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Laboratory-scale evaluation of fluidized bed reactor technology for biotreatment of maleic anhydride process wastewater

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Fluidized bed reactor (FBR) technology has emerged in recent years as an attractive approach for the biotreatment of chemical industry wastestreams. A laboratory-scale FBR study was conducted to investigate the feasibility of utilizing FBR technology for the biotreatment of maleic anhydride wastewater generated during manufacturing operations. The maleic anhydride wastestream contains a mixture of maleic acid, fumaric acid, phthalic acid and di-*n*-butylphthalate (DBP). The FBR removed >98% of chemical oxygen demand (COD) and total organic carbon (TOC) from the wastewater at a chemical loading rate of 4.86 kg of COD m^{-3} bed day^{-1}. Maleic acid, fumaric acid or phthalic acid were not detected in the FBR effluent indicating removal of these diacids. Residues of DBP adsorbed to granular activated carbon (GAC) stabilized at low levels indicating that the >99% removal efficiency for DBP in the FBR resulted from microbial degradation. Solids measurements showed microbial biomass levels on the GAC ranging from 10500 to 32400 mg L^{-1} and effluent solids production ranged from 0.027 to 0.041 kg solids kg^{-1} COD treated. This laboratory-scale study demonstrated that FBR technology was highly effective for the biotreatment of the maleic anhydride wastestream and may offer several advantages over traditional activated sludge systems.

Keywords: fluidized bed reactor; granular activated carbon; biotreatment; biocarrier; maleic wastewater; di-*n*-butylphthalate

Introduction

Technology for use of immobilized bacteria, configured primarily as a fluidized bed reactor (FBR), has emerged over the past few years as an effective biotreatment approach that has potential widespread application. FBRs utilize high densities of chemical-degrading bacteria attached to a biosupport, usually sand or granular activated carbon, to achieve rates of chemical degradation which are much faster (shorter hydraulic residence times) than those achieved in conventional activated sludge systems [12]. FBRs are capable of treating wastestreams which contain both moderately high and low levels of chemicals. Furthermore, FBRs are more resistant to system upsets, less susceptible to chemical toxicity, produce less sludge, and require smaller reactor sizes than conventional systems [6,13].

Maleic anhydride is manufactured for use as a commodity chemical. Although wastewater from the production process can be biotreated by a continuous activated sludge process, the wastewater must first be pretreated to remove di-*n*-butylphthalate (DBP) levels to acceptable loading levels. Aerobic biological treatment has the potential to mineralize the organic constituents of process wastes to carbon dioxide and water. The efficiency of FBR biotreatment of the maleic anhydride wastestream depends on the degradability of the organic components. Previous reports suggest that maleic and fumaric acid can be eliminated from water through complete microbial destruction to carbon dioxide [2] and many microbial species can utilize DBP as a sole carbon source [5,7]. Studies with activated sludge demonstrated a high removal efficiency (>88%) of DBP from contaminated wastewaters [8]. In addition, shake flask tests with mixed microbial populations have shown that phthalic acid is a biologically degradable acid [10].

A laboratory-scale study was conducted to evaluate the feasibility of FBR technology as a more effective alternative for the biotreatment of maleic anhydride wastes. The primary objectives of the study were to determine the performance of FBR technology for removal of total chemicals, measured as loss of chemical oxygen demand (COD), and the specific removal of DBP and maleic acid. In addition, this study determined the relationship between chemical loading and effluent quality at four chemical loading rates. The study also included measurements of the microbial solids generated during operation of the FBR, total sludge discharge from the reactor and levels of DBP residues on the granular activated carbon (GAC) and wasted sludge.

Materials and methods

Design of the laboratory-scale fluidized bed reactor

A laboratory-scale fluidized bed reactor (FBR) was operated with the primary objective of carbonaceous COD removal from the maleic anhydride wastewater and specific removal of DBP. A thorough description of the design, construction and operation of the FBR, and a schematic, has been previously published [6]. The reactor was filled with 20 L of dechlorinated water and approximately 2.7 kg of GAC. The particle size of the carbon was 0.85–1.5 mm (12 × 20 mesh). The initial unfluidized bed height was 61 cm. Fluidization of the carbon bed was achieved by upflow recycling of water at 4.53 L min^{-1}. This represented an upflow velocity of 74.4 cm min^{-1} and hydraulic loading rate of approximately 138 L min^{-1} m^{-3}. The volume of the

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carbon bed was 6.8 L and the initial fluidization height of the carbon bed was 88 cm (40% bed expansion). Maleic wastewater was metered into the recycle stream by a peristaltic pump (Fluid Metering, Inc, Oyster Bay, NY, USA) which delivered feed to the FBR at a rate of 0.5–5 ml min^{-1}. Pure oxygen was delivered into the recycle stream using a mass flow controller (Model VCD 1000, Porter Instrument Co, St Louis, MO, USA). A dissolved oxygen (DO) probe was used to detect the level of oxygen at the recycle port. Dissolved oxygen levels in the liquid headspace at the point of recycle were maintained at 2–4 mg oxygen L^{-1} throughout the study.

