

## Bio-argumentation for purifying VOCs

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### Abstract

The SepaTech Micro-bubble System has been applied to bio-argumentation by introducing an ERP KB-12 strain into contaminated soil with volatile organic compounds such as benzene. The ERP KB-12 strain can decompose benzene under aerobic conditions and effectively reduce the odor derived from contaminants in a short time. As a result of bio-argumentation at the old site of N company's Kobe factory in Chuo-ku, Kobe, we succeeded in improving the odor by injecting a relatively small amount of the ERP KB-12 strain. The odor before implementing bio-argumentation recorded about 960 on average in some plots, but it was irreversibly reduced to almost 0 about 24 hours after injection. By combining the ERP KB-12 strain and SepaTech Micro-bubble System, it is possible to effectively purify volatile organic compounds such as benzene in situ.

### Key words

bio-argumentation, micro-bubble, aerobic micro-organisms, volatile organic compounds, in situ purification

### 1. Introduction

Recently, due to the relocation problem of the Tokyo central wholesale market to Toyosu, the issue of soil contamination by volatile organic compounds (VOCs), typified by benzene, has attracted attention. Since odors from VOCs directly affect the human body, decompositions of these VOCs are important for purifying contaminated soil. Also, in conventional research, aerobic micro-organisms are considered effective for biological decomposition of VOCs (Katayama, 2010). As a purification technique using aerobic micro-organisms, an "Air Sparging Method" has been devised in which micro-organisms and air are directly injected into the soil (Kiryama et al., 2009), however, two pumps are required for sending both the micro-organisms and air, so the construction scale is increased. The use of anaerobic micro-organisms in situ has also been studied in recent years. The rate of purification is slower than that of aerobic micro-organisms (Ito and Takahata, 2008). There are difficulties with handling in an aerobic environment for culturing, management of construction and so on.

The Micro-bubble System (Patent No. 6104399) developed by Earth RePure, SepaTech® is a device that generates fine bubbles (micro-bubbles) with a diameter of 50 µm or less in water. It is mainly used for purification of water pollution, and has a good track record of its application (Tamura et al., 2014). Since the generated micro-bubbles are sufficiently small compared with the spaces between the soil particles, they can penetrate the soil as water moves, and they stay in water without levitation and then collapse. It is known that active oxygen is generated when the bubble collapses (Takahashi et al., 2007), and it is considered effective for purification of contaminated soil by decomposition of organic substances. Furthermore, it is

also known that crushing of bubbles causes super-saturation of dissolved oxygen concentration in water (Ebina et al., 2013). We have tried to purify VOCs in situ by utilizing two properties of active oxygen derived from bubbles and the activation of aerobic micro-organisms due to increased dissolved oxygen. We could obtain positive results and report as follows.

### 2. Method

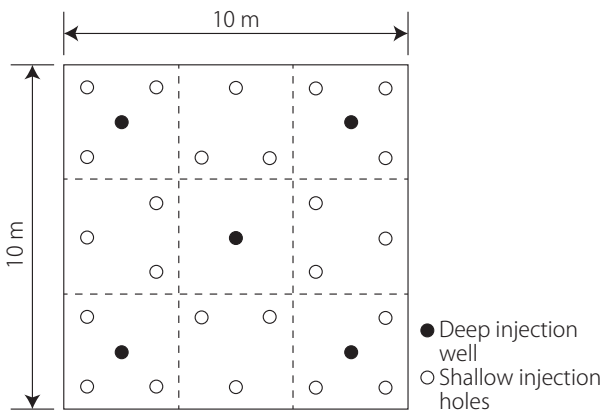
#### 2.1 Benzene decomposition by the ERP KB-12 strain

Benzene decomposition ability of the ERP KB-12 strain was tested in an aerobic environment in water. Three two-liter plastic bottles were prepared and filled with 1 liter of pure water and 0.1 ml of benzene. They were thoroughly stirred. One of them was sampled immediately after stirring and used as the control. In the other two bottles, 50 mL of the ERP KB-12 strain culture solution was added and stirred well again, then put at room temperature. One of the two was sampled after 30 minutes, and the other was sampled after 60 minutes. For the three samples, we commissioned Kankyo Research Co., Ltd. to measure the concentration of benzene in the water. Analysis was carried out according to the JIS K0125 5.2 method and by using HS-GC/MS (JMS-Q1050GC/ JEOL Ltd.) under a temperature rise from 40 °C (1 min) → 60 °C (2 °C/min) → 230 °C (15 °C/min). 4-Bromofluorobenzene was used as an internal standard.

