LIMESTONE LINERS TO PROTECT GROUNDWATER QUALITY AGAINST ORGANIC WASTEWATER SEEPAGE

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(Received 22 December, 1994; accepted 6 September, 1995)

Abstract. Crushed limestone was tested as a sealing liner for organic wastewater storage facilities. This material was compacted in laboratory columns and exposed in quadruplet to three levels of wastewater total solids (TS of 0.6, 1.3 and 2.6%). A fourth set of quadruple columns was used to monitor the total nitrogen (TN) loading rate using 1.3% TS wastewater. The crushed limestone cores measured 310 mm in depth by 98 mm in diameter and were exposed to a typical wastewater depth of 290 mm. Wastewater TS and ambient temperatures had a marked effect on seepage and TN loading rates. If the wastewater contains at least 1.3% TS, the seepage and N loading rate can be limited to 2×10^{-8} m s^{-1} and 200 mgN m^{-2} d^{-1}, respectively. Ambient temperatures below 5 °C caused the TN loading rate to increase 7 fold, while those above 5 °C favoured nitrifying and denitrifying activity, thereby reducing seepage TN.

Key words: liner, limestone, wastewater

1. Introduction

Facilities used for the storage of solid organic wastes, such as livestock manures, require a hard floor for the circulation of machinery. As flooring material, crushed limestone has been used to replace poured reinforced concrete at a cost reduction of 75%. Once in place, this material hardens quickly and retains the wastewater running off the solid organic waste. A laboratory study was conducted to investigate the impact of such a sealing liner on groundwater quality. Using 310 mm limestone columns exposed to 290 mm of wastewater, the laboratory study measured seepage rates under 2×10^{-8} m s^{-1} and a TN loading rate for the underlying material of less than 600 mg m^{-2} d^{-1}. Accordingly, crushed limestone liners can meets North American environmental requirements to contain wastewater with a TS over 1.3%, under conditions above freezing.

2. Literature Review

When exposed to a liquid containing organic particles, a porous medium generally loses some of its permeability. The main groups of sealing mechanisms have been identified as physical, biological and chemical (Barrington *et al.*, 1990).

Physical sealing occurs when the solid particles of the wastewater are larger than the medium's pores and become trapped there in. Any process reducing the

Water, Air, and Soil Pollution **92:** 315–327, 1996.

cross sectional area of the medium's pores has a negative effect on the flow of liquids as well as on the permeability of the system.

Biological sealing results mainly from the formation of gums and polysaccharides by microorganisms. These hydrocarbons generally possess, on their surface, a high density of positively charged sites (Russell, 1989) and adhere to the sides of the medium's flow channels. The pores therefore become clogged when exposed to a significant quantity of biological by-products (Tollner *et al.*, 1983).

Chemical sealing is induced when the wastewater reacts with the particles of the porous medium. Gleization is a chemical process occurring under saturated conditions whereby hydrocarbons contained in the wastewater feed anaerobic microorganisms which reduce and solubilize the soil's metal oxides. As a result, these key soil aggregating metals leave the soil without macropores, thus with a lower permeability (McConkey *et al.*, 1990).

Exposed to organic wastewater, crushed limestone offers the conditions necessary to bring about all three types of sealing mechanisms, physical, biological and chemical. Nevertheless, the sealing must be extensive enough to reduce the medium's seepage and TN loading rate below 10^{-8} m s^{-1} and 600 mg m^{-2} d^{-1}, respectively, as required by most environmental authorities in North America. Although phosphorous can move rapidly in saturated soils, TN has always been of greater issue as it can lead to nitrate leaching with little soil adsorption and absorption.

