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# Denitrification of a Nitrate-Rich Synthetic Wastewater using various Wood-based Media Materials

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## ABSTRACT

This laboratory study examined the use of various wood materials as a carbon source in horizontal flow filters to denitrify nitrate-nitrogen ($NO_3$-N) from a synthetic wastewater. The filter materials were: sawdust (*Pinus radiata*), sawdust and soil, sawdust and sand,

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and medium-chip woodchippings and sand. Two influent concentrations of $NO_3$-N, 200 mg $L^{-1}$ and 60 mg $L^{-1}$, loaded at 2.9 to 19.4 mg $NO_3$-N $kg^{-1}$ mixture, were used. The horizontal flow filter with a woodchippings/sand mixture and an influent $NO_3$-N concentration of 60 mg $L^{-1}$, which operated over a study duration of 166 days, performed best, yielding a 97% reduction in $NO_3$-N at steady-state conditions.

*Key Words:* Horizontal flow filters; denitrification; intermittent sand filtration; nitrate-nitrogen; wood materials.

## INTRODUCTION

In Ireland, nitrate-nitrogen ($NO_3$-N) pollution of surface and drinking waters constitutes a potential environmental problem. A recent study [1] estimated that the percentage pollution attributed to agriculture was 18%, 38% and 51% in the case of rivers and streams that were seriously, moderately, and slightly polluted, respectively. Land spreading is the most common method employed for the treatment of dairy wastewaters and may contribute to this problem.

In land spreading, the recharge rate, the time of year of application, the hydraulic conductivity of the soil, the depth of soil to the water table and/or bedrock, and the concentration of nutrients and suspended sediment in the wastewater are some of the defining parameters that determine the movement of nitrates through the soil to the water table. The recommended maximum rate of application is 5 mm per hour and the quantity applied should not exceed 50 $m^3$ per hectare by single tanker application. [2, 3] This means that large land areas are required for the effective treatment of dairy parlour washings. In order to reduce the nitrates below the maximum allowable concentration (MAC) of 11.3 mg $NO_3$-N $L^{-1}$, the applied nitrogen may be reduced by prior treatment.

Intermittent dosing of wastewater onto sand filters is considered to be an efficient and economic treatment method for dairy wastewaters. Healy et al. [4] examined a stratified intermittent sand filter column (0.9 m deep, and 0.3 m in diameter) for the treatment of synthetic effluent resembling dairy parlour washings for a period of 806 days. The column was operated in both single-pass and recirculation modes. In single-pass mode, under a hydraulic loading rate of 6.7 L $m^{-2}$ $d^{-1}$, the Tot-N was reduced by 27-41 %, with an effluent $NO_3$-N concentration of 165±45 mg $L^{-1}$. By recirculating the sand filter effluent through an anoxic zone at a rate of three times the influent flow to the system to give a sand filter column hydraulic loading rate of 26.7 L $m^{-2}$ $d^{-1}$, denitrification occurred, resulting in an effluent $NO_3$-N concentration of 60±6 mg $L^{-1}$. In some field situations it would be necessary to further reduce the single-pass effluent concentration of 165±45 mg $L^{-1}$ and the recirculated effluent concentration of 60±6 mg $L^{-1}$ before the wastewater could be applied to the land to prevent nitrate contaminating the groundwater.

Conventional methods for the removal of nitrogen, including continuously moving biofilm reactors [5], sequencing batch biofilm reactors [6], trickling filters [7], activated sludge systems [8], and fluidized-bed biofilm reactors [9], have shown good potential for biological nitrogen removal.

