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Improvement of Deodorization Ability by Producing a New Z/M Bio-carrier

Min-Jae Lee[1], Byung-Moon Jin[2], Kyung-Yae Hyun[3]*

[1]Yusung Engineering CO., LTD, Yangsan-si, 626-851, Korea

[2]Depart. of Physics, Dong-Eui University, Busan 614-714, Korea

[3]*Depart. of Clinical Laboratory Science, Dong-Eui University, Busan 614-714, Korea

Abstract

Odors from sewage treatment plants or various sewage are removed according to diverse methods. However, odors emerging from the treatment process, in particular, cause fatal issues in health management, such as adverse effects and respiratory diseases, for the life environment near the plants as well as employees in the plants. Those also play a role as a negative factor by decreasing a house price in a nearby area and hindering activity. Hence, techniques to remove sewage and odors from factories have been studied with various methods including physical and biological methods. However, in previous studies, it was found that physicochemical treatment methods increased a treatment cost due to secondary sewage produced and that biological treatment methods were not able to play a role as an appropriate carrier, which made microorganisms not get settled. Therefore, odor treatment ability has not been completely demonstrated. In the present study, we used *Acidithiobacillus thiooxidans* developed in the previous study and mixed Z carrier and M carrier at the appropriate ratio to investigate the efficiency of deodorization and how much odor treatment ability is improved by *Acidithiobacillus thiooxidans* well get settled. The carrier layer in deodorization had a large porosity, but we mixed Z-carrier, which is alkaline, and M-carrier, which has small pores and is strong acid. Using that Z/M carrier, we confirmed that A. thiooxidans well got settled to exhibit appropriate deodorization. Therefore, we conducted this study to investigate applicability of Z/M carrier, which has never been applied in Korea, in the deodorization mode in order to provide basic data for deodorization.

Keywords: *Bio-carrier, Z-carrier, M-carrier, Acidithiobacillus thiooxidans*

1. Introduction

Odors from waste water and sewage produced by sewage treatment plants or chemical plants are removed according to diverse methods. However, odors emerging from the treatment process, in particular, cause fatal issues in health management, such as adverse effects and respiratory diseases, for the life environment near the plants as well as employees in the plants. Those also play a role as a negative factor by decreasing a house price in a nearby area and hindering activity. One of the related problems is that the environment authorities has not been established a quantitative assay for odors and the number of plants which have deodorization equipment in use is small. Thus, it is hard to efficiently figure out fundamental and established deodorization equipment. In addition, suitability of deodorization equipment has not been evaluated and detailed plans have not been prepared so efficient deodorization is not properly performed. In Korea, physicochemical methods, such as adsorption, combustion and washing, and biological methods for deodorization are used. Physicochemical methods can stably treat contaminants, but those require a high maintenance cost and importantly produce secondary contaminants. In addition, biological treatment methods are not enough to play a role as an appropriate carrier, which made microorganisms not get settled. Thus, odor treatment ability has not been completely demonstrated. In the present study, we used *Acidithiobacillus thiooxidans*[1] developed in the previous study and mixed Z carrier and M carrier at the appropriate ratio to investigate the efficiency of deodorization and how well *Acidithiobacillus thiooxidans* gets settled. The biggest problem of the current biofilter system is H_2S which is dissolved in water to become sulfuric acid to acidify the environment where most bacteria cannot grow. Bacteria used for deodorization generally grow at pH 6 to 8 and therefore its survival rate decreases as the pH is getting lower. Furthermore, porous ceramic is used as a carrier and the pore hole of this carrier is much larger than bacteria so it is hard for bacteria to get settled[2～6].

To improve those drawbacks, bacteria well growing in the acidic environment and carriers for bacteria to get settled are required[7～9]. Using *A. thiooxidans*, we studied the deodorization efficiency of an improved carrier by investigating the decomposition efficiency of noisome odor gas to find out how well Z/M carrier we made is growing in the actual environment.

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2. Theory

2.1 Definition of odor and the relevant laws

An odor is defined as 'H_2S, mercaptan, amine, other irritating gas materials' according to Clean Air Conservation Act by Ministry of Environment, and also a smell giving displeasure and distaste by stimulating the olfactory sense. In other words, an odor is a harmful smell which exists with various ingredients(22 types) mixed and stimulates the olfactory sense to damage the pleasant life. Among common odors we can easily find, H_2S has a smell of a rotten egg, mercaptan has a smell of a rotten vegetable and amine has a smell of fish. H_2S and ammonia are typical odor producing materials.
Korea Ministry of Environment designated complex odors and designated odor materials and defined the odors effluent quality standards and the extent of establishment of effluent quality standards. As Clean Air Conservation Act is strengthening every year, the odors effluent quality standards[10] tend to be tightened.[Table 1]

