Synthesis of a New Type Poly(vinyl alcohol)/Peat/Bamboo Charcoal/KNO_3 Composite Bead Used as Biofilter Material

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ABSTRACT: A new type poly(vinyl alcohol) (PVA)/peat/bamboo charcoal (BC)/KNO_3 composite bead was prepared, which has a diameter of 2.4–6.0 mm and a density of 1.133 g/cm^3 and is a porous spherical particle. The biochemical kinetic behaviors of *n*-butyl acetate in PVA/peat/BC/KNO_3 spherical composite bead biofilter (BC biofilter) and PVA/peat/granular activated carbon (GAC)/KNO_3 spherical composite bead biofilter (GAC biofilter) were investigated. The values of half-saturation constant K_s for BC biofilter and GAC biofilter were 27.89 and 27.95 ppm, respectively. The values of maximum reaction rate V_m for BC biofilter and GAC biofilter were 13.49 and 13.65 ppm/s, respectively. Zero-order kinetic with the diffusion limitation was regarded as the most adequate biochemical reaction model for the two biofilters. The microbial growth rate and biochemical reaction rate for two biofilters were inhibited at higher inlet concentration, and the degree of inhibitive effect was more pronounced in the inlet concentration range of 100–800 ppm. The biochemical kinetic behaviors of the two biofilters were similar. The maximum elimination capacity of BC biofilter and GAC biofilter were 111.65 and 122.67 g C/h m^3 bed volume, respectively. The PVA/peat/BC/KNO_3 composite bead was suitable as a biofilter material. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1782–1787, 2011

Key words: poly(vinyl alcohol) (PVA); peat; synthesis; composites; biological application of polymers

INTRODUCTION

The removal of volatile organic compounds (VOCs) from a polluted air stream using a biological process is highly efficient and has low installation and operation/maintenance costs. Biofiltration technology offers environmental advantages: it does not generate undesirable byproducts by converting 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 subsequently 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 in the biofiltration process. Therefore, the filter material property is an important factor in obtaining optimal pollutant removal. The optimal filter material should have the following characteristics: high moisture holding capacity, porosity, available nutrients, compression strength, and pH buffer capacity.[1]

Granular activated carbon (GAC) has large surface area and porosity. It has been shown that the microorganism can colonize GAC and form a biofilm.[2,3] The use of GAC in a bioscrubber could improve the transfer of hydrophobic VOCs from gas to liquid phase.[4] An activated carbon filter was used as a buffer and placed before a biofilter for treating a fluctuating concentration of toluene. The biofilter performance could be enhanced if the waste gas entering the activated carbon filter was relatively dry.[5] Different amount of GAC mixed with the base biofilter material could enhance the biofilter performance.[6] Biofiltration of VOCs on a GAC biofilter could enhance the availability of VOCs for microorganism because VOCs adsorbed on to GAC remained for a higher column residence time for microbial degradation. The affinity of VOCs with GAC was an important parameter controlling the biodegradation process.[7] GAC was found to be an effective biofilter media for toluene biofiltration, and the maximum elimination capacity (EC) of 872.5 g/m^3 h was observed at the inlet load of 1104.5 g/m^3 h.[8] Therefore, combining adsorption and biofiltration technologies would be a very promising alternative, and the adsorbed pollutants represent a further available source for microbial growth to enhance the EC. Hence, a filter material blend with GAC would

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enhance the adsorption capacity, moisture holding capacity, and porosity of filter material. A spherical poly(vinyl alcohol) (PVA)/peat/GAC/KNO_3 composite bead was prepared and was proven suitable as a filter material in the biofiltration process in our previous works.[9] The diffusivity of nutrient within the filter material was an important control factor for achieving good biofilter performance.

Bamboo is a perennial plant and is abundant in Taiwan. Bamboo charcoal (BC) is an environmentally functional material and developed fast in recent years because bamboo grows very fast and has short harvest cycle. Hence, making BC does not destroy forest and environment. BC has the adsorption capacity as the activated carbon has and can replace the wood charcoal.[8,10] BC is good in strength and can bind with a variety of molecules because it contains network of pores of various shapes and sizes.[11] Bamboo carbonized at 400°C and treated with diluted sulfuric acid is effective for removing NH_3 from aqueous solution.[10] The acid-treated bamboo root biomass could be a good adsorbent for the removal of Cu^{+2} and Zn^{+2} ions from industrial effluents.[12] Therefore, BC could blend with PVA, peat, and KNO_3 to form a PVA/peat/BC/KNO_3 spherical composite bead, which would 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.