Physical sealing can develop at the surface of and within a layer of crushed limestone if its pore size is small enough. The pore size of any porous medium is related to the particle size distribution and degree of compaction (Kovacs, 1981):

$$D_o = \{4N_o/(1 - N_o)\}/D \tag{1}$$

where

D_o is the equivalent pore size of the porous medium, m;
N_o is the porosity of the dry medium, fraction;
D is the equivalent particle size of the medium, defined as:

$$D = \{1/[\delta S_i/D_i]\} \tag{2}$$

where

δ is a shape coefficient ranging between 9 to 12 and 30 to 50 for spherical and plate-like particles, respectively, dimensionless;
S_i is the mass fraction of the i^{th} group of particles;
D_i is the average diameter of the i^{th} group of particles, m;

The hydraulic conductivity of a porous medium can therefore be estimated from D, if the particles are not consolidated or aggregated, such as those of crushed limestone:

$$K = \{g/(5v)\}\{(N_o^3/(1 - N_o)^2\}D^2 \tag{3}$$

where

K is the hydraulic conductivity of the medium,m s^{-1};
g is the gravitational constant, 9.81 m s^{-2};
v is the kinematic viscosity of the liquid infiltrating the medium, $1.005 \times 10^{+6}$ m^2 s^{-1};

Biological sealing will occur both within and at the interface of the crushed limestone layer if the environment is moist, nutrients are available and the pH as well as the temperatures range from 5.5 to 8.5 and 5 to 35 °C, respectively (Overcash *et al.*, 1983; Alexander, 1977). Organic wastewater, such as manure runnoff, is rich in microorganisms, hydrocarbons, water, and minerals. It therefore provides all the seed organisms as well as the necessary nutrients and moisture to start and support bacterial activity. The temperature of the medium is determined by the ambient conditions and the protection offered by the depth of wastewater above the limestone liner. The pH of the seepage can be controlled under 8.5 if carbon dioxide is present to precipitate the dissolved calcium. This reaction can reduce the pH from 12 to 8.0 and 7.5 if the solution's CO_2 concentration ranges from 0.1 to 1.0%, respectively (Russell, 1989).

Chemical sealing can occur within the crushed limestone layer in conjunction with biological activity. The CO_2 contained in the wastewater precipitates the dissolved calcium at the entrance of and within the pores through the following chemical reaction (Moeller *et al.*, 1983):

$$Ca^{+2} + CO_2 + 2\,OH^{-1} \rightleftharpoons CaCO_3 + H_2O\,.$$

The result is the direct clogging of the pores within the layer of crushed limestone.

3. Materials and Method

The experiment was conducted using 2.6% TS wastewater obtained from solid dairy manure that had been stored outside uncovered. The wastewater was diluted two and four times to obtain TS of 1.3 and 0.6%, representing typical TS ranges (Loehr, 1974). The quarry limestone had a calcium carbonate content over 85%. The manure wastewater and crushed limestone were characterized before initiating the experiment.

