toluene, dimethyl sulfate and dimethyl sulphide. The determination of ammonia was carried out by the spectrophotometry of Nessler reagent. Other substances are determined using an atmospheric detector.

The odor produced was sampled by an anti-reverse suction device consisting of an atmospheric sampler, a beaker, a funnel, a glass tube and a rubber tube. The odor was absorbed for 4 minutes with 50ml, 0.5mol/L of H₂SO₄ as the absorbent. The colorimetric tube was rinsed with absorbent solution and 10ml was taken for test.

To verify the accuracy of RAE 3000, one sample was collected and detected by RAE 3000 and gas chromatograph. The results were listed in Table1. The results of S1 and S2 were detected by RAE 3000, and the results of S3 were detected by gas chromatograph. The results showed that the differences between the two methods were not significant, and indicated that the odor concentrations determined by RAE 3000 were reliable.

| Sample | isobutylene (μg/L) | hydrogen sulphide (μg/L) | dimethyl sulfate (μg/L) | dimethyl sulphide (μg/L) | toluene (μg/L) |
|--------|-------------------|--------------------------|-------------------------|--------------------------|----------------|
| S1     | 33.25             | 69.07                    | 1372                    | 14.37                    | 26.30          |
| S2     | 36.51             | 68.36                    | 1478                    | 13.61                    | 25.94          |
| S3     | 34.79             | 69.16                    | 1450                    | 14.00                    | 25.55          |

2.4 QA and QC

Impurities such as ferric ion, organic matter and sulphide may be contained in the absorbed samples, which may interfere with the determination of the absorbance of samples. Interference can be removed by the following methods:

Adding 0.50ml sodium potassium tartrate solution to the absorption sample can eliminate the interference of ferric trivalent ions. When the sample produced heterochromic interference measurement, dilute hydrochloric acid can be added to remove the interference. When there are some interference caused by the formation and precipitation of certain organic substances in the sample, the absorbent sample can be acidified to a pH of no more than 2 with 0.1mol/l hydrochloric acid before colour comparison, and then boiled to remove the interference.

3. Results and discussion

3.1 The deodorization of deodorant DO1

As shown in Figure 1, the ammonia has the highest removal efficiency, followed by isobutylene, dimethyl sulphide, hydrogen sulphide, toluene and dimethyl sulfate. It is pointed out in the literature that wood acetic acid solution can significantly reduce ammonia in the air, and boric acid also can react with ammonia gas. When ammonia gas is dissolved in water, ammonia molecules and water molecules can combine to form ammonium hydroxide (NH₃•H₂O) which could be ionized into ammonium ion (NH₄⁺) and hydroxide ion (OH⁻) ions. Hydroxide ions then combine with hydrogen ions (H⁺) in boric acid to form water, allowing continuous inhalation of ammonia gas [13]. Ammonia gas could react with ferrous sulfate to form iron hydroxide and ammonium sulfate, and it also can effectively reducing the content of ammonium in odor gas. In addition, the deodorant contains abundant organic acid, which reacts with ferric hydroxide to improve the reaction speed. Relevant literatures have pointed out that methenamine plays an important role in the absorption of hydrogen sulphide [10], [14]. The relatively higher removal rate of hydrogen sulphide in this experiment may ascribe to the methenamine in deodorant.

It can be seen from the figure 2 that isobutene has the highest removal efficiency when compares to other substances, followed by hydrogen sulphide, dimethyl sulfate, dimethyl sulphide, toluene and ammonia. Hydrogen sulphide is easy to be reduced because of its low valence state. Compared with the DO11, the removal rate of ammonia gas dropped significantly. Isobutylene can reach up to 40%, hydrogen sulphide and dimethyl sulfate up to 20%. The optimal reaction time reduced to 10min, with rapid deodorization and consumption. After 30 minutes, the odor concentration goes up again.
Figure 1. The removal rate of deodorant DO11 to isobutene, hydrogen sulphide, toluene, dimethyl sulfate, dimethyl sulphide and ammonia

Figure 2. The removal rate of deodorant DO12 to isobutene, hydrogen sulphide, toluene, dimethyl sulfate, dimethyl sulphide and ammonia

Figure 3. The removal rate of deodorant DO13 to isobutene, hydrogen sulphide, toluene, dimethyl sulfate, dimethyl sulphide and ammonia
It can be seen from the figure 3 that the biggest change of the deodorant is that the deodorizing time is shorter and the deodorizing efficiency is obviously decreased. The deodorization efficiency for several gases in odor tends to be the same. This is mainly because the concentration of the drug is lower and the reaction time is lower. After 10min, the odor concentration gradually increased, indicating that the deodorant had been consumed completely. In general, the deodorization effect is not good enough.