Recently, we had indicated that the process for degradation of VOCs in PVA/peat/GAC/KNO_3 composite bead biofilter could be divided into three phases: lag, exponential growth, and stationary phases, and the exponential growth and stationary phases are important for controlling the removal efficiency of biofilter.[9,13] This article investigates the preparation of a PVA/peat/BC/KNO_3 spherical composite bead and the biochemical kinetic behaviors of *n*-butyl acetate in this composite bead biofilter. The relationship of *n*-butyl acetate inlet concentration with the microbial growth rate and biochemical reaction rate are studied. To verify whether PVA/peat/BC/KNO_3 spherical composite bead is suitable as biofilter material, the biochemical kinetic behaviors of *n*-butyl acetate between PVA/peat/BC/KNO_3 spherical composite bead biofilter (BC biofilter) and PVA/peat/GAC/KNO_3 spherical composite bead biofilter (GAC biofilter) are compared.

EXPERIMENTAL

Materials

Peat (industrial grade from KekkilaOyj, Tuusula, Finland) was dried at 105°C before use. It has a dry density of 90 kg/m^3, a pH of 5.5, a pore volume of 96%, and an organic substance content of 91%. Boric acid, sodium monobasic phosphate, sodium dibasic phosphate, potassium nitrate, and *n*-butyl acetate (extra pure grade from Union Chemical, Hsinchu, Taiwan) were used as received. PVA powder (industrial grade from Chung Chun Petrochemical, Hsinchu, Taiwan), GAC (industrial grade from Taipei Chemical, Hsinchu, Taiwan), and BC (industrial grade from local shops) were also used as received.

Preparation procedures of PVA/peat/BC/KNO_3 spherical composite bead

Peat and BC were sieved between 16 and 35 mesh (average diameter, 0.85 mm). Peat (50 g) was added into a 13.8% KNO_3 aqueous solution (200 mL) in a 500-mL beaker to form peat mixture. BC (25 g) was added into 25 mL water in a 100-mL beaker to form BC mixture. Both mixtures were sealed with paraffin and kept at 25°C for approximately 24 h for the peat and BC to adsorb KNO_3 and water and reach equilibrium. PVA powder (50 g) was added into a 6.0% KNO_3 aqueous solution (500 mL) in a 1000-mL beaker, and, then, the mixture was heated to 90°C for dissolution. Once the PVA powder was completely dissolved, both peat/KNO_3 and BC mixtures were slowly added into the PVA/KNO_3 mixture at 90°C. The PVA/peat/BC/KNO_3 mixture was stirred for 1.5 h at 90°C and cooled to 40°C. The mixture was slowly siphoned and dripped into a 6% boric acid aqueous solution (1000 mL) for 10 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 $NaH_2PO_4{\cdot}2H_2O$ and 335 g $Na_2HPO_4{\cdot}12H_2O$ in 450 mL water. Finally, the bead was washed with distilled water and dried at 140°C for 24 h. The dried PVA/peat/BC/KNO_3 composite beads were stored in desiccators at room temperature before use. The composite bead has a diameter of 2.4–6.0 mm and density of 1.133 g/cm^3 and is a porous spherical particle. The procedures for preparing PVA/peat/GAC/KNO_3 composite beads were similar as described above and only the BC was replaced with GAC.

Biofilter experiments

The biofilter systems consisted of two biofilter columns and contained a VOCs influent gas supply system as shown in Figure 1. The biofilter columns and the VOCs flask were set in an isothermal transparent acrylic chamber and an isothermal water bath, respectively. The temperature of biofilter column and VOCs flask was maintained at 30°C. The biofilter column was composed of four sections connected in series; each section has a transparent

