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Original Article

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REMOVAL OF DICHLOROMETHANE FROM WASTE GAS STREAMS USING A HYBRID BUBBLE COLUMN/BIOFILTER BIO-REACTOR: EFFECT OF EMPTY BED RETENTION TIME AND KINETIC OF BIOFILTRATION

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ABSTRACT:

Introduction: Dichloromethane (DCM) is an air pollutant emitted mainly through industrial application. In this study, removal of DCM from waste gas streams using a pilot-scale hybrid bubble column/biofilter (HBCB) bioreactor was studied in steady state.

Materials and methods: The hybrid bioreactor had two compartments: bubble column bioreactor and biofilter.The experiments were carried out with relatively constant concentration of DCM (approximately 240 ppm) and variable empty bed residence time (EBRT) of 50, 100, 150 and 200 s in steady state.

Results: The average DCM removal efficiency of the HBCB bioreactor at EBRT of 200 and 150 s were 79 and 71%, respectively, but further reduction of EBRT significantly decreased the DCM removal efficiency. DCM removal rate was determined to be in the range of 12.1 g/m^3.h to 19.6 g/m^3.h. The first order rate equation best described the kinetic data of biofiltration (R^2>0.99) with kinetic constant of 0.0114 1/s. The mixed liquor characterization indicated that the daily adjustment of pH and EC was sufficient to prevent any limitation in the performance of the HBCB bioreactor.

Conclusions: This study showed that the HBCB bioreactor could be an efficient, economical and flexible option for DCM removal from waste gas streams.

INTRODUCTION

In recent years, concerns regarding environmental contamination by dichloromethane (DCM, CH_2Cl_2), otherwise known as methylene chloride, have been increased due to its elevated levels in the ambient air and its adverse health effects. DCM is a synthetic volatile organic compound (VOC) without known natural sources. Dichloromethane is a moderately hydrophobic and highly

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volatile compound. Due to its special properties, DCM has many industrial applications such as paint stripping and removing production, metal cleaning and degreasing process, pharmaceutical manufacturing, adhesive manufacturing, polyurethane foam production, film base manufacturing, polycarbonate resin production and solvent formulation. Worldwide utilization of DCM has been estimated to be about 600,000 tons/year in 2004 [1-4].

The main route of human exposure to DCM is inhalation of the ambient air, although DCM may be absorbed via drinking water and food. The acute health effects of DCM inhalation are mainly nervous system disorders including visual, auditory and motion dysfunctions; although these effects are reversible once exposure ceases, but prolonged exposure to high concentration of dichloromethane may cause to fatality. The chronic health effects of dichloromethane exposure consist of central nervous system (CNS) damages, cardiac effects, liver and lung cancers and mammary gland tumors [5-8].

In order to control DCM emission from industrial facilities, several treatment technologies has been developed which mostly are belong to physical and chemical methods. These technologies including incineration, adsorption, catalytic oxidation and wet scrubbing are involved with several disadvantages such as high capital costs, high energy consumption, need for activated carbon replacement or regeneration, catalystconsumption and/or chemical requirement [9-11]. With increasing importance of environment protection and preservation aspects, biological treatment technologies have been taken into more consideration. The biological reactors, such as biofilter, bioscrubber, biotrickling filter, etc. will benefit from several advantages including high cost-efficiency, being environmental friendly, high reliability and flexibility and simplicity of operation [12-14]. Under aerobic biodegradation, DCM is oxidized to CO_2 and HCl as the end products, although intermediate products may be produced as formaldehyde, formic acid and formyl chloride where DCM is not oxidized completely [15-18]. Biofilter as a cost-effective reactor is packed with media which support a surface and sometimes supply nutrients for growth of microorganisms, but this reactor cannot treated gas stream with a high concentration of DCM, because HCl produced from the decomposition of DCM lowers pH and disrupts the bioreactor performance. In contrast, liquid phase bioreactors such as bubble column bioreactor are not sensitive to high concentrations of acid-producing pollutants [17, 19].

