

Kinetic behaviors between acetone and composite bead in biofilter

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ABSTRACT. In this study, the kinetic behaviors between acetone and composite bead were investigated. The microbial growth rate decreases with increasing the average inlet concentration and increases with increasing the operation temperature at the average inlet concentration ranging from 50 to 300 ppm and the operation temperature ranging from 30 to 40°C. The microbial growth rate would be inhibited as the average inlet concentration increases and the inhibitive effect is more pronounced at the higher operation temperature. The microbial growth rate would be enhanced as the operation temperature increases and the enhance effect is more pronounced at the higher average inlet concentration. The value of maximum rate V_m and half-saturation constant K_s are range from 0.04 to 0.05 g-C/h-kg packing material and from 37.19 to 42.77 ppm, respectively. The biochemical reaction model could be regarded as the zero-order kinetic with the diffusion rate limitation. The biochemical reaction rate decreases with increasing the average inlet concentration and increases with increasing the operation temperature. The biochemical reaction rate would be inhibited at the high average inlet concentration and the inhibitive effect is more pronounced at the lower operation temperature. The biochemical reaction rate would be enhanced as the operation temperature increases and the enhance effect is more pronounced at the higher average inlet concentration. The maximum elimination capacity of biofilter increases with increasing the operation temperature. The value of critical and maximum elimination capacity are ranging from 0.07 to 0.15 and from 0.13 to 0.16 g-C/h-kg packing material, respectively.

1 INTRODUCTION

The removal of volatile organic compounds (VOCs) from a polluted air stream using a biological process is high efficient and has low installation and operation/maintenance costs. Biofiltration technology offers environmental advantages; it does not generate undesirable byproducts and converts many organic and inorganic compounds into harmless oxidation products (e.g., water and carbon dioxide). Biofiltration involves the passage of a polluted air stream through a packed bed containing microorganisms immobilized within a biofilm attached to the bed packing material. Contaminants are transferred to the interface between the gas and biofilm and are then absorbed into the biofilm. Contaminants are then used as carbon and/or energy sources for the

microorganisms within the biofilm. The solid filter material provides a nutrient source and matrix for the attachment of microorganisms. So, the filter bed is the heart of a biofiltration system and the filter material property is an important factor to obtain optimal pollutant removal. The optimal filter material should have the following characteristics: high moisture holding capacity, porosity, available nutrients and pH buffer capacity (Deviney *et al.*, 1999).

A wide range of filter materials including compost, peat and soil have been studied and found to be effective bed materials for specific contaminants and gas streams (Williams and Miller, 1992; Hodge *et al.*, 1991; Bohn, 1993). These natural materials are compact and crack causing higher bed head loss and uneven flow distribution as the filter bed is operated over a period of time. The result causes the efficiency of VOC removal to decrease. So, the filter bed usually requires a blending of some inert materials to prevent the occurrence. Polystyrene, gypsum, perlite, wood chips, and branches have been used as inert materials to blend into the bed (Ottengraf and Konings, 1986; Peters *et al.*, 1993). The oxidation of sulfur, nitrogen, and chlorine-containing compounds would produce acid intermediates or an end product to lower the bed pH and subsequently reduce the efficiency of VOCs removal. Calcium carbonate, marl and oyster shells have been used to buffer the acid product (Ergas, 1994; Ottengraf and van den Oever, 1983). Carbon, nitrogen and phosphorus are three important nutrients for microbial growth and metabolism. Carbon is supported by the VOCs in the air stream, however nitrogen and phosphorus must both be provided by the filter material. Nitrogen can make up about 15% of microbial cell dry weight and therefore it is a major constituent of microorganism proteins and nucleic acids (Carlson and Leiser, 1966). Since nitrogen is such a large percentage of cell mass, it can be a limiting nutrient if adequate amounts are not available in the biofilter material. Inorganic nitrogen (ammonia, nitrate, or nitrite) is water-soluble and can be considered as the available nitrogen nutrient for microorganisms utilized. Generally, inorganic nitrogen is not initially present in the filter material and is formed by the mineralization of organic nitrogen in the filter material and by recycling of nitrogen through the mineralization of cells. A spherical PVA/peat/KNO₃ composite bead has been prepared and has proved suitable as a filter material in the biofiltration process and the diffusivity of nutrient within the filter material would be an important control factor to achieve good biofilter performance (Chan and Lin, 2004). Granular activated carbon (GAC) has sufficient surface area and porosity, adding GAC into the biofilter would enhance the adsorption capacity, moisture holding capacity and porosity of filter material. Therefore, a PVA/peat/KNO₃/GAC composite bead would be a highly performance filter material. VOCs degradation by microorganisms in the biofilter is affected by various factors such as moisture content, pH, temperature, flow rate and concentration of contaminant. To study the effects of the operation temperature and inlet VOCs concentration on the composite bead biofilter performance would promote the application of the composite bead on the biofilter. This article investigates the biochemical kinetic behaviors between acetone and composite bead. The composite bead is the spherical PVA/peat/KNO₃/GAC composite bead. The relationships of the microbial growth rate and biochemical kinetic rate with the operation temperature and inlet VOCs concentration are also investigated.