Maleic process wastewater feed

The feed for the FBR was the raw maleic process wastewater from a water sump. This wastestream was analyzed during routine maleic anhydride manufacturing operations and reported to have an average of 5000 mg L^{-1} maleic acid, 1011 mg L^{-1} fumaric acid, 1400 mg L^{-1} phthalic acid and 1025 mg L^{-1} DBP. The wastewater feed drum received for use in the FBR feasibility study had a COD of 7500 mg L^{-1} and a total organic carbon content of 3000 mg L^{-1}. The pH of the waste was about 4.0 and it was adjusted to neutrality with 50% sodium hydroxide. The feed was supplemented with 0.15% (w/v) ammonia chloride and 0.03% (w/v) dipotassium phosphate.

Microbial inoculation and start-up

A carbon adsorption phase preceded the microbial inoculation of the carbon support matrix. Maleic wastewater was pumped into the FBR at a rate of 1.62 kg COD m^{-3} day^{-1} for one week. A total of 10 L of waste was applied to the bed. No oxygen was fed into the reactor during the preadsorption phase to eliminate the possibility of chemical oxidation of feed components or aerobic microbial growth. Adsorption of wastestream chemicals onto the carbon support served as a concentrated initial food source for the microbial biomass after microbial inoculation and reactor start-up.

The source of inoculum for the FBR was 1 L of secondary return sludge from the American Bottoms wastewater treatment plant (Sauget, IL, USA), and a microbial isolate capable of degrading phthalic acid esters. The activated sludge was homogenized by low-speed mixing in a Waring blender before addition to the FBR column to prevent clumping of the biomass and to promote better adherence of the sludge to the carbon support. The bacterial isolate was previously isolated after extensive culturing on di-2-ethylhexylphthalate. The pure culture was grown in 0.5 L of L-salts medium [9] supplemented with 100 mg L^{-1} DBP. The culture was centrifuged at 11 300 × *g* for 5 min and the supernatant phase was discarded. The pellet was resuspended in 500 ml of the L-salts medium, and added to the top of the reactor column. Oxygen flow to the recycle water was established and the reactor was initially fed raw maleic wastewater at an influent feed rate of 0.8 kg COD m^{-3} day^{-1}. Acclimation of the inoculum to the raw waste was detected by an increase in oxygen uptake and a decrease in the COD of the FBR effluent. As the microorganisms acclimated to the wastewater and colonized the GAC to produce a biofilm, the particle density of the carbon decreased. The attached biomass continued to grow and the subsequent decrease in carbon density expanded the height of the fluidized bed to 106.7 cm. When the bed height exceeded 106.7 cm, an electric stirrer sheared away biomass from the carbon and the biomass was either recycled within the reactor or discharged from the system through the effluent port.

Chemical loading to the reactor

The step-change increase in chemical loading to the reactor for the entire study is represented in Table 1. The FBR was fed at 1.6 kg COD m^{-3} day^{-1} while the microbial inoculum acclimated to the maleic wastewater. After approximately 3.5 weeks, the feed rate was increased to 3.2 kg COD m^{-3} day^{-1}. This chemical loading rate was maintained for 3 weeks before increasing the influent flow rate to 4.8 kg COD m^{-3} day^{-1}. A chemical load of approximately 4.8 kg COD m^{-3} day^{-1} was considered a design loading rate since previous research showed that full-scale reactors using conventional oxygenation systems become oxygen limited beyond this loading rate. When the design chemical loading rate had been maintained for 9 days, the influent flow was increased to a final rate of 8.0 kg COD m^{-3} day^{-1}. This rate was chosen as the final chemical loading rate to examine the performance of the FBR during unexpected high chemical loadings.

