A New Type Synthetic Filter Material for Biofilter: Poly(Vinyl Alcohol)/Peat Composite Bead

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ABSTRACT: In this study, a new type of poly(vinyl alcohol) (PVA)/peat composite bead was prepared and was proved suitable as a filter material in the biofiltration process. The composite bead is a porous spherical particle and has a diameter of 2.4–6.0 mm and a density of 0.69 kg/cm^3. It contains 3.25 mg N/g dry solid and 2.91 mg P/g dry solid. The equilibrium moisture content of the composite bead for adsorption and holding experiments is 50.5 and 66.8% by wet basis, respectively. The initial compression strength of the composite bead is 0.32 kg/cm^2. It has higher moisture holding capacity and compression strength than pig manure compost filter material. The adsorption behavior of ethyl acetate and composite bead follows the Freundlich adsorption isotherm. The composite bead has buffer capacity and could keep the filter bed at pH = 6.9–7.2 during operating. The percentage of removed ethyl acetate was 99% for up to 33 days as the composite bead adsorbed nutrients. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 3248–3255, 2003

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

INTRODUCTION

Removal of gas-phase volatile organic compounds (VOC) from a polluted air stream by a biological process is a high-removal efficiency, low-installation and operation/maintenance cost and good reliability technology. Most importantly, biofiltration does not generate undesirable byproducts and converts many organic and inorganic compounds into harmless oxidation products (e.g., water and carbon dioxide). Biofiltration is one such technology involving 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 used as carbon and/or energy sources for the microorganisms within the biofilm.

In the biofiltration process, the solid filter material provides a nutrient source and matrix for the attachment of microorganisms. Therefore, the filter bed is the heart of a biofiltration system and the filter material property is an important factor used to obtain optimal pollutant removal. The optimal filter material should have the following characteristics[1–7]: (1) high moisture holding capacity for preventing dried bed and moisture content between 40 and 60 wt % (by wet basis) for sustaining biological activity. (2) Pore volume of filter bed and diameter of 60 wt % particles (d_{60}) should be greater than 80% and 4.0 mm. The high porosity could reduce the head loss and ensure even distribution of incoming waste gas. (3) Having available nutrients for optimal microbial growth is required. (4) The pH and temperature of the bed during operating must maintain between 7 and 8 and 20 and 40°C, respectively, for promoting biological oxidation.

A wide range of filter materials have been studied.[8–10] Compost, peat, and soil have been observed to be an effective bed material for specific contaminants and gas streams. Those natural materials would appear compact and crack to cause higher bed head loss and uneven flow distribution as the filter bed operated over a period of time. The result would cause the VOC removal efficiency to decrease. Therefore, the filter bed usually requires blending 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.[11–12] The oxidation of sulfur, nitrogen, and chlorine-containing compounds would produce acid intermediate or an end product to lower the bed pH and subsequently reduce the VOC removal efficiency. Calcium carbonate, marl, and oyster shells have been used to buffer the acid product.[13,14]

If a spherical filter material could be synthesized and its characteristics would correspond to the optimal filter material required, it would be an innovative packing material in the biofiltration process. Poly(vinyl alcohol) (PVA) was a hydrophilic polymer and it could capture water by the OH group. Thus, PVA used as a bonding agent and blended with natural

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packing material to make a spherical particle would be suitable as a filter material in the biofiltration process.

PVA blended with activated sludge and fixated with boric acid to produce a spherical bead with a diameter of 3 mm. It is found that the total organic carbon (TOC) removal efficiency of the bead is 93% in the 0.5–2.35 kg TOC/L-day wastewater and the bead is undissociated after operating 40 days.[15] PVA blended with activated sludge and fixated with boric acid and phosphate to produce a spherical bead with a diameter of 3 mm. It is found that the phosphorylated bead have remarkably higher stress than an unphosphorylated bead.[16] The use of a spherical composite bead produced by the PVA blend with fibrous materials and fixated with boric acid and phosphate as a filter material in the biofiltration process is unavailable in the literature.

This study investigates the synthesis and characteristic analysis of a spherical composite bead and proves it is suitable as a filter material in the biofiltration process. The composite bead is prepared by blending PVA with peat and fixing with boric acid and phosphate. The characteristic analysis is the moisture adsorption capacity, moisture holding capacity, and VOC adsorption capacity of the composite bead. The variation of VOC removal efficiency, pH, and head loss is recorded during the biofilter operation. The VOC is ethyl acetate.