Rodgers and Burke [5] used a continuously moving biofilm reactor for the treatment of high strength wastewater. The system comprised six reactors in series: one anaerobic, one anoxic and four aerobic reactors. In the anaerobic and anoxic reactors, plastic modules of specific surface area 240 $m^2$ $m^{-3}$ moved up and down but were always submerged in the wastewater, whereas, in the aerobic reactors, the plastic modules moved vertically up and down, in and out of the wastewater. Average $NO_3$-N removals of 0.42 kg $NO_3$-N $m^{-3}$ $d^{-1}$, based on bulk fluid volume of the reactors, were measured in the study. In an experiment on two fluidized-bed biofilm reactors, each comprising 2 kg of sand with an average grain size of 0.84 mm and subjected to nitrogen loading rates ranging from 6.3 to 16 kg N $m^{-3}$ $d^{-1}$ [9], maximum $NO_3$-N removals of 12 kg N $m^{-3}$ $d^{-1}$, based on the volume of the fluidized bed, were measured.

Horizontal flow [10] or vertical flow [11] denitrification filters using a carbon source as the filter media may also reduce nitrate concentration. Carbon sources such as corn [10] (97% $NO_3$-N removal) and sawdust [11, 12] (92-99% $NO_3$-N removals) have been used effectively to denitrify wastewaters. Although studies have indicated that horizontal flow filters are capable of denitrifying 60-100% of $NO_3$-N up to an influent $NO_3$-N concentration of 125 mg $L^{-1}$ [10, 13], the denitrification process appears to be very dependent on the ambient water temperature [10, 13, 14] and oxygen content of the filter. [13]

The aim of this paper was to examine the efficiencies of four carbon mixtures (sawdust, sawdust and soil, sawdust and sand, and woodchippings and sand) in the treatment of water with two $NO_3$-N concentrations of 200 mg $L^{-1}$, similar to single-pass sand filter effluent (165±45 mg $NO_3$-N $L^{-1}$), and 60 mg $L^{-1}$, similar to recirculation sand filter effluent (60±6 mg $NO_3$-N $L^{-1}$) from the study on dairy parlour washings of Healy et al. [4]

## MATERIALS AND METHODS

Six horizontal flow filters were used in this study (Table 1) and were constructed using sawdust or woodchippings as the carbon filter source. For the influent concentration of 60 mg $NO_3$-N $L^{-1}$, the filter mixtures were: (i) sawdust and soil; (ii) sawdust; (iii) woodchippings and sand. For the influent concentration of 200 mg $NO_3$-N $L^{-1}$, the filter mixtures were: (i) sawdust and soil; (ii) sawdust and sand; (iii) woodchippings and sand. The carbon source to sand or soil volume ratio was 1. Each of the six reactor tanks (Figure 1) measured 430 mm long by 320 mm wide, and had a height of 260 mm. Within each reactor tank, the horizontal flow filter was 315 mm long by 320 mm wide and 260 mm high, and the upstream and downstream vertical boundary of the filter consisted of a porous nylon membrane supported on a steel wire frame. 2 litres of bulk fluid containing heterotrophic bacteria from an aerobic biofilm unit for chemical oxygen demand (COD) removal were used to seed the filters at 3 incremental depths during construction.

The nitrate-amended influent water was made up using potassium nitrate ($KNO_3$) mixed in tap water and the water flow of 1 L $d^{-1}$ into each reactor tank was regulated by a

Mariotte vessel (positioned on a hydraulic jack), which delivered the water through a 3 mm narrow bore tube . The tube was positioned under the water surface in a chamber between the upstream tank wall and the filter. A similar chamber collected the outflow from the filter and the effluent flowed through apertures located near the top of the downstream wall of the reactor tank, ensuring that the wood materials were totally submerged.

Almost daily analyses of the effluent water quality parameters were carried out over a maximum study duration of 180 days. The water quality parameters measured were: $NO_3$-N (automated hydrazine reduction method; tested on a Konelab analyser, type 955, Finland), colour (APHA Platinum-Cobalt standard method), and dissolved organic carbon (DOC) (combustion-infrared method; tested on a Total Organic Carbon Analyser, model no. TOC-5000A, Shimadzu Corp., Japan). Almost daily measurements of water temperature, influent and effluent dissolved oxygen and pH were taken. All water quality parameters were tested in accordance with Standard Methods. [15] $NO_3$-N removal rates (g $NO_3$-N $m^{-3}$ $d^{-1}$) in each filter were calculated using the difference in $NO_3$-N concentration entering and leaving the filter, the average daily flow rate (1 L $d^{-1}$), and the volume of each filter (0.0262 $m^3$). $NO_3$-N removal rates were also calculated in terms of the mixture mass (mg $kg^{-1}$ mixture $d^{-1}$).