Table1. Laws related to 22 odor materials[10]

Component	Effluent Quality Standard (ppm)		Time of application
	Manufacturing area	Elsewhere	
Ammonia	2 ↓	1 ↓	from 02. 10. 05.
Metylmercaptan	0.004 ↓	0.002↓	
H_2S	0.06 ↓	0.02 ↓	
Dimetylsulfide	0.05 ↓	0.01 ↓	
Dimethyl disulfide	0.03 ↓	0.009↓	
Trimetylamine	0.02 ↓	0.005↓	
Acete aldehyde	0.1 ↓	0.05↓	
Styrene	0.8 ↓	0.4 ↓	
Propionaldehyde	0.1 ↓	0.05↓	
Isobutylene-Isoprene Aldehyde	0.1 ↓	0.029↓	
n-Valeraldehyde	0.02 ↓	0.009↓	
i-Valeraldehyde	0.006 ↓	0.003↓	
Toluene	30 ↓	10 ↓	from 01.01.08
Xylan	2 ↓	1 ↓	
Methyl ethyl ketone	35 ↓	13 ↓	
Methyl isobutylketone	3 ↓	1 ↓	
Isobutylene-acetate	4 ↓	1 ↓	from 01.01.10
Propionic acid.	0.07 ↓	0.03 ↓	
n-Butyrate	0.002 ↓	0.001↓	
n-Valeric acid	0.002 ↓	0.0009 ↓	
i-Valeric acid	0.004 ↓	0.001 ↓	
i-Isobutylalcohol	4.0 ↓	0.9 ↓	

2.2 Types of deodorization and deodorization techniques

The dictionary definition of deodorization is to remove smells. Removing odors which give displeasure and distaste to the life environment is called deodorization. Materials causing most odors are gas and volatile materials. The principle and techniques to remove air pollutants are generally used. Deodorization techniques are classified into physical methods, chemical methods and biological methods. Among three techniques, the most efficient deodorization technique should be selected depending on the environment of odor sources[11][Table 2].

Table 2. Types of deodorization technique

Types	Technique	
Physical method	Washable(water, charcoal, suspension)	
	Air cooling condensation (water cooling, air cooling	
	Dilution method(atmospheric diffusion)	
	Adsorption method(charcoal, zeolite)	
chemical method	Burning method	Direct, Catalytic burning method
	Chemical treatment	Acid, Alkali washing, Liquid chemical washing, Oxidize method, Neutralize method, , Liquid catalytic method
Biological method	Soil filter adsorber	
	Activated sludge system	
	Bio-filter	
	Compost deodorization	
	Degradation of enzyme	

3. Methods

3.1 Pretreated deodorization

Pretreated deodorization provided by YooSung Engineering is being used in sewage treatment plant, swinery, livestock wastewater treatment plant, slaughterhouse, food factory and various chemical plants.
The most offending issue is the environment composition for the growth of microorganisms in carriers of biofilter. To achieve this, the pretreatment process is combined with the front part to adjust temperature and pH in advance in complex deodorization.
[Fig. 1] shows biofiltering deodorization equipment with a fan cooler which sends air inside by inhaling odor gas; the pretreatment part including the first filter where odor gas

passes the polyurethane form layer and pall ring layer downstream and the second filter where odor gas passes the pall ring layer and polyurethane form layer upstream; the main body where odor gas comes through from the above pretreatment part, and in which the porous ceramic carrier layer and acid clay carrier layer are installed; and the outlet where clean gas comes through from the above main body after odor ingredients are removed from odor gas, and then is released through an installed separator and a demister into the air.

