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Development of a biofilter with water content control for research purposes

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ABSTRACT

A traditional packed bed biofilter was operated as a CSTR by using internal recycle and combined with water content control. Sufficient headspace mixing eliminated interparticle gas phase concentration profiles in the compost bed. A hydrophilic membrane, hydraulically connecting the compost to a water chamber, maintained under vacuum, controlled the water content in the compost. Changing the matric potential from −20 to −300 cm H_2O decreased the elimination capacity (EC) of toluene by 50%. The reactor design allowed easy manipulation of dissolved components in the liquid phase while controlling the unsaturated water content in the compost. Nitrogen was identified as limiting the biomass growth for the particular composts tested. The addition of either ammonia or nitrate increased the steady state EC significantly ($7 \rightarrow 76\,g\,m^{-3}\,h^{-1}$). The EC versus toluene concentration profile was easily generated and displayed a typical mass transfer-limited system up to a concentration between 100 and 200 ppm, followed by a biomass-limited system with increasing toluene concentration. This reactor permitted a better exploration of environmental influences on biofiltration performance than the traditional long column biofilter.

1. Introduction

Biofiltration is an air pollution control method that can treat a large variety of odorous and volatile organic compounds. A critical aspect of biofilter operation is the control of the water content of the bed material [1]. Although this is widely recognized, water content control has received little formal attention. Too little water will reduce microbial activity and irreversibly damage the packing material. Too much water fills the biofilter pores and reduces the mass transfer rates of pollutants, oxygen and waste products. It also leads to structural problems, increased pressure drops in the biofilter bed and excessive leachate production [2].

The common goal (or assumption) of most laboratory-scale catalytic reactors, including biofilters, is plug flow for the gas phase with no radial or axial gradients in environmental parameters, and only contaminant concentration changing along the length of the reactor. As biofiltration is an oxidative reaction, temperature can vary axially and radially, but the use of narrow diameter reactors can minimise temperature gradients. However, a small reactor diameter relative to particle diameter increases the potential of by-pass, broadening the residence time distribution and complicating the estimation of intrinsic elimination capacity [3].

Water content is especially difficult to control in biofilters. The inlet gas stream is usually humidified, but the water content can still change for a number of reasons including insufficient inlet humidity (drying), cooling of a warm, water-saturated inlet stream (wetting), microbial heat generation raising the absolute humidity (drying), water generation from oxidation (wetting), cooling/heating at reactor surfaces (wetting/drying). The variation of water content is virtually impossible to eliminate over the long periods of time in biofilters without active manipulation [4].

Control of the water content in a traditional packed bed biofilter requires a reliable on-line measurement of water content and a way to manipulate the water content. On-line measurement of water content is traditionally limited to gravimetric (bed weight), electromagnetic (TDR, capacitive, resistive), neutron probe or tensiometry [2]. None of these are techniques are particularly easy in laboratory-scale reactors due to size issues and are either spot measurements or bulk average measurements, so the water content can still vary through the reactor. The only way to raise the water content is to add liquid water gravimetrically to the top of the biofilter or by injecting an aerosol in the inlet gas stream [5]. Therefore, the water content will vary both with time and position in the reactor as the water periodically permeates through the bed. If the bed becomes too wet, it is very difficult to lower the water content uniformly during operation. These measurement and control issues are a problem for biofilters at all scales. However, from a research perspective, if water content influences performance, rigorous control at the laboratory-scale is desirable, similar to other traditionally

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well-controlled variables such as inlet concentration and temperature.

The water content is defined either by the physical amount of water in the medium (mass or volume ratio) or the potential energy of the water in the medium compared to the reference state of free water (ψ). Bohn and Bohn [2] outlined the relationships between the physical water content and the water potential in regards to biofiltration and the concept of water potential is explored in more detail in Papendick and Campbell [6]. Water activity (a_W) and water potential are related through the following relationship.

$$\psi = \frac{RT}{V_W} \ln a_W \quad (1)$$

where R is the universal gas constant, T is temperature and V_W is the partial molal volume of water (1.8×10^{-5} m^3 mole^{-1}). The exponential relationship means water potential is a more useful term for wet material (biofilters) and water activity for dry materials or water with a high solute concentration. The increasingly negative value of water potential for drier materials is consistent with water flowing spontaneously from regions of high potential to low potential. The unit of water potential is J m^{-3} but is often reported as vacuum as either Pascal or height difference in a water manometer (1 J m^{-3} = 1 N m^{-2} = 1.02×10^{-4} cm). Typical water activities in biofilters are above 0.9996 corresponding to water potentials higher than −500 cm [2].

Matric potential (ψ_m) is the dominant component of the water potential in porous media such as soil or compost. The other components of water potential include osmotic potential, gravimetric and pressure potential [2]. The matric potential is generated by the capillary forces of pores and particle surfaces adsorbing water. At saturation, all of the pores are filled with liquid water and the matric potential is zero. When a gravitational or a suction force is applied to the saturated porous medium, water drains from the medium until equilibrium between gravity and the matric potential is established at a lower water content [6]. As the potential decreases, implying drier material, smaller and smaller pores empty. A matric potential of −500 cm implies all nominal pores with a diameter greater than 5.8 μm are air-filled, based on a simple capillary model. However, in a real heterogeneous material, the water distribution is complicated by bottlenecks, dead end pores and other irregularities.