As the initial poor performance of the filters was attributed to the high dissolved oxygen (DO) of the influent waters, the DO was reduced by the daily addition of sodium sulphite ($Na_2SO_3$) to the Mariotte vessels after 113 days of operation. The woodchippings/sand filter with an influent $NO_3$-N concentration of 60 mg $L^{-1}$ was set up subsequent to the other reactor tanks, and from its start of operation, $Na_2SO_3$ was added to its influent waters.

RESULTS AND DISCUSSION

Figures 2 and 3 illustrate the performance of the filters throughout the duration of operation. The woodchippings/sand filter with an influent $NO_3$-N concentration of 60 mg $L^{-1}$ produced a consistently low effluent $NO_3$-N concentration of 2±3 mg $NO_3$-N $L^{-1}$ (Table 1). In this filter, the $NO_3$-N removal rate was 2.2±0.1 g $NO_3$-N $m^{-3}$ $d^{-1}$ on a filter bulk volume basis and 2.8±0.1 mg $NO_3$-N $kg^{-1}$ mixture $d^{-1}$ on a mixture mass basis. This is considerably less than the $NO_3$-N removal rate of 56 mg $NO_3$-N $kg^{-1}$ paper $d^{-1}$ (approximately 7.5 g $NO_3$-N $m^{-3}$ $d^{-1}$) achieved by Volokita et al. [13]on a laboratory column packed with shredded newspapers treating drinking water. The woodchippings/sand filter with an influent $NO_3$-N concentration of 200 mg $L^{-1}$ removed 3.3±1 g $NO_3$-N $m^{-3}$ $d^{-1}$ (3.5±1.1 mg $NO_3$-N $kg^{-1}$ mixture $d^{-1}$) and had an effluent $NO_3$-N concentration of 114±27 mg $L^{-1}$ (Table 1). Stabilisation of the effluent $NO_3$-N concentration to the values tabulated in Table 1 normally occurred within a period of approximately 25 days, which is the approximate average water retention time for all the mixtures. This was particularly noticeable in the sawdust reactor tank (Figure 2).

Initially, the poor $NO_3$-N removals in the filters were attributed to the high DO concentrations in the influent waters (influent DO concentrations ranged from 3.7 to 7.3 mg $L^{-1}$). Following the daily addition of $Na_2SO_3$ to the Mariotte vessels (after 113 days of operation), the DO in the influent water reduced to an average concentration of 1.5 mg $L^{-1}$. Only the performance of the woodchippings/sand mixture for the influent concentration of 200 mg $NO_3$-N $L^{-1}$ appeared to be affected by the influent DO reduction where the effluent $NO_3$-N concentrations, before and after the daily additions of $Na_2SO_3$, were 149±18 mg $L^{-1}$ and 114±27 mg $L^{-1}$, respectively.

Throughout the study, the effluent from the filters, excluding the woodchippings/sand filters, had a pH and a DO concentration ranging from 7.5 to 7.7 and 0.8 to 2.4 mg $L^{-1}$, respectively. As the addition of the low DO influent waters did not greatly affect the performance of these filters, DO was not limiting in these filters. In the woodchippings/sand filters, the low effluent DO (0.5±0.1 and 0.6±0.1 mg $L^{-1}$ at influent $NO_3$-N concentrations of 60 mg $L^{-1}$ and 200 mg $L^{-1}$, respectively) suggested the occurrence of denitrification within the filters. [16]