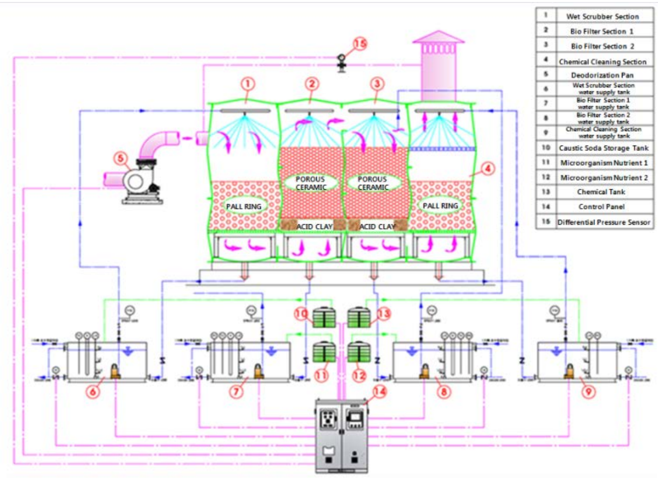

Fig. 1 Preconditioning filter Plan

3.2. Z/M-carrier selection

Other companies are commonly using four microorganisms(*Bacillus subtilis*, *Bacillus circulans*, *Rhodopseudomonas palustri*, *Thiobacillus sp*.) for bio deodorization. However, as the environment laws have strengthened, the effluent limitations and regulations are being tightened and therefore deodorization with higher efficacy and efficiency is required. Carriers are being developed in Korea, but efficient deodorization has not been achieved. In the present study, we use Z carrier and M carrier, which have been already used, to find out the appropriate ratio for the most efficient deodorization.
Oxidation of H_2S, one of ingredients of odor gas, decreases the pH to 2~4 and therefore we selected sulfur-oxidizing bacteria which well grow in this environment. We investigated *Thiobacillus Sp*. confirmed to have sulfur-oxidizing capacity in our previous study, and then selected *A. thiooxidans*. In addition, porous ceramic carriers currently used have a large pore so microorganisms cannot get settled well and are very alkaline. Thus, we selected Z/M carrier which has a smaller pore and mixed with acid clay at a constant ratio[Fig. 2].

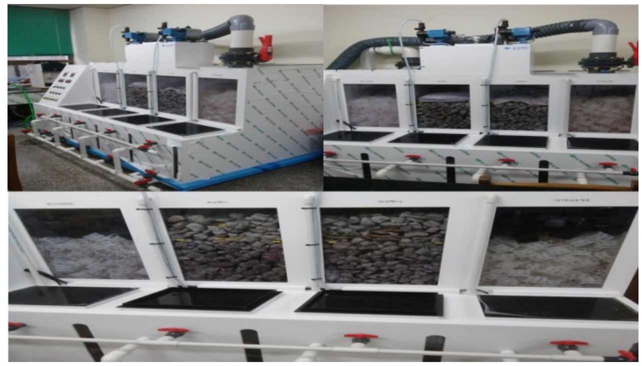

Fig. 2 Test bio-filter using the Z/M carrier layer

3.3. Z/M bio-carrier production

3.3.1 Z-ceramic carrier

Types of carrier used for bio-filter are diverse. Microorganisms used by most bio deodorization manufacturers are limited so alkaline carriers, the bacteria growing environment, are generally used.
Korea Institute of Construction Materials sent the result of analysis of ingredients with Z carrier currently used, as shown in [Table 3].
In addition, to measure the accurate pH, we requested Korea Testing and Research Institute. In the result, the pH was 0.50% in 10.3 N, P was not detected, K was mg/kg and cation exchange capacity was 5 meq/100 g. The reason of the use of alkaline carriers is that the pH of oxidized water needs to become neutral because the ingredients of odor gas generally have a large amount of H_2S. We used an artificial soil ceramic carrier(Korea), as Z carrier, produced by Daewoo. Co.,

Table 3. Ingredient analysis results of Z-ceramic carrier

Test item		Result	Test method
Chemical component(%)	SiO_2	72.1	KS E 3808 :2003
	Fe_2O_3	2.0	
	Al_2O_3	15.1	
	CaO	3.2	
	MgO	1.1	
	K_2O	4.2	
	SO_3	0.1	

.3.2 M-Montmorillonite carrier

In M-Montmorillonite carrier introduced in this section, microorganisms can be well attached and grow, but this carrier, unlike Z carrier, is composed of particles. Thus, it is hard to maintain an individual shape so fabric called ‘Sia’ is used to make a pocket to keep the shape, which is inconvenient. As the features of M carrier, acid clay, the main ingredient, improves adsorption, decolorization and

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catalysis through a chemical reaction so this natural mineral product is used for purification and adsorption of petrochemicals, and as a catalyst. We used acid clay DC-260(Korea) from DONGHAE CHEMICALS, as M carrier. The ingredient table and the chemical anaylsis are shown in [Table 4-1. Table4-2]

Table 4-1. Ingredient tale of M-carrier acid clay
Particle size distribution (average values)

Size range	Content(%)
> 20Mesh(0.84㎜)	1.5
30Mesh(0.59㎜)~20Mesh(0.84㎜)	25
60Mesh(0.25㎜)~30Mesh(0.59㎜)	72
< 60Mesh(0.25㎜)	1.5

Table 4-2. Chemical anaylsis (average values)

Component	Content(%)
SiO_2 (Silica)	65.2
Al2O3 (Aluminum oxide)	13.0
Fe_2O_3 (Ferric oxide)	6.0
MgO (Magnesium oxide)	1.7
CaO (Calcium oxide)	0.5
Na_2O (Sodium oxide)	0.5
K_2O (Potassium oxide)	0.5
IG-Ioss	9.0

3.3.3 Z/M carrier composition

To use advantages of two carriers as described above, we calculated the condition that backpressure does not appear, decided the ratio of 7:3, and named this carrier Z/M carrier.