Chemical analysis of carbon and sludge for di-n-butylphthalate

Analysis for DBP residues on the GAC and microbial sludge were performed by gas chromatography/mass spectrometry (GC/MS). Throughout the biotreatment study, carbon samples of approximately 10 g were taken from the top of the reactor bed. The samples were extracted by weighing 2.0 g of the carbon into an extraction thimble. Sodium sulfate (10 g) was added to the carbon and the sample was thoroughly mixed. Samples were then taken and continuously extracted for 14 h using methylene chloride in a soxhlet extraction apparatus. A 100-ml sample of sludge was removed from the carbon bed at the end of the FBR biotreatment study. A 10-g sample (wet weight) of the sludge was mixed with 2 g of sodium sulfate and extracted with methylene chloride using ultrasonic agitation. The methylene chloride extracts from the carbon and sludge extractions were analyzed using a Hewlett Packard HP 5890 GC/MS. The gas chromatograph was equipped with a DB-5 capillary column (J & W Scientific, Folson, CA, USA), 30 m × 0.32 mm i.d. (film thickness 0.25 μm). Helium was used as a carrier gas and the column head pressure was maintained at 5–7 psi. The column temperature was maintained at 50°C for 4 min and then increased to 300°C at a rate of 8°C min^{-1}. The limit of detection was 1 μg DBP g^{-1} (wet weight) of carbon or biomass.

Chemical analysis of maleic wastewater feed and FBR effluent

Effluent samples from the FBR were taken from the recycle port at a minimum of three times each week for COD analysis. The influent feed to the FBR was analyzed for COD each time a new 20-L batch of feed was used. Samples were filtered through a 0.45-μm pore size filter

Table 1 Chemical oxygen demand and total organic carbon of FBR influent and effluent

Days after start-up	Chemical loading (kg COD m^{-3} day^{-1})	HRT[a] (h)	Influent conc. (mg L^{-1})		Effluent conc. (mg L^{-1})	
			COD	TOC	COD	TOC
1	1.6	120	7500	3000	525	230
12	1.6	120	7500	3000	70	11
19	1.6	120	7500	3000	20	15
23	1.6	120	7500	3000	40	11
26	1.6	120	7500	3000	20	10
30	3.2	60	7500	3000	40	25
33	3.2	60	7500	3000	55	21
36	3.2	60	7500	3000	175	67
40	3.2	60	7500	3000	400	170
43	3.2	60	7500	3000	727	292
47	3.2	60	7500	3000	350	235
50	3.2	60	7500	3000	380	91
51	4.8	40	7500	3000	180	91
55	4.8	40	7500	3000	130	41
57	4.8	40	7500	3000	90	43
59	4.8	40	7500	3000	100	58
60	8.0	24	7500	3000	180	77
61	8.0	24	7500	3000	210	79
68	8.0	24	7500	3000	160	74

[a] HRT = hydraulic residence time.

and analyzed at time of collection using the test tube colorimetric procedure of the Hach Chemical Co (Loveland, CO, USA), which is similar to method 5220 D in Standard Methods for the Examination of Water and Wastewater [1]. Effluent samples for total organic carbon analysis were also collected three times each week. A 30-ml filtered sample was acidified to pH 2.0 and stored at 4°C until analysis. Total organic content of the reactor effluent was analyzed using the standard procedure for the O I Corp Model 700 Total Organic Carbon Analyzer (O I Corp, College Station, TX, USA).

Maleic process wastewater was analyzed at the start of the biotreatment study for DBP. Reactor effluent samples of 40 ml each were also analyzed throughout the study for the presence of DBP. The water samples were filtered (0.45 μm) then extracted with methylene chloride. The methylene chloride extracts were analyzed using the method described above for carbon and sludge extractions. The minimum detection level was 1 μg DBP L^{-1}.

Maleic acid, fumaric acid and phthalic acid concentrations in the raw wastewater and FBR effluent samples were analyzed by a Dionex Capillary Electrophoresis System (Dionex System, Dionex Corp, Sunnyvale, CA, USA) using indirect UV detection. The instrument used a 67 cm long × 75 μm i.d. × 375 μm o.d. fused-silica capillary column filled with a pH 7.1 sodium phosphate/potassium phosphate buffer. A 15 000 V current was applied across the column to induce separation of the three diacids. The limit of detection of maleic and fumaric acid was 5 mg L^{-1} and was 20 mg L^{-1} for phthalic acid.

Biomass measurements

Biomass levels were measured in the fluidized bed several times during each of the four chemical loading rates. Volumetric samples of GAC were taken from 25 cm and 80 cm depths below the top of the fluidized bed. Biomass attached to the carbon matrix was measured using a gravimetric/heat volatilization method previously described [11]. Biomass estimations were used to determine total biomass present at each chemical loading rate, to calculate feed to mass ratio at each influent flow rate, and to determine sludge retention time.