Washout of significant amounts of DOC were noted in the initial stages of operation for all the filters. Initial DOC concentrations normally ranged from 37 to 171 mg $L^{-1}$, before stabilising to concentrations between 11 and 43 mg $L^{-1}$ (Table 1). In the woodchippings/sand filter for an influent concentration of 60 mg $L^{-1}$ this was particularly noticeable, where initial DOC effluent concentrations of 171±74 mg $L^{-1}$ were measured (Figure 4). Similar results were obtained by other researchers [10, 11], who attributed the high effluent DOC to a large amount of energy available in the carbon source. Similarly, high colour levels were noted in the effluent from the filters, with values ranging from 34±18 PtCo for the sawdust/soil mixture at 200 mg $NO_3$-N $L^{-1}$ to 617±306 PtCo for the woodchippings/sand mixture at 60 mg $L^{-1}$. However, tests on the effluent organic content from the woodchippings/sand reactor tank at 60 mg $NO_3$-N $L^{-1}$ influent indicated that the organic carbon release from the system was relatively small with effluent biochemical oxygen demand (BOD) and COD concentrations of around 30 and 50 mg $L^{-1}$, respectively.

## Sizing of Pilot-Scale Plant

Under a loading rate of 2.9 mg $NO_3$-N $kg^{-1}$ mixture $d^{-1}$, the laboratory-scale woodchippings/sand mixture removed 97 % of $NO_3$-N with an influent $NO_3$-N concentration of 60 mg $L^{-1}$. Being mindful of the possible differences between laboratory synthetic effluent and dairy farm wastewaters, it is estimated, using removal rates from this study, that a mass of about 1 x $10^5$ kg of this filter mixture would be required to treat 5000 L $d^{-1}$ of wastewater with a similar $NO_3$-N concentration. Using the bulk density of 780 kg $m^{-3}$ (Table 1), a volume of 132 $m^3$ of the woodchippings/sand mixture would be required for adequate treatment of effluent $NO_3$-N (Table 2).

## CONCLUSION

On the basis of the horizontal flow filter study, deoxygenated influent water at a loading rate of 2.9 mg $NO_3$-N $kg^{-1}$ $d^{-1}$ on a woodchippings/sand horizontal flow filter yielded a 97 % reduction in $NO_3$-N when applied at an influent $NO_3$-N concentration of 60 mg $L^{-1}$ at an average temperature of 17$^{o}$C for 166 days. This study suggests that a woodchippings/sand mixture could be used to further denitrify the $NO_3$-N concentration in an effluent from a recirculating sand filter treating dairy parlour wastewater.

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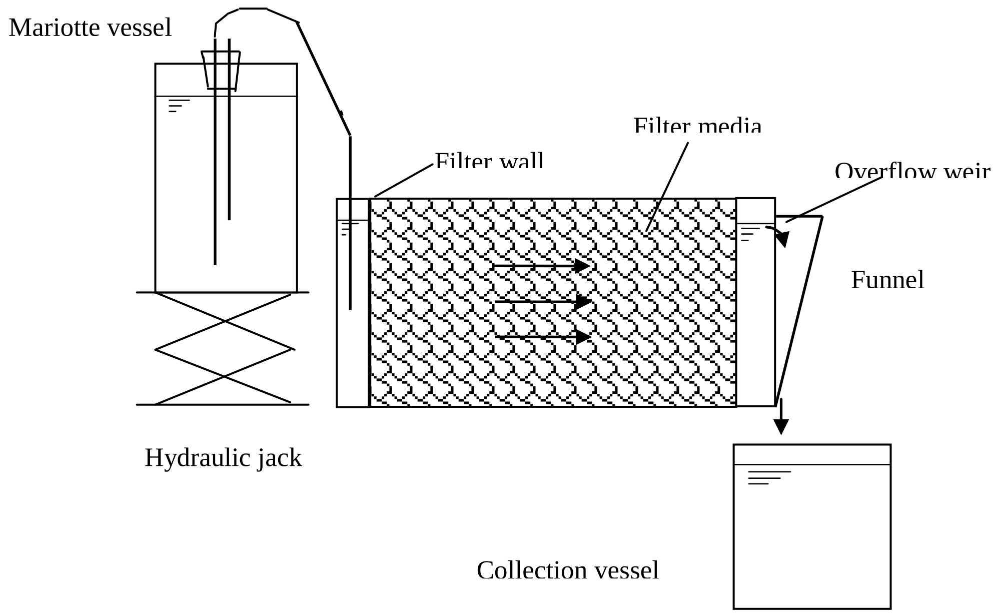
FIGURE CAPTIONS