2 EXPERIMENTAL AND METHODS

Descriptions of material used, preparing process of composite bead and biofilter experiments are almost given in our previous work (Chan and Lin, 2004). The new materials acetone (extra pure grade from Union Chemical Co., Hsinchu, Taiwan) and

granular activated carbon (GAC) (industrial grade from Taipei Chemical Co. Ltd., Hsinchu, Taiwan) were used as received. GAC (25g), sieved between 16 and 35 mesh (average diameter, 0.85 mm), was added into 25 mL water in a 100 mL beaker. The mixture were sealed with parafilm and kept at 25 °C for about 24 h in order for the GAC to adsorb water and reach equilibrium. Once the PVA powder was completely dissolved, both peat/KNO₃ and GAC mixture was slowly added into the PVA/KNO₃ mixture at 90 °C. As the filter material appeared before packing, it was immersed in 0.384M KNO₃ aqueous solution for about 12h to adsorb KNO₃ and reach equilibrium.

3 RESULTS AND DISCUSSION

The variation in the percentage of removed VOCs over time in an air stream with velocities exceeding 100 mh⁻¹, an acetone average inlet concentration in the range of 50-300 ppm, and a relative humidity of more than 95%, through a composite bead filter bed is shown in Figure 1 (only the average inlet concentration 100 ppm and operation temperature 30 °C is shown). We have found that the variation in the percentage of removed VOCs over time for the composite bead biofilter could be divided into six phases according to the microbial growth phases based on the number of viable cells with times. (Reynold, 1982) Since the microbial growth rate (phase II) and biochemical reaction kinetic (phase III) are the important factors for controlling the removal efficiency of biofilter, we investigate the effect of microbial growth rate and biochemical reaction rate on the inlet VOCs concentration and operation temperature.

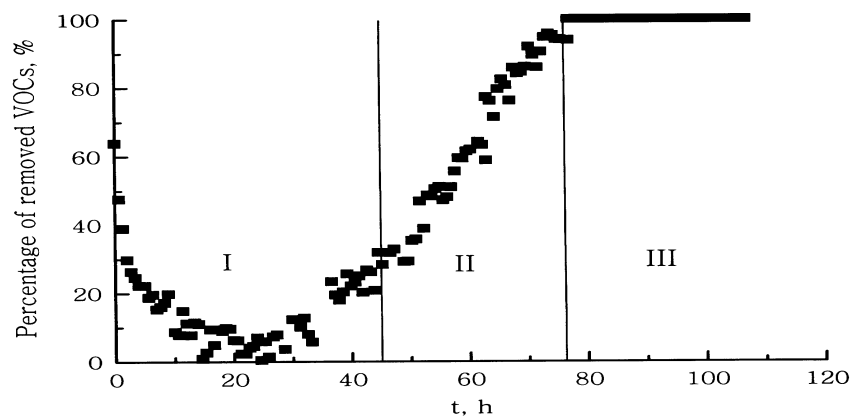


Figure 1. Percentage of removed VOCs over operation time (t) at the average inlet concentration 100 ppm and operation temperature 30°C.

