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Removal of dichloromethane from waste gases with a bio-contact oxidation reactor

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Abstract

Dichloromethane (DCM) is a kind of volatile organic compound (VOC), and many biological technologies have been studied and applied to meet the treatment of the waste gases. In this paper, a new bio-contact oxidation reactor, in which biofilm attached on the assembly semi-soft plastic media filled in column, was set up to removal DCM from waste gases. The influences of empty bed residence time (EBRT), temperature, pH and organic load on the removal efficiency (RE) and the elimination capacity (EC) of DCM were investigated and discussed. The optimum operation conditions were obtained as the temperature of 20–30 °C, pH 6.0–7.0 and EBRT of 28.3 s for the inlet gas concentration range of 500–1260 mg/m^3. Under the optimum operation conditions, the average removal efficiency of DCM was higher than 82%, at the inlet concentration of DCM lower than 1260 mg/m^3. The maximum elimination capacity (EC_{max}) of DCM in the bio-contact reactor was higher than that in the biofilters reported in the literature under the same operation conditions.

Keywords: Bio-contact oxidation reactor; Biological technology; Dichloromethane (DCM); Volatile organic compound (VOC)

1. Introduction

Dichloromethane (DCM, or methylene chloride) are used widely as organic solvents and vesicants. The global consumption of DCM is about 600,000 tonnes in 2004, making an increasing trend stilly. Although some DCM containing wastes are incinerated, it can be assumed that the greater part of the DCM produced is eventually lost to the environment. Due to its low boiling point (40.1 °C) and high vapor pressure (47 kPa at 20 °C), significant amounts of DCM reach the environment via gaseous emissions. DCM is a kind of irritative compound with fragrant odor, which is harmful to respiratory system and central nervous system of mankind. The emission control of DCM and other VOCs has been the subject of recent environmental regulations in China and other countries. The relevant enterprises are thus required to adopt appropriate technologies to reduce these VOCs in the emissions. The current control technologies for these VOCs, such as thermal incineration and wet scrubbing, are usually costly, especially in cases when the concentrations of these pollutants are not very high.

Biological techniques, such as biofilters, bioscrubbers, biotrickling filters, rotating drum bioreactors, suspended bacteria columns, and membrane bioreactors have been studied and applied successfully to solve polluted air emission problems containing VOCs and odour over the past decades, due its less expensive and more effective than other traditional methods, particularly when the pollutant concentration is low and volume is large [1,2].

The removal of DCM based on the biofilters [3–5] and suspended bacteria reactors [6,7] has been investigated by some previous studies. However, no research report has been published in biological contact oxidation reactors for the waste gases purification, a fixed-biofilm process commonly used to treat wastewaters, characterized by many advantages such as higher operational flexibility, more even for the distribution of nutrients, shorter reaction time, greater processing capability and no bed clogging occurring unlike biofilters [5]. The work presented in this paper is to focus on both developing a bio-contact oxidation reactor to treat VOCs and obtaining the optimum operation parameters for purifying the gas streams containing DCM.

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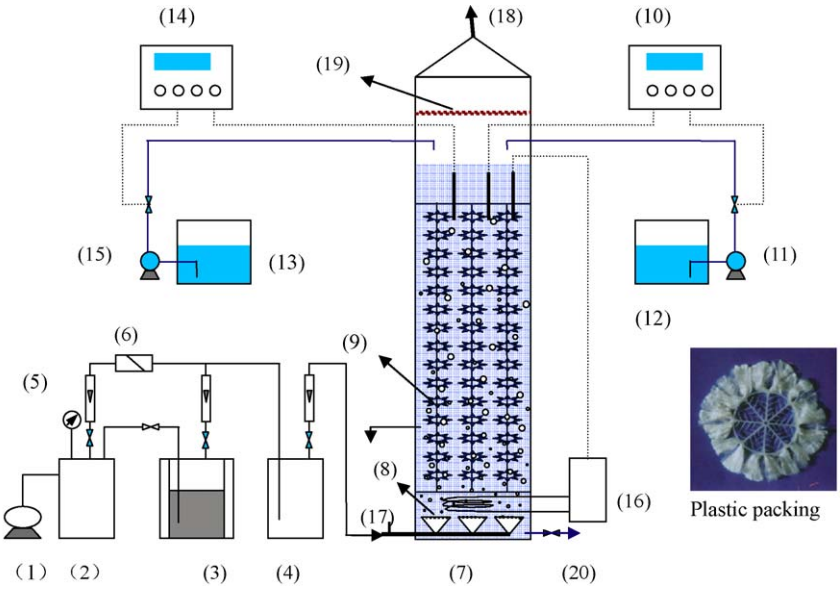