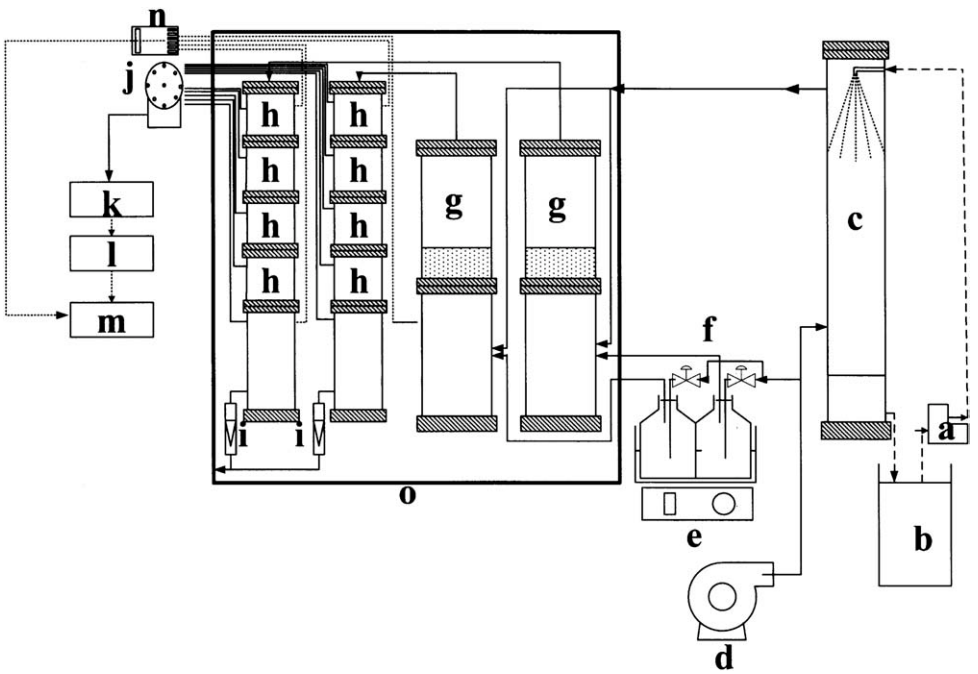

Figure 1 Schematic diagram of the biofilter system: (a) water pump, (b) water bath, (c) water spray tower, (d) air pump, (e) isothermal water bath, (f) VOC flask, (g) mixing chamber, (h) composite bead, (i) flow meter, (j) autosampling port, (k) gas chromatograph, (l) transfer interface, (m) PC, (n) thermometer, and (o) isothermal transparent acrylic chamber.

acrylic resin pipe with an inner diameter of 8 cm and a height of 7.5 cm, which was packed to a height of about 4 cm with filter material. The bulk density of filter material as packed was 348.3 kg dry composite bead/m^3 bed volume. The influent gas was divided into two streams: one stream was bubbled through a VOC liquid in a 2.5-L Erlenmeyer flask to make evaporated VOC, and the other stream flowed through a water spray tower by increasing humidity to over 95%. The two streams were mixed in a mixing chamber and then allowed to flow into the biofilter column. *N*-butyl acetate was poured into Erlenmeyer flask.

Before packing, the filter material was immersed in a 0.384*M* KNO_3 aqueous solution to adsorb KNO_3 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 the seeding was performed with activated sludge obtained from the sludge thickener of an industrial wastewater plant. The suspended solids were allowed to settle for 4 h, and the supernatant was discarded to concentrate the sludge. The seeding step consisted of mixing 250 mL of concentrated sludge with 70 g composite beads in a 500-mL beaker. The so produced composite beads covered with biological attachment were placed into the biofilter. The desired inlet VOCs concentration in this study was 100, 400, 800, 1200, and 1600 ppm. Each desired inlet VOCs concentration was obtained by adjusting the amount of evaporated VOCs and was maintained at this concentration during the period of biofilter operating. The gas flow rate was maintained at 0.102 m^3/h for all experiments, and, consequently, the empty bed residence time of biofilter column was 28 s. As the stationary phase had been maintained for more than 3 days, the biofilter operation was stopped according to the variations of VOCs removal efficiency with operation time. One biofilter column always operated at an inlet concentration of 400 ppm representing the control biofilter column for each experiment. Then, new filter material was repacked, and the operation procedures described above were carried out to start another experiment with the desired inlet concentration. The VOCs concentration in the inlet and exit air streams of each section was determined by autosampling and analyzing using gas chromatography (Model GC-8A from Shimadzu, Tokyo, Japan). The VOCs removal efficiency was calculated by the difference in the VOCs concentration between the inlet and exit air streams. The relative standard deviation and relative error of the experimental measurements were less than 2% and 5%, respectively.