In the log growth phase (phase II), the microbial growth rate increases exponentially and is represented by the following equation (Valsaraj, 1995)

$$\frac{dX}{dt} = k_g X \quad (1)$$

where X is the number of viable cells per unit volume, k_g is the microbial growth rate and t is the operation time. The concentration of VOCs in the exit stream (C) is inversely proportional to the number of viable cells per unit volume in the bed, so equation (1) can be converted into

$$\frac{dC}{dt} = -k_g C \quad (2)$$

Integration of equation (2) yields

$$\ln\left(\frac{C}{C_0}\right) = -k_g t \quad (3)$$

where C_0 is the concentration of VOCs in the inlet air stream. A plot of $\ln(C/C_0)$ versus t should correspond to a line, allowing k_g to be determined.

The variations of k_g with average inlet concentration for three operation temperatures (30, 35 and 40 °C) are shown in Figure 2. It is found that the k_g value decreases with increasing the average inlet concentration among three operation temperatures. The result indicates that the microbial growth rate would be inhibited as the VOCs concentration increases and high VOCs concentration would produce inhibitive effect on the metabolic activity of the microbial population. The slope of the linear relationship between k_g and average inlet concentration at 30, 35 and 40°C are 2.78×10^{-4} , 3.68×10^{-4} and $5.10 \times 10^{-4} \text{ ppm}^{-1} \text{ h}^{-1}$, respectively. The result indicates that the inhibition effect is more pronounced at the higher operation temperature.

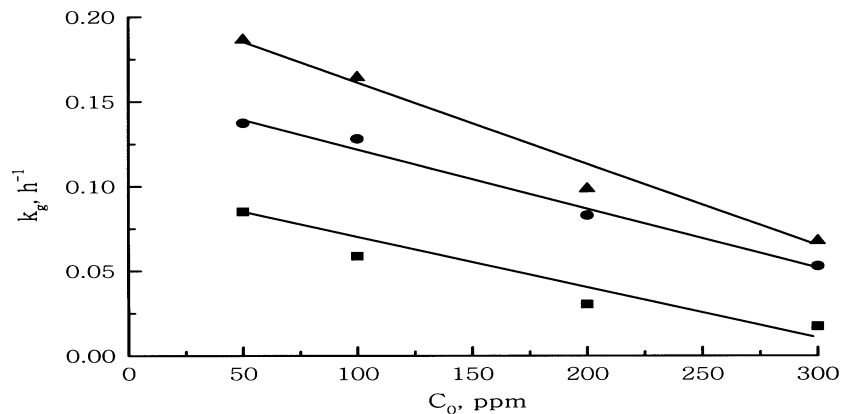


Figure 2. The variation of k_g with average inlet concentration (C_0) for various temperatures: (■) 30°C, (●) 35°C, (▲) 40°C.

The relationship between the microbial growth rate and temperature can be expressed as

$$\log k_g = \log k_{g0} + T \log \Phi \quad (4)$$

where k_{g0} is constant and Φ is temperature correction coefficient. A plot of $\log k_g$ versus T should correspond to a straight line. The variations of $\log k_g$ with operation temperature for four average inlet concentrations (50, 100, 200 and 300 ppm) are shown in Figure 3. It is found that the microbial growth rate increases with increasing operation temperature. The calculated Φ of average inlet concentration 50, 100, 200 and 300 ppm are 1.082, 1.108, 1.124 and 1.146, respectively. The results indicate that the microbial growth rate would be enhanced as the operation temperature increases and the enhance effect is more pronounced at the higher average inlet concentration.