Fig. 1. Schematic of the bio-contact oxidation system for air pollution control. (1) Air pump; (2) buffer-storage; (3) gas generator; (4) mix-buffer; (5) gas-rotameter; (6) non-return; (7) bio-reactor; (8) air sparger; (9) pack materials; (10) pH control system; (11) peristaltic pump; (12) buffer base; (13) nutrient water reservoir; (14) electrical conductivity control system; (15) liquid pump; (16) temperature control system; (17 and 18) inlet and outlet sample port; (19) demister; (20) effluent.

2. Materials and methods

2.1. Bio-contact oxidation reactor

The schematic diagram of the bio-contact oxidation reactor was shown in Fig. 1. The set consisted of three parts: gas loading units, reactor with packing materials and conditioning unit for the liquid part. The bio-contact oxidation reactor was constructed from Plexiglas tubing with a length of 1000 mm and an internal diameter of 200 mm. The reactor was installed with assembly semi-soft media which were constructed by plastic ring and synthetic fiber string. The configuration of the media was shown in Fig. 1. The media had a theoretical specific surface area of 1538 m^2/m^3. These semi-soft media were not clogged owing to the special configuration and large specific surface area, and microorganisms that were attached onto the media would be able to accumulate faster. The packing bed was 400 mm in height, resulting in an effective volume (V_e) of 12.56 L. When in operation, the reactor was filled with nutrient water to a depth of 600 mm that resulted in the submergence of all packing.

The synthetic waste gas stream, simulated the waste gas exhausted by a local chemical plant, was produced by passing compressed oil-free air (1 and 2) through a water-bathed vessel containing liquid DCM (3). The saturation of DCM in gas phase was controlled by temperature of the water bath. Air streams carrying DCM was first mixed with the major air steam in the buffer (4). The concentrations of DCM were controlled by adjusting the flux of two air streams, regulated by two rotameters (5). Non-return valve (6) was installed in order to prevent contamination of the major section with pollutant vapors.

When in operation, the air stream entered the reactor (7) through air diffusers (8), located at the bottom of the reactor to supply sufficient oxygen to the biomass and transfer the contaminants from gas phase into liquid phase where it was degraded by biomass attached on packing and suspended in liquid (9). During the biodegradation of DCM, the by-product of hydrochloric acid may be generated and accumulated in the liquid. Some conditions should be adjusted continuously. The pH of the system was maintained at 6.5 ± 0.5 with a pH-controller (type 3675, Taiwan) (10) coupled to a peristaltic pump (11) which added buffer water containing NaOH and K_2HPO_4 (12). The concentration of NaCl in the system was kept at a constant level of 100–200 mmol/L to void inhibiting effects, recorded by continuous measurement of the electrical conductivity of the liquid phase [4,8]. The nutrient water was renewed periodically through a nutrient water feed system, consisting of a reservoir (13), a electrical conductivity control apparatus (14) and a pump (15) to control the concentration of NaCl in reactor. The temperature-controlled system (16) consisted of a coil with cold water and an electric heater coupled with a constant thermometer.

2.2. Adaptation and immobilization

The strain *Pseudomonas*, GD11 [8], was used for the degradation of DCM. At a pH 6.0–7.0 and a temperature of 25–30 °C, the maximum growth rate of this organism is 1.8 per day, and the yield of biomass on DCM is 0.12 g dry weight biomass on per gram of DCM degraded. For the pure culture of *Pseudomonas*, GD11, the specific activity amounts to 0.12 g DCM/g VSS h.