EXPERIMENTAL

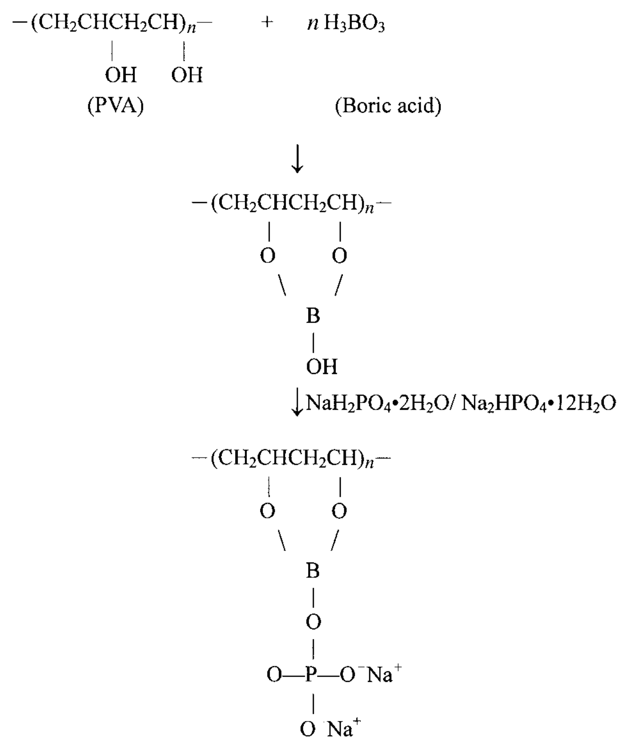
Materials

Industrial grade peat was dried at 105°C before use. Boric acid, sodium monobasic phosphate, sodium dibasic phosphate, and ethyl acetate (extrapure grade from Union Chemical Co., Hsinchu, Taiwan) were used as received. PVA powder (industrial grade from Chung Chun Petrochemical Co. Ltd., Hsinchu, Taiwan), pig manure compost (industrial grade from Taiwan Sugar Corp., Chu-nan, Taiwan), and fern chips (industrial grade from Pao Shan Co., Hsinchu, Taiwan) were also used as received.

Synthesis of composite

Peat (10 g), sieved between 16 and 35 mesh (average diameter, 0.85 mm), was added into an amount of water (40 g) in a 100-mL beaker. It was sealed with parafilm and kept for about 24 h for peat to adsorb water and reach equilibrium. PVA powder (10 g) in water (100 mL) was heated to 90°C for dissolution. As the PVA powder was completely dissolved, the adsorbed water peat was slowly added into the PVA aqueous solution at 90°C. The PVA/peat mixture was stirred for 1.5 h at 90°C and then cooled to 40°C. The mixture was slowly siphoned and dripped into a 6% boric acid aqueous solution (1000 mL) for 10 min. The step of reacting with boric acid was to decrease the PVA hydrophilic property and form a bead. Then, the bead was transferred into a phosphate aqueous solution and stirred for 1 h. The phosphate aqueous solution was prepared with 150 g $NaH_2PO_4 \cdot 2\ H_2O$ and 335 g $Na_2HPO_4 \cdot 12\ H_2O$ in 450 mL water. Finally, the bead was washed with distillated water and dried at 140°C for 24 h. The step of reacting with phosphate was to increase the stress strength of the bead. The dried PVA/peat composite bead was stored in a desiccator at room temperature before use.

The above reaction process can be proposed as the following scheme:



Characteristic analysis

Moisture adsorption/holding capacity experiments

The apparatus of the experiments including an adsorption column and an influent gas supply system was shown in Figure 1. The adsorption column was composed of two sections of transparent acrylic resin pipe with an inner diameter of 15 and 30 cm, respectively, where the lower section was used for uniformly distributed air stream and the upper section was used for adsorption. The adsorption section was made by two transparent acrylic resin pipes: the outside pipe with an inner diameter of 15 and 30 cm, and the inside pipe with an inner diameter 8 and 20 cm. The influent gas stream flows through a water spray tower to increase its humidity to more than 95%. The moisture adsorption experiments were processed so that the