The purpose of this work is to rigorously control environmental parameters, especially water content and contaminant concentration to investigate the degradation of air-borne toluene by compost. To accomplish this, a traditional packed bed biofilter reactor was operated as an approximate CSTR to eliminate temperature and concentration gradients in the compost layer, and combined with the suction cell technique used in soil science to control water content.

2. Methods

2.1. Reactor design: CSTR approximation

The goal of this work is to develop a CSTR-type reactor for measuring intrinsic catalytic kinetics for biofilter packing material. The main goal is to minimise as many gradients as possible in the active compost bed including interparticle gas phase concentration, temperature and water content. This contrasts with the typical packed bed reactors where most of the parameters change along the length, diameter and/or time in the reactor.

There are two general design options for fluid flow to achieve CSTR-type operation, external or internal recycle (Fig. 1) [3]. Fig. 1a shows a packed bed reactor (volume = V_1) converted to a CSTR using external recycle. The feed concentration is diluted by the large volume of recycled fluid and the single pass conversion is minimal. As long as the recycle flow rate (F_2) is much higher than the feed rate (F_1) ($F_2/F_1 > 20$), the system approaches CSTR operation [7].

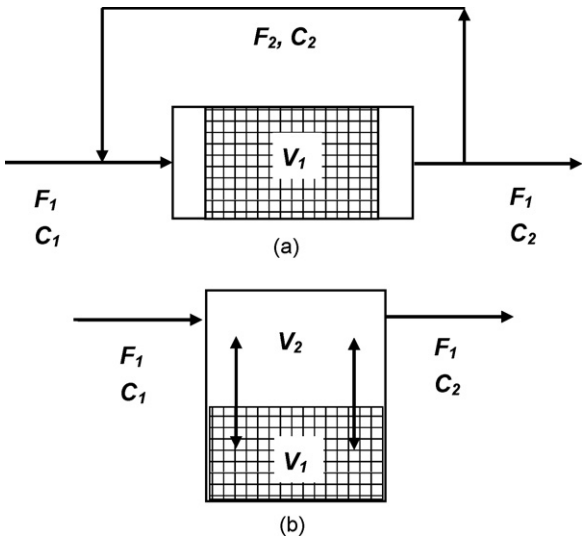

Fig. 1. The two design options for operating a fixed bed biofilter as a CSTR. (a) External recycle with F_1 and F_2 the feed flow rate and recycle flow rate respectively, C_1 and C_2 the inlet and outlet concentrations of the contaminant respectively and V_1 is the volume of the catalyst bed. (b) Internal recycle with V_2 the volume of the internal reservoir.

A packed bed reactor can also be converted to a CSTR-type operation using an internal reservoir to provide recycle (Fig. 1b). In this case, the inlet concentration is diluted by the volume of the internal reservoir (V_2) and the concentration in the compost layer (V_1) is the same as the outlet concentration. As long as the internal reservoir is mixed sufficiently to eliminate any concentration gradients and to provide sufficient exchange with the compost layer, a CSTR is approximated [8].

Internal recycle is used in this work (Fig. 1b). As the reactor approximates a CSTR, Eq. (2) describes the mass balance on the contaminant, where EC is the traditional biofiltration elimination capacity (g m^{-3} h^{-1}).

$$\frac{dC}{dt} = \frac{F_1}{(V_1 + V_2)}(C_1 - C_2) - \frac{(\mathrm{EC})V_1}{(V_1 + V_2)} \quad (2)$$

At steady state, the removal efficiency (f) is given by Eq. (3).

$$f = \frac{C_1 - C_2}{C_1} = \frac{(\mathrm{EC})V_1}{C_1 F_1} \quad (3)$$

The main design variables for the reactor are flow (F_1), compost volume (V_1), the internal reservoir volume (V_2) and the desired fractional conversion. The fractional conversion has to be large enough to not be compromised by contaminant analysis uncertainty. The compost volume (V_1) is limited by the ability to control water content (see next section). With V_1, f and an estimate for EC, the flow rate can be determined. The volume of the internal reservoir does not affect the steady state removal efficiency (Eq. (3)), and only increases the hydraulic residence time of the system. If V_2 is increased relative to F_1, the hydraulic residence time ($(V_1 + V_2)/F_1$) increases and steady state takes longer to achieve. If it is increased further, perfect mixing of the reservoir is eventually impractical. If V_2 is decreased, at some point the assumption of perfect mixing in the internal reservoir and between the internal reservoir and the compost layer would be false. Therefore, a design based on Fig. 1b with good mixing will eliminate interparticle concentration and temperature gradients and eliminate by-pass in the compost bed. However this basic design does not eliminate water content changes.

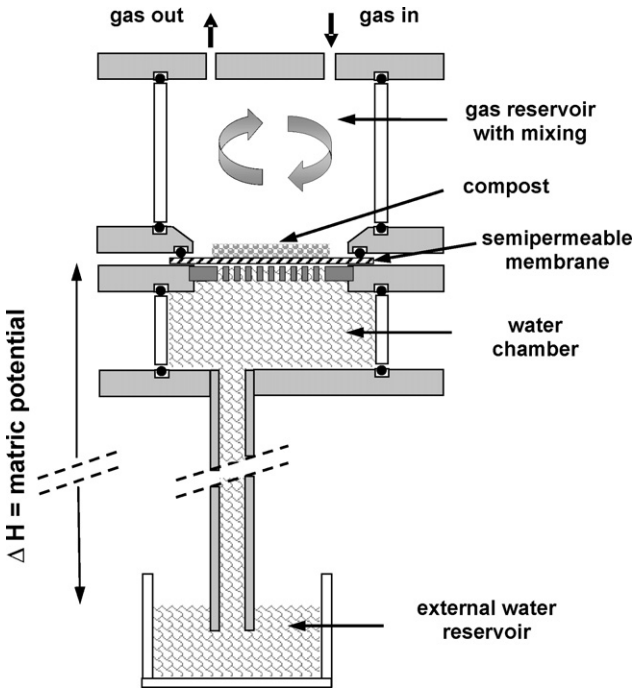

Fig. 2. A cut-away of the biofilter system used to approximate a CSTR with water content control. A semi-permeable membrane and an external water reservoir were used for controlling matric potential.

