

PREPARATION OF A POLY (VINYLALCOHOL) (PVA)/PEAT/ORGANOCLAY /KNO₃ COMPOSITE BEAD AS BIOFILTER MATERIAL FOR BIOFILTRATION OF VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

In this study, a PVA/peat/organoclay/KNO₃ spherical composite bead was prepared and was proved suitable as a biofilter material. This composite bead was a porous spherical particle with a diameter of 3.0-5.0 mm, a density of 1.23 g/cm³ and a porosity of about 50%. The organoclay was prepared by hexadecyl trimethyl ammonium bromide (HDTMA) exchanged clay. The biochemical kinetic behaviors of n-butyl acetate in the spherical PVA/peat/HDTMA-clay/KNO₃ composite bead biofilter (Clay biofilter) and PVA/peat/granular activated carbon (GAC)/KNO₃ spherical composite bead biofilter (GAC biofilter) were investigated. The values of half-saturation constant K_s for Clay biofilter and GAC biofilter were 69.86 and 38.49 ppm, respectively. The values of maximum reaction rate V_m for Clay biofilter and GAC biofilter were 23.77 and 22.97 ppm/s, respectively. Diffusion-limited Zero-order kinetic was regarded as the most adequate biochemical reaction model. The microbial growth rate k_g and biochemical reaction rate k_d for two biofilters were inhibited at higher inlet concentration. The degree of inhibitive effect was more pronounced in the GAC biofilter in microbial growth process and that was almost the same in two biofilters in the biochemical reaction process. The maximum elimination capacity for Clay biofilter and GAC biofilter was 139.10 and 154.67 g-C/h-m³ bed volume, respectively. The PVA/peat/HDTMA-clay/KNO₃ composite bead was suitable as a biofilter material.

Keywords: Poly (vinyl alcohol) (PVA), Organoclay, Composite bead, Biofilter material, Biofiltration.

1. INTRODUCTION

The removal of volatile organic compounds (VOCs) from a polluted air stream using a biological process is efficient and economical. Biofiltration technology offers environmental advantages: it does not generate undesirable by-products as many organic and inorganic compounds are converted 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 subsequently absorbed into

the biofilm. Contaminants are then used as carbon and/or energy sources for the microorganisms within the biofilm. The filter material acts as a source of nutrients and a matrix to hold the microorganisms during the biofiltration process. Therefore, the properties of the filter material are key to obtaining optimal pollutant removal. The optimal filter material should have the following characteristics: a high moisture-holding capacity, porosity, available nutrients, compression strength, and a pH buffer capacity (Deviney *et al.*, 1999).

Clays are natural fine-grained materials that are composed primary of a group of crystalline minerals. Clays are layered with interlayer spaces and the layers may be electrically and mechanical stability, possess a variety of structural and surface properties and have high values of cation exchange capacities, thus making clays an excellent group of adsorbents. However, their sorption capacity for organic molecules is very low because the hydrophilic nature of the mineral surface. The surfaces of clay-minerals can be transferred from hydrophilic to hydrophobic by the inorganic-organic ion-exchange process. The ion-exchange process is the exchangeable inorganic cations in the interlayer of natural clays replaced by a variety of organic cations. The organic cations often used in the inorganic-organic ion-exchange process were the quaternary ammonium cations such as example tetramethylammonium (TMA), trimethylphenylammonium (TMPA), tetrabutylammonium (TBA) and tetraethylammonium (TEA) etc. (Janes and Boyd, 1990; Akcay *et al.*, 2005; Akcay, 2004; 2006). The organoclays were found to be good sorbents for removing the toxic organic pollutants from the aqueous solution (Wu *et al.*, 2001; Bouras *et al.*, 2001; 2007; Zhu and Zhu, 2007). We had found that the adsorption capacity of HDTMA exchanged clay composite beads was about 4.4 times that of natural clay composite beads for adsorbing methyl ethyl ketone (Chan and Lai, 2012).