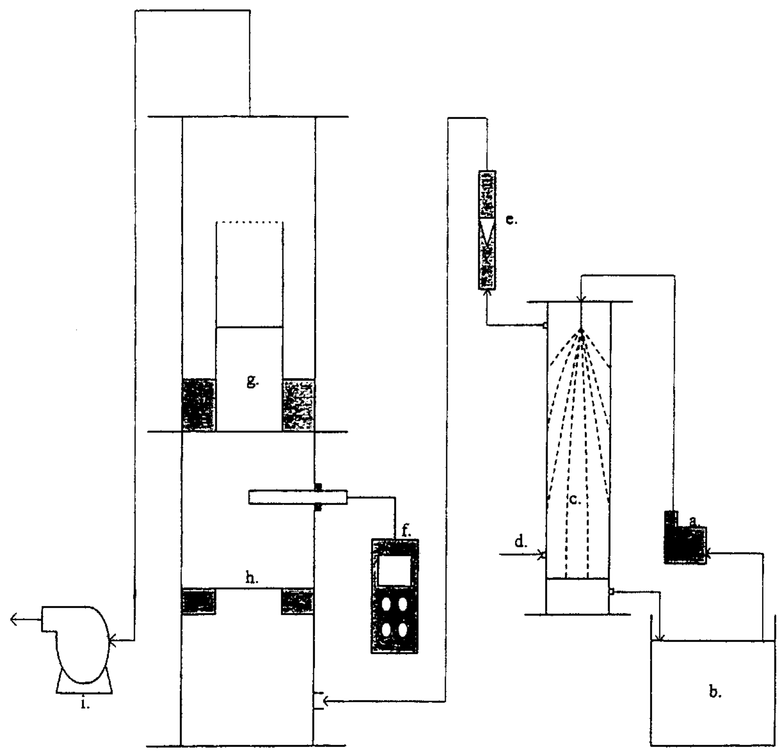


Figure 1 Schematic diagram of moisture adsorption/holding capacity experiments: (a) water pump, (b) water bath, (c) water spray tower, (d) air inlet, (e) flow meter, (f) humidity meter, (g) filter material, (h) sieve wire, (i) air pump.

dried PVA/peat composite bead was packed with 10 cm height in the inside pipe. The PVA/peat composite bead was weighed every 1 h for the initial 6-h region and then every 24 h until the weight of the PVA/peat composite reached equilibrium. The procedures of the moisture holding experiment are the same as those of the moisture adsorption experiment, but the packing material is the wetted PVA/peat composite bead. Moisture content of the wetted packing bead must be higher than 2.0 g water/g solid (dry basis).

VOCs adsorption experiments

VOCs adsorption experiments were carried out by shaking 1.0 g dried PVA/peat composite bead with 250.0 mL air and with the desired ethyl acetate concentration in a glass-stoppered Erlenmeyer flask at a constant temperature bath. The concentration of ethyl acetate in the air was analyzed by a gas chromatograph (Model GC 8700F; China Chromatographic Equipment Co., Taipei, Taiwan) until the adsorption reached equilibrium (about 6 h). The amount of adsorbed ethyl acetate was calculated by the difference of the concentration of ethyl acetate in the air before and after adsorption.

Compression experiments

The composite bead strength was measured by the stress–stain test.[17] In a two-arm balance, a composite bead was placed in the hole of a metal holder stand on one arm of the balance and a tested needle (1 mm diameter with a flat top) was just connected on the bead surface. As a suitable weight was placed on the other arm of the balance, a strain reading (position of metal holder) was carried out by using a cathetometer (accuracy, 1/10 mm). The placed weights were 0, 20, 40, 80, 160, 300, and 500 g. The moisture content of the composite bead must be humidified to 1.5 (dry basis) before testing. The volume compression ratio of the bead was calculated by the ratio of the compressed length of the bead to its original length.

The volume compression of the filter bed was measured by packing wetted filter material with 10 cm height in an inner diameter of 8 cm of transparent acrylic resin pipe; then, a flat plate was placed on the top surface of the bed. A suitable weight was placed on the flat plate and a strain reading (position of flat plate) was recorded by using a cathetometer (accuracy, 1/10 mm). The placed weights were 200, 400, 1000, 1500, 2000, 3000, 4000, and 5000 g. The moisture content of the filter material before testing was as before. The volume compression ratio of the bed was calculated by the ratio of the compressed length of the bed to its original length.