Z-carrier with the volume of 3×3×4(m) was installed in biofilter in actual deodorization and then M carrier was filled up to 1.7 m on Z carrier according to approximate calculation. To prevent M carrier from overflowing, 'Sia' was used to make a pocket so water and air could go through and M carrier did not overflow.

3.4 Composition of the biofilter environment for the mediation pumping station

To adjust a flow rate of inflow gas to seven seconds, the formula of SV(space velocity) was used. Space velocity is the number of times gas with a volume of the charge layer passes per unit time and was calculated by dividing by the volume of the charge layer. It is faster than the actual flow of fluid because of various structures or fillings installed in the inner space, and changes complicatedly depending on the location. Thus, it is the apparent velocity calculated by dividing mass flow by superficial cross-sectional area.

Therefore, when the flow rate of odors is F [m3/h], SV[h-1] is F / VR and the gas flow rate of a blower was 350[m3/min] calculated by dividing F by the amount of carriers and pall rings(VR) installed to determine 7-second flow rate.[12,13,14] In addition, using panels in deodorization, we adjusted the optimum colony temperature(30°C) for *A. thiooxidans*.[6,15]

The carrier composition was exchanged from Z-ceramic carrier to Z/M carrier to adjust the pH to be acidic. Before microorganisms were seeded, carriers and pall rings were washed.

4. Result and discussion

Identification of the growth of *A. thiooxidans* in actual biofilter

We cultured *A. thiooxidans* in the laboratory and created the environment in order to grow it in actual biofilter. *A. thiooxidans* was seeded in the test. After that, MW medium was supplied and then we checked whether bacteria grew well in actual biofilter. To check whether bacteria grew well after *A. thiooxidans* was seeded and MW medium was supplied, the color and the pH of bacteria in the biofilter circulatory flask[Fig. 3] were compared. In the result, yellowish red bacteria[Fig. 4] turned red[Fig. 5]. In addition, microorganisms were adsorbed by sulfur added after seeding and precipitated as shown in [Fig. 6]. Furthermore, it was confirmed by checking changes in pH for several days that *A. thiooxidans* grew well in actual biofilter. We confirmed applicability of a deodorization mode using Z/M carrier which has never been applied in Korea. Therefore, our study will be able to provide basic data for deodorization.

Fig. 3 Microorganism circulatory flask of actual biofilter

Fig. 4 Changes in color from yellowish red after *A. thiooxidans* was seeded

Fig. 5 Red *A. thiooxidans* after cultured

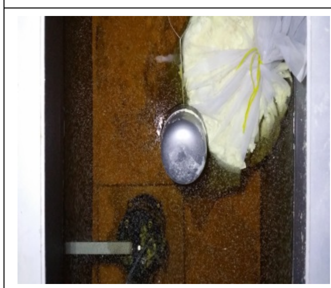
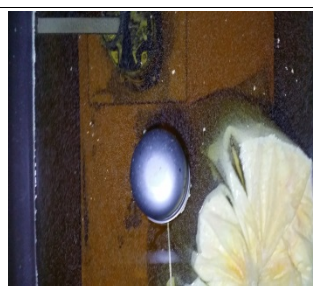
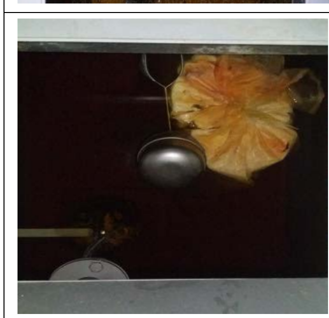
Bio-filter 1(1day,5day,15day)	Bio-filter 2(1day,5day,15day)
	
	

Fig. 6 *A. thiooxidans* combined with sulfur and precipitated to the ground

5. Conclusion

We used *A. thiooxidans* which can remove H_2S and ammonia(NH_3), the most common ingredients in noisome odor gas, at the same time and has sulfur-oxidizing capacity in order to study the characteristics of Z/M carrier produced with alkaline Z carrier and acidic M carrier at the ratio of 7:3. The result was applied to actual biofilter to determine removal efficiency of odor gas. In conclusion, it was confirmed that *A. thiooxidans* grew well in actual biofilter and that biofilter system could remove nine water-soluble odor ingredients including H_2S and ammonia at the same time.

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