Recently, the spherical polyvinyl alcohol (PVA)/peat/granular activated carbon (GAC)/KNO₃, (PVA)/peat/bamboo charcoal/KNO₃ and (PVA)/peat/nitrocellulose/KNO₃ composed beads were prepared and were proven suitable as a filter material in the biofiltration process in our previous works (Chan and Peng, 2008; Chan and Chang, 2011; Chan and Ho, 2011). Therefore, blending organoclay with PVA, peat, and KNO₃ to form a spherical PVA/peat/organoclay/KNO₃ composite bead could then be used as the filter material in the biofiltration process. However, such filter material has not previously been reported and details of the biodegradation kinetic behaviors in this composite bead biofilter are scant. This article investigates the preparation of a spherical PVA/peat/organoclay/KNO₃ composite bead and the biochemical kinetic behaviors of n-butyl acetate in this composite bead biofilter. The relationships of the n-butyl acetate inlet concentration to the microbial growth rate and biochemical reaction rate are studied. In order to verify the PVA/peat/organoclay/KNO₃ spherical composite bead is suitable as biofilter material, the biochemical kinetic behaviors of n-butyl acetate between PVA/peat/organoclay/KNO₃ spherical composite bead biofilter (Clay biofilter) and PVA/peat/GAC/KNO₃ spherical composite bead biofilter (GAC biofilter) are compared.

2. MATERIAL AND METHODS

2.1. Materials

Clay (industrial grade from Pai Can Chemical, Hsinchu, Taiwan) was 1.84 μm in average diameter and had a cation exchange capacity (CEC) of 87 meq/100g. Peat (industrial grade from KekkilaOyj, Tuusula, Finland) was dried at 105°C before use, and it has a dry density of 90 kg/m³, a pH of 5.5, a pore volume of 96%, and an organic substance content of 91%. Poly(vinyl alcohol) (PVA) powder (industrial grade from Chung Chun Petrochemical, Hsinchu, Taiwan), granular activated carbon (GAC) (industrial grade from Taipei Chemical, Hsinchu, Taiwan), hexadecyl trimethyl ammonium bromide (HDTMA) (extra pure grade from Merck Chemical, Darmstadt, Germany), boric acid, sodium monobasic phosphate, sodium dibasic phosphate, potassium nitrate, silver nitrate and n-butyl acetate (extra pure grade from Union Chemical Co., Hsinchu, Taiwan) were used as received.

2.2. Preparation Procedures of PVA/Peat/Organoclay/KNO₃Spherical Composite Bead

Clay (25g) was dispersed in 100 mL of deionized water at room temperature followed by mixing for 1h at 90°C. The HDTMA (18.72g) was dissolved in 100 mL of deionized water at room temperature and slowly added to the clay dispersion. The clay/HDTMA mixture was stirred for 2 h at 90°C and then cooled to room temperature. The mixture was put in an ultrasonic oscillator at room temperature for 1h and then was centrifuged at 3000 rpm for 40 min. The clear liquid was decanted from the top and the residual HDTMA exchanged clay (HDTMA-clay) was washed with deionized water several times until no bromo ions were detected with AgNO₃ solution. Peat was sieved between 16 and 35 mesh (average diameter, 0.85 mm), and then 50g of peat was added to a 13.8% KNO₃ aqueous solution (200 mL) in a 500mL beaker to form an aqueous peat/KNO₃ dispersion. This dispersion was sealed with parafilm and kept at 25°C for approximately 24 h to allow the peat to adsorb KNO₃ and water and reach equilibrium. PVA powder (50g) was dispersed in a 6.0% KNO₃ aqueous solution (500 mL) in a 1000 mL beaker, and the dispersion was then heated to 90°C for dissolution. Once the PVA powder was completely dissolved, both the HDTMA exchanged clay and the peat/KNO₃ dispersions were slowly added to the PVA/KNO₃ aqueous solution at 90°C. The PVA/peat/HDTMA-clay/KNO₃ mixture was stirred for 1.5 h at 90°C and then cooled to 40°C. The mixture was slowly siphoned and added dropwise to a 6% boric acid aqueous solution (1000 mL) for 30 min, leading to the formation of a bead. The beads were subsequently transferred into a phosphate, aqueous solution and stirred for 30 min. The phosphate aqueous solution was prepared with 150 g NaH₂PO₄· 2H₂O and 335 g Na₂HPO₄· 12H₂O in 450 mL water. Finally, the bead was washed with distilled water and dried at 140°C for 24 h. The dried PVA/peat/HDTMA-clay/KNO₃ composite beads were stored in desiccator at room temperature before use. The composite bead was a porous spherical particle with a diameter of 3.0-5.0 mm and density of 1.23 g/cm³. The procedures for preparing PVA/peat/GAC/KNO₃ composite beads were described in our previous work (Chan and Peng, 2008).