Effluent solids and sludge measurements

The majority of excess biomass that detached from the GAC, or that was physically sheared off the carbon by the stirrer, floated out of the column through the recycle port and was collected in the FBR settling basin. Small particles of biomass that remained in the effluent were pooled in an effluent carboy. Sludge trapped in the settling basin and the effluent carboy were measured at each loading rate to determine sludge production. Representative 100-ml samples from both the sludge settling basin and the effluent carboy were taken for the determination of total suspended solids. The level of total suspended solids accumulated over a selected time period was analyzed using the Method 2540 D in Standard Methods for the Examination of Water and Wastewater [1]. Quantitation of total solids produced per mass of COD loaded into the reactor was conducted as previously described [6].

Results

Chemical loading and removal in the FBR

The removal of organic carbon from maleic wastewater by the FBR was determined by measuring the COD and total organic carbon of the influent and effluent throughout the 68-day study (Table 1). Chemical loading and COD removal efficiency during each of the four chemical loading rates is presented graphically in Figure 1. At the time of start-up, the FBR effluent had an initial COD of 525 mg L^{-1} due to the input of 10 L of maleic wastewater during the

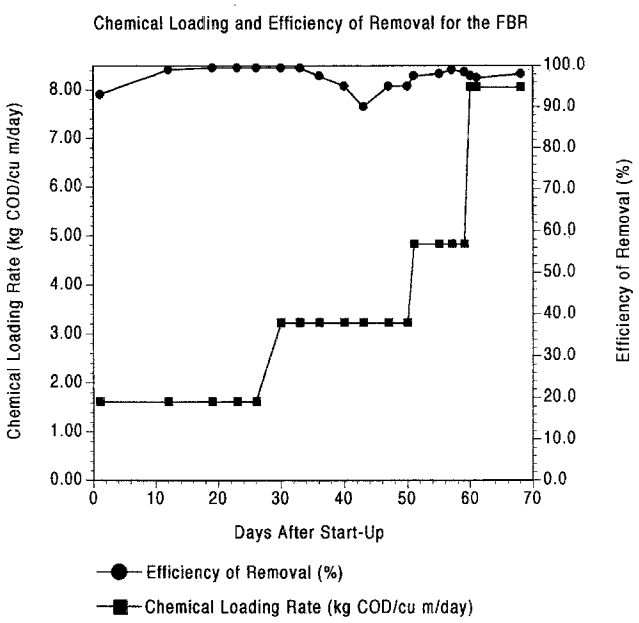

Figure 1 Chemical oxygen demand (COD) loading rate and efficiency of COD removal during FBR treatment of maleic wastewater.

pre-adsorption phase. The COD of the effluent decreased to 20–40 mg L^{-1} during the 29-day acclimation period while chemical loading to the reactor was 1.6 kg COD m^{-3} day^{-1}. The total organic content of the effluent was also very low ($\leq$15 mg L^{-1}). This represented a >99% chemical removal efficiency (based on COD and total organic carbon measurements). The FBR maintained this high level of removal of COD and total organic carbon during days 30–35 of the 3.2 kg COD m^{-3} day^{-1} loading rate phase. However, from day 36–43, an increase occurred in the residual COD of the FBR effluent. The reactor returned to high performance by day 50 and was operating at a 95% chemical removal efficiency at the end of the 3.2 kg COD m^{-3} day^{-1} loading phase. Similarly, at the end of the design loading phase of 4.8 kg COD m^{-3} day^{-1} (days 51–59), the COD of the reactor effluent was 100 mg L^{-1} and total organic carbon was 50 mg L^{-1}. This represented a 98.5% COD and 98% total organic carbon removal efficiency. The maximum chemical loading rate of 8.0 kg COD m^{-3} day^{-1} (1.5 × design loading) produced a biotreated effluent containing 160 mg L^{-1} COD and 74 mg L^{-1} total organic carbon. This represented 98% and 97.5% removal of COD and total organic carbon, respectively, by the FBR at the end of the study during high chemical loading.

di-n-butylphthalate residues on GAC and sludge

One of the main advantages of using GAC as a support in FBRs is its provision of high surface area per unit weight (1000 m^2 g^{-1}) and chemical adsorptive capacity. The presence of activated chemical-binding sites on the carbon allowed for selective adsorption of DBP from the maleic anhydride wastewater. DBP has a moderate carbon adsorption capacity of 220 mg g^{-1} carbon, as determined by previously reported specific carbon adsorption isotherms [4]. Studies on the comparative removal of toxic water pollutants by activated sludge treatment processes have shown that DBP can be associated with the suspended solids in the process sludge. Concentrations of DBP can accumulate on the sludge to levels that are several-fold higher than present in the process effluents being biotreated [8]. Material balance calculations for DBP in the maleic anhydride wastewater required analysis of both the carbon and sludge in the FBR to determine if removal of DBP from the effluent resulted from microbial degradation or was due to adsorption of the compound on the carbon and biomass.