Pilot experiments

The pilot system consisting of two biofilter columns and containing a VOC influent gas supply system is

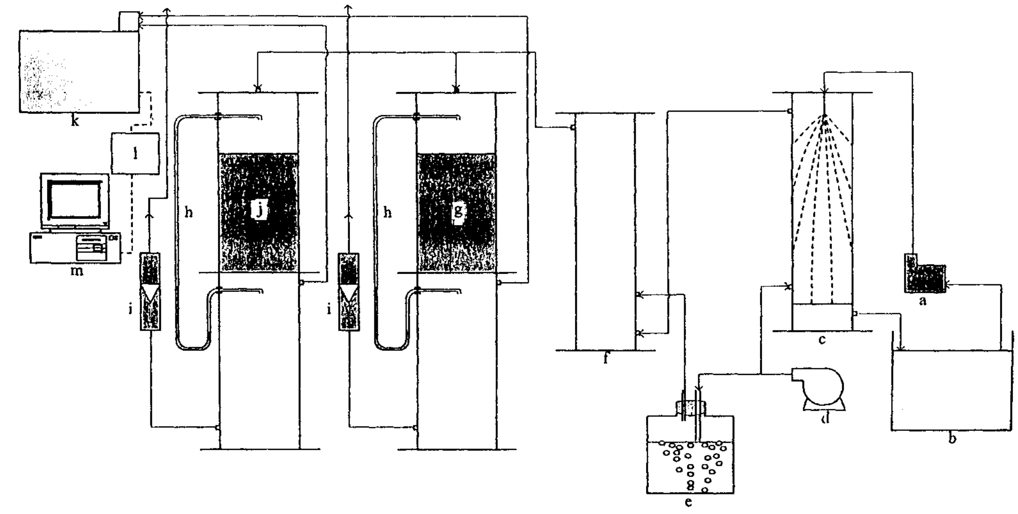


Figure 2 Schematic diagram of the biofilter system: (a) water pump, (b) water bath, (c) water spray tower, (d) air pump, (e) VOC bottle, (f) mixing chamber, (g) composite bead bed, (h) pressure gauge, (i) flow meter, (j) pig manure compost bed, (k) GC, (l) transfer interface, (m) PC.

shown in Figure 2. The biofilter column with an inner diameter of 8 and 30 cm height transparent acrylic resin pipe was made and packed with 20-cm-high filter material. The influent gas was divided into two streams: one steam 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 95%. The two streams were mixed in a mixing chamber and then flowed into the biofilter column. Ethyl acetate was used as VOC.

Two biofilter columns were packed with PVA/peat composite bead and pig manure compost materials, respectively. The pig manure compost material was nine parts pig manure compost blend with one part fern chips and one part $CaCO_3$ in weight. As the filter material appeared before packing, its moisture content must be humidified to 1.5 (dry basis) and the seeding was performed with activated sludge. The VOC concentration in the inlet and exit air stream was taken by auto-sampling and analyzed gas chromatography (GC). The VOC removal efficiency was calculated by the difference of the VOC concentration in the inlet and exit air stream.

RESULTS AND DISCUSSION

The PVA/peat composite bead prepared from the above process is a porous spherical particle with a density of 0.69 kg/m^3 and containing 3.25 mg N/g dry solid and 2.91 mg P/g dry solid. The diameter range of the dried bead is between 2.4 and 6.0 mm and the average diameter is about 4.0 mm. The bead would be swelled about 5% at a moisture content of 1.5.

Moisture adsorption/holding capacity

The moisture content variation of PVA/peat composite bead with time for passing through the velocity at 100 m/h and relative percentage humidity of more than 95% air stream are shown in Figure 3. For moisture adsorption capacity, the moisture adsorbed by the bead increased sharply at the initial region and then reached an equilibrium value after 33 h. The equilibrium moisture content adsorbed by the bead equaled 1.02 (dry basis). The equilibrium value converted into a wet basis equaled 50.5% that corresponded to the moisture content of the optimal filter material required (between 40 and 60%). The result indicated that the PVA/peat composite bead was suitable as a filter material and was sufficient to sustain the biological activity as the bead adsorbed equilibrium moisture. For moisture holding capacity, the moisture holding in the bead decreased sharply at the initial region and then decreased to an equilibrium value after 22 h. The equilibrium moisture content holding in the bead equaled 1.46 (dry basis). The value converted into a wet basis equaled 66.8% that also corresponded to the moisture content of the optimal filter material required. The equilibrium moisture content of the bead held was higher than that of the bead adsorbed by 0.44. The bead adsorbed equilibrium water before the moisture holding capacity test and was dried for the moisture adsorption capacity test. Thus, all pores in the bead were filled with the moisture captured by the OH group of PVA before testing and some moistures in the pore could not be removed during the moisture holding capacity test.

