Hydrogen sulfide biological removal efficiency by vermicompost horizontal biofilter

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Abstract. To efficiently treat hydrogen sulfide (H2S) from contaminated air, we designed a fixed carrier horizontal biofilter. The biofilter system was packed with vermicompost as baffle plate. The inlet concentration and the thickness of media on the removal efficiency were studied. Furthermore, a final product analysis and the macro-kinetics of bio-degradation were also evaluated. The results showed that the horizontal biofilter can be started quickly, favorable removal efficiencies of H2S were proved and reached nearly100% when the inlet concentration lower than 350 mg m-3. The thickness of vermicompost affected the H2S removal efficiency. It was found that the nutrient elements of vermicompost increased, especially the sulfur increased significantly. In addition, in kinetic analysis, the semi-saturation constant and maximum removal rate of H2S were calculated to be 417.1 mg m-3 and 1428.6 g m-3 d-1. The results presented in this study the horizontal vermicompost biofilter was effective for removing H2S contaminated air, and will be valuable for further research and engineering applications.

1. Introduction

Hydrogen sulfide(H2S) is a colorless and toxic acid contaminants gas, which is widely emitted in petroleum refining, paper making, chemical industry, municipal treatment facilities such as landfill, Sewage Treatment and aquaculture. H2S not only damages the living environment of mankind, undermines public health, and harms growth of animals and plants, but also accounts for a potential hazard to the society. Air quality control regulations on H2S emission in these years have become more and more stringent. The Scientific Advisory Board on Toxic Air Pollutants (USA) prescribes an acceptable range for H2S in the environment of 20-100 ppb with an instantaneous threshold of 50 ppm [1]. To reduce the toxicity and other negative effects of H2S and improve the quality of the environment, H2S pollution must be effectively removed.

Biofiltration outperforms physical-chemical methods for such advantages as high treatment efficiency, ecological and environmental friendliness, and cost-effectiveness. Aita et al. used sawdust immobilized acidithiobacillus thiooxidans biofilter for the treatment of biogas rich in H2S (10,000 ppmv), and achieved an average removal rate of 75±13% and a maximum removal rate of 97% [2]. Das et al. studied the H2S treatment process by composting and biochar filter, and found that the removal performance was improved by adding biochar to the original compost filler [3]. Biofilter is performed mostly by a vertical reactor in most research. Nevertheless, it is susceptible to such
problems as filler compaction, increased pressure drop, and low treatment efficiency after long-time operation. In this study, to address the above shortcomings of vertical reactors, a horizontal multi-layer bioreactor with vermicompost as the media was designed to treat H2S contaminated air under the condition of room temperature and continuous air flow, and its purification performance and biodegradation kinetics were evaluated to provide guidance for further research and engineering application.

2. Materials and Methods

2.1. Selection of packing media

The packing media is where microorganisms grow, and its performance directly affects the growing environment of microorganisms. The selection of suitable packing media is of great importance to the high treatment effect with biofiltration. In this experiment, vermicompost was collected from a vermicomposting reactor of dewatered municipal sewage and sludge, which was used as the packing media due to its high-water holding capacity, large specific surface area, richness in beneficial microorganisms and nutrient components. Screened by a sieve with a pore diameter of 2.36 mm-4.75 mm, the vermicompost was then naturally loaded into the bioreactor. For the vermicompost for testing, the pH was 7.15, the humidity was 58.65%, the bulk density was 717.59 g L\(^{-1}\), the specific surface area was 7.65 m\(^2\) g\(^{-1}\), the conductivity was 2195 µs cm\(^{-1}\), and the C/N was 10.35. Contents of other nutrient ingredients are shown in Table 1.

2.2. Experimental equipment and operation

The experimental bioreactor was horizontal and consisted of three parts: pre-treatment system, bioreactor and tail gas absorption device. The main structure of the vermicompost bioreactor was made of polymethyl methacrylate (PMMA), in a form of cuboid (400 mm × 210 mm × 130 mm). Four vermicompost filling boxes (80 mm × 200 mm × 120 mm) made of polytetrafluoroethylene mesh cloth were placed inside. The effective volume of vermicompost was 7.37 L. Five gas sampling ports were provided along the length of the reactor. A certain concentration of H\(_2\)S gas from the cylinder was measured by rotameter with pressure stabilization, entered the gas buffer bottle, went through an activated carbon air filter and got mixed with the pre-humidified fresh air, and finally generated the simulated exhaust gas required for the experiment. The simulated exhaust gas entered the reactor from the left side, got purified by microorganisms attached to the filler and finally absorbed by sodium hydroxide. The experimental device is shown in Fig. 1. The gas flow shows a horizontal "S" type. H\(_2\)S was continuously supplied to the bioreactor at room temperature, and the air flow was adjusted through the gas flow meter to reach the concentration of H\(_2\)S at 20-500 mg m\(^{-3}\). The gas residence time was 106 s.
2.3. Analysis and statistical methods