The levels of DBP adsorbed on the carbon bed (with attached biomass) were measured at several time-points during the study and are shown in Table 2. Pre-adsorption of the carbon with maleic anhydride wastewater before the reactor was inoculated resulted in an accumulation of 28 μg DBP g^{-1} carbon (wet weight determination). This represented a total mass of 50.4 mg of DBP on the carbon bed (based on 2700 g total carbon per FBR bed). After the FBR was inoculated, levels of absorbed DBP decreased to 6 μg g^{-1}, then increased to 73 μg g^{-1} by day 41 (chemical loading rate of 3.2 kg COD m^{-3} day^{-1}). However, there was no further increase in absorbed levels of DBP as the final chemical loading increased to 8.0 kg COD m^{-3} day^{-1} (day 75), indicating the FBR maintained a steady-state where DBP loading equaled DBP biodegradation.

Both GAC and bacterial sludge have good capacities for DBP adsorption and it was necessary to ascertain the total mass of influent DBP accumulated on the GAC and biomass to account for DBP loss due to biodegradation. Analysis of biomass collected from carbon and effluent during operation of the FBR at the maximum chemical loading rate of 8.0 kg COD m^{-1} day^{-1} showed an accumulation of 4.74 μg DBP g^{-1} biomass (wet weight). Since total biomass on the reactor bed at this maximum chemical loading rate was determined to be 363.75 g, the level of DBP on the attached biomass was 1.73 mg. In a similar calculation, the maleic anhydride wastewater contained 76 mg L^{-1} of DBP, and a total chemical load of 19.23 g of DBP was added to the FBR during the 68-day biotreatment study (based on volumetric flow rate). The final concentration of DBP on the carbon at day 68 was 38 μg g^{-1} carbon. Therefore, 102.6 mg of DBP was absorbed onto the 2700 g FBR bed by the end of the biotreatment study. Based on the above quantifications for DBP absorption on GAC and biomass, 0.5% of the total mass of DBP added to the reactor was accumulated on the GAC and 0.009% of the total influent

Table 2 Selective adsorption of di-*n*-butylphthalate onto granular activated carbon

Days after start-up	Chemical loading (kg COD m^{-3} day^{-1})	DBP (μg g^{-1} carbon)[a]
Control	0.0	4
Pre-adsorption	1.6	28
1	1.6	6
9	1.6	24
19	1.6	58
29	3.2	54
33	3.2	60
41	3.2	73
68	8.0	57

[a] Concentration values are based on wet weight determination. Estimated limit of detection is 1 μg g^{-1}.

DBP accumulated on the attached biomass. The minimal adsorbtive loss of DBP to the GAC and biomass indicated that microbial degradation was the primary mechanism responsible for removal of DBP from maleic anhydride wastewater.

Chemical analysis of FBR effluent

Measurements of COD and total organic carbon are good overall measurements of biotreatment efficiency, but do not address the removal of specific wastestream components by the FBR. Effluent samples were analyzed several times at each chemical loading rate for maleic acid, fumaric acid, phthalic acid and DBP to determine primary degradation of the wastewater constituents (Tables 3 and 4). The theoretical occurrence of wastestream components in the FBR effluent, assuming no chemical adsorption onto carbon in the reactor and no biodegradation, was calculated using the following mass balance equation:

$$C_e = C_o\,(1 - e^{-t(Q/V)}) \qquad (1)$$

where:

C_e = Concentration of chemical in effluent (mg L^{-1})
C_0 = Concentration of chemical in influent (mg L^{-1})
t = Days held at specific influent flow rate
Q = Volumetric flow rate (L day^{-1})
V = Total volume of the FBR (L).