For the adaptation, a 1000 mL flask containing culture medium was seeded with the strain, obtained from a local pharmaceutical wastewater treatment plant. The mineral medium for batch growth experiments was composed following Hartmans and Tramper [5]. The pH varied in the range 6.0–7.0 and the temperature was maintained at 25–30 °C. The synthetic waste gas stream was introduced into the flask. After 6–7 days, the quantity of the activated sludge increased gradually. Analysis results showed that the removal efficiency of the flask for DCM

Table 1
Additional nutrients used for microbial growth

Compounds	Concentration (mg/L)
K_2HPO_4	250
$(NH_4)_2SO_4$	1000
$FeSO_4{\cdot}7H_2O$	1

reached 98% corresponding to the initial removal efficiency of below 10%. In the subsequent 2 days, no obvious decrease in the removal efficiency of DCM was observed and the adaptation was completed.

In the pilot plant experiments the medium was based on tap water, which had a composition comparable to the medium for batch experiments, with respect to all spore elements. Additions followed Diks and Ottengraf [3] (listed in Table 1). The biomass, coming from flask, was put into the bio-contact oxidation reactor described earlier. The culturing was continued until the steady-state biomass loading on the plastic packing materials. After 8 days, a stable biofilm was formed on the plastic packing materials. At last, the amount of biomass in column was about 2.23 kg VSS/m^3 assumed by weighing method.

2.3. Analytical method

The concentration of DCM in the gas phase and in the liquid phase was determined by the gas chromatography. Polluted air was pumped through 0.1 mL sampling loops for automatic injection into a Hewlett Packard type 5890(2) gas chromatography, filled with a 15-m HP-50+ column and operated isothermally at 90 °C, the carrier gas used was hydrogen (H_2) and detection was with a flame ionization detector (FID). The retention time was 0.8 min for DCM. From the inlet and outlet gas phase concentrations the removal efficiency (or degree of conversion) was thus determined.

The attached biomass was measured by weighing method. For measuring biomass attached to media, the biofilm attached media were first washed with distilled water to remove some impurities, then dried and weighed. The biomass samples were then digested in the solution of 0.2N NaOH. Thereafter, the clean media were washed again with distilled water, dried and weighed. Unused media were also analyzed as a blank to determine the weight loss. The biomass was calculated by deducing the net media weight together with the weight loss of media from the weight of biofilm attached media.

3. Results and discussion

3.1. Effect of gas EBRT on the elimination capacity

The empty bed retention time (EBRT) τ is calculated as follow:

$$\tau = \frac{H}{u_g} \times 3600 \quad (1)$$

In this equation, H is the height of the packed bed, 0.4 m; u_g is the superficial gas velocity, m/h. The units of τ is s. The

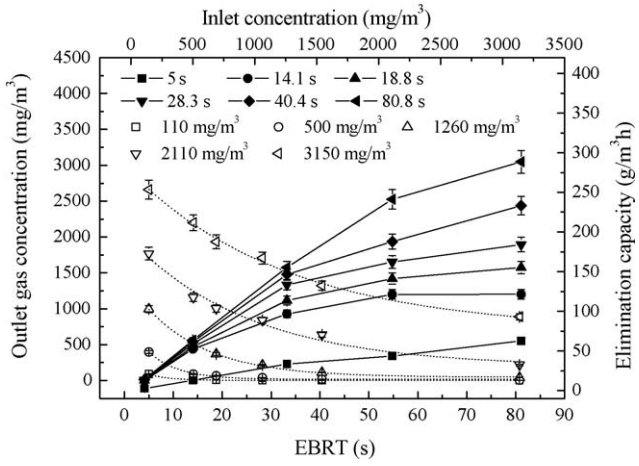

Fig. 2. Outlet gas concentration and the elimination capacity in the bioreactor as a function of EBRT and inlet concentration.