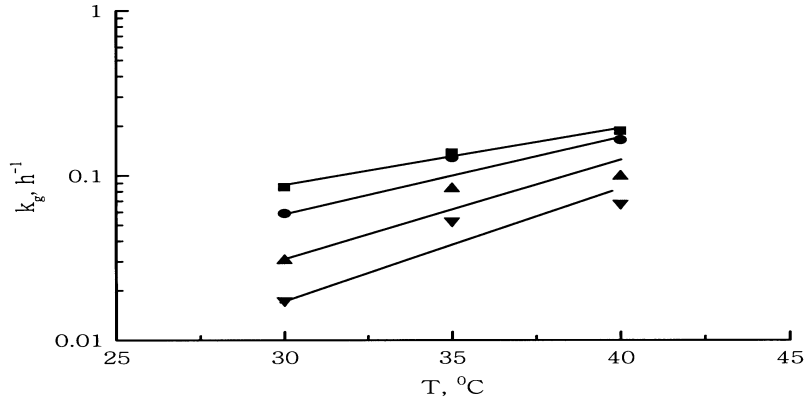


Figure 3. The variation of $\log k_g$ with operation temperature (T) for various average inlet concentrations: (■) 50 ppm, (●) 100 ppm, (▲) 200 ppm, (▼) 300 ppm.

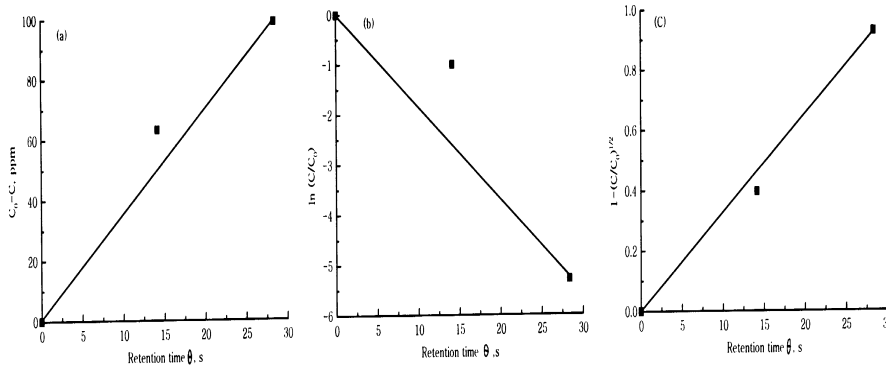


Figure 4. Plot of (a) $C_0 - C$ versus θ , (b) $\ln(C/C_0)$ versus θ , (c) $1 - (C/C_0)^{1/2}$ versus θ .

In the maximum stationary phase, the population of viable cells is at a relatively constant value. Under the steady-state conditions, the substrate utilization rate by microbial has been proposed by Ottengraf. There are three situations may be encountered in a biochemical reaction system and corresponding equations could be derived from the Michaelis-Menten relationship to express the rates of biochemical reaction for each situation as follow:

First-order kinetic

$$\ln(C/C_0) = -k_1\theta \quad (5)$$

Zero-order kinetic with reaction rate limitation

$$C_0 - C = k_0\theta \quad (6)$$

Zero-order kinetic with diffusion rate limitation

$$C = C_0 [1 - \theta (a k_0 D_e / 2mC_0\delta)^{1/2}]^2 \quad (7)$$

where a is the interfacial area per unit volume, D_e is the effective diffusion coefficient, m is the distribution coefficient of the component, θ is the retention time, δ is the biofilm thickness and k_0 and k_1 are the zero- and first-order reaction rate coefficient, respectively. However, in order to conveniently use, it is necessary to define a new parameter, $k_d = (a k_0 D_e / 2mC_0\delta)^{1/2}$. It can be seen that k_d is a function of the operating

conditions of the biofilter system, and k_d is constant under steady-state conditions. Therefore, Equation (7) can be rewritten as

$$1-(C/C_0)^{1/2} = k_d\theta \quad (8)$$

The plots of $\ln(C/C_0)$ versus θ , C_0-C versus θ and $1-(C/C_0)^{1/2}$ versus θ calculated from the data of the phase III in Figure 1 are shown in Figure 4. It is found that three plots are almost linearly, so it is difficult to judge which model is suitable. Assume a plug air flow in the biofilter column, the following equation based on the Michaelis-Menten equation is obtained (Yani *et al.*, 1998)