Analysis of the raw maleic wastewater influent showed 1500 mg L^{-1} maleic acid, 134 mg L^{-1} fumaric acid, 291 mg L^{-1} phthalic acid, and 76 mg L^{-1} DBP. Using Equation 1, the expected concentration of diacids and DBP in the FBR effluent at day 12 of the acclimation phase (chemical loading rate of 1.6 kg COD m^{-3} day^{-1}), if biodegradation and adsorption were not occurring, were: 870 mg L^{-1} maleic acid, 78 mg L^{-1} fumaric acid, 169 mg L^{-1} phthalic acid and 44 mg L^{-1} DBP. Although 273 mg L^{-1} of maleic acid was present in the FBR effluent after the pre-adsorption phase, analysis of the FBR effluent during the acclimation phase revealed no diacids or DPB present. After 47 days, the FBR reached steady-state equilibrium, where the concentration of maleic acid, fumaric acid, phthalic acid and DBP in the FBR effluent, without biodegradation or adsorption, would be expected to equal the concentration of each compound in the influent maleic wastewater feed. The chemical loading rate during steady-state equilibrium was 3.2 kg m^{-3} day^{-1}. During operation of the reactor at steady-state equilibrium, the biomass became stressed due to a lack of sufficient nitrogen and phosphorus in the chemical feed. A subsequent decrease in COD removal efficiency occurred on days 40–50, and a small quantity of fumaric acid and phthalic acid was detected in the FBR effluent. After nitrogen/phosphorus addition to the raw feed, the FBR returned to the expected COD removal efficiency of 98% at day 56 and fumaric acid and phthalic acid were not detected. Analysis of the FBR effluent at the 4.8 kg and 8.0 kg COD m^{-3} day^{-1} loading rates showed no detectable levels of maleic acid, fumaric acid, phthalic acid or DBP. Since previous data had shown minimal accumulation of DBP on the carbon and sludge and since the acidic components of maleic wastewater do not significantly adsorb to activated carbon, these data indicated the primary removal mechanism of the organic constituents from the maleic anhydride wastestream was microbial degradation. Furthermore, FBR effluent analyses of filtered samples during the 67-day biotreatment study indicated no detectable levels of DBP above the minimum detection limit of 1 mg L^{-1}. On day 68 of the study, a final 1-L effluent sample was taken

Table 3 Analysis of FBR effluent for the presence of maleic acid, fumaric acid and phthalic acid[a]

Days after start-up	Load rate[b]	Maleic acid	Fumaric acid	Phthalic acid
0	1.6	273	ND	ND
12	1.6	ND	ND	ND
19	1.6	ND	ND	ND
22	1.6	ND	ND	ND
26	1.6	ND	ND	ND
29	3.2	ND	ND	ND
33	3.2	ND	ND	ND
36	3.2	ND	ND	ND
40	3.2	ND	27	ND
43	3.2	ND	20	15[c]
47	3.2	ND	19	12[c]
51	4.8	ND	ND	19[c]
56	4.8	ND	ND	ND
58	4.8	ND	ND	ND
59	4.8	ND	ND	ND
62	8.0	60	ND	ND
67	8.0	ND	ND	ND

[a] ND indicates not detected. Analyses were done by capillary zone electrophoresis. Detection limits for maleic acid and fumaric acid were 5 ppm, and phthalic acid was 20 ppm.
[b] Chemical loading rate presented as kg COD m^{-3} day^{-1}.
[c] Significant instrument response was observed but values were below the minimum quantitation limit of 20 ppm.

Table 4 Analysis of FBR effluent for di-*n*-butylphthalate

Days after start-up	Loading rate (kg COD m^{-3} day^{-1})	DBP[a] (mg L^{-1})
0	1.6	ND[b]
12	1.6	ND
19	1.6	ND
22	1.6	ND
26	1.6	ND
29	3.2	ND
33	3.2	ND
36	3.2	ND
40	3.2	ND
43	3.2	ND
47	3.2	ND
51	4.8	ND
56	4.8	ND
58	4.8	ND
59	4.8	ND
62	8.0	ND
67	8.0	ND
67[c]	8.0	<0.001

[a] Di-*n*-butylphthalate.
[b] ND indicates that levels of DBP were not detected in filtered effluents above the minimum detection limit of 1 ppm.
[c] End-point filtered effluent sample taken for low-level analysis of DBP. Minimum detection limit was 10 ppb.

and concentrated for low-level analysis of DBP. The level of DBP in the effluent sample was below 10 μg L^{-1}, showing a removal efficiency of $\geq$ 99.99%. These data indicated that FBR biotreatment was promising for achieving clarified effluent with DBP concentrations within acceptable guidelines for surface water discharge.