2.2. Reactor design: water content control

Fo most non-biological systems, a system as described in Fig. 1 is sufficient to control most environmental parameters. For this work, the water content control is also required and the gas phase is ill-suited to do this. Water content control is added by contacting the compost with a water chamber using a hydrophillic membrane (Fig. 2) [9]. The membrane provides hydraulic continuity between the compost and the water reservoir. The water chamber is placed under a vacuum by lowering the external water reservoir below the water chamber. The vacuum forms because air can not pass through the pores of the membrane and the free surface of the external reservoir is lower than the membrane. Therefore, the setup is effectively a hanging water column. This technique is commonly used in soil physics to measure or manipulate the water content of soils. It is important to note that since the hydrophilic membrane stops convective air flow (at pressure differentials below the bubble point), the gas reservoir is not under vacuum. The gas reservoir operates at effectively atmospheric pressure other than the slight pressure increase due to gas flow.

Changing the height between the external water reservoir and the membrane varies the magnitude of the vacuum applied to the water-side of the membrane. Because of the hydraulic continuity across the membrane, the vacuum controls the matric potential in the compost and thus the physical amount of water in the compost at equilibrium. This arrangement allows equilibrium of water potential and the dissolved nutrients between the water chamber and the water in the compost. If the matric potential in the compost rises due to condensation or oxidative water production, excess water drains away from the compost into the water chamber. If the matric potential in the compost decreases due to evaporation, water is absorbed into the compost from the water chamber. The same applies to dissolved components, with movement between the compost and the water chamber driven by concentration gradients.

2.3. Experimental setup

Three reactors were used to collect data. The reactors were autoclaved at 121 °C for 20 min before assembly to eliminate biological growth in the water reservoirs. Toluene was supplied to a reactor by either using a compressed air cylinder supplemented with 100 ppm toluene (BOC Ltd., NZ) or using a diffusion tube to evaporate liquid toluene into the air stream at a constant rate [10]. The diffusion tube system used clean, compressed air passing over a vertical tube (1.5–6.4 mm ID and 116–170 mm long) connected to the headspace of a reservoir containing liquid toluene in a water bath. By varying the bath temperature between 5 and 55 °C and the length and diameter of the vertical tube, inlet toluene concentrations were varied between 15.5 ± 1.2 and 640.2 ± 22.1 ppm. In the systems using a diffusion tube, higher equilibrium reactor concentrations were obtained by increasing the temperature of the water bath. This increased the diffusion flux of the toluene and increased the inlet concentration and the load of the incoming gas stream. Once water bath temperatures exceeded 55 °C, a larger diameter and/or shorter length diffusion tube was installed and the water bath temperature was lowered. Typically flow rate was not varied. In the case of the toluene-supplemented air bottle, the only parameter that could be changed was the flow rate and the equilibrium reactor concentrations that could be achieved were below <100 ppm. A manual flow controller (32505 Series, Cole-Parmer) in combination with a flow meter (250 mL, Gilmont, Accucal) controlled the inlet airflow rate between 18 and 24 ± 1 mL min^{-1}.

All tubing was 1/4 in. copper or 314 stainless steel (SS). The toluene-laden air was humidified with a shell-in-tube humidifier (Perma Pure LLC). The reactor reservoirs were constructed from 5 mm thick, 100 mm OD glass pipe. The upper gas reservoir was 1.2 L and the water reservoir was 0.4 L. The lid and separator plates were constructed from 10 mm thick, 314 SS and sealed with Viton o-rings. The membrane was a mixed cellulose ester, diameter 90 mm, pore size 0.45 μm (Advantec MFS Inc.). The air was able to slowly diffuse through the continuous water phase in the membrane and formed air bubbles on the bottom side of the membrane. The lower the matric potential, the faster they formed. These bubbles did not affect performance dramatically but decreased the contact area and slightly changed the matric potential by displacing water. A purge tube in the water chamber facilitated air bubble removal from beneath the membrane and liquid exchanges. Further details are available in Beuger [11].

Each reactor and humidifier was placed in a temperature-controlled box at 30 °C. The reactor headspace was agitated by either external recirculation using a diaphragm pump (22.6 L min^{-1}) (toluene-loaded air bottle) or direct agitation with a 4-blade turbine, 10 cm OD at 100 RPM (diffusion tube). The diffusion tube was very sensitive to pressure fluctuations caused by the diaphragm pump and toluene-supplemented air was supplied directly.