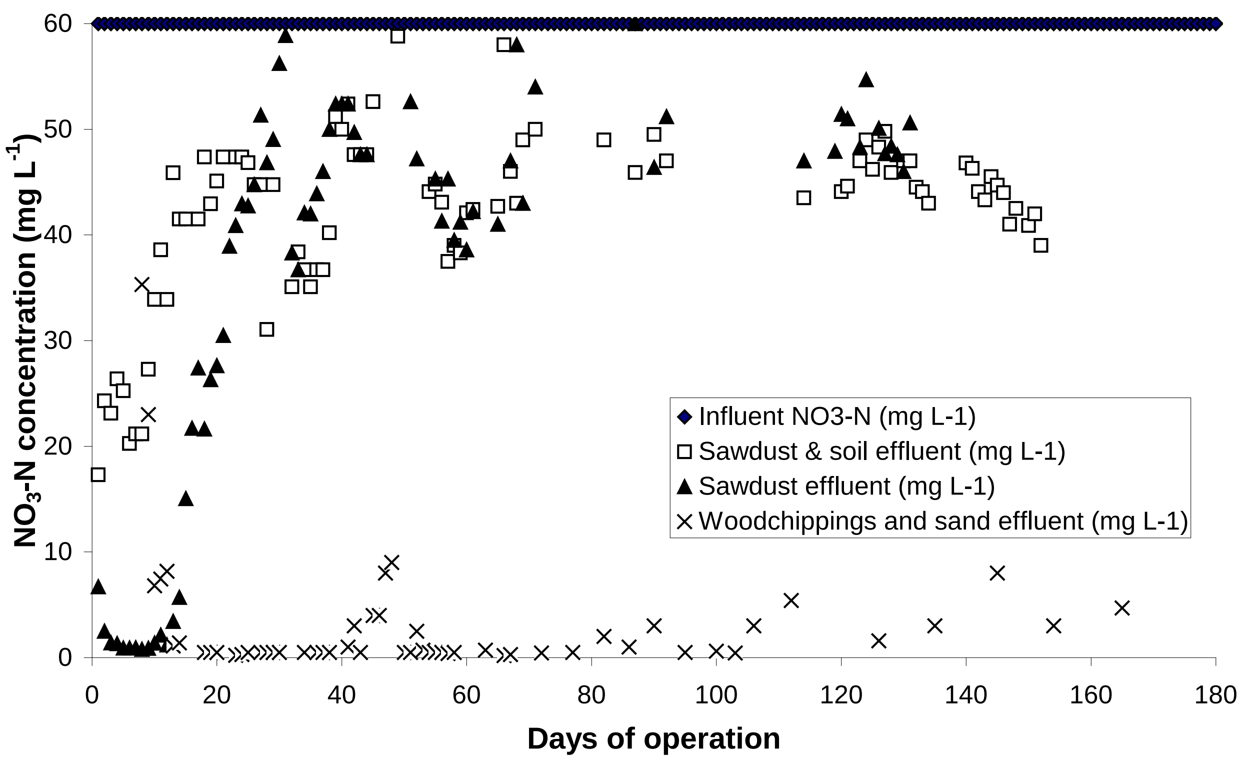
***Figure 1.*** The laboratory filter used in this study.