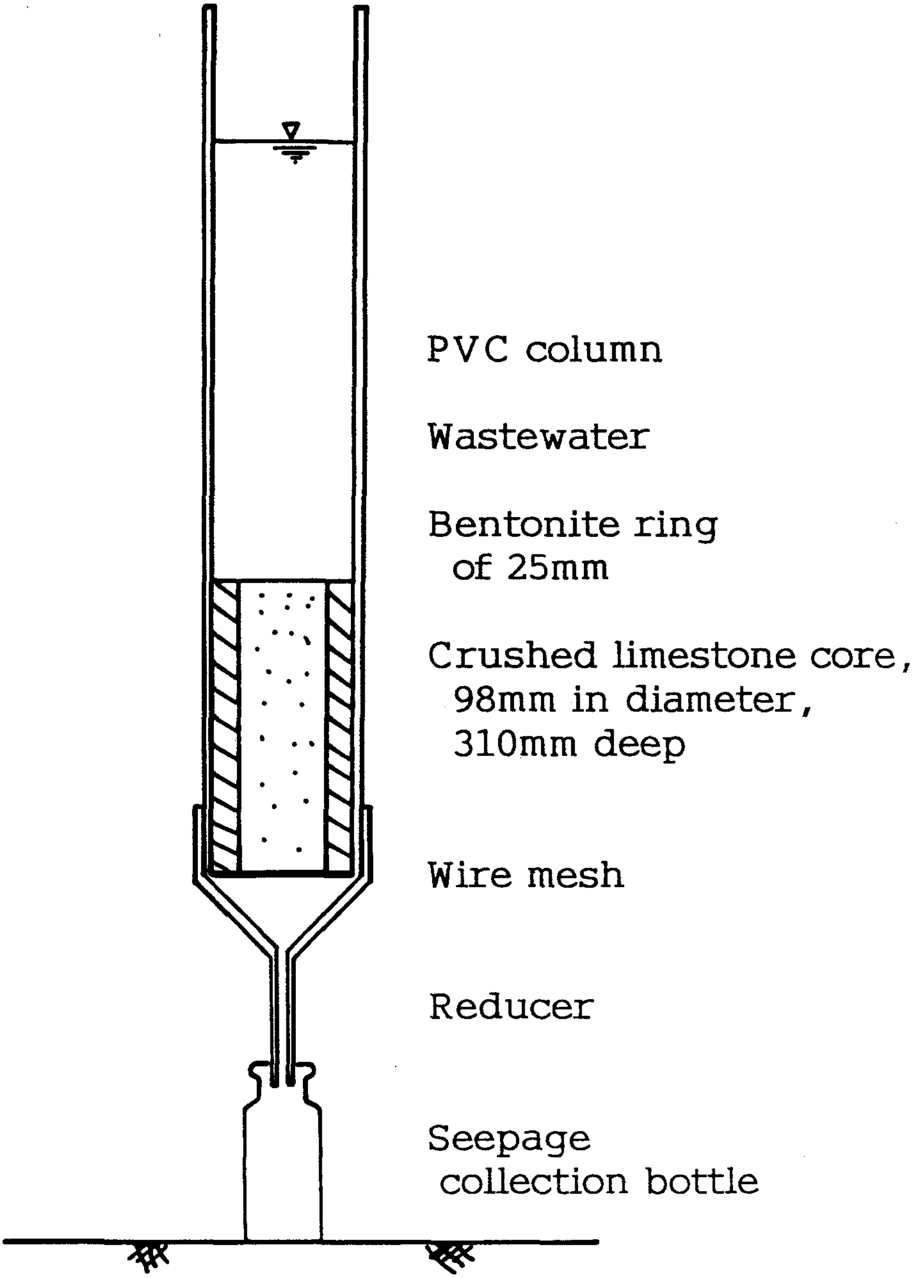

Figure 1. The experimental columns.

The experimental columns (Figure 1) were made of 900 mm long PVC (Polyvinyl Chloride) tubing, 148 mm in inside diameter. The 310 mm deep limestone core was enclosed in an outer 25 mm ring of bentonite and was held in place in each column

Table I
Characteristics of manure wastewater

Characteristic	Value	
	Initial	Final
Total solids, %	2.6 (0.01)	1.3 (0.01)
TKN, mg L^{-1}	1130 (101.3)	333 (73.1)
NH$_4$–N, mg L^{-1}	883 (0.15)	76 (0.01)
NO$_3$–N, mg L$_{-1}$	112 (0.01)	190 (0.01)
TN, mg L^{-1}	1242 (157.6)	523 (73.1)
pH	8.0 (0.1)	8.0 (0.1)
Particle size, % by mass		
>300, μm	4 (0.72)	
250–300, μm	2 (0.04)	
75–250, μm	2 (0.31)	
75–20, μm	10 (2.43)	
20–1, μm	50 (7,53)	
<1, μm	32 (3.18)	