Two types of compost were tested, Compost 1 ("Results", a general commercial brand) and Compost 2 ("Plus Extra", Parkhouse Garden Supplies, produced from bark, animal effluent and grass). Both composts were sieved using a mesh no. 6 (3.36 mm opening). The compost was loaded onto the membrane using a 53 mm ID ring of 1.6, 3.0 or 5.0 mm height as a guide, lightly tamped down and then the ring was removed. Typically, the mass of dry compost loaded was ~1.8 g for 3 mm deep layers. The ring also left a gap on the membrane between the reactor wall and the compost layer. This facilitated the drainage of the occasional condensate that ran down the reactor wall and minimised the transient increase in compost water content.

All reported elimination capacity values were obtained by averaging daily measurements (minimum of 7 days) after steady state was obtained. The time to achieve steady state varied depending

on whether matric potential (8–15 days) or toluene concentration (2–5 days) was changed. A specific matric potential in the compost was achieved by placing the external water reservoir below the membrane at the desired height. The matric potential changes were rapid from one level to another. The external reservoir was open to the atmosphere. The matric potential values were corrected for the pressure in the reactor headspace. The matric potential of −300 cm was accomplished by sealing the external water reservoir and creating and monitoring a vacuum in the headspace.

Water retention curves were created using a hanging water column with a membrane similar to the reactor system. All matric potentials were reported as a vacuum measurement in units of height of a water column (cm). All water contents were determined after a minimum equilibration time of 7 days at the applied matric potential. The compost was dried at 105 °C at 24 h. Gravimetric water contents (θ_g) were reported as mass of H_2O per mass of dry compost ($g_w\ g_{DC}^{-1}$). Volumetric water contents (θ_v) were calculated based on dry bulk density of 270 kg m^{-3}.

The traditional column biofilter consisted of a 60 cm, 1 in. ID Quickfit glass pipe with a bed depth of 58 cm. The empty bed residence time for the humidified air was 0.9 min at toluene feed concentrations manipulated from 10 to 350 ppm. The bed was operated at ambient temperatures. The initial water content was 1.54 $g_w\ g_{DC}^{-1}$ and the final water content after 1750 h was 1.26 $g_w\ g_{DC}^{-1}$.

Toluene concentrations at the reactor inlet and outlet were measured daily using gas chromatography (Varian CP-3800) with a flame ionization detector, a capillary column (Chrompack Cp-Sil 5 CB) and helium as the carrier gas. The temperature of the injector, oven and detector were 220, 180 and 200 °C respectively. Gas samples of 0.2 mL were taken at the inlet and outlet of the reactor using a 1 mL gas tight syringe (SGE). Peak areas were quantified using a calibration curve determined from samples from prepared air/toluene mixtures. The calibration curve was reconfirmed periodically with no significant variation. All reported uncertainties represent one standard deviation.

Different nutrient solutions replaced the tap water in the water reservoirs in some experiments (Table 1). Between each experiment, the water in the reservoirs was drained before addition of the next nutrient solution. The solutions were autoclaved prior to addition at 121 °C for 20 min.

3. Control experiments

3.1. Leak testing and abiotic losses

Before any degradation experiments were conducted, the complete experimental setup was pressurised and checked for leaks. The humidifier feed reservoir was monitored and water consumption measurements confirmed the entering relative humidity was ~100%. To verify no abiotic toluene losses, the system was operated with a 90 ppm toluene feed without compost in the reactor.

Table 1
Details of the nutrient addition experiments.

Experiment	Nutrient	Concentration (g L^{-1})	Duration (days)
1	NH_4Cl	1.0	8
2	NH_4Cl	1.0	10
3	K_2HPO_4	0.8	14
	NaH_2PO_4	0.7	14
4	$MgSO_4{\cdot}7H_2O$	0.4	11
	$FeSO_4{\cdot}7H_2O$	0.0035	11
	$CaCl_2{\cdot}2H_2O$	0.02	11
5	$NaNO_3$	1.0	17

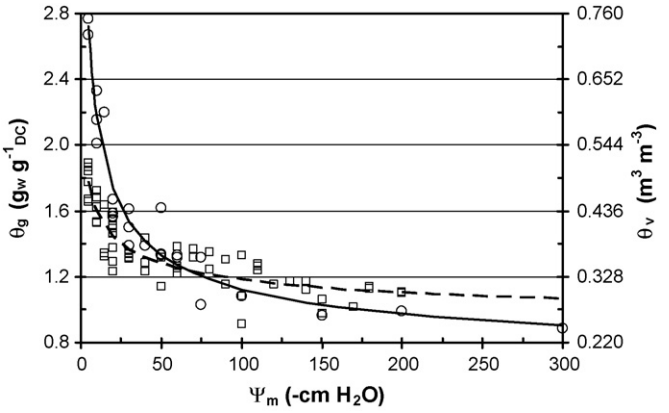

Fig. 3. Water retention data and model fit for Compost 1 (○) and Compost 2 (□). The solid line (Compost 1) and dashed line (Compost 2) correspond to the van Genuchten model fit. A bulk density of 270 kg m^{-3} was used to convert between gravimetric and volumetric water contents.

No toluene loss was observed after the initial equilibration between the air phase and the water reservoir. Undoubtedly, some toluene was continuously absorbed in the water phase and subsequently lost to the air through the external water reservoir but the rate was less than could be measured.