$$C_{ln}/R = K_s/V_m + C_{ln}/V_m$$

where $C_{ln} = (C_0-C)/\ln(C_0/C)$, $R = (C_0-C)/\theta$, K_s is saturation constant and V_m is maximum reaction rate. The plot of C_{ln}/R versus C_{ln} for three operation temperatures is shown Figure 5 (only the operation temperature 30°C is shown). The calculated K_s and V_m for three operation temperatures are range from 37.19 to 42.77 ppm and from 0.04 to 0.05 g-C/h-kg packing. If the substrate concentration is very low ($K_s \gg C_0$), it approaches 1st-order kinetic; the substrate concentration is very high ($K_s \ll C_0$), it approaches zero-order kinetic with reaction rate limitation. Since the values of K_s and C_0 are comparable, the biochemical reaction model could be regarded as the zero-order kinetic with diffusion rate limitation.

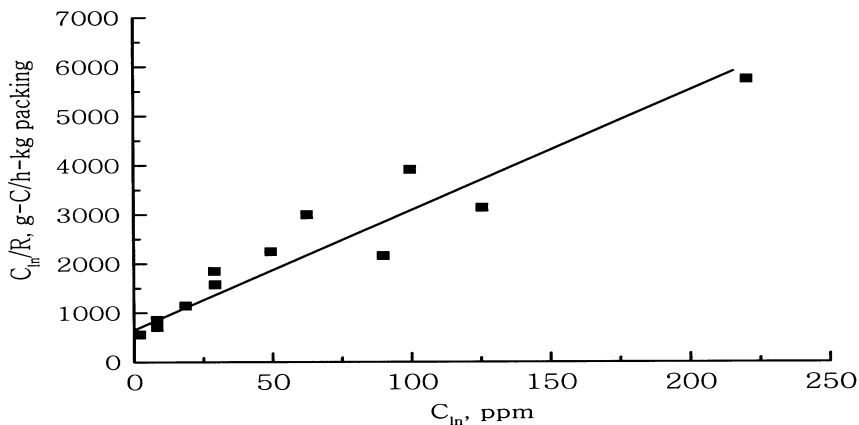


Figure 5. Plot of C_{ln}/R versus C_{ln} for biofilter at operation temperature 30°C .

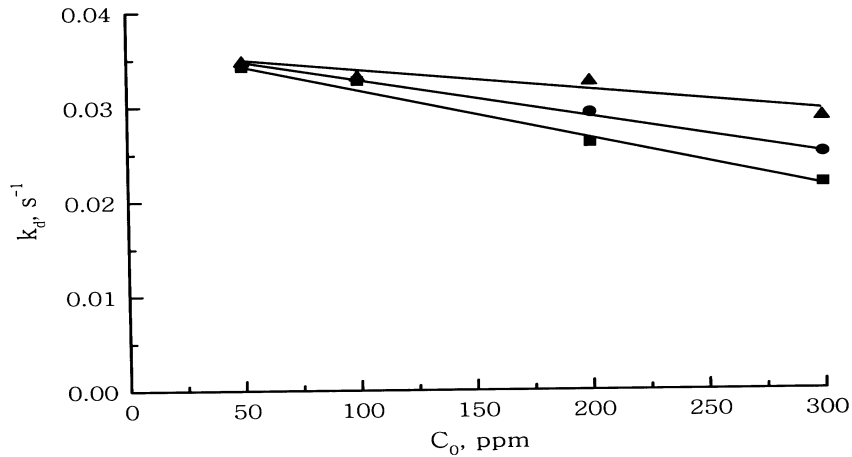


Figure 6. The variation of k_d with average inlet concentration (C_0) for various temperatures: (■) 30°C, (●) 35°C, (▲) 40°C.