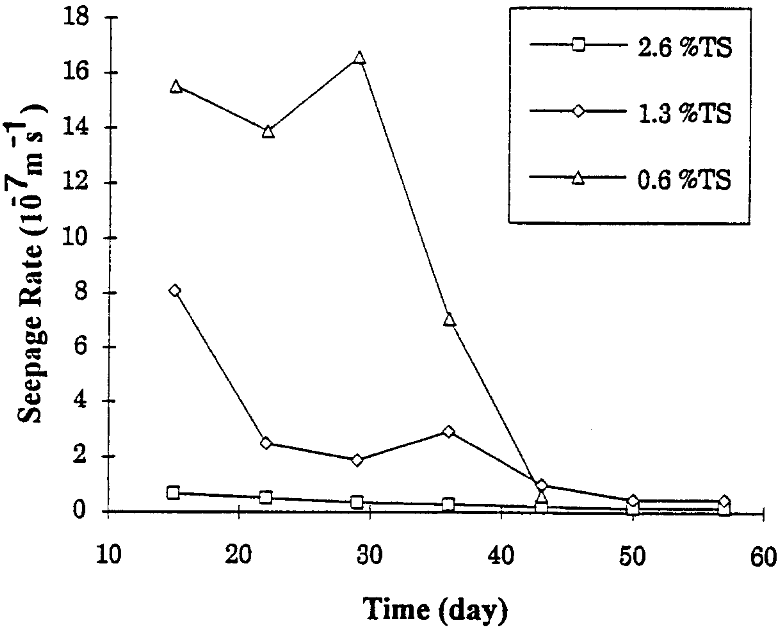

Figure 2. Seepage rate of treatments 1, 2 and 3, where the columns were refilled with their own seepage to compare the effect of TS on levels of sealing.

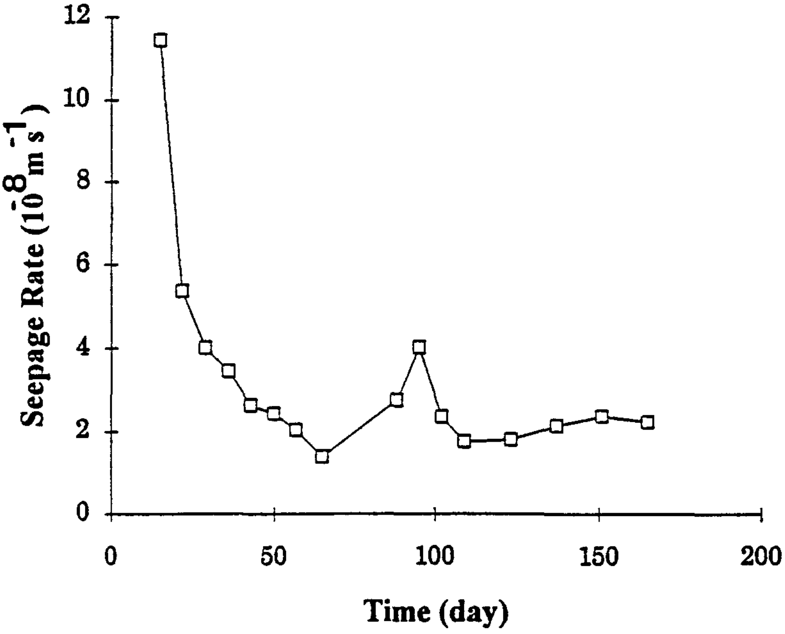

Figure 3. Seepage rate of treatment 4 where the columns were refilled with wastewater to observe sealing under field conditions.

by a porous geotextile over a metal mesh. The top portion of the columns was filled with 290 mm of manure wastewater. A reducer under the column collected all seepage and was used to determine the seepage and TN loading rates.

A set of 16 experimental columns were built to test four treatments in quadruplets. The first three treatments were designed to establish the effect of wastewater TS on the seepage rate using three levels of wastewater TS:

- 0.6%, for treatment 1;
- 1.3%, for treatment 2;
- 2.6%, for treatment 3.

These 12 experimental columns were refilled with their own seepage to maintain equivalent physical sealing conditions among all columns (Barrington *et al*, 1987).