3.2. Water retention curves

The relationship between matric potential and gravimetric/volumetric water content was determined for the two composts (Fig. 3). Several empirical relationships relate volumetric water content (θ_v) to matric potential (ψ_m), the most popular being the van Genuchten equation (Eq. (1)) [12].

$$\theta_v = (\theta_s - \theta_r)\left[\frac{1}{1+(\alpha\psi_m)^n}\right]^m + \theta_r \quad (4)$$

The parameters θ_s, θ_r, α, and n are fitting parameters and were determined using a least squares method on all data points (Table 2) covering the matric potential range from −5 to −300 cm. The parameter m is related to n by the relationship $m = 1 - n^{-1}$.

At the wettest condition of −5 cm, Compost 1 held considerably more water (2.8 $g_w\ g_{DC}^{-1}$) than Compost 2 (1.9 $g_w\ g_{DC}^{-1}$) Decreasing the matric potential from −5 to −50 cm lowered the water content more dramatically in Compost 1 (52%) than Compost 2 (29%) (Fig. 3). The large drop in both cases was attributed to drainage of the large interparticle pore spaces. These pores held large quantities of water but drained easily. Decreasing the matric potential from −50 to −300 cm reduced the water content more gradually, 30% for Compost 1 and 15% for Compost 2. This was most likely due to the higher capillary forces generated by smaller diameter pores in the individual compost particles. At matric potentials below −50 cm, both compost types approached a water content of approximately 1.1 $g_w\ g_{DC}^{-1}$ (~50% wet basis). Little hysteresis in water content was observed for either compost as is sometimes observed in mineral soils. This lack of hysteresis was similar to that

Table 2
Fitted parameters of the van Genuchten model for relating matric potential to volumetric water content in both types of compost evaluated.

Parameter	Compost 1	Compost 2
α (cm^{-1})	0.654	3.673
n	1.484	1.294
θ_s ($m^3\ m^{-3}$)	1.233	0.857
θ_r ($m^3\ m^{-3}$)	0.161	0.205

observed by Hon and Gostomski [36] when determining unsaturated hydraulic conductivity for composts.

3.3. Water content control

Experimental runs in each reactor were operated as long as possible and individual runs moved through a series of EC steady states at different matric potentials and/or outlet concentrations. Stoppages were normally due to a mechanical failure or the need for reactor modifications. The average run length was 50–60 days. At these times, the gravimetric water content was measured to confirm the assumption that the reactor controlled the water content accurately and fresh compost was normally added upon restarting. However, regular sampling during a run was impossible because of the small amount of compost in the reactor, typically ~2 g. The results showed that after discounting for specific cases of experimental errors, the equilibrium water content in the reactors corresponded with the water retention curves with an average ψ_m uncertainty of ±9.6 cm and an average θ_g uncertainty of ±0.18 $g_w\ g_{DC}^{-1}$ indicating good control of the water content in the reactor.

One common practical problem was condensed water falling into the reactor during sampling, especially from the metal clamping ring holding the o-ring against the membrane (Fig. 2). The small absolute amount of compost made one or two drops of water significant. The reactor design addressed this type of water addition in the medium term, as any excess water was pulled away from the compost. However, if water dripped on the compost during dismantling, the gravimetric water content appeared higher than the true equilibrium value. The upper, inside edge of the rings were beveled to stop water accumulation and the gas inlet tube was modified, so infrequent water droplets drained to the side of the reactor and did not drop directly on the compost.

On one occasion, a water content discrepancy could not be attributed to known experimental errors, such as water droplets or insufficient time to equilibrate at a new matric potential prior to sampling (5–7 days). The system had spent 26 days at −300 cm, prior to increasing the matric potential to −20 cm for 28 days, subsequent to sampling. The compost was 0.36 $g_w\ g_{DC}^{-1}$ drier than expected, which implied a matric potential of −55 cm rather than the −20 cm applied to the system. Because of the extended period at a low matric potential, the compost could have become less hydrophilic, inhibiting rewetting [2]. The drier conditions of the compost at −300 cm could have also stimulated the growth of fungi, which have been observed to inhibit wetting in soils [13,14]. Both of these explanations imply a changed water retention curve and additional work at lower matric potentials is required, however the majority of the results were at higher potentials and the results indicated good water content control.

3.4. Mass transfer within the compost layer

Good mixing between the free space above the compost layer and the interparticle, air-filled pore space was required. This ensured that all of the compost was exposed to the same toluene gas phase concentration and that this concentration was the same as the exiting gas concentration (which was measured). A number reactor features contributed to this requirement,

- direct agitation of the free space;
- a thin compost layer (~3 mm);
- gas diffusion coefficients are four orders of magnitude greater than liquid diffusion coefficients.

Smoke tests implied almost instantaneous gas mixing in the upper chamber. In addition, a series of experiments were operated at different compost thicknesses. Insufficient mixing would have manifested as a decreasing elimination capacity (EC) with increasing compost thickness at the same outlet concentration. The standard thickness of the compost layer was 3 mm, so two additional thicknesses were tested, 1.6 and 5.0 mm. The compost was acclimated at 5.0 mm depth and −20 cm matric potential. The 3.0 and 1.6 mm depths were obtained by removing compost and repacking. Each thickness was operated in excess of 12 days after achieving a constant outlet concentration (24.5 ± 4.4 $g\ m^{-3}\ h^{-1}$ and flow (22.1 ± 0.9 $mL\ min^{-1}$). In all three cases, the dry bulk density was a similar 260 ± 10 $kg\ m^{-3}$.