***Figure 2.*** Daily effluent $NO_3$-N (mg $L^{-1}$) for an influent $NO_3$-N concentration of 60 mg $L^{-1}$.

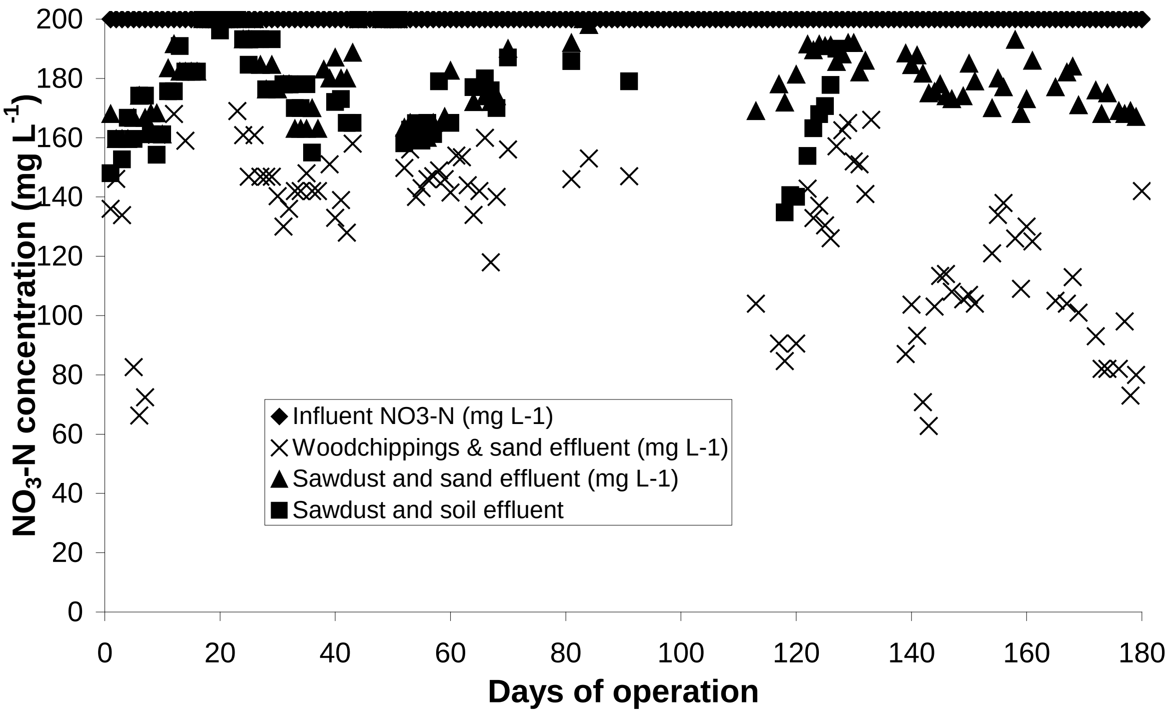
***Figure 3.*** Daily effluent $NO_3$-N (mg $L^{-1}$) for an influent $NO_3$-N concentration of 200 mg $L^{-1}$.