With the comparison of the deodorization rate of the different concentrations of deodorant 1, it’s obvious that the deodorization effects have a positive correlation with the concentration of deodorant, and it decreased with the decreasing of deodorant concentration. In addition, the deodorant could react quickly with odor, and the maximum deodorization efficiency could be reached within 10 min.

Generally speaking, the deodorization rate is not good enough, for the removal rate of most odor composition is less than 50%. However, it works for some of the odor composition, such as isobutene, ammonia gas, and hydrogen sulphide.

The boric acid and wood vinegar in DO1 effectively reduced the concentration of ammonia, and methenamine reacted with hydrogen sulphide, but the removal efficiency was not ideally. After the spray, the odor concentration did not decrease significantly, but the effect of peppermint essence covered up parts of the odor, making the sensory deodorization effect seems better.

3.2 The deodorization of deodorant DO2

It can be seem from Figure 4, compared with DO1, DO2 has a high removal rate for toluene and dimethyl sulphide, but has a relatively lower removal rate for isobutene, hydrogen sulphide, and dimethyl sulfate. It is speculated that the increased concentration of fungicide in DO2 could kill the bacteria that will change the biochemical reaction in rubbish.

The Figure 5 shows that the deodorization rate decreased significantly with decreasing of the deodorant concentration. The highest removal rate was only 18% (methyl sulphide), and the rest substances were about 10%. The results indicated that the increase of the concentration of wood vinegar, fungicide and mixed acids could not enhance the deodorization efficiency, and by contrast, the odor removal rate of DO1 is better than DO2. It indicated that the deodorization efficiency is not only related to the amount of each of the constituents of the deodorant, but the ratio of the constituents is also important. In addition, the deodorization efficiency is significantly related to the concentration, and it increase with the increasing of the deodorant concentration.

3.3 Comparison of the deodorization efficiency with commercial deodorant
In order to verify the commercial value and estimate the deodorization efficiency level when compares to other commercial deodorant, one kind of commercial deodorant (DO3) was chosen to compare the deodorization efficiency with the best performance deodorant DO11. The commercial deodorant DO3 was also diluted as DO11, and they were sparged in the same experiment box with the same condition. The results showed in Figure 6.

![Figure 6](image_url)

**Figure 6.** The removal rate of commercial deodorant (DO3) to isobutene, hydrogen sulphide, toluene, dimethyl sulfate, dimethyl sulphide and ammonia

With the comparison of Figure 1, the removal rates of DO11 for all the odor gas were higher than DO3 except isobutene. The odor gas could be decreased quickly within 10 to 20 min for DO11, and it is more than 30 min for DO3. It seems like that the deodorization efficiency of DO11 was better than DO3. And the cost of DO11 is only 60% of DO3.
One kind of ecological deodorant was applied by Lu et al to remove the NH$_3$ and H$_2$S, and the results indicated that, the removal rate of NH$_3$ and H$_2$S could up to 99% under optimal conditions [15], and the relatively high removal rate also reported in other literature [16]. However, the deodorization rate seems relatively low in this experiment, including the commercial deodorant. In fact, the declared deodorization rate is much better than its performance in this experiment. The possible reason may ascribe to the relative small volume of the experiment box. The odor gas could emit continuously in the small space, so the detected odor concentration include the new emitted part. By contrast, the high removal rate of odor reported in literatures were carried out in smaller space and use discontinuous odor source, so they can get the relatively higher removal rate. It means that, the real deodorization rate for our deodorant is possible higher than the results described above. And the results of the control group provide the evidence that the odor gas concentration increased when no deodorant was sparged.

4. Conclusion
The deodorant developed in this paper could effectively reduce the concentration of odor gas, and the deodorization efficiency is higher than the commercial deodorant. The deodorization efficiency is increased with the increasing of the deodorant concentration. However, the increase of the concentration of parts of the component of deodorant could not significantly increase the deodorization rate, and the ratio of the different component is plays an important role in the deodorization.

5. Acknowledgements
This study is supported by Xiamen science and technology plan project (3502Z20183064) and the Fujian Science and Technology Guiding Project (2018Y0079). We also thank the support of Key Laboratory of Environmental Biotechnology (XMUT), Fujian Province University.

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