RESULTS AND DISCUSSION

The variations in VOCs removal efficiency with operation time are shown in Figure 2 (only the inlet concentration of 400 ppm is shown). It was found that the variations in VOCs removal efficiency with

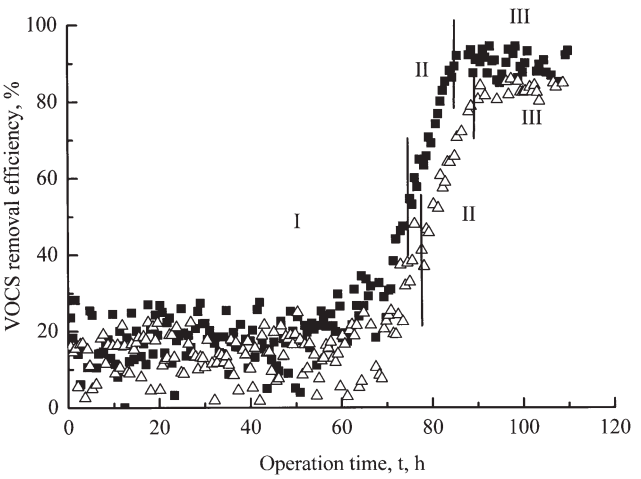

Figure 2 The variations of VOCs removal efficiency with operation time t for two biofilters at an inlet concentration of 400 ppm: (■) BC biofilter and (△) GAC biofilter.

operation time appeared in three phases: lag phase (Phase I), exponential growth phase (Phase II), and stationary phase (Phase III).[9,13] Only the biochemical kinetic behaviors in the exponential growth phase and stationary phase were studied in this work.

Microbial growth process

In the exponential growth phase (Phase II), the microbial growth rate increased exponentially and was represented by the following equation[13,14]

$$\ln(C/C_0) = -k_g t \tag{1}$$

where C and C_0 are the concentration of VOCs in the exit and inlet air stream, respectively. A plot of $\ln(C/C_0)$ 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 in k_g values with inlet concentration C_0 for BC and GAC biofilters are shown in Figure 3. The k_g values of BC biofilter were slightly smaller than those of GAC biofilter. The result indicated that the microbial growth rate in the BC biofilter was slightly smaller than that in the GAC biofilter. The k_g value sharply decreased with increasing inlet concentration in the concentration range of 100–800 ppm, and, then, it slightly decreased with increasing inlet concentration in the concentration range of 800–1600 ppm. The reason was that an increase in the inlet concentration generally would enhance the transfer rate of the VOCs from the gas phase to the biofilm. This phenomenon could explain the fact that more microorganisms were caused to participate in the biodegradation. However, high concentrations of some recalcitrant VOCs may produce inhibitive effects on the metabolic activity of the microbial population.[15] Therefore, the result indicated that the inhibitive effect predominated, and the microbial growth rate was inhibited at higher inlet concentration.

The linear profiles in the inlet concentration range of 100–1600 ppm could be divided into two regions. The slope of the linear profiles in the inlet concentration range of 100–800 ppm for BC and GAC biofilters were 1.69×10^{-4} and 1.81×10^{-4} h^{-1} ppm^{-1}, respectively. The values in the inlet concentration range of 800–1600 ppm for BC and GAC biofilters were 6.75×10^{-6} and 7.92×10^{-6} h^{-1} ppm^{-1}, respectively. These results indicate that the degree of inhibitive effect was more pronounced in the low inlet concentration range (from 100 to 800 ppm) and was almost of the same sensitivity for both biofilters.

Biochemical reaction process

In the stationary phase, the population of viable cells was at a relatively constant value. The earliest and commonly used biofiltration model under steady state condition was proposed by Ottengraf. The three basic situations of Ottengraf model was first-order kinetics, zero-order kinetics with reaction limitation, and zero-order kinetics with diffusion limitation.[16,17] The corresponding equations expressed the rates of biochemical reaction for each situation as follows:

1. First-order kinetic

$$\ln(C/C_0) = -k_1\theta \tag{2}$$

2. Zero-order kinetic with reaction limitation

$$C_0 - C = k_0\theta \tag{3}$$

3. Zero-order kinetic with diffusion limitation

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

where k_1, k_0, and k_d are the rate coefficient of first-order kinetic, zero-order kinetic with reaction limitation, and zero-order kinetic with diffusion limitation, respectively.[18]

The substrate utilization rate by microbes 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[18]: 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