***Figure 4.*** Daily effluent DOC for the reactors used in this study.

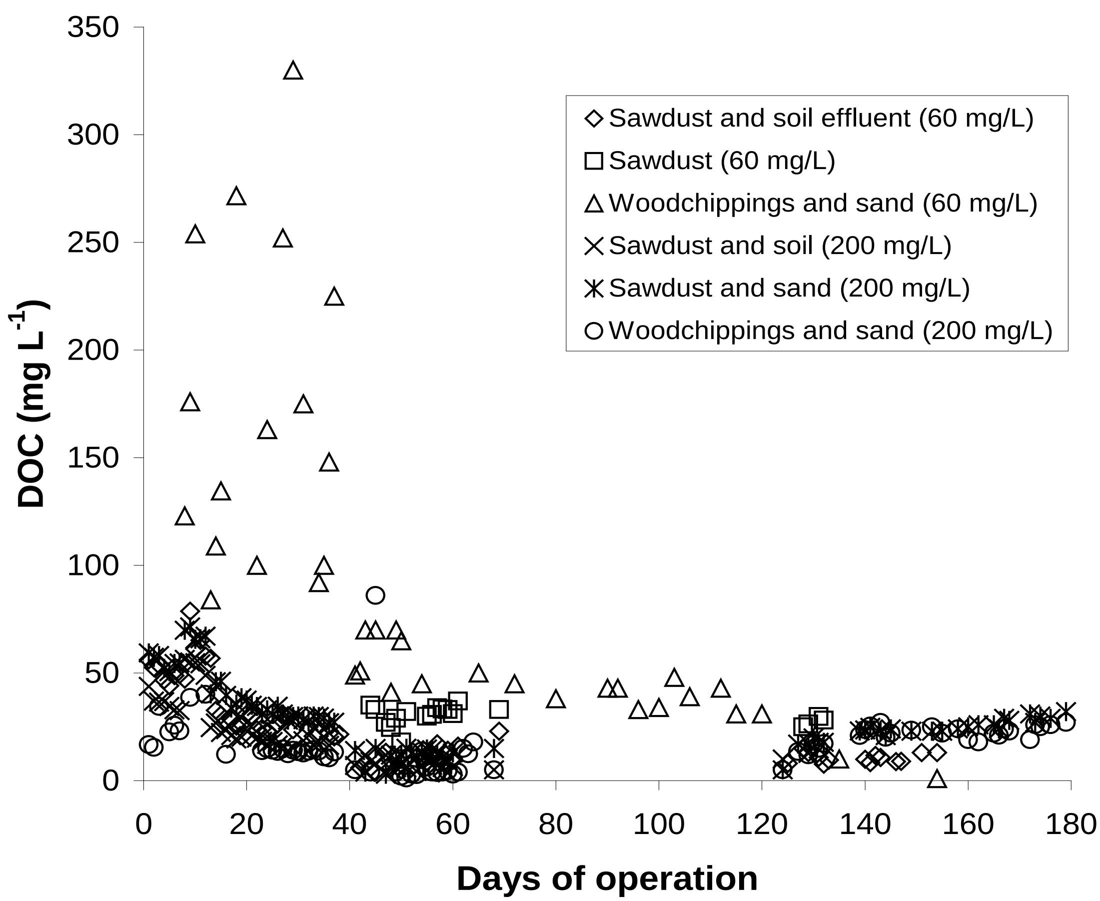

Mariotte vessel
Filter media
Filter wall
Overflow weir
Funnel
Hydraulic jack
Collection vessel



60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
NO3-N concentration (mg L-1)
Days of operation
Influent NO3-N (mg L-1)
Sawdust & soil effluent (mg L-1)
Sawdust effluent (mg L-1)
Woodchippings and sand effluent (mg L-1)



200
180
160
140
120
100
80
60
40
20
0
NO3-N concentration (mg L-1)
0
20
40
60
80
100
120
140
160
180
Days of operation
Influent NO3-N (mg L-1)
Woodchippings & sand effluent (mg L-1)
Sawdust and sand effluent (mg L-1)
Sawdust and soil effluent



350
300
250
200
150
100
50
0
0
20
40
60
80
100
120
140
160
180
DOC (mg L-1)
Days of operation
Sawdust and soil effluent (60 mg/L)
Sawdust (60 mg/L)
Woodchippings and sand (60 mg/L)
Sawdust and soil (200 mg/L)
Sawdust and sand (200 mg/L)
Woodchippings and sand (200 mg/L)

***Table 2***. Sizing of a prototype-scale treatment plant[†] using woodchippings/sand mixture.

| Laboratory $NO_3$-N loading rate[‡] | Prototype-scale hydraulic loading rate | Weight required | Pilot-scale volume reqd. |
|---|---|---|---|
| mg $NO_3$-N $kg^{-1}$ mixture $d^{-1}$ | L $d^{-1}$ | kg | $m^3$ |
| 2.9 | 5000 | 1 x $10^5$ | 132 *(11x12x1m)* |

† Based on the effluent $NO_3$-N concentration from a recirculating sand filter (60 mg $L^{-1}$) from a 100 cow farm with each cow producing 50 L $d^{-1}$.

‡ Using the $NO_3$-N loading rate on the woodchippings/sand mixture at 60 mg $NO_3$-N $L^{-1}$.