relation of outlet gas concentration's influencing with EBTR at five different inlet gas concentration (110, 500, 1260, 2110 and 3150 mg/m^3) was shown in Fig. 2. From Fig. 2 it was found that the influencing variations of EBRT were different on the outlet gas concentration (or removal efficiency) under the various inlet gas concentrations. The different values of apparent rate constant (k) were calculated first order model as 0.243, 0.166, 0.078, 0.040 and 0.031 s^{-1}, with five correlation coefficients (R^2) of 0.997, 0.993, 0.999, 0.982 and 0.997. The values of k went down as the inlet gas concentration increased, and the good correlation coefficient indicated that there was good fit between the experimental data and the first order equation at the various inlet concentrations. Two factors (transport and biodegradation) should be considered for the phenomena of the bioreactor elimination process. Fig. 2 showed that the higher removal efficiency of 92.0% of reactor purifying waste gas containing DCM was obtained at EBRT of 28.3 s for a lower inlet gas concentration of 500 mg/m^3, due to an adequate biodegradation capacity from the experimental results, indicating that the mass-transfer from gas phase to biomass became the main factor limiting the removal efficiency. For higher inlet gas concentration of 3150 mg/m^3, the biodegradation capacity got full. It was unavoidable to get a very lower removal efficiency of 45.8% at EBRT of 28.3 s than for a higher inlet gas concentration of 3150 mg/m^3. It similarly indicated that the DCM biodegradation rate became another main factor limiting the removal efficiency. The optimum EBRT was selected as 28.3 s for the inlet gas concentration range of 500–1260 mg/m^3.

3.2. Effect of temperature on the removal efficiency

In this experiment, the effect of temperature on the DCM removal efficiency (RE) of the bioreactor was determined. Two situations were considered: one was at a relatively long EBRT of 80.8 s and high inlet concentration of 3150 mg/m^3 and the second was at a short EBRT of 14.1 s and a very low inlet concentration of 110 mg/m^3. From Fig. 3, the effect of the temperature on these two situations was markedly different. The DCM removal efficiency was little affected by the temperature

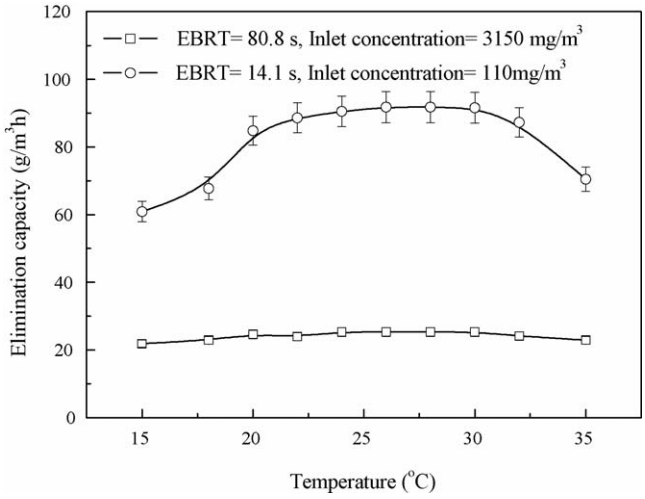

Fig. 3. Temperature effect on specific elimination capacity in the bioreactor.