The specific surface area of vermicompost was measured by a specific surface area analyser (JW-BK200, Germany), the pH value was determined by a pH meter (pH-3C, Shanghai, China), and the water content through the loss on ignition (LOI) method, the total nitrogen (TN) though the microwave digestion-kjeldahl method, the total phosphorus (TP) through the alkali fusion – Mo-Sb anti spectrophotometric method, the total potassium (TK) through the NaOH fusion - flame spectrophotometry, and the SO$_4^{2-}$ and TS through ion chromatography with Dionex ICX-1000 (SHIMADZU, Japan). The amount of H$_2$S concentration was periodically determined by gas chromatography (GC-2014, Shimadzu, Japan) with a flame photometric detector (FPD) and DB-5 capillary column (15 m ×ø 0.53 mm × 1.0 um, Hewlett Packard, USA). Nitrogen was used as the carrier gas. The data were measured repeatedly three times in the experiment, the graph data were statistically analyzed by SPSS22.0 software, and the data were processed and plotted by Sigmaplot16.2 software.

3. Results and Discussion

3.1. $H_2S$ concentration and removal efficiency of the system

In the biological treatment of hydrogen sulfide exhaust gas, sulfur-oxidizing bacteria and sulfur-oxidizing archaea are usually used to oxidize H$_2$S into odourless substances such as CO$_2$, H$_2$O and SO$_4^{2-}$ [4]. During this experiment, no nutrient was added. The effect of removing H$_2$S through vermicompost biofilter is shown in Fig. 2. The results showed that the H$_2$S removal rate was 74.9% when the reactor was started, but reached over 90% in 3 days, and was close to 100% when the inlet concentration was less than 350 mg m$^{-3}$, indicating that a large number of sulfur-oxidizing microorganisms were enriched in vermicompost. As the biofilter continued to work, the microbial activity increased and the microbial number reached a certain amount, and the H$_2$S removal rate remained stable.
3.2. Impact of thickness on H$_2$S removal efficiency

Hydrogen sulfide samples from different thickness (1*-80 mm, 2*-160 mm, 3*-240 mm and 4*-320 mm) were periodically investigated to determine the distribution of H$_2$S. The influence of thickness on the removal efficiency of H$_2$S and changes in concentration are demonstrated in Fig. 3. The results showed that the removal efficiency the H$_2$S improved as the thickness increased. This was because when the filler layer thickens, the path and contact area of hydrogen sulfide through the filler layer expanded, and the time of reaction with vermicompost would prolong; therefore, the higher removal efficiency was obtained. The filler of each layer made the different contributions to the H$_2$S removal efficiency. When the inlet gas concentration is lower than 350 mg m$^{-3}$, the H$_2$S removal rate at 80 mm was more than 50%, and which was the main area for deodorization, indicating that there were abundant sulfur-oxidizing microorganisms in this layer of vermicompost to adsorb and degrade a great amount of H$_2$S. When the inlet air concentration was further increased, the contributions at 160 mm and 240 mm gradually increased.
3.3. Changes of nutrients and metabolic products

Vermicompost can be used as agricultural organic fertilizer, so more and more researchers has focused on the nutrients of vermicompost. Table 1 shows the changes of nutrients and metabolic products in vermicompost and the control during hydrogen sulfide treatment. The results showed that TN and TP contents in vermicompost increased significantly. The increase in TN may be due to the mineralization of organic nitrogen which was facilitated by the catalytic action of microorganisms on nitrogen conversion during the adsorption and degradation of hydrogen sulfide by vermicompost, while the continuously introduced H₂S gas into the reactor contained N components. There are lot of phosphorus-solubilizing bacteria in the final of vermicomposting, and it contains high content of organic matter [5]. When organic matter is degraded, CO₂ and organic acids are produced and can accelerate the release of phosphorus, which is able to further increase the total phosphorus content. At the same time, it was found that the content of TK in vermicompost increased with the operating time. Biological treatment of H₂S is a process of acid production by microorganism, which can transform insoluble potassium into soluble potassium in the vermicompost, which plays an important role in the increase of K content. Sulfur is the fourth most important nutrient element for plants following nitrogen, phosphorus and potassium applied in agriculture [6]. As shown in the experimental results, the content of TS in the vermicompost after H₂S treatment significantly increased, and the vermicompost with H₂S removed can become an effective sulfur fertilizer.