In this study, in order to benefit from advantages of both biofilter and bubble column bioreactor, a hybrid bubble column/biofilter (HBCB) bioreactor was developed and studied for DCM removal from waste gas streams to determine the optimized operational conditions.

MATERIALS AND METHODS

Experimental apparatus

The schematic diagram of the experimental set-up is shown in Fig. 1. The experimental set-up consisted of three parts: gas loading unit, the HBCB bioreactor including the bubble column bioreactor and biofilter and conditioning unit (for humidification of the biofilter medium and nutrient and trace element supply). Polluted inlet gas stream was produced by blending ambient air stream with a small amount of air stream containing DCM in a mixing chamber. The inlet gas stream was first entered to the bubble column bioreactor by an air diffuser, and then was dispersed to the biofilter located above the bubble column bioreactor in an upflow mode. By using this arrangement, the required humidity for microbial activity in the biofilter was mainly provided by passing the inlet gas stream through the bubble column bioreactor. The HBCB bioreactor was a Plexiglas tube with an inner diameter of 5 cm and effective heights of 25 and 38 cm for the bubble column bioreactor and biofilter, respectively. The packing media of the biofilter were made of polystyrene (Bee-Cell 2000, DANAQ, Denmark) with bulk porosity of 87% and specific surface area of 650 m^2/m^3.

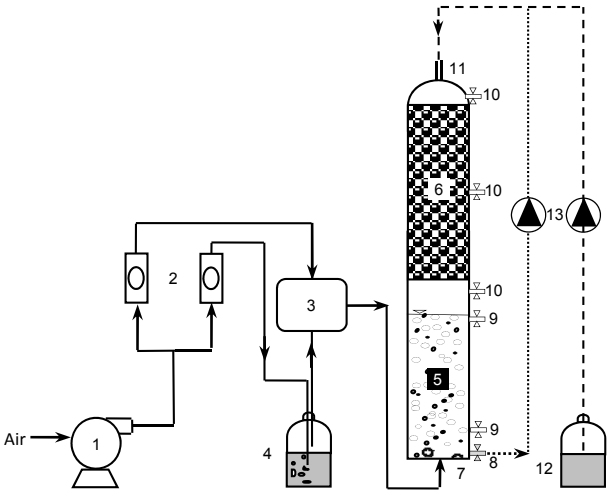

Fig. 1. The experimental set-up used in this study: (1) air compressor, (2) air flowmeter, (3) mixing chamber, (4) DCM vaporization chamber, (5) bubble column bioreactor, (6) biofilter, (7) gas inlet, (8) drainage port, (9) liquor sampling port, (10) gas sampling port, (11) gas outlet, (12) nutrient reservoir and (13) peristaltic pumps.

Microorganisms and culture media

For microbial inoculation of the HBCB bioreactor, a mixed microbial culture was derived from an activated sludge pilot plant treating 4-chlorophenol polluted wastewater. After the microbial seeding, the HBCB bioreactor was run in mixed liquor recirculation mode (from bottom of the bobble column bioreactor to top of the biofilter) nearly 30 days for acclimatization of the bacteria to DCM and biofilm development on the biofilter media. Following this period, normal operation of the HBCB bioreactor was started at a gradually increasing DCM concentration from 5 to 30 ppm during 30 days to complete the start-up stage.

The nutrients and trace elements were added to the HBCB bioreactor once a day. The nutrient stock solution consisted of NH_4Cl and NaH_2PO_4 at concentrations of 1911 and 387 mg/L, respectively. The constituents of the trace element stock solution and their concentrations were $FeSO_4.7H_2O$ at 500 mg/L, $ZnSO_4.7H_2O$ at 400 mg/L, $C_{10}H_{14}N_2Na_2O_8.2H_2O$ at 250 mg/L, $CoCl_2.6H_2O$ at 50 mg/L, $CuSO_4.5H_2O$ at 30 mg/L, $MnCl_2$ at 20 mg/L, H_3BO_3 at15 mg/L, $NiCl_2.6H_2O$ at 10 mg/L and $(NH_4)_6Mo_7O_{24}.4H_2O$ at 10 mg/L. For preparation of the nutrient and trace element solution, a volume of 1 mL from each stock solution was poured to a volumetric flask and then reached to 100 mL by tap water. The prepared solution was poured from top of the biofilter and after passing through biofilter bed was added to the mixed liquor of the bobble column bioreactor. After addition of the solution, the mixed liquor was recirculated from top of the biofilter for 30 min to complete humidification of the biofilter medium and washout of the excess biofilm and waste materials from DCM biodegradation. Finally, an equal volume of the added solution to the mixed liquor was discharged from the bioreactor. With regard to the effective volume of the bubble column bioreactor (500 mL) and the mixed liquor discharge regime (100 mL/d), the hydraulic retention time (HRT) in the bubble column bioreactor was 5 d.