Biomass measurements

Biomass attached to the carbon particles was determined by gravimetric measurement of the volatile mass of the attached biofilm. Samples were collected from 25 cm below the surface of the bed at several time periods during each of the four chemical loading set-points. The density of the biomass was related to chemical loading rate: Biomass increased with increased chemical loading rate (Table 5). There was 15 500 mg L^{-1} biomass on the carbon support 2 weeks after reactor start-up. A two-fold increase in chemical loading (3.2 kg COD m^{-3} day^{-1}) produced a 60% increase in biomass (25 000 mg L^{-1}), and the bed expanded 30 cm above initial fluidization height (90 cm to 120 cm). Wash-out of the carbon bed was prevented by removing the excess biomass and returning the expanded bed height to 106.7 cm. At the design chemical loading rate of 4.8 kg COD m^{-3} day^{-1}, there was a further increase in biomass to 29 000 mg L^{-1} and periodic sludge wasting was needed to prevent wash-out of the bed into the effluent. During the highest chemical loading (8.0 kg COD m^{-3} day^{-1}) the biomass levels increased to 48 500 mg L^{-1}. However, no further bed expansion occurred and there was a brown discoloration of the biomass. Since maleic wastewater feed was not pretreated to remove suspended chemical solids, chemical sludge associating with the biomass may have accounted for the increased bed density and the brown discoloration of the biofilm.

Feed to mass ratio

The biomass levels and chemical loading rates were used to calculate the feed to mass ratio for the FBR during selected periods of operation with influent wastewater having 7500 mg L^{-1} of COD.

The feed to mass ratio (*F/M*) was calculated using the following equation:

$$F/M = \frac{(S_o - S_e)\cdot Q}{X_v t \cdot V_{bed}} \qquad (2)$$

where:

S_o = Influent COD (mg L^{-1})
S_e = Effluent COD (mg L^{-1})
Q = Influent flow rate (L day^{-1})
X_V = Biomass on the carbon (mg L^{-1})
t = Time (days)
V = Volume of the fluidized bed (L).

Table 5 Biomass levels and feed-to-mass ratios for the FBR during biotreatment of maleic anhydride wastewater

Days after start-up	Chemical loading (kg COD m^{-3} day^{-1})	HRT (h)	Biomass (mg L^{-1})	Feed/mass ($days^{-1}$)
26	1.6	120	15 500	0.11
52	3.2	60	25 000	0.12
60	4.8	40	29 000	0.15
67	8.0	30	48 500	0.15

The feed to mass ratio remained relatively constant with each increase in COD loading to the FBR, and ranged from 0.11 to 0.15. Although the chemical loading rate was increased 5-fold, only a 45% increase in the feed to mass ratio was exhibited. Furthermore, the feed to mass ratio for both of the final chemical loading set-points of 4.8 kg COD m^{-3} day^{-1} and 8.0 kg COD m^{-3} day^{-1} was 0.15.

Solids and sludge production

Total solids production per unit COD was calculated for six time periods during operation of the FBR (Table 6). These time periods provided data for each chemical loading set-point. Total solids production was determined by summing both the amount of sludge collected in the sludge trap over a given period of time and the total suspended solids in the reactor effluent. The total solids production remained stable throughout the study with the exception of the second time period of operation. The addition of a nitrogen and phosphorous source to the influent feed during this period enhanced the microbial growth rate and the level of biomass on the carbon rapidly increased. The carbon column expanded 15 cm and the excess biomass was removed by the bed clipping device. Stripping the excess biomass from the carbon produced temporarily high levels of total suspended solids in the effluent, and biomass levels increased 5-fold to 1300 mg L^{-1}. Sludge trapped in the settling basin increased 2-fold producing a total solids to COD ratio which was artificially high. Reliable total solids to COD ratios were attainable at the chemical loading rates of 4.8 kg COD m^{-3} day^{-1} and 8.0 kg m^{-3} day^{-1}, where the FBR performed steadily and the average total solids/COD ratio ranged from 0.027 to 0.041 kg solids kg^{-1} of COD treated.

Sludge retention time

Sludge retention time, or sludge age, is defined as the average length of time the biomass is under aeration and is calculated using the following equation:

Table 6 Total solids[a] production by the FBR during selected periods in operation of the FBR

COD treated (g)	Chemical loading (kg COD m^{-3} day^{-1})	Trapped sludge (g)[b]	Effluent solids (g)[b]	Solids/COD treated (g g^{-1})
151	3.2	9.2	4.0	0.087
43	3.2	5.0	6.0	0.260
227	4.8	7.0	2.3	0.041
918	8.0	9.1	15.9	0.027
594	8.0	15.5	0.4	0.027
270	8.0	5.5	0.3	0.033

[a] Total solids is the sum of total suspended solids in the reactor effluent and sludge accumulation in the settling trap.
[b] Dry weight determination.

$$\text{Sludge age} = \frac{X_V}{\Delta X_V} \quad (3)$$

where:

X_V = Total biomass in the reactor (g)
ΔX_V = Quantity of biomass wasted (g day^{-1}).