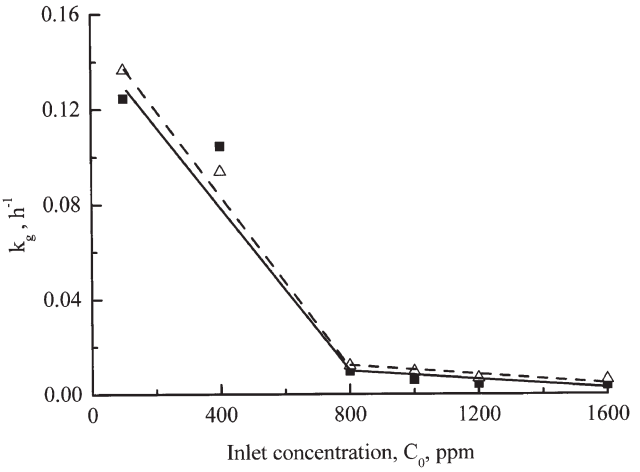

Figure 3 The variations of k_g values with inlet concentration for two biofilters: (■, —) BC biofilter and (△, ---) GAC biofilter.

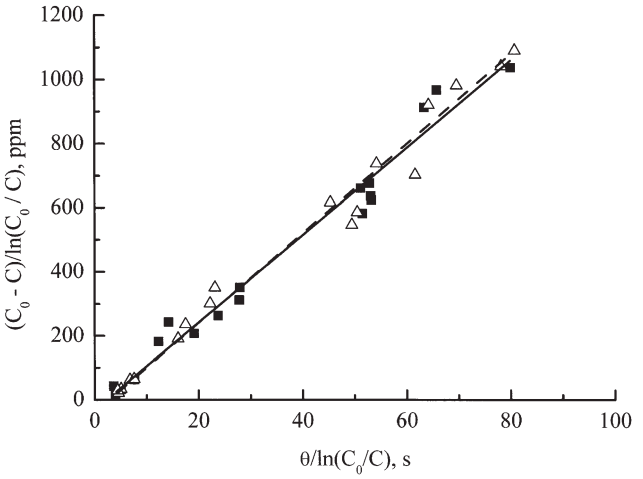

Figure 4 Plot of $(C_0 - C)/\ln(C_0/C)$ versus $\theta/\ln(C_0/C)$ for two biofilters: (■, —) BC biofilter and (△, ---) GAC biofilter.

comparable with K_s, the reaction rate expression could not be simplified, and the Ottengraf diffusion limiting model was found to be the most approximate expression.

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[14]

$$(C_0 - C)/\ln(C_0/C) = V_m[\theta/\ln(C_0/C)] - K_s \qquad (5)$$

where K_s is the half-saturation constant and V_m is the 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 plot of $(C_0 - C)/\ln(C_0/C)$ versus $\theta/\ln(C_0/C)$ for BC and GAC biofilters are shown in Figure 4. The calculated K_s values for BC biofilter and GAC biofilter were 27.89 and 27.95 ppm, respectively. The calculated V_m values for BC biofilter and GAC biofilter were 13.49 and 13.65 ppm/s, respectively. The C_0/K_s values for BC biofilter and GAC biofilter were found to be 3.58–57.37 and 3.58–57.25, respectively. The results indicated that the relationship of C_0 and K_s does not correspond to Situation 1 or 2, and it corresponds to Situation 3 for two compounds. Therefore, the concentration C_0 was comparable with K_s, and zero-order kinetic with diffusion limitation was regarded as the most adequate biochemical reaction kinetic model 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 5. The k_d values of BC biofilter were also slightly smaller than those of GAC biofilter. The result indicated that the biodegradation rate in the BC biofilter was also slightly smaller than that in the GAC biofilter. The k_d value also sharply decreased with increasing inlet concentration in the concentration range of 100–800 ppm, and, then, it also slightly decreased with increasing inlet concentration in the concentration range of 800–1600 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. Microorganism was almost poisoned as the inlet concentration was greater than 800 ppm.