Bioreactor operation

All of the experiments were performed in a continuous upflow mode at ambient laboratory temperature (20 ± 2 ˚C). The experiments were performed in four stages (so called stages I, II, III and V) by variable gas flow rates (0.375, 0.500, 0.750 and 1.500 L/min) and approximately constant DCM concentration of 240 ppm (848 mg/m^3). In the experimental stages I, II, III and V, the total empty bed retention time (EBRT) of the HBCB bioreactor were 50, 100, 150 and 200 s, respectively. The corresponding values of the total DCM loading rates were 15.3, 20.5, 30.7 and 61.9 g/m^3.h, respectively.

Kinetic analysis of biofiltration

In this study, kinetic data of biofiltration were analyzed using the zero-order, zero-order limited by mass transfer, half-order, first-order, second-order and Michaelis-Menten rate equations. The linear forms of these equations are presented below as Eqs. (1)-(6) [20-23]:

$$C_0 - C = k_0 t \quad (1)$$

$$1 - (C / C_0)^{0.5} = k_d t \quad (2)$$

$$C_0^{0.5} - C^{0.5} = 0.5k_{0.5}t \quad (3)$$

$$\ln\frac{C_0}{C} = k_1 t \quad (4)$$

$$\frac{1}{C} - \frac{1}{C_0} = k_2 t \quad (5)$$

$$\frac{t}{\ln(C_0/C)} = V_m \frac{(C_0 - C)}{\ln(C_0/C)} - K_s \quad (6)$$

where, C_0 (mg/m^3) and C (mg/m^3) are the inlet and outlet concentrations, respectively; t (s) is retention time; k_0 (mg/m^3.s) is the zero-order reaction rate constant; k_d is the constant of zero-order limited by mass transfer reaction rate; $k_{0.5}$ (mg$^{0.5}$/m$^{1.5}$.s) is the half-order reaction rate constant; k_1 (1/s) is the first-order reaction rate constant; k_2 (m^3/mg.s) is the second-order reaction rate constant and K_s (mg/m^3) and V_m (mg/m^3.s) are the Michaelis-Menten model constants. Linear regression coefficient (R^2) and the average percentage errors (ε%) calculated according to the below equation were used to determine the fitness between the experimental data and predicted values by the kinetic models:

$$\varepsilon\% = \frac{\sum_{i=1}^{N}\left|\frac{C_{exp} - C_{theo}}{C_{exp}}\right|}{N} \times 100 \quad (7)$$

where the subscripts 'exp' and 'theo' show the experimental and calculated values and N shows the number of observations [24].

Analytical methods

In addition to measurement of DCM concentration in gas phase, the quality characteristics of the mixed liquor were also analyzed during the start-up and experimental stages. DCM concentration in both gas and liquid phases was determined by a gas chromatograph (Varian CP-3800) equipped with flame ionization detector (GC/FID). Type of the capillary column was CP-Sil 8 CB with length of 30 m, inner diameter of 0.32 mm and film thickness of 0.25 µm. The injection FID temperature was raised from 35 ˚C (1 min) to 100 ˚C at rate of 16 ˚C/min and held for 5 min. Air samples were taken from gas sampling port with gas-tight syringe and injected to the GC/FID. The volume of aqueous samples was 5 mL that collected by using 10 mL vials sealed with screw cap and PTFE–silicon septum. The vials were then transferred to the GC/FID and analyzed with the headspace analytical technique [25, 26]. In order to determine fraction of the DCM mineralization, CO_2 concentration was measured in gas samples using GC/FID. All of the other quality parameters of the mixed liquor including pH, electrical conductivity (EC), chloride (Cl^-), mixed liquor suspended solids (MLSS) and chemical oxygen demand (COD) were measured according to the instructions of Standard Methods [27].