2.3. Biofilter Experiments

The apparatus and operation of the biofilter system were described in our previous work (Chan and Peng, 2008). N-butyl acetate was used as VOC. Before packing, the filter material was immersed in a 0.384 M KNO₃ aqueous solution to adsorb KNO₃ and to reach equilibrium (approximately 12 h). The bead moisture content was humidified to more than 1.5 g water/g dry composite bead, and seeding was performed with activated sludge obtained from the sludge thickener of an industrial wastewater plant. The desired inlet VOC concentration in this study was 100, 400, 800, and 1200 ppm. Each desired inlet VOC concentration was obtained by adjusting the amount of evaporated VOC, and this concentration was maintained during the period of biofilter operation. The gas flow rate was maintained at 0.102 m³/h for all experiments, and consequently the empty bed residence time (EBRT) of the biofilter column was 28 s. When the stationary phase had maintained for more than 3 days, biofilter operation was stopped based on the change in the VOC removal efficiency with operation time. New filter material was then packed into column and the operation procedures described above were carried out to start another experiment with the desired inlet concentration. The VOC concentration in the inlet and exit air streams of each section was determined by auto-sampling and gas chromatography (GC) (Model GC-8A from Shimadzu, Tokyo, Japan). The VOC removal efficiency was calculated by evaluating the difference in VOC concentration between the inlet and exit air streams. The relative standard deviation and relative error in the experimental measurements were less than 2% and 5%, respectively.

3. RESULTS AND DISCUSSION

The variations of VOC removal efficiency with operation time are shown in Figure 1. (note that only the inlet concentration of 400 ppm is shown). It was found that the variations of VOC removal efficiency with operation time appeared in three phases: the lag phase (phase I), exponential growth phase (phase II) and stationary phase (phase III) (Chan and Peng, 2008). Only the biochemical kinetic behaviors in the exponential growth phase and stationary phase was studied in this work.

3.1. Microbial Growth Process

In the exponential growth phase (phase II), the microbial growth rate increased exponentially and was represented by the following equation (Valsaraj, 1995; Chan and Peng, 2008)

$$\ln(C/C_0) = -k_g t \quad (1)$$

where C and C₀ are the concentration of VOC in the exit and inlet air stream, respectively. A plot of ln(C/C₀) versus t should correspond to a straight line, and k_g can be determined. The microbial growth rate k_g at various inlet concentrations was calculated from the data in phase II and Eq. 1.