Now, comparing the moisture holding capacity between the composite bead and nature filter materials

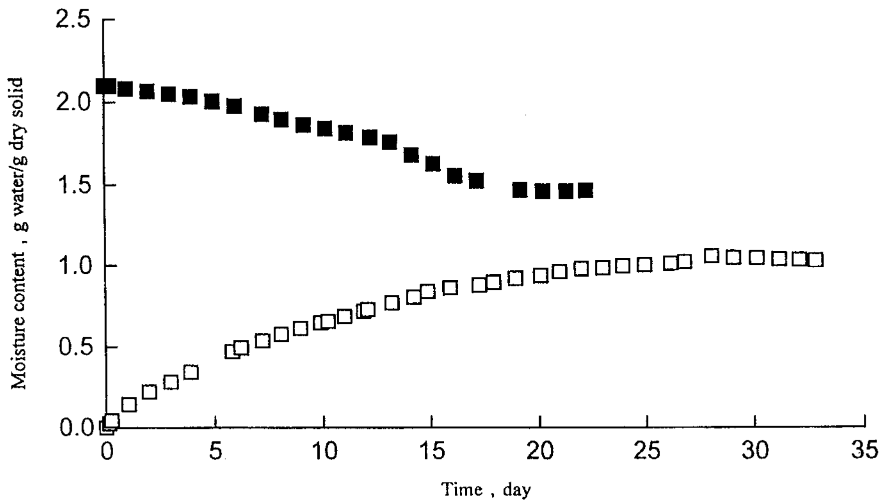


Figure 3 The variation of moisture content of composite bead with time for the moisture adsorption/holding capacity experiments: moisture adsorption experiment (□), moisture holding capacity experiment (■).

proved that the composite bead is suitable as a filter material. The relationships of moisture content of PVA/peat composite bead, peat, and pig manure compost with time for passing through the velocity at 100 m/h, and relative percentage humidity of more than 95% air stream are shown in Figure 4. The relationship of moisture content with time is linear for three kinds filter materials. The slope of the curves of PVA/peat composite bead, peat, and pig manure compost are −0.0183, −0.0914, and −0.0424, respectively. The results indicated that the order of moisture holding capacity for three kinds filter materials is PVA/peat composite > pig manure compost > peat. Thus, the PVA/peat composite bead has the best moisture holding capacity and is the most suitable as a filter material among the three kinds of filter materials.

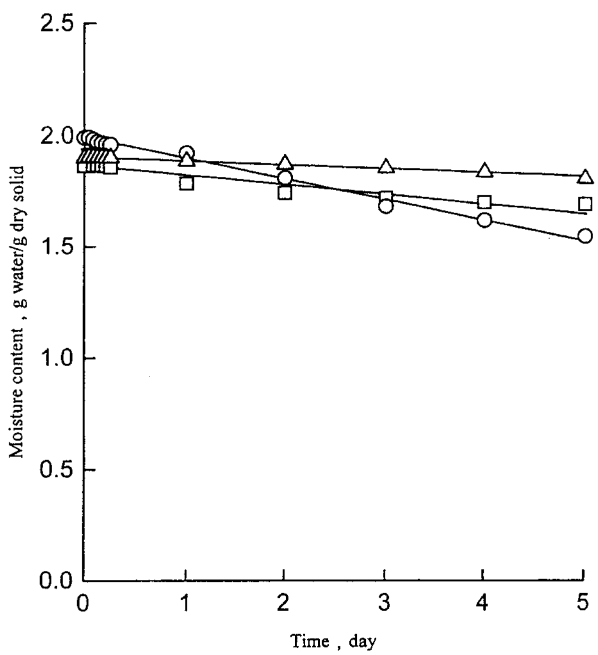


Figure 4 The variation of moisture content of filter material with time for three kinds filter materials: pig manure compost (□), peat material (○), composite bead (△).