Excess sludge and total suspended solids were collected for 7 days while operating the FBR at the design loading rate of 4.8 kg COD m^{-3} day^{-1}. Total solids removed were 1.33 g day^{-1}. Sludge age of the FBR was calculated to be 5.4 months (based on biomass concentration of 29000 mg L^{-1}). Repeating this calculation at the high chemical loading rate using a biomass concentration of 48500 mg L^{-1} and an average total solids removal of 1.36 g day^{-1} gave a sludge retention time of 4.4 months.

Discussion

This laboratory-scale study demonstrated the feasibility of FBR technology for biotreatment of the maleic anhydride process wastestream. The FBR achieved consistently high treatment efficiencies, with ≥98% of the wastewater COD and total organic carbon removed during operation at design chemical loading rate. Chemical analyses of the FBR effluent for specific components of the maleic anhydride wastestream showed removal efficiencies ≥99.9% for maleic acid, fumaric acid, phthalic acid and over 99.99% removal of DBP at all loading rates. These high chemical removal rates indicate that the microbial biomass acclimated rapidly to the wastestream components and maintained good removal efficiencies in response to increased chemical loading.

The use of GAC as the biocarrier in an FBR offers a number of advantages. Activated carbon has the ability to adsorb a wide range of organic compounds including moderate quantities of DBP from the maleic anhydride wastewater. The carbon bed in the FBR was pre-absorbed with low levels of DBP prior to microbial inoculation and reactor start-up. Activated carbon with adsorbed substrate has been reported to enhance microbial growth rates up to 100% compared to growth rates on a non-adsorbing media such as sand [3]. The rapid acclimation of the FBR to the maleic anhydride wastewater was probably assisted by the ability of the activated carbon to concentrate soluble organic compounds from the maleic wastewater as substrate to stimulate the growth and assimilation of microbial biomass on the carbon. In addition, one of the primary advantages of carbon is the provision of chemical adsorption as a mechanism of chemical removal in addition to microbial degradation. DBP was detected on the GAC after the pre-adsorption phase and throughout the study. However, concentrations of DBP on the carbon did not increase over time even though chemical loading to the FBR was increased 5-fold during the 68-day study. This indicates that chemical adsorption onto the carbon and microbial regeneration of active sites on the carbon was occurring throughout the study. Furthermore, the presence of chemical adsorption as a chemical removal mechanism in FBRs provides additional protection of effluent quality during system upsets or chemical surge-loadings. In these cases, the adsorbed chemicals are retained in the reactor on the carbon until they are degraded by microorganisms. This property of GAC may be particularly important in the operation of a full-scale system, where the carbon will serve to store excess substrate and resist excursion in performance efficiency caused by fluctuation in feed strength, composition and flow rate.

The rough surface texture and large surface area of the carbon support media contributed to the high biomass levels sustained in the FBR. The biomass concentrations of 15500–48500 mg L^{-1} were 10× greater than normally maintained in a conventional suspended growth system. The biomass levels were dependent on the organic loading rate and increased with each increase in chemical loading rate. The ability of the FBR to maintain high COD and total organic carbon removal efficiencies at each increase in chemical loading was primarily due to this concomitant increase in biomass levels in response to increased feed rates.

Sludge management is an essential part of the wastewater treatment process. The cost of sludge handling and disposal may account for at least 50% of the total operating costs for a biological treatment system [14]. The FBR produced a significantly low total solids ratio of 0.027–0.041 kg solids kg^{-1} COD (based on wet weight of solids). In addition, the average sludge retention time during steady state operation of the FBR was 5.4 months, which is 8-fold higher than reported for suspended systems. However, FBRs are known to produce finer, less settleable solids in effluents which may be more difficult to remove and handle. The relationship between mean cell residence time (sludge age), total sludge production, and overall costs for clarification, sludge management and wastewater treatment is important since total sludge management costs decrease as sludge age increases and sludge production decreases. One explanation is that longer sludge ages result in a greater degree of secondary microbial autooxidation of biomass in the reactor which decreases the overall sludge produced by the FBR.

The FBR achieved ≥97% removal of the COD and total organic carbon of the wastewater within 60 days and this removal efficiency was maintained at chemical loading rates as high as 8.0 kg COD m^{-3} day^{-1}. In addition, the organic diacids and DBP were below detection limits in filtered FBR effluent throughout the study. Only trace levels of DBP were absorbed to the sludge or carbon biocarrier. The high performance and reliability of the FBR in this study indicates that FBR technology is feasible for reducing maleic process wastes.

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