The variations of k_g values with inlet concentration C_0 for two biofilters are shown in Figure 2. The k_g value decreased from 7.39×10^{-2} to $0.38 \times 10^{-2} \text{ h}^{-1}$ for Clay biofilter and from 9.47×10^{-2} to $0.55 \times 10^{-2} \text{ h}^{-1}$ for GAC biofilter as the inlet concentration was increased from 100 to 1200 ppm. The result indicated that the microbial growth rate decreased with increasing inlet concentration. Increasing the inlet concentration generally enhanced the transfer rate of the VOC from the gas phase to the biofilm. This phenomenon could explain why more microorganisms then took part in the biodegradation. However, high concentrations of some recalcitrant VOCs may produce inhibitive effects on the metabolic activity of the microbial population (Leson and Winer, 1991). Therefore, the result indicated that the inhibitive effect predominated and the microbial growth rate was inhibited at higher inlet concentration. The k_g values of the Clay biofilter were slightly smaller than those of the GAC biofilter. The slope of the linear profiles in this inlet concentration range for Clay and GAC biofilters was 6.47×10^{-3} and $8.19 \times 10^{-3} \text{ h}^{-1} \text{ ppm}^{-1}$, respectively. These results indicated that the microbial growth rate in the Clay biofilter was also slightly smaller than that in the GAC biofilter, and the degree of inhibitive effect was more pronounced in the GAC biofilter.

3.2. Biochemical Reaction Process

In the stationary phase, the population of viable cells remained relatively constant. The earliest and most commonly used steady-state biofiltration model was proposed by Ottengraf. Ottengraf model for first-order kinetics, reaction-limited zero-order kinetics and diffusion-limited zero-order kinetics have been considered (Ottengraf and Van Den Oever, 1983; Ottengraf, 1986), and the following equations express the biochemical reaction rate for each of these scenarios:

1. First-order kinetic

$$\ln(C/C_0) = -k_1 \theta \quad (2)$$

2. Reaction-limited zero-order kinetic

$$C_0 - C = k_0 \theta \quad (3)$$

3. Diffusion-limited zero-order kinetic

$$1 - (C/C_0)^{1/2} = k_d \theta \quad (4)$$

where k_1 , k_0 and k_d are the rate coefficient of first-order kinetic, reaction-limited zero-order kinetic and diffusion-limited zero-order kinetic, respectively (Yang and Allen, 1994).

In order to verify the biochemical reaction kinetic model, assume there was a plug air flow in the biofilter column and the following equation was derived from the Michaelis-Menten equation (Valsaraj, 1995)

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

where K_s is half-saturation constant and V_m is maximum reaction rate. A plot of $(C_0 - C)/\ln(C_0/C)$ versus $\theta/\ln(C_0/C)$ should correspond to a straight line, and K_s and V_m can be determined. The substrate utilization rate by microbial was generally expressed by the Michaelis-Menten relationship. Under the steady state of microbial population, three possible situations may be

encountered in a biochemical reaction system (Yang and Allen, 1994): Situation (1) if the substrate concentration was very low ($K_s \gg C_0$), the reaction rate expression could be simplified to first-order kinetic; Situation (2) if the substrate concentration was very high ($K_s \ll C_0$), the reaction rate expression could be simplified to zero-order kinetic; Situation (3) if the substrate concentration C_0 was comparable with K_s , the reaction rate expression could not be simplified and the Ottengraf diffusion-limited model was found to be the most approximate expression.

The plot of $(C_0-C)/\ln(C_0/C)$ versus $\theta/\ln(C_0/C)$ for Clay and GAC biofilters was shown in Figure 3. The calculated K_s values for Clay biofilter and GAC biofilter were 69.86 and 38.49 ppm, respectively. The calculated V_m values for Clay biofilter and GAC biofilter were 23.77 and 22.97 ppm/s, respectively. The C_0/K_s values for Clay biofilter and GAC biofilter were found to be 1.43-17.17 and 2.60-31.18 respectively. The results indicated that the relationship of C_0 and K_s does not correspond to Situation 1 or 2; it corresponds to Situation 3. Therefore, the concentration C_0 was comparable with K_s , and the diffusion-limited zero-order kinetic was regarded as the most adequate model for the kinetics of the biochemical in this study. The k_d value of two biofilters at various inlet concentrations was calculated from the data in phase III and Eq. (4).