RESULTS AND DISCUSSION

Effect of DCM loading rate on bioreactor performance

One of the most important parameters for assessing the performance of a bioreactor is its acceptable range of pollutant loading rates, so that when a bioreactor can be efficiently operated at high pollutant loading rates, the bioreactor is evaluated as an appropriate option for removal of the relevant pollutant [3]. Profiles of DCM concentration in the inlet and outlet of the HBCB bioreactor and the bioreactor performance for DCM removal are shown in Fig.2. The overall removal efficiency of DCM in Stages I and II were relatively high (79 and 71%, respectively), but in the next stages, the bioreactor efficiency was decreased significantly, so that in Stage IV with an EBRT of 50 s, the overall efficiency was as low as 32% and DCM concentration decreased from 837-892 mg/m^{3}to 565-647 mg/m^3. Fig.3 shows the effect of DCM loading rate on the removal rate and efficiency of the HBCB bioreactor. Based on Fig.3, with increasing the loading rate from 15.3 g/m^3.h to 61.9 g/m^3.h, the removal efficiency increased (from 79 to 32%) directly and the removal rate decreased (from 12.1 to 19.6 g/m^3) inversely. Also, in the equal DCM loading rate, DCM removal rate and efficiency of the biofilter were higher than the corresponding values of the bubble column bioreactor.

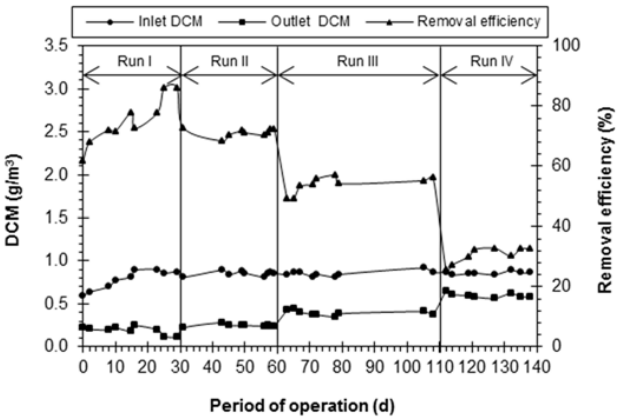

Fig. 2. The overall performance and efficiency of HBCB bioreactor in DCM removal from the gas phase.

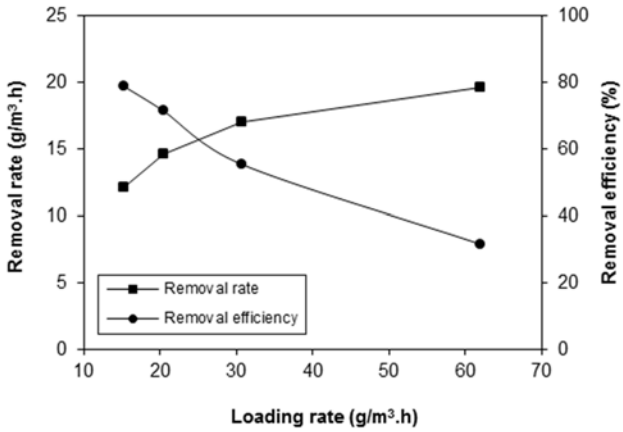

Fig. 3. Effect of DCM loading rate on the removal rate and efficiency in HBCB bioreactor.