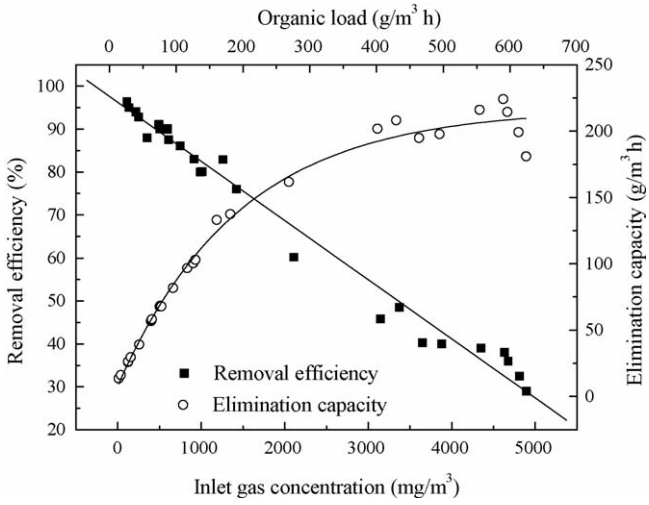

Fig. 4. Removal efficiency and elimination capacity at various inlet gas organic loading EBRT of 28.3 s, a temperature of 28 ± 1.0 °C, and pH values of 6.0–7.0.

under a low inlet concentration (110 mg/m^3) and high superficial gas velocity (102 m/h), indicating once more that the removal efficiency of DCM in the bioreactor was mainly mass transfer limited. Hartmans and Tramper [5] explained this similar phenomena in bio-trickling filter that the temperature dependency of the diffusion coefficient, which results in a higher mass-transfer resistance at lower temperatures, is compensated by the increased solubility of DCM at these lower temperatures (a lower partition coefficient) resulting in an increased driving force for mass transfer. However, a gradual change from a reaction-limited situation at the lower temperature (15–20 °C) to a partially mass-transfer-limited situation in the higher temperature range (25–30 °C) took place with the higher inlet concentration of DCM and a relatively low superficial gas velocity. Thus, the optimum temperature for treating the waste gas of DCM ranged from 20 to 30 °C.

3.3. Effect of organic load on the elimination capacity

The effect of DCM load on bio-contact oxidation reactor performance was investigated in Fig. 4, at an EBRT of 28.3 s, a temperature of 28 ± 1.0 °C, and pH values of 6.0–7.0.

It was found that the inlet gas concentration might make a well effect on the performance of the bioreactor as shown in Fig. 4. The removal efficiencies decreased rapidly and sloped linearly as the inlet gas concentration increased. Under above optimum operated conditions, the average removal efficiency of DCM was over 82% as the outlet concentration of DCM lower than 1260 mg/m^3.

The elimination capacity (EC) was a function of the organic load at gas load below 180 g/(m^3 h) in Fig. 4, explaining the existence of mass-transfer resistance in liquid phase. At lower gas velocities and higher inlet concentrations of DCM, resulting in a much higher driving force for mass transfer, specific elimination capacities as high as 200 g/(m^3 h) were achieved. When DCM load was beyond 400 g/(m^3 h), the elimination capacity of DCM did not increase obviously with the increase of organic load, indicating that this degrade rate of biomass followed zero-order kinetics in this concentration range, in agreement with "the reaction limited" theory [9].

Due to the toxicity, organism activity might be restrained at high concentration of DCM. DCM was somewhat easier to be degraded as a bacterial growth substrate at a low concentration. However, It was found that the maximum elimination capacity (EC_{max}) of DCM in bio-contact oxidation reactor was about 200 g/(m^3 h), and higher than those in the biofilters with the maximum elimination capacities of DCM of 157 g/(m^3 h), as reported in literature [3]. The elimination capacity began to decrease as the organic load beyond 590 g/(m^3 h), exploring the elimination efficiencies of DCM were controlled mainly by the degrade rate of biomass in the bio-contact oxidation reactor at a higher organic load.

3.4. Comparison to other biological gas treatment methods

Diks and Ottengraf [3] investigated the removal of DCM from waste gases in a biological trickling filter experimentally as well as theoretically within the concentration range of 0–10,000 mg/m^3. A maximum DCM elimination capacity of 157 g/(m^3 h) was observed at a superficial liquid velocity of 3.6 m/h. The developed "Uniform-Concentration Model" showed to predict the filter performance close to the numerical solutions.

In study by Vanderberg Twary et al. [6] conducted in a 1.2 L gas lift loop volume, contaminated gases containing DCM and toluene were introduced into the bioreactor via a non-porous diffuser. The liquid was buffered to maintain a neutral pH and inoculated with *Hyphomicrobium* sp. strain DM-2 and *Rhodococcus rhodochrous strain* OFS. The optimal treatment was achieved at a gas flow rate of 0.142 m^3/h which provided sufficient oxygen without loss of biomass.