The EC at a layer thickness of 1.6 mm (5.9 ± 0.6 $g\ m^{-3}\ h^{-1}$) was ~25% lower then at 3 mm (7.9 ± 0.7 $g\ m^{-3}\ h^{-1}$) and 5 mm (7.8 ± 0.7 $g\ m^{-3}\ h^{-1}$). However, the thinnest layer was difficult to pack evenly, affecting the volume estimate used in the determination of EC. In this reactor system, EC was calculated based on the volume of the compost layer (V_1 in Fig. 1) and not the total reactor volume ($V_1 + V_2$). Converting the EC to a mass basis ($\mu g\ g^{-1}\ h^{-1}$), the removal rates at 1.6 mm (28.5 ± 1.6 $\mu g\ g^{-1}\ h^{-1}$), 3 mm (29.1 ± 1.3 $\mu g\ g^{-1}\ h^{-1}$) and 5 mm (30.2 ± 1.3 $\mu g\ g^{-1}\ h^{-1}$) were similar. So it was concluded interparticle mass transfer did not restrict the EC. Therefore, no significant concentration gradient existed through the gas phase of the compost layer.

3.5. Elimination capacity

The initial EC for both compost types prior to nitrogen addition was low (2.7–21.0 $g\ m^{-3}\ h^{-1}$ at a load between 14.0 and 56.6 $g\ m^{-3}\ h^{-1}$) in the recycle reactor. These low values were not an artefact of the new reactor system, as a comparable EC value (steady state of 4.8 ± 0.7 $g\ m^{-3}\ h^{-1}$) was observed in the traditional column reactor over a period of 20 days at an initial water content of 1.54 $g_w\ g_{DC}^{-1}$ for Compost 1. This EC value was the average obtained in the constant EC region ($f < 100\%$) at inlet concentrations ranging from 20 to 125 ppm and a loads varying from 6 to 30 $g\ m^{-3}\ h^{-1}$. The column reactor was not used for any other experiments because water content control was not possible.

The EC values reported for toluene vary considerably. Auria et al. [15] reported EC values between 15 and 150 $g\ m^{-3}\ h^{-1}$, Morales et al. [16] reported ECs between 8 and 190 $g\ m^{-3}\ h^{-1}$ and Sun et al. [17] between 0 and 40 $g\ m^{-3}\ h^{-1}$. Therefore, both composts had a low initial EC at the conditions of operation and the internal recycle with matric content control was not the cause of the low value.

4. Results and discussion

4.1. Influence of matric potential on performance

The steady state EC was determined at a variety of matric potentials for Compost 1 and a limited range for Compost 2 (Fig. 4). The maximum EC occurred at approximately −20 cm for both compost types, but with a fairly broad maximum for Compost 1. However at higher (>−20 cm) and lower (<−90 cm) matric potentials, the EC dropped by ~50% for Compost 1. The decrease in EC for Compost 2 was more severe below −20 cm but potentials lower than −40 cm were not tested. The maximum plateau in EC was attributed to a number of influences. At low potentials, organisms directly respond by producing compatible solutes and extracellular polysaccharides. In bacteria, the compatible solutes are often amino acids [18]. As this system was nitrogen limited (see next section), the microorganisms would have had trouble raising the internal concentration of amino acids. In addition, as the potential decreased, sufficient hydration of enzymes on the cell surface would have been more difficult as the free water layer retreated into smaller pores [19]. At very high potentials, the excess water and any extracellular polysaccharides would have increased the mass transfer resistance and therefore

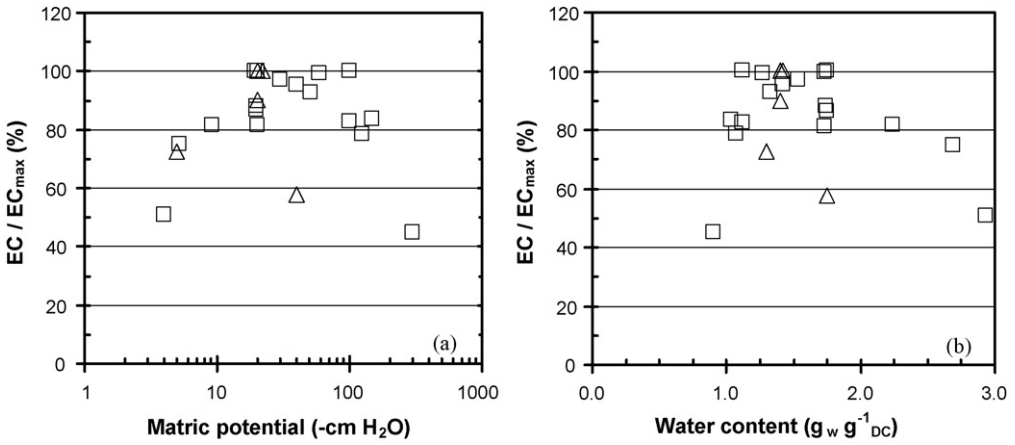

Fig. 4. Influence of the matric potential (a) and the water content (b) on the ratio of the actual EC compared to the highest EC measured in the run (EC_{max}) for Compost 1 (□) and Compost 2 (△).

lowered the EC. There was also the possibility that community diversity might have changed as function of water potential and thereby influencing the EC. Changes in diversity were not tested and the literature is inconclusive on this [17,20].