Because of the various environmental conditions applied in different studies, the maximum DCM elimination capacity alone is not an appropriate indicator to compare different bioreactors or methods and other operational parameters such as DCM outlet concentration, removal efficiency, pH, temperature, amount of waste generation, etc. should be taken into consideration. The performance of several bioreactors in the removal of DCM from gas phase is given in Table 1. Ravi et al. [28] reported the maximum DCM elimination rate of 20.1 g/m^3.h in the loading rate of 31.5 g/m^3.h (with removal efficiency of 64%) for a compost biofilter. Ergas et al. [29] observed that the maximum DCM elimination rate of a biofilter was 10.3 g/m^3.h with removal efficiency of 98%. Based on Table 1, the highest DCM elimination rate as much as 455 g/m^3.h has been obtained by a biotrickling filter.

Although the maximum DCM removal rate of the HBCB bioreactor was not the highest one, but was promising in comparison with that of the biofilters. In addition to suitable elimination capacity, other advantages of the HBCB bioreactor consisted of low wastewater generation, low liquid recirculation, regular humidification of the biofilter inlet gas by passing through the bubble column bioreactor, low pressure drop, no bed clogging, etc. On the other hand, the operating conditions applied in this study were the simplest situations, including the use of mixed microbial culture, bioreactor operating at room temperature (while some studies have been carried out at higher temperatures), the daily adjustment of pH and EC (whereas in most other studies, pH and EC were adjusted instantaneously). Consequently, the suitable DCM elimination capacity and the inexpensive and simple operation increase the possibility of full-scale application of the HBCB bioreactor [15, 30].

Effect of DCM loading rate on mixed liquor quality

The mixed liquor quality is a very important aspect to provide suitable conditions for the growth and activity of DCM degrading microorganisms [15, 31]. During DCM biodegradation, hydrochloric acid is produced and decreases the pH of the bioreactor environment. Hence, pH of the DCM treating bioreactors should be neutralized to provide a suitable environment for microorganisms activity [32, 33]. Daily changes in the mixed liquor pH as a function of DCM loading rate is shown in Fig.4. By increasing DCM loading rate, higher reduction in the mixed liquor pH occurred daily, so that in the highest loading rate, pH decreased until 6.04. According to the results of the previous studies, the decreased pH values would not be inhibitor for microbial activity.

Table 1. The efficiency and performance of some bioreactors used for DCM removal from gas streams

Type of bioreactor	Loading rate ($g/m^3.h$)	Removal rate ($g/m^3.h$)	Removal efficiency (%)	pH	Temperature (˚C)	Reference
Biotrickling filter	-	157	-	-	-	[36]
Biotrickling filter with polypropylene media	174.5	103.5	59.3	7.0	25	[2]
Biotrickling filter with polypropylene media and inoculated with *Hyphomicrobium GJ21*	145.7	102	70	7.8-8.0	20-22	[37]
Biotrickling filter with polypropylene media and inoculated with mixed microbial culture	534.5	455	85	6.5±0.5	28	[30]
Compost biofilter inoculated with mixed microbial culture	10.5	10.3	98	-	-	[29]
Compost biofilter inoculated with mixed microbial culture	30	20.1	67	7.0	Room temp.	[28]
Completely stirred tank bioreactor inoculated with *Hyphomicrobium*	127.2	117	92	7.0	30	[15]
Completely stirred tank bioreactor with two-liquid-phase and inoculated with *Hyphomicrobium*	516.2	351	68	7.0	30	[15]
Bio-contact oxidation reactor inoculated with *Pseudomonas GD11*	400	200	50	6.0-7.0	28±1	[3]
HBCB bioreactor with polypropylene media and inoculated with mixed microbial culture	61.9	19.6	32	6.0-8.1	20±2	This study

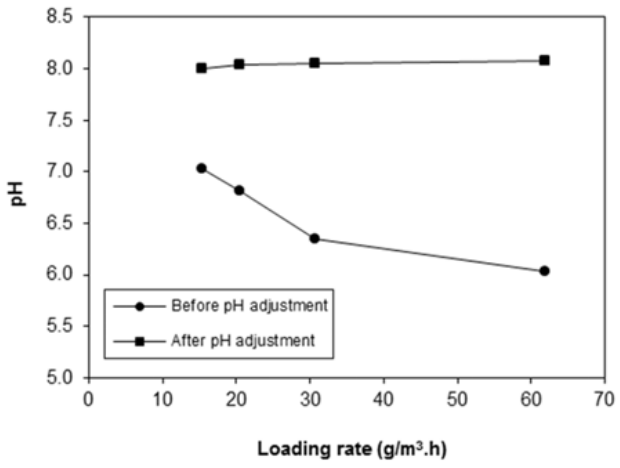

Fig. 4. Effect of loading rate on the mean daily changes in mixed liquor pH.