Adsorption isotherms

The adsorption isotherm for the ethyl acetate adsorbed on the PVA/peat composite bead can be analyzed by the Langmuir adsorption isotherm and the Freundlich adsorption isotherm. The Langmuir adsorption isotherm is expressed as

$$C_e/q_e = 1/Qb + C_e/Q \tag{1}$$

and the Freundlich adsorption isotherm is expressed as

$$\ln q_e = \ln K_f + 1/n \ln C_e \tag{2}$$

where C_e is the equilibrium concentration of the ethyl acetate in the air stream (mg/L); q_e is the amount of adsorbed ethyl acetate (mg) per gram of PVA/peat composite bead; Q is the maximum amount of adsorbed ethyl acetate (mg) per gram of PVA/peat composite bead; b is the Langmuir constant (L/mg); and K_f and n are the Freundlich constants, respectively.

The Langmuir and Freundlich plots of the data of ethyl acetate adsorbed on the PVA/peat composite bead at 25°C are shown in Figure 5. The relationship between C_e/q_e versus C_e and $\ln q_e$ versus $\ln C_e$ are linear, and the values of coefficient of correction for the C_e/q_e versus C_e and $\ln q_e$ versus $\ln C_e$ plots are 0.8640 and 0.9864, respectively. The results indicated that the value of coefficient of correction for the Freundlich plot was closer to 1.0 than that for the Langmuir

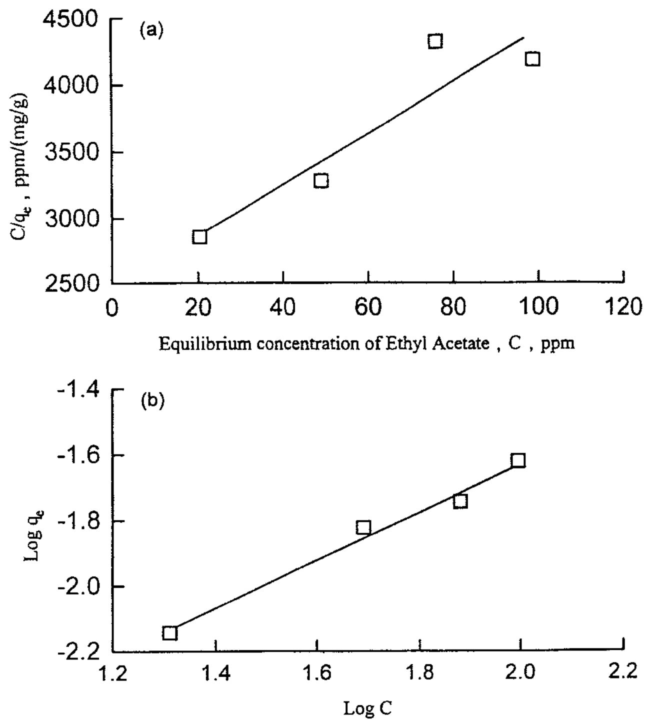


Figure 5 (a) Langmuir and (b) Freundlich plots for the adsorption of ethyl acetate and composite bead at 25°C.

plot. Thus, the adsorption behavior of the composite bead followed the Freundlich adsorption isotherm. The K_f and n values calculated from eq. (2) are 0.0449 and 1.354, respectively.

Compression strength

The volume compression ratio of various wetted composite beads with stress is shown in Figure 6. The volume compression ratio increased sharply at low stress and then slowly reached 0.76 at a stress of 4.0 kg/cm^2. The result exhibited that the wetted composite bead had a rubberlike and elastic property. Therefore, it was difficult to rupture and the bead strength at break could not be determined. According to published literature,[16] the bead strength could be determined from the slope of the initial linear portion of the volume compression ratio–stress curve. Thus, the initial strength of bead is 0.32 kg/cm^2 and is about 1.30 times higher than the PVA/activated sludge composite bead.[16]

The bed volume compression ratio of the wetted composite bead, peat, and pig manure compost filter materials with various stress is shown in Figure 7. The order of bed volume compression ration over the stress ranging from 0 to 190 g/cm^2 for the three kinds of filter materials is composite bead $<$ pig manure compost $<$ peat. The bed volume compression ratio of the wetted composite bead, peat, and pig manure compost filter materials at a stress of 190 g/cm^2 are 16, 37, and 23%, respectively. The results indicated that the composite bead has the lowest bed volume compression ratio among three kinds of filter materials. Thus, the composite bead bed would have the largest porosity and produce the lowest pressure drop among three kinds of filter materials as the air stream passed through.