Some studies developed an airlift bioreactor to meet the treatment of waste gases. Zuber et al. [7] used the results of 3 years of bench-scale treatment of DCM in a 3-phase airlift bioreactor (sand:water:air) to estimate scale-up to a full scale treatment

Table 2
Comparison of the performance on removal of DCM in three different biological reactors

	Bio-trickling filter	Suspended bacteria column	Bio-contact oxidation reactor
Packing materials	Ceramic saddle	–	Assembly plastic
Interfacial area (m^2/m^3)	750	–	–
Void volume (%)	68	–	–
Biomass amount, kg VSS/m^3	3.75	0.52	3.26
EBRT (s)	60	30	28.3
Maximum elimination capacity (g/(m^3 h))	157	–	200
Nutrient distribution	Uneven	Even	Even
Biomass distribution	Uneven	Even	Even
Biomass management	Backwash once a monthly	No management	No management
Bed clogging	Clogging	No clogging	No clogging
Pressure	Unstable	Stable	Stable

system. In a bench-scale reactor of 0.83 m liquid height containing 195 kg sand/m^3 reactor volume, DCM concentration was reduced from 3000 mg/m^3 to 300 mg/m^3. A basic vestment cost of $1,74,300 would be needed to construct an airlift with sand media to treat 100 m^3/h of air containing 2 mg/L DCM to 99.5% removal. Additional operating costs for energy, chemicals, water and personnel time averaged to $79,720/year.

This study showed the DCM removal efficiency increased from 80.0 to 96.0% at an inlet gas concentration of 110 to 1260 mg/m^3 and an EBRT of 28.3 s, the biomass in the bio-contacting oxidation reactor was much more evenly distribution within the medium, due to the submergence of all packing into nutrient water. Although there was gradual biomass accumulation within the packing materials, no bed clogging occurred in performance. The amount of attached biomass in the volume was maintained about 2.23 kg VSS/m^3.

A comparison of the relevant operating condition was summarized in Table 2. It showed that a considerable surface was offered in biological trickling filters filled with low void packing materials, conducing to the cling of biomass suspended in liquid phase. However, the spongy media in bio-trickling filters was found fully filled with biomass, resulting in bed clogging. The distributions of nutrient, pollutant load and oxygen on the biomass were uneven. Compared to these biofilters, the nutrients, oxygen, pollutant load and biomass were even under the air stream stirring continuously distribution in bio-contact oxidation reactor. The bio-contact oxidation reactor could also maintain long-term stable performance without cleaning extra biomass, for the adequate space existing among the assembly packing. The DCM removal efficiency was over 80.0% and the elimination capacity of DCM was 103 g/(m^3 h) at an inlet gas concentration of 1010 mg/m^3 and an EBRT of 28.3 s, indicating that the biomass accumulated within the packing material and enhanced the elimination efficiency. No clogging occurred and pressure drop kept stable in the performance. Compared to suspended bacteria column, higher amount of biomass in the system was observed.

4. Conclusions

Following conclusions can be drawn based on this study:

(1) Biological treatment of contaminated gases can be achieved using a new bio-contact oxidation reactor.
(2) The optimum operation conditions of bio-contact oxidation reactor for treating waste gas of DCM was the temperature range of 20–30 °C, pH 6.0–7.0 and EBRT of 28.3 s for the inlet gas concentration range of 500–1260 mg/m^3. Under the optimum operation conditions, the average removal efficiency of DCM was higher than 82%.
(3) Unlike conventional biofilters, the bio-contact oxidation reactor can maintain long-term stable performance without bed clogging occurring. However, more tests are still needed for optimizing the design and the operation of the bio-contact oxidation reactor, especially in such as cost reducing and amount of biomass per volume enhancing, similar to suspended bacteria columns [7].

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