Fig.5 shows soluble and suspended COD and MLSS concentrations of the mixed liquor in the experimental stages. The soluble COD concentration of the mixed liquor was not changed with the DCM loading rate, because the soluble COD was mainly related to the gas phase DCM concentration which was approximately constant during the experiments. With increasing the DCM loading rate, MLSS and suspended COD concentrations (as an indirect indicator of MLSS) were elevated in a non-linear trend. MLSS and suspended COD concentrations of the mixed liquor were in the range of 166-219 $g/m^3$and 114-154 g/m^3, respectively. Due to the applied environmental conditions, microbial mass of the bioreactor was mostly in the form of turbidity and floc formation was apparently negligible.

Chloride concentration and EC are the factors causing environmental osmotic pressure and affect the growth and activity of DCM degrading microorganisms [15, 34]. Chloride (Cl^-) concentration and EC of the mixed liquor at different DCM removal rates are presented in Fig.6. As illustrated in Fig.6, Cl^- concentration and EC of mixed liquor were linear functions of the DCM

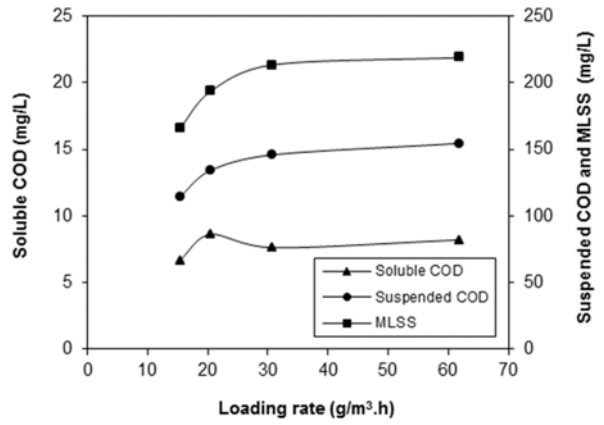

Fig. 5. Variations of the mixed liquor quality parameters (soluble and suspended COD and MLSS concentrations) at different DCM loading rate

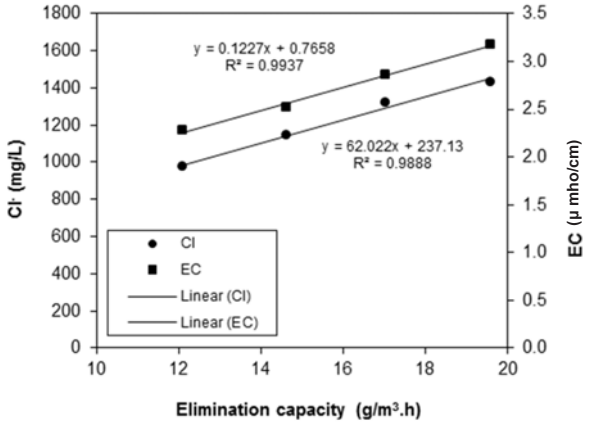

Fig. 6. Chloride concentration and EC of the mixed liquor as a function of DCM removal rate.

removal rate. Linear regression analysis indicated that per 1 g/m^3.h DCM removal rate, Cl^- concentration and EC of the mixed liquor were increased 62 g/m^3 and 122 µ mho/cm, respectivee ly. According to the stoichiometric equation of DCM oxidation to CO_2, 2 moles Cl^- are produced versus 1 mole DCM degradation. Based on the equation, the observed increase in Cl^- concentration of the mixed liquor was about 25% of the stoichiometric value. The causes for this result could be incomplete mineralization (intermediate compounds formation) and exhaustion of Cl^- in the form of HCl vapor [34]. Measurement of CO_2 in the inlet and outlet gas straems showed that the proportion of mineralization was about 76%. Lack of complete mineralization of DCM has also been reported in some other studies [35]. The highest average Cl^- concentration and EC of the mixed liquor were respectively 1433 g/m^3 and 3181 µmho/cm in the different stages of the HBCB bioreactor operation that would not be inhibitor for microbial activity [15, 34].