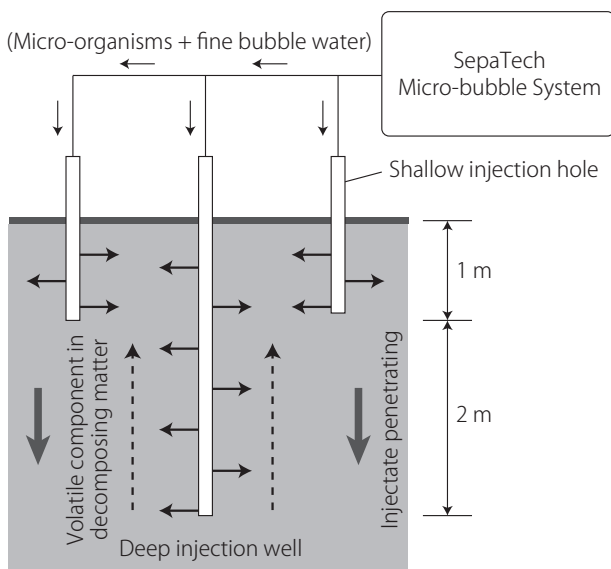
The ability of the ERP KB-12 to improve the odor was also tested. As in the examination of the decomposition ability, 1 liter of pure water and 0.1 mL of benzene were put into 2 liter plastic bottles and stirred well. 50 mL of the ERP KB-12 strain culture solution was added to one bottle (+ KB-12 plot). Another bottle, without adding the ERP KB-12 was the control. The bottles were stirred and then left at room temperature for 30 minutes. After that, in each headspace, the benzene concentration in the air was measured using a GASTEC No. 121S detection tube.

## 2.2 Bio-augmentation of VOCs

Bio-augmentation of VOCs were carried out at the old site of N company's Kobe factory in Chuo-ku, Kobe. The main contaminants in the target area were 1,2-dichloroethane and benzene (Goto et al., 2009). In addition, the preliminary survey found that contaminated soil was distributed within 3m from the surface of the ground. In the construction, as shown in Figure 1, a 10 square meter treatment section was set up, five 3 meter depth injection wells, and twenty-four 1 meter depth shallow injection holes were excavated (Figure 1 (a)), and then a disinfectant injection pipe was inserted. The inserted pipe was connected to the SepaTech Micro-bubble System, and a decomposing agent, which was a mixture of an aerobic micro-organism (the ERP KB-12 strain), and micro-bubble water, were injected. The injection amount of the decomposing agent was 0.02 % of the volume of the purification target



(a) Distribution of deep injection wells and shallow injection holes in each from a plane view



(b) Scheme of decomposing agent injection

Figure 1: SepaTech Micro-bubble System applied to the system purifying VOCs in situ

area of each section (for example, 0.06 m<sup>3</sup> per section if the depth was 3 m). The deep injection wells were aimed to directly inject micro-organisms into the contaminated soil, and the shallow injection holes were aimed for further decomposition of newly generated VOCs due to penetration from the top of the mixture solution and bio-degradation occurring in the deep layer (Figure 1 (b)). Construction was completed in a total of 16 days from February 23rd to March 10th, 2009. The effect of the decomposing agent was evaluated by using an odor measuring device (Shin-Ei OMX-GR). We measured five times in total, before injection, and 3 hours, 6 hours, 24 hours, and 30 hours after injection. The odor was measured immediately above the deep well of each treatment section.

## 3. Results and evaluation

Figure 2 shows the results of an odor reduction experiment of benzene in an aerobic environment by using the ERP KB-12 strain. The + KB-12 plot was slightly cloudy, and it can be distinguished from the control (Figure 2 (a)). The detection tube indicated the benzene concentration in the headspace in the + KB-12 plot was 20 ppm (Figure 2 (b)), and 120 ppm or more (Figure 2 (c)) in the control. Therefore, the ERP KB-12 strain can reduce benzene concentration in the air to at least 16 % or less in 30 minutes, and it is considered that the odor can be effectively improved.

On the other hand, the benzene concentration in water decreased as time elapsed after injection of the ERP KB-12 strain (Figure 3). However, the rate of reduction was less than 50 % before mixing after 30 minutes, and 16 % after 60 minutes.

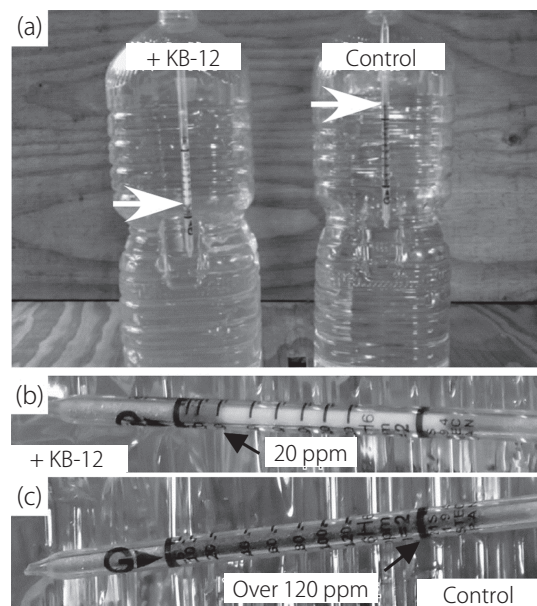


Figure 2: Decomposition of benzene by the ERP KB-12 strain  
Notes: (a) Each plot at the time of measurement (the arrow indicates the position for reading the value.); (b) The detection tube in + KB-12 plot shows 20 ppm; (c) The detection tube in the control plot shows over 120 ppm.