Pilot operating

The percentage of removed ethyl acetate with various times for exceeding the velocity of 100 m/h, ethyl acetate average concentration of 400 ppm, and relative percentage humidity of more than 95% air stream

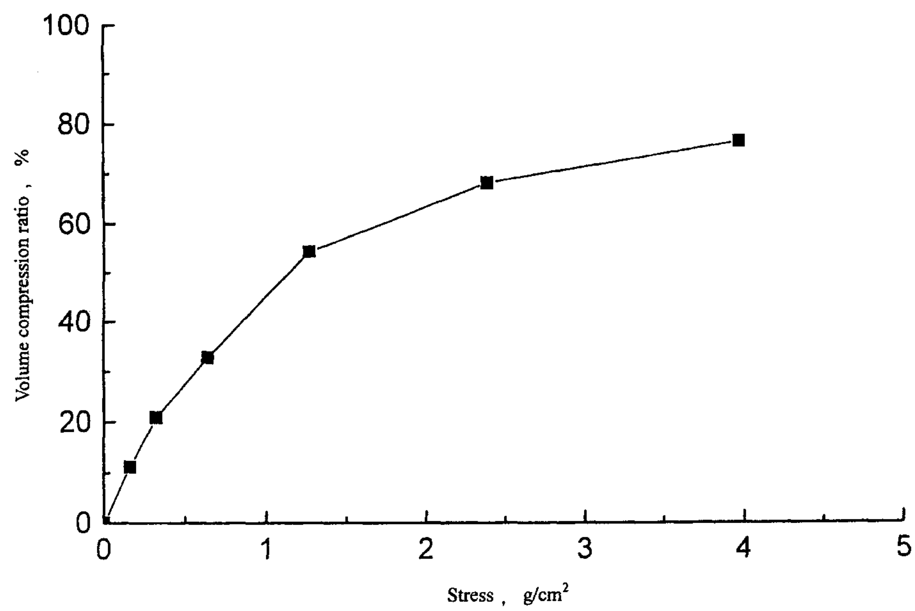


Figure 6 The variation of volume compression ratio of wetted composite bead with stress.

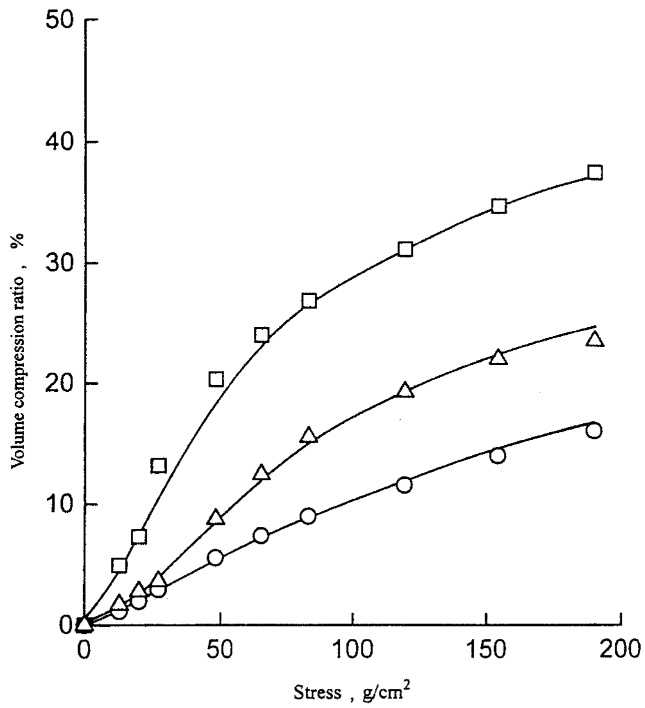


Figure 7 The variation of volume compression ratio of filter bed for three kinds filter materials: pig manure compost (□), peat material (△), composite bead (○).

through the PVA/peat composite bead and pig manure compost filter beds are shown in Figure 8. It is found that the percentage of removed ethyl acetate increases to 100% after operating 1 day for the pig manure compost filter bed, but it is about 20% in the initial 4 days and about 5% in the 4–10 days for the PVA/peat composite bead filter bed. The results indicate that the removed ethyl acetate is adsorbed by the composite bead and un-biodegraded by the microorganism in the initial 10 days for the composite bead filter bed. The reason is that the percentage of removed ethyl acetate would decrease as the amount of ethyl acetate adsorbed by the composite bead accumulates and gradually reaches saturation, and no available nutrient in the composite bead could be diffused out to support the microbe growing during the initial 10 days. Thus, available nutrients in the composite bead bed support the microbe growing at the initial stage.