Kinetic analysis of biofiltration

General equation expressing the biofiltration rate predicts the removal efficiency and exhaust gas quality [20-23, 35]. Biofiltration kinetic parameters of the zero-order, zero-order limitedby mass transfer, half-order, first-order, second-order and Michaelis-Mentenrate equations are presented in Table 2. According to Table 2, the first-order rate equation is the most consistent with the kinetic data (R^2>0.99 and ε%<2.2). The constant of the first order rate equation was obtained 0.0114 1/s, which indicating the relatively high removal rate of DCM in the biofilter. The high removal rate decreases biofilter volume and from an economic point of view is highly desirable and important [20]. Kinetic data of DCM biofiltration also showed a high compatibility with the Michaeilis–Menten equation. The constants of the Michaeilis–Mentenmodel, K_s and V_m (saturation and the maximum reaction rate constants, respectively), were determined 2150 mg/m^3 and 108 g/m^3.h, respectively (R^2>0.98 and ε%<0.6). Kinetic of gas stream biofiltration has been studied in some previous researches. it was reported that kinetic of biofiltration of *n*-butyl alcohol and *iso*-butyl alcohol had the most conformity with the zero order limited by mass transfer rate equation [21]. The kinetic data also showed good fitness with the Michaeilis–Menten model, where K_s and V_m for *n*-butyl alcohol were 9 mg/m^3 and 613 g/m^3.h, respectively, and for *iso*-butyl alcohol were calculated 8 mg/m^3 and 584 g/m^3.h, respectively.

CONCLUSIONS

In this research, the HBCB bioreactor was designed with combining the bubble column bioreactor and biofilter and its performance for DCM removal from waste gas streams was studied in the EBRT range of 50-200 s. In the DCM loading

Table 2. Analysis of biofiltration kinetic using of the zero-order, half-order, first-order, second-order and Michaelis-Menten rate equations

Rate equation	Rate constants		R^2	ε%
	Parameters	Values		
Zero-order				
limited by reaction	k_0 (g m^{-3} s^{-1})	0.0045	0.421	19.7
limited by mass transfer	k_d	0.0045	0.968	6.2
Half-order	$k_{0.5}$ ($g^{0.5}$ $m^{-1.5}$ s^{-1})	0.0035	0.911	9.1
First-order	k_1 (s^{-1})	0.0114	0.995	2.1
Second-order	k_2 (m^3 g^{-1} s^{-1})	0.0325	0.905	11.6
Michaelis-Menten	K_s (g m^{-3})	2.15	0.982	0.5
	V_m (g m^{-3} s^{-1})	0.0301		

rate range of 15.3-61.9 g/m^3.h, the highest elimination rate of 19.6 g/m^3.h occurred at the highest loading rate and the highest removal efficiency of 79% was observed at the lowest loading rate. The results of linear regression analysis indicated that per each 1 g/m^3.h of the DCM removal rate, Cl^-concentration and EC of the mixed liquor increased 62 g/m^3 and 122 µmoh/cm, respectively. Kinetic analysis of biofiltration showed that the first-order rate equation could be regarded as the most adequate reaction rate model (R^2>0.99 and ε%<2.2) and the reaction rate constant of DCM removal was acquired 0.0114 1/s. The major advantages of the HBCB bioreactor consisted of relatively high DCM removal rate, small amount of waste production, little need to mixed liquor recirculation, low pressure drop and no fouling of biofilter bed.

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COMPETING INTERESTS

The authors declare that they have no competing interests.

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ETHICAL CONSIDERATIONS

Ethical issues (including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc) have been completely observed by the authors.

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