Treatment 4 was designed to monitor TN loading rates. All columns of treatment 4 were filled with 1.3%TS wastewater and refilled with more wastewater in order to represent actual field conditions.

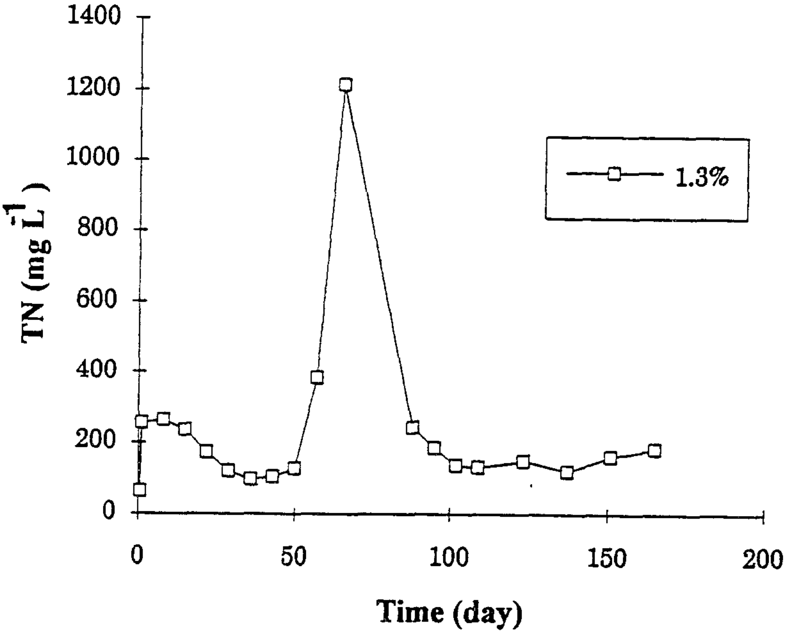

Figure 4. Seepage TN for treatment 4.

The seepage rates were monitored over 45 days for treatments 1, 2 and 3, and 165 days for treatment 4 by measuring the volume of liquid collected under each experimental column. The seepage rate was calculated as:

$$S = V/A/t \tag{4}$$

where

S is the seepage rate in m s^{-1}
V is the volume of seepage collected under the column during time t, m^3,
A is the cross sectional area of the limestone core, m^2,
t is the time during which V was collected, s.

For treatment 4, the TN loading rate was measured and calculated from the seepage rate and the concentration of N in the seepage:

$$L = 8.64 \times 10^{-7}[N]S \tag{5}$$

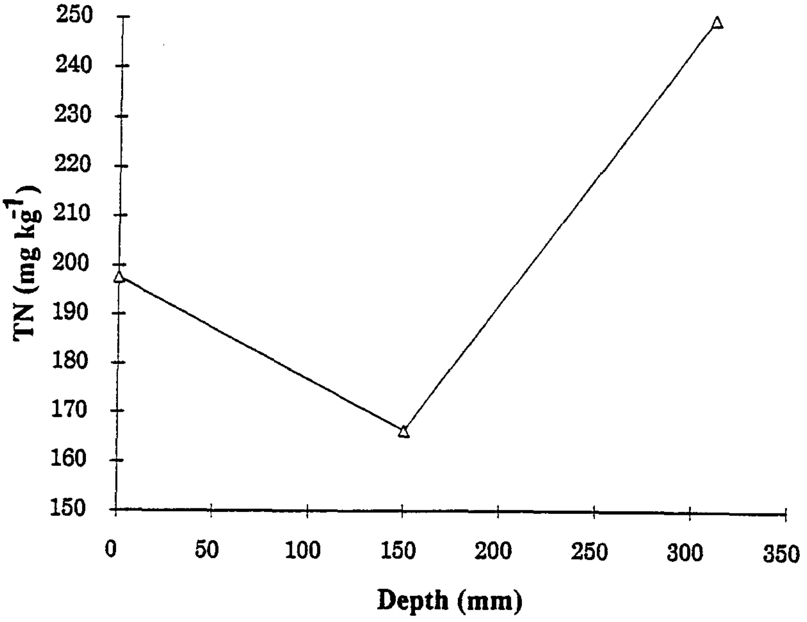

Figure 5. Limestone core TN after 165 days of experimentation.