Nitrogen is an essential nutrient for microbial growth and the available nitrogen is in inorganic form as ammonia or nitrate type. Thus, the composite bead biofilter is shut down and the nitrate-type nutrient is added into the composite bead. The steps are as follows: the composite beads are taken out from the biofilter column and immersed in 10% KNO_3 aqueous solution for adsorbed nitrate. As the composite beads adsorbed nitrate to reach equilibrium (about 12 h), they were repacked into the column and continued operating. It is found that the percentage of removed ethyl acetate increased to more than 99% after the repacking column operated for 2 days. The result indicated that the nutrient is a limiting factor for the composite bead bed having low ethyl acetate removal efficiency during the initial 10 days. The pressure drop of the composite bead bed and compost filter material bed are 0 and 2 mm H_2O, respectively.

The percentage of removed ethyl acetate stayed at more than 99% removal level during the following 33 operating days. It has about 0.71 g ethyl acetate/h biodegraded and converted into water and carbon dioxide products by microorganisms at the high removal level. The pH value of the composite bead bed over the operating period is in the range of 6.9 and 7.2. The results indicated that the pH of the composite

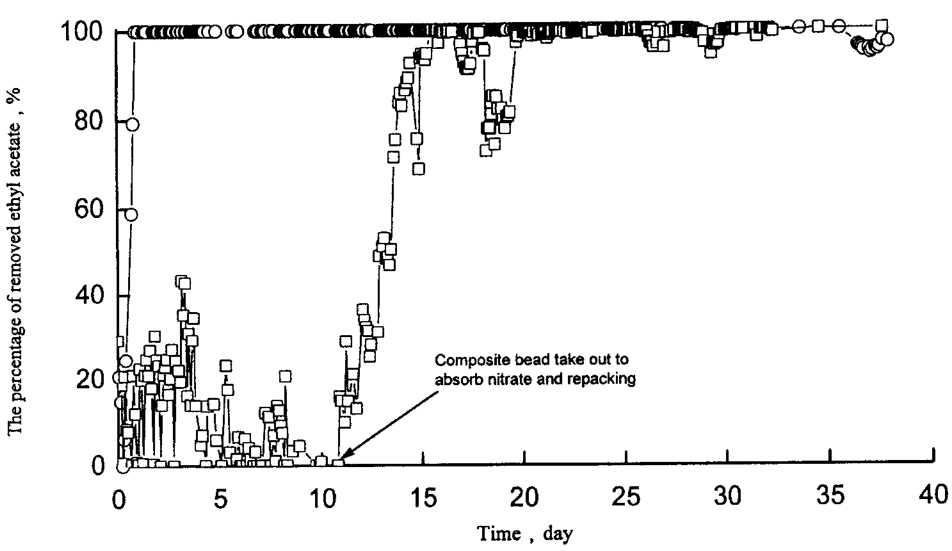


Figure 8 The percentage of removed ethyl acetate with various times for two kinds of biofilter: pig manure compost filter (○), composite bead filter (□).

bead bed stayed in a neutral range over the operating period. The reason is that the composite bead had been immersed in the phosphate solution during the preparation process and the phosphate solution is a pH = 7.2 buffer solution. Thus, the composite bead has a buffer capacity to lead the composed bead bed in keeping in a neutral range during operation.

CONCLUSION

A new PVA/peat composites bead is prepared and is proved suitable as a filter material in the biofiltration process. The composite bead has a diameter of 2.4–6.0 mm, has a density of 0.69 kg/cm^3, and is a porous spherical particle. It contains 3.25 mg N/g dry solid and 2.91 mg P/g dry solid. The equilibrium moisture content of the composite bead for adsorption and holding experiments is 50.5 and 66.8% by wet basis, respectively. The initial compression strength of the composite bead is 0.32 kg/cm^2. It has higher moisture holding capacity and compression strength than pig manure compost filter material. The adsorption behavior of ethyl acetate and the composite bead follows the Freundlich adsorption isotherm. The composite bead has buffer capacity and could keep the filter bed at pH = 6.9–7.2 during operating. The percentage of removed ethyl acetate could be more than 99% for 33 days as the composite bead adsorbed nutrients.

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