The variations of k_d values with inlet concentration C_0 for two biofilters are shown in Figure 4. The k_d value decreased from 4.66×10^{-2} to $0.73 \times 10^{-2} \text{ h}^{-1}$ for Clay biofilter and from 4.75×10^{-2} to $0.83 \times 10^{-2} \text{ h}^{-1}$ for GAC biofilter as the inlet concentration increased from 100 to 1200 ppm. The result indicated that the biodegradation rate was also inhibited at higher inlet concentration. Microbial metabolic activity would decrease with increasing the amount of n-butyl acetate dissolved in the biofilm because the dissolved n-butyl acetate would produce toxicity for the microorganism. The k_d values of the clay biofilter were slightly smaller than those of the GAC biofilter. The slope of the linear profiles in this inlet concentration range for Clay and GAC biofilters was 3.67×10^{-3} and $3.66 \times 10^{-3} \text{ h}^{-1} \text{ ppm}^{-1}$, respectively. These results indicated that the biodegradation rate in the Clay biofilter was also slightly smaller than that in the GAC biofilter, and the degree of inhibitive effect was almost the same in both biofilters.

Overall, the microbial growth rate and biochemical reaction rate were inhibited at higher inlet concentration. The degree of inhibitive effect was more pronounced in the GAC biofilter in microbial growth process and that was almost the same in both biofilters in the biochemical reaction process.

3.3. Elimination Capacity

Elimination capacity (EC) and load were calculated according to equations presented below:

$$EC = Q (C_0 - C) / V \quad (6)$$

$$\text{Load} = Q C_0 / V \quad (7)$$

where Q is the flow rate of inlet air steam and V is the bed volume of filter material when packed. Under low load conditions, the elimination capacity essentially equals the load, and the system is calculated to be at 100% removal efficiency. As the load on the system is increased, a point is reached where the overall load exceeds the overall elimination capacity, causing removal

efficiencies less than 100%. This point is typically called the critical load or critical elimination capacity. As the load is increased further, a maximum overall elimination capacity will eventually be reached. This maximum overall elimination capacity is independent of contaminant concentration and residence time within a reasonable range of operating conditions (Ottengraf, 1986). The relationship between the elimination capacity (EC) of biofilter and the load for two biofilters is shown in Figure 5. The maximum elimination capacity of the Clay biofilter and GAC biofilter were 139.10 and 154.67 g-C/h-m³ bed volume, respectively. The result indicated that the maximum elimination capacity of the GAC biofilter was slightly greater than that of the Clay biofilter. Thus, the PVA/peat/organoclay/KNO₃ composite bead was suitable as biofilter material.

4. CONCLUSIONS

A new type PVA/peat/organoclay/KNO₃ composite bead was prepared. It was a porous spherical particle with a diameter of 3.0-5.0 mm, a density of 1.23 g/cm³ and a porosity of about 50%. The organoclay is prepared by hexadecyl trimethyl ammonium bromide (HDTMA) exchanged clay. The biochemical kinetic behaviors of n-butyl acetate in the spherical PVA/peat/HDTMA-clay/KNO₃ composite bead biofilter (Clay biofilter) and PVA/peat/GAC/KNO₃ spherical composite bead biofilter (GAC biofilter) were investigated. Diffusion-limited Zero-order kinetic was regarded as the most adequate biochemical reaction model. The microbial growth rate k_g and biochemical reaction rate k_d were inhibited at higher inlet concentration. The degree of inhibitive effect was more pronounced in the GAC biofilter in microbial growth process and that was almost the same in both biofilters in the biochemical reaction process. The microbial growth rate k_g , biochemical reaction rate k_d , and maximum elimination capacity in the Clay biofilter was slightly smaller than those in the GAC biofilter. The PVA/peat/HDTMA-clay/KNO₃ composite bead was suitable as a biofilter material.

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