A limited number of papers in the biofiltration literature have looked at the effect of water content directly. Morales et al. [21] used a dynamic drying study to estimate a critical water content for peat degrading toluene. They found that below 1.4 $g_w\ g^{-1}$, there was insufficient flux of water from the interior of individual particles to the biofilm on the particle surface to maintain optimum EC. Cox et al. [22] also performed a dynamic drying experiment and showed a fairly linear relationship between water content and EC for yeast on perlite degrading styrene.

Auria et al. [23] showed a broad water content optimum for peat degrading ethanol (0.82–2 $g_w\ g^{-1}$) but then an 82% drop in drier conditions (0.5 $g_w\ g^{-1}$) which was similar to this work. Wang and Govind [24] found an optimum removal rate for isopentane at a initial water contents of 0.54 $g_w\ g_{DC}{}^{-1}$ for compost and 0.64 $g_w\ g^{-1}$ dry peat. At lower initial water contents, the removal dropped away steeply, but at higher water contents, the drop was more gradual for both materials. Although their work followed the same trend reported here, the optimums were at much lower water contents, possibly reflecting the much lower solubility of isopentane [25] or possibly that the water retention curves for their peat and compost were much different than the compost in this work.

Poulsen and Jensen [26] showed a significant EC difference for ammonia removal as a function of water content between two different compost types. They concluded that one compost had a higher proportion of small pores and therefore the water was less available to the organisms. If correct, this would manifest as a lower matric potential at equivalent gravimetric water content. These different reports showing different optimum rates at different gravimetric water contents for the same contaminant combined with our results (optimum θ_g in Compost 1 of 1.7 $g_w\ g_{DC}{}^{-1}$ versus 1.4 $g_w\ g_{DC}{}^{-1}$ in Compost 2) raises the possibility that matric potential and not gravimetric water content is a better measure of water's influence on EC [2]. In addition, from the practical side, matric potential is still likely to be a more useful measurement tool, since the addition of bulking agents such as bark chips or pumice to the compost can change the water retention curve of the mixture dramatically. These bulking agents generally retain significantly less water at the same matric potential. It is unlikely, that the gravimetric water content of a fairly inert bulking agent would directly influence the biofilm in the compost at a given matric potential at equilibrium. However, additional compost sources would have to be evaluated to determine the range of the optimum matric potential. In the case of reduced sulfur and nitrogen contaminants, the need to remove acidic compounds produced by oxidation could put an additional constraint on the system where excess water is required to flush these non-volatile waste products.

Only a few research groups have actively controlled the unsaturated water contents. Holden et al. [27] conducted short term, batch experiments down to very low matric potentials (−15,000 cm) with a device similar to this work but more suitable to lower matric potentials. With pure cultures of *P. putida* deposited directly on a semi-permeable membrane, they observed that the matric potential had little effect on VOC degradation rates with non-growing cultures. Ranasinghe and Gostomski [28] using a similar setup as in this work, but in short-term, batch mode with a different compost type, controlled the matric potential over a smaller range at wetter conditions (−6 to −36 cm). The elimination capacity dropped from 155 to 24 $g\ m^{-3}\ h^{-1}$ as the matric potential decreased. This means a six-fold reduction of elimination capacity over a small range of matric potentials. The matric potential influence in both cases were different than observed here, but both reports were operated in batch mode and therefore not at steady state. Also, in the case of the second study, data was collected below 100 ppm but the EC was assumed not to be a function of toluene concentration. However, this work has demonstrated that toluene concentrations below 100 ppm can lower the EC (see subsequent section).

4.2. Nutrient addition

The water reservoir beneath the membrane allowed manipulation of the concentration of soluble compounds without changing the water content in the compost. To test this, a 1.0 $g\ L^{-1}$ NH_4Cl solution was added at 1650 h to Compost 2. After 24 h, the EC increased six-fold and after 48 h the EC reached a steady state of $39.8 \pm 3.0\ g\ m^{-3}\ h^{-1}$ (Fig. 5). The toluene removal was 93%. The NH_4Cl solution was removed from the reservoir and replaced with tap water. For five days, the EC remained constant. The load was increased from 43.3 ± 3.0 to $68.2 \pm 7.7\ g\ m^{-3}\ h^{-1}$ at 2010 h. The EC increased initially, but it slowly decreased to the steady state value at the previous load by 2300 h. Another addition of NH_4Cl solution (1.0 $g\ L^{-1}$) at 2466 h increased the steady state EC to $59.4 \pm 1.7\ g\ m^{-3}\ h^{-1}$.

Additional nutrients were tested sequentially for their impact on EC (Table 1). A phosphate buffer at pH 6.5 was added with no significant change in EC. The addition of magnesium sulfate, iron sulfate and calcium chloride also had no effect. The addition of 1.0 $g\ L^{-1}$ $NaNO_3$ almost doubled the EC. A further increase in the load showed similar results as before with a maximal EC of 114 $g\ m^{-3}\ h^{-1}$ at

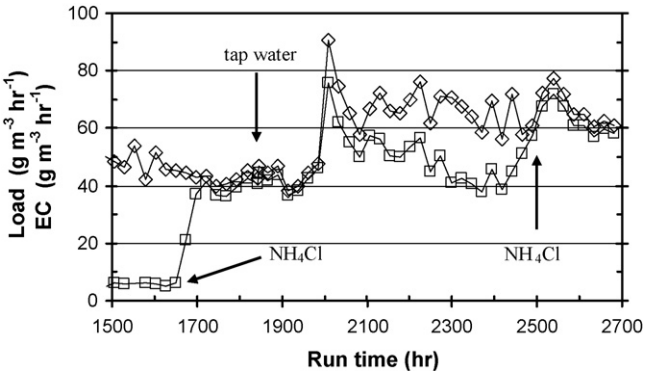

Fig. 5. The elimination capacity, (□) and load, (◊) for native Compost 2 followed by the addition of 1.0 g L^{-1} NH_4Cl (first arrow) and tap water (second arrow) and addition of 1.0 g L^{-1} NH_4Cl (third arrow) to the water reservoir.