The linear profiles in the inlet concentration range of 100–1600 ppm could be also divided into two regions. The slope of the linear profiles in the inlet concentration range of 100–800 ppm for BC and GAC biofilters were 4.03×10^{-5} and 5.80×10^{-5} h^{-1} ppm^{-1}, respectively. The values in the inlet concentration range of 800–1600 ppm for BC and GAC biofilters were 5.61×10^{-6} and 5.86×10^{-6} h^{-1} ppm^{-1},

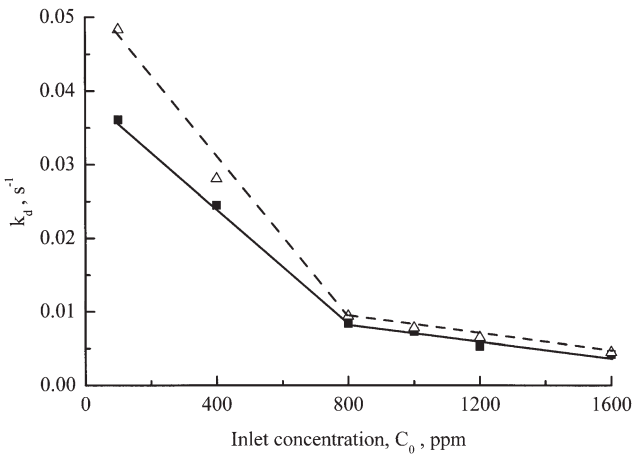

Figure 5 The variations of k_d with inlet concentration for two biofilters: (■, —) BC biofilter and (△, ---) GAC biofilter.

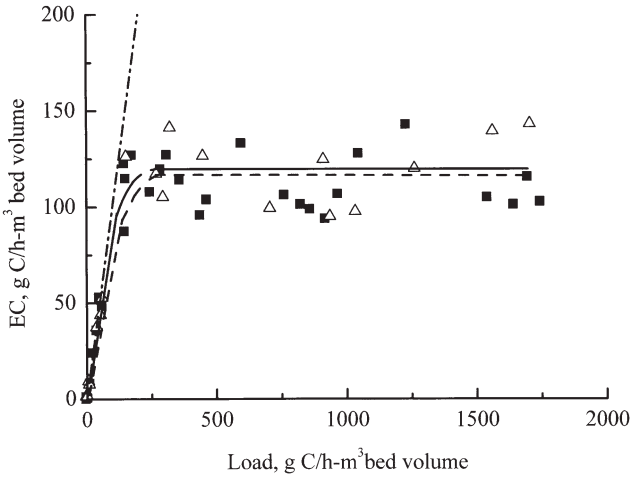

Figure 6 The variations in elimination capacity (EC) with load for two biofilters: (■, —) BC biofilter, (△, ---) GAC biofilter, and (-●-) 100% removal.

respectively. These results indicate that the degree of inhibitive effect was more pronounced in the low inlet concentration range (from 100 to 800 ppm) and was almost of the same sensitivity for 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 low inlet concentration range for both biofilters. Thus, the biochemical kinetic behaviors of the two biofilters were the same.

Elimination capacity

EC and load were calculated according to equations presented below:

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

$$\mathrm{Load} = QC_0/V \quad (7)$$

where Q is the flow rate of inlet air steam and V is the bed volume of filter material as packed. Under low load conditions, the EC essentially equals the load, and the system is calculated to be at 100% removal efficiency. By increasing the load on a system, a point will be reached where the overall load will exceed the overall EC, generating removal efficiencies less than 100%. This point is typically called the critical load or critical EC. As the load continues to increase, a maximum overall EC will eventually be reached. This maximum overall EC is independent of contaminant concentration and residence time within a reasonable range of operating conditions.[17] The relationship of EC of biofilter versus load for two biofilters is shown in Figure 6. The maximum EC of BC biofilter and GAC biofilter was 111.65 and 122.67 g C/h m^3 bed volume, respectively. The result indicated that the maximum EC of GAC biofilter was slightly greater than that of BC biofilter. Thus, the PVA/peat/BC/KNO_3 composite bead was suitable as a biofilter material.

CONCLUSIONS

In this study, a new type PVA/peat/BC/KNO_3 composite bead was prepared and was proved suitable as biofilter material. The composite bead has a diameter of 2.4–6.0 mm and a density of 1.133 g/cm^3 and is a porous spherical particle. The biochemical kinetic behaviors of *n*-butyl acetate in PVA/peat/BC/KNO_3 spherical composite bead biofilter (BC biofilter) and PVA/peat/GAC/KNO_3 spherical composite bead biofilter (GAC biofilter) were investigated. Zero-order kinetic with the diffusion limitation could be regarded as the most adequate biochemical reaction model. Microbial growth rate k_g and biochemical reaction rate k_d of both biofilters were inhibited at higher inlet concentration, and the degree of inhibitive effect was more pronounced in the low inlet concentration range. The biochemical kinetic behaviors of two biofilters were the same. The PVA/peat/BC/KNO_3 composite bead was suitable as a biofilter material.

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