where

L is the TN loading rate or the quantity of TN seeping through the limestone core, mg N m^{-2} d^{-1},

$[N]$ is the seepage TN concentration, mg L^{-1},

S is the seepage rate, m s^{-1}

The fluctuation in wastewater depth over the limestone cores was limited to 2% by refilling the columns each time a seepage volume of 500 mL was collected. A sample of the seepage was collected every two weeks for the analysis of pH, TKN, NH_4–N and NO_3–N. The effect of cold temperatures was observed when, after 45 days of seepage, the ambient temperature was gradually dropped from 20 to −10 °C. The lowest temperatures were reached on day 55. At that time, only the columns associated with treatment 4 were thawed and observed at ambient temperatures of 20 °C until day 165.

On day 165, the limestone cores of treatment 4 were drained and sampled at three depths, 0–40 mm, 130–170 mm and 260–300 mm. These samples were analyzed for TKN, NH_4–N and NO_3–N.

Chemical and physical analyses of all experimental materials were carried out according to standard methods (APHA *et al.*, 1990; Lamb, 1969). TKN was

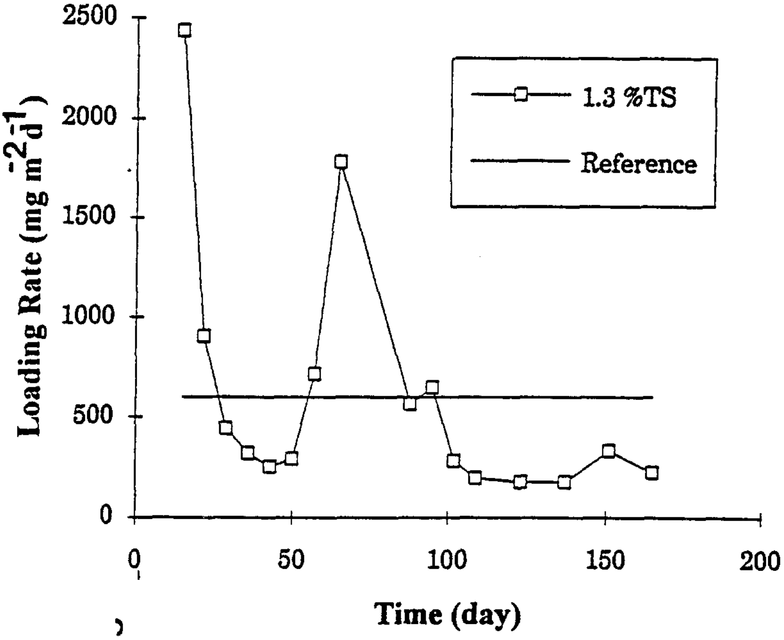

Figure 6. TKN loading rate for treatments 4.

determined using a selective ammonia probe after digestion in sulphuric acid. NH_4–N and NO_3–N were quantified using selective electrodes. Limestone particle size was determined using the dry sieve and the hydrometer methods. The size of the solid particles of the wastewater was determined using the wet sieve method followed by a filtration method using decreasing filter pore sizes. A standard Proctor test was carried out on the crushed limestone to establish the relationship between moisture content and compaction dry bulk density. The results of this test were used to compact the limestone in the columns, to 90% of their optimum density, this level replicating non ideal field compaction conditions.