Tab.1 Variation of nutrients and metabolic products in vermicompost and the control during hydrogen sulfide treatment (g kg⁻¹). Values are the means ± standard errors (n=3).

| Sample Number | Parameters | TN   | TP   | TK   | TS   | SO₄²⁻ |
|---------------|------------|------|------|------|------|-------|
|               | Initial vermicompost |       |      |      |      |       |
| CK            |            | 23.59±0.37 | 5.95±0.42 | 2.12±0.30 | 71.66 ± 0.1 | 10.35±0.35 |
| 1#            |            | 24.15±0.85 | 6.81±0.62 | 2.53±0.23 | 130.01±0.52 | 19.08±0.31 |
| 2#            |            | 25.09±1.05 | 8.61±0.30 | 2.36±0.15 | 113.04±0.85 | 17.54±0.25 |
| 3#            |            | 25.11±0.95 | 7.85±0.45 | 2.28±0.25 | 106.67±0.53 | 16.37±0.20 |
| 4#            |            | 25.33±0.67 | 8.71±0.25 | 2.21±0.18 | 95.24±0.25  | 14.79±0.15 |
|               | Final vermicompost |       |      |      |      |       |

SO₄²⁻ is the final converted product of the biological treatment of H₂S. It can be seen from Table 1 that the content of SO₄²⁻ increased significantly after the start of the reactor and the content of SO₄²⁻ in the sample 1# was the largest, and there was no significant difference in the content of SO₄²⁻ in the different layers. The reason was that in this study, the simulated exhaust gas passed through vermicompost from left to right; the 1# had an exposure to high concentration of H₂S, leading to a higher growth and reproduction rate of sulfur-oxidizing microorganisms; the majority of H₂S was adsorbed and degraded at 1#. This was similar to the results of Li et al. [7]. As the running time extended, the content of SO₄²⁻ in vermicompost increased gradually, and no adverse effect of the accumulation of SO₄²⁻ in this range on the removal of H₂S by the biological filtration system was found. In conclusion, a wide application of vermicompost treated with H₂S in agriculture can be expected.
3.4. Kinetic analysis

In the process of removing H$_2$S contaminated air using vermicompost, mass transfer and biodegradation occurred simultaneously. The transfer and diffusion of H$_2$S took place in the gas phase, while the biodegradation took place in the biofilm. If that airflow was a plug flow, microorganisms in the filler were uniformly distributed, the oxygen required for aerobic respiration of microorganisms in the biofilm was sufficient, and the malodorous hydrogen sulfide gas was adsorbed and degraded in the vermicompost bioreactor through a single enzyme catalytic reaction, there is no product inhibition. The modified Michaelis–Menten equation [8] was used in estimating the removal rate of H$_2$S in the vermicompost biofilter, in accordance with the assumptions bio-degradation into a rate-limiting step.

$$\frac{1}{R} = \frac{K_s}{V_m C_{in}} + \frac{1}{V_m}$$  \hspace{1cm} (1)

Where $R$ is the apparent removal rate, g H$_2$Sm$^{-3}$ d$^{-1}$, $C_{in}$ is the log mean concentration $[(C_{in}-C_{out})/\ln(C_{in}/C_{out})]$, g H$_2$S m$^{-3}$. $V_m$ (maximum apparent removal rate) and $K_s$ (saturation half constant) for the gas phase can be calculated by plotting(1/R) against (1/$C_{in}$). Steady state H$_2$S removal data obtained from biofilter was used as inputs to equation.1 to calculate the kinetic constants ($K_s$ and $V_m$), to biodegrade H$_2$S under different conditions using Lineweaver-Burk method. The results were shown in Fig.4. The regression equation was given as $y = 0.292x + 0.0007$. $K_s$ and $V_m$ for the horizontal biofilter were 417.1 mg m$^{-3}$ and 1428.6 g m$^{-3}$ d$^{-1}$, respectively. The high values of $K_s$ and $V_m$ obtained in this experiment indicated that the sludge-based vermicompost as the packing material was suitable for the growth of sulfur-oxidizing bacteria and had a strong ability to adsorb and degrade H$_2$S malodorous gas.

4. Conclusions

The horizontal vermicompost biofilter was proved able to treat H$_2$S from contaminated air and the removal efficiency was close to 100%. H$_2$S removal efficiency of biofilter improved with the increase of filler thickness at the same gas residence time and other conditions. Furthermore, it was found that the major product for biofilter was sulfate ion after long operation, and the vermicompost treated with H$_2$S can be used as agricultural organic fertilizer. The bio-kinetic constants, $K_s$ and $V_m$ for the horizontal biofilter were 417.1 mg m$^{-3}$ and 1428.6 g m$^{-3}$ d$^{-1}$, respectively. The results from this work revealed horizontal biofilter packed with vermicompost has a good performance without nutrition, and would be used as a guidance for the design and operation of industrial-scale systems.

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