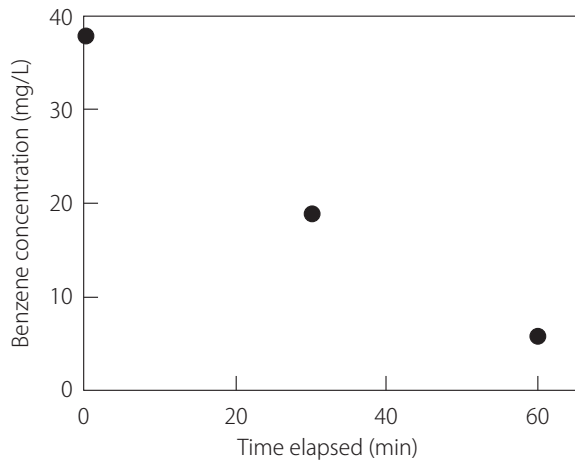


Figure 3: Benzene concentration in water decreased after injection of the ERP KB-12 strain

It was less gradual than in the headspace. The effect of odor reduction may be greater than the actual decomposition of contaminants. These results show that the ERP KB-12 strain can effectively decompose benzene in a short time, and it can be said that the odor is improved by the decomposition of benzene.

The results of bio-augmentation at the old site of N company's Kobe factory are shown in Figure 4. The construction was carried out for 28 sections (2,800 m<sup>2</sup> in total) colored in Figure 4. The numerical value of each section is the average of the odor measured value of five deep wells in the same section. The maximum value of the average before construction was about 960 in section E-5 and a few sections showed almost the same value. In such high odor-value sections, there were some injection wells in which the odor value reached to the

0 hour (construction just started)

	A	B	C	D	E	F	G	H	I	J	K
1											
2								71.4	42.2		
3							142.4	131.4	51.6	40.5	315.3
4	173.0	948.4	104.6	523.8	732.6				327.8	368.8	105.2
5	42.0	433.4	364.5		956.8				182.6	89.2	103.2
6		625.2	370.2	231.2	111.0				188.4		97.8

3 hours later

	A	B	C	D	E	F	G	H	I	J	K
1											
2								23.6	16.0		
3							26.2	59.0	14.4	12.5	156.8
4	9.5	139.8	1.2	78.0	109.0				28.6	66.8	47.4
5	1.5	193.0	15.75		128.4				23.0	27.0	24.8
6		205.0	42.2	52.6	20.0				83.8		43.0

6 hours later

	A	B	C	D	E	F	G	H	I	J	K
1											
2								2.4	3.6		
3							6.4	3.2	3.0	1.5	44.3
4	0.0	26.6	0.0	27.2	25.6				20.2	16.0	7.8
5	0.0	18.6	0.0		21.6				8.2	17.0	4.2
6		30.4	6.2	0.0	5.8				24.6		47.8

24 hours later

	A	B	C	D	E	F	G	H	I	J	K
1											
2								0.0	0.8		
3							0.0	0.0	0.0	0.0	7.8
4	0.0	2.8	0.0	4.2	0.0				0.0	1.4	0.0
5	0.0	2.4	0.0		1.6				1.4	4.0	0.0
6		0.0	0.0	0.0	0.0				2.8		11.0

30 hours later

	A	B	C	D	E	F	G	H	I	J	K
1											
2								0.0	0.0		
3							0.0	0.0	0.0	0.0	0.8
4	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0
5	0.0	0.0	0.0		0.0				0.0	0.0	0.0
6		0.0	0.0	0.0	0.0				0.6		0.0

Figure 4: Time elapsed after injection of the decomposing agent at each section

Note: Darker color indicates higher value.

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upper limit of 999. The average value in the section was calculated by using 999 for the provisional odor value. When the measured value reached the upper limit, 999 was used as a measurement value to calculate each section average value.

The measured odor values drastically decreased in all plots 3 hours after injection of the decomposing agent. 6 hours after injection, the odor was reduced to a value where nobody felt the odor in almost all the plots, but in some sections (for example, section E-5 and section B-4), which showed high odor values before construction, the odor still remained. The odor values further decreased 24 hours after injection, and became quite low values even in the high odor-value sections. The odors of all the sections were improved 24 hours after injection, and then this condition continued until 30 hours after injection. Therefore, it is considered that the VOCs, which were the origin of the odor, were irreversibly purified.

#### 4. Conclusion

In situ purification (bio-augmentation) of VOCs, typified by 1,2-dichloroethane and benzene, by applying the SepaTech Micro-bubble System was investigated. The ERP KB-12 strain, which was found to be capable of efficient decomposition of benzene, was used for bio-augmentation. The measured odor values before purification showed a high value of about 960 at the maximum, but decreased irreversibly to nearly 0 about 24 hours after injection of the decomposing agent. Therefore, it was clarified that VOCs can be effectively purified by application of the SepaTech Micro-bubble System. Since the SepaTech Micro-bubble System is a very compact system, integrating the bubble generating part and the liquid sending pump, it is considered to be useful for purification in a limited space such as the underground of a building, similar to the underground space of the Toyosu market, or inside the tunnel of a mine.

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