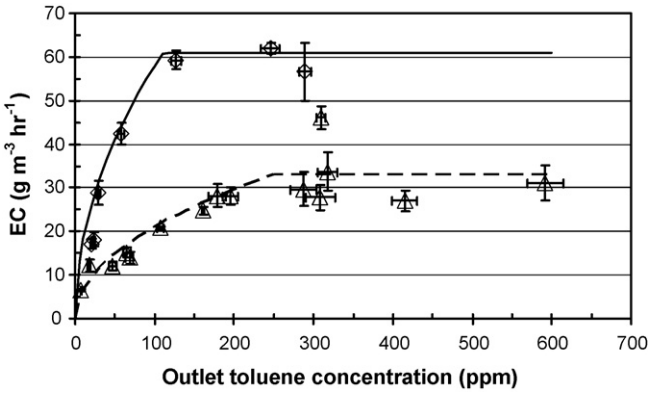

Fig. 6. The relationship between the outlet (residual) toluene concentration and the EC at two different biomass loadings. Both experiments were conducted at a $\psi_m = -20$ cm.

a load of 120 g m^{-3} h^{-1}. After removing the nitrate solution, a steady state was maintained for 7 days at 76.3 ± 3.4 g m^{-3} h^{-1} (load 97.1 ± 4.2 g m^{-3} h^{-1}). These results indicated that nitrogen was the main growth-limiting nutrient in the system. In addition, the reactor design permitted these sequential experiments to be conducted at unsaturated conditions without the need to flush the compost to remove different nutrients.

A sharp increase in EC after nitrogen addition has been observed before. After obtaining a steady state toluene EC of 8 g m^{-3} h^{-1}, Morales et al. [16] stopped toluene addition and added gaseous ammonia to a biofilter. Upon restarting toluene addition, the EC subsequently increased to 80 g m^{-3} h^{-1} after 2 days, and then dropped to a steady state of 30 g m^{-3} h^{-1} after 15 days. Cherry and Thompson [29] also observed a spike in the EC followed by a small increase in the steady state values after a nutrient injection.

Following a similar logic to that proposed by Cherry and Thompson [29], the EC profile after nitrogen addition was caused by a transition from maintenance metabolism to growth followed by a return to maintenance metabolism in regards to toluene consumption rates. At steady state, there was no net biomass growth and all toluene consumption was for maintenance requirements at a lower rate. Removal of the nitrogen restricted further growth, but the net increase in biomass increased the volumetric toluene consumption for maintenance, causing the higher steady state EC.

In this case, the toluene degraders grew when supplemented with both ammonia and nitrate as a nitrogen source. This result was consistent with typical toluene degraders present in compost such as *P. putida* [30]. The temporary increase in EC when the toluene load was increased at 2010 h was most likely due to a temporary production of extracellular polysaccharides or another energy storage compound as reported by Delhomenie et al. [31].

4.3. Toluene concentration influence on EC

The relationship between the equilibrium reactor concentration (outlet concentration) and the EC was explored at $\psi_m = -20$ cm at two different biomass loadings (Fig. 6). Each data point represents a steady state of typically 5 days. A transition from one residual concentration steady state to another typically took 1–2 days. The results follow the general conceptual model put forward by Ottengraf and Vandenoever [32], where at low concentrations the EC was lower due to incomplete the biofilm penetration. The EC rose with increasing residual toluene concentrations, eventually becoming constant as the biofilm was fully utilised. These results were similar to those typically obtained on the length of a typical long column biofilter; but in this case, all the compost experienced the same concentration and environmental conditions. In addition, the resolution of this system was not limited by the number of sample ports nor obtaining sufficient degradation over a bed section to calculate a reliable EC.

No drop in EC at high toluene concentrations was observed in these experiments. The maximal residual concentration was 600 ppm at a load of 426 ± 11 g m^{-3} h^{-1}. Toluene inhibition was seen at an inlet concentration above 1090 ppm and loads above 1000 g m^{-3} h^{-1} [33]. Oxygen limitation at high toluene loads would have lowered the EC also. Villaverde et al. [34] and Smith et al. [35] observed oxygen limitations at toluene concentrations greater than 400 and 593 ppm respectively, which was close to the maximal concentration used in these experiments. Thus, it was possible that at higher residual toluene concentrations, oxygen would have become limiting but probably not significantly over the majority of the range tested.

5. Conclusions

These results demonstrate the advantage of a biofilter reactor using internal recycle along with water potential control compared to a traditional plug-flow (long column) reactor when investigating environmental influences on specific removal rates. Water content changes can easily change the EC by a factor of two. A typical laboratory integral reactor, unless operated at very high water contents (trickle bed) is most likely subject to water content dynamics, thereby clouding the interpretation of results if water content is not controlled. Additionally, the water chamber in this system means soluble compounds can be added evenly to the porous medium without changing the water content or overloading the top of the column. In addition, soluble compounds can be removed without the need for excessive washing of the entire column.

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