The variation of k_d with average inlet concentration for three operation temperatures is shown in Figure 6. It is found that k_d decrease with increasing average inlet concentration, and its decrease rate at operation temperature 30, 35 and 40 °C are 5.601×10^{-5} , 4.048×10^{-5} and 2.340×10^{-5} $\text{ppm}^{-1} \text{s}^{-1}$, respectively. The results indicate that biochemical reaction rate would be inhibited as the inlet concentration increases, and the inhibition effect is more pronounced at lower operation temperature. The plot of $\log k_d$ versus T for four average inlet concentrations are shown in Figure 7. It is found that k_d increases with the operation temperature. The calculated Φ at average inlet concentration 50, 100, 200 and 300 ppm are 1.0015, 1.0012, 1.0221 and 1.0279, respectively. The results indicate that the biochemical reaction rate would be enhanced as the operation temperature increases and the enhance effect is more pronounced at the higher inlet concentration. The relationship of elimination capacity (EC) of biofilter versus load for three operation temperatures is shown in Figure 8 (only operation temperature 30 °C is shown). The critical and maximum elimination capacity at 30, 35 and 40 °C are 0.07 and 0.13, 0.11 and 0.15, and 0.15 and 0.16 gC/h-kg packing, respectively. The results indicate that both elimination capacities increase with increasing the operation temperature.

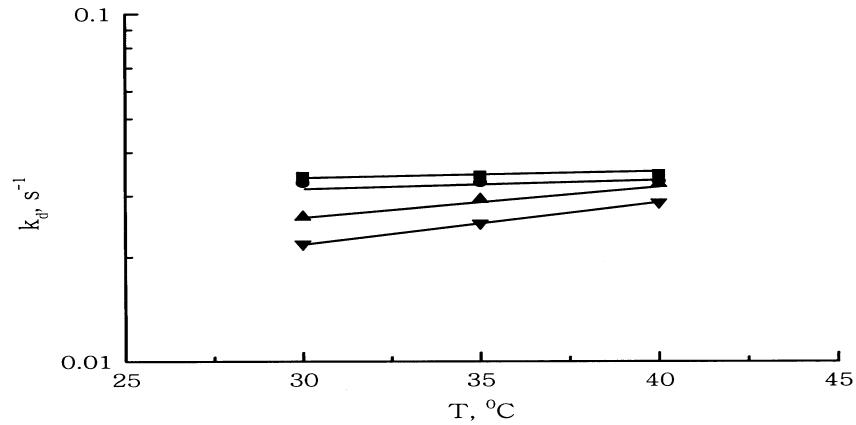


Figure 7. The variation of $\log k_d$ with operation temperature (T) for various average inlet concentrations: (■) 50 ppm, (●) 100 ppm, (▲) 200 ppm, (▼) 300 ppm.

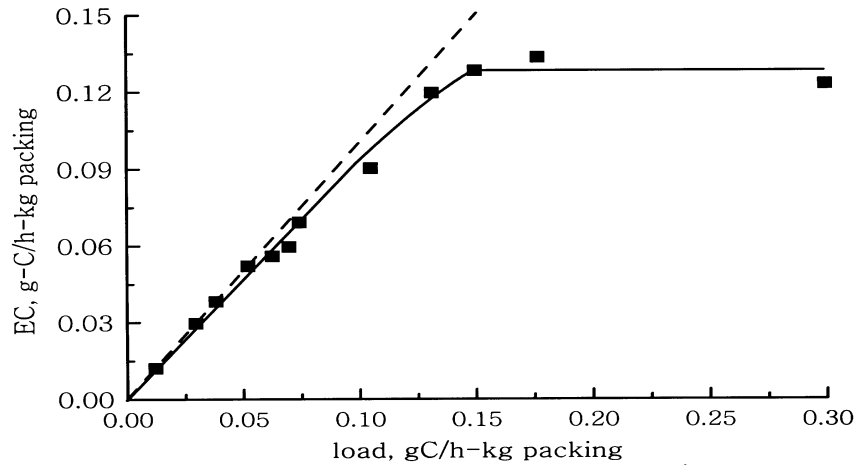


Figure 8. Plot EC versus load for biofilter at operation temperature 30°C.

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