4. Results and Discussion

The manure wastewater had a particle size distribution, ranging mostly (82%) under 20 μm and a TS, TKN and pH of 2.6%, 1242 mg L^{-1} and 8.0, respectively (Table I). This wastewater was diluted twice and four times to obtain the required TS level of 1.3 and 0.6%. That wastewater diluted to 1.3% was stored until the end of the experiment to refill the columns of treatment 4. At the end of the experiment,

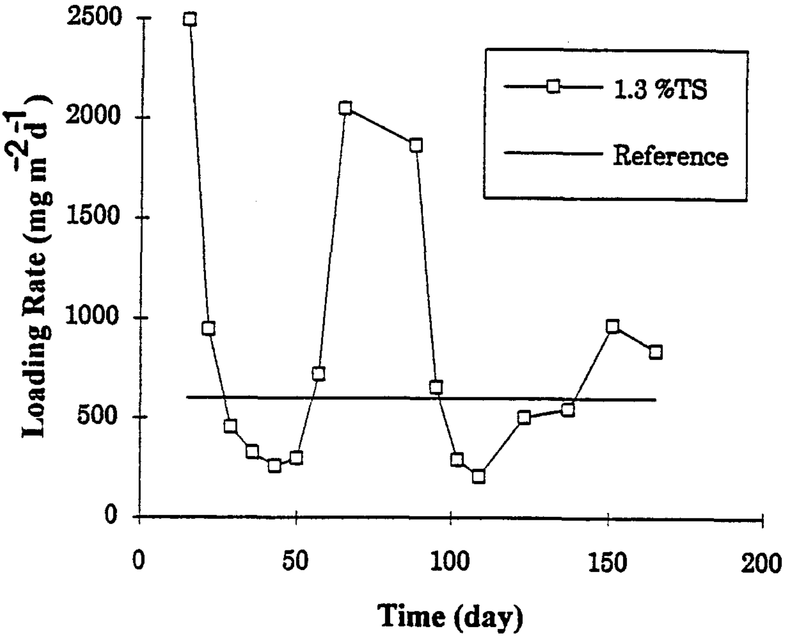

Figure 7. TN loading rate for treatment 4.

the 1.3% TS wastewater demonstrated a TKN and pH of 333 mg L^{-1} and 8.0, respectively.

Based on the measured particle size and hydraulic conductivity, the crushed limestone had an equivalent particle and pore size of 8 and 9μm, respectively, despite the larger particle diameter ranging mainly (84%) between 0.075 to 1.700 mm (Table II). When the particle size is well distributed, the small particles become lodged between the larger ones consequently reducing the equivalent pore size. Only 40% of the wastewater particles were found to be smaller than the equivalent pore size of the crushed limestone cores. This implies that sealing will occur as long as the physical mechanisms are assisted by biological and chemical processes which reduce the pore size of the medium through the deposit of gums and dissolved particles inside the flow channels, respectively. Otherwise, the wastewater particles are larger than the pores and will be transported with the seepage through the limestone layer.

The TS level of the wastewater had a significant effect (99% confidence level) on the seepage rate (Figure 2). The 0.6% TS wastewater reached a low seepage rate of 6.0×10^{-8} m s^{-1} on day 45 and increased thereafter. This increased seepage rate is to be expected with low TS wastewater as the physical seal leaches and

Table II

Crushed limestone cores

Characteristic	Value
Particle size,%	
> 1.700 mm	2.6 (0.16)
1.700–0.425 mm	27.1 (0.82)
0.425–0.250 mm	31.0 (3.46)
0.250–0.150 mm	13.8 (0.90)
0.150–0.075 mm	14.7 (1.99)
0.075–0.020 mm	7.8 (0.89)
<0.020 mm	3.0 (0.15)
Proctor Compaction test	
Humidity,% by weight	Bulk density, kg dm L^{-1}
4.8	1.82
7.8	1.92
9.2	2.14
11.6	1.48
Dry density, kg L^{-1}	1.92 (0.07)
Measured K, m s^{-1}	2.15×10^{-6} (0.22×10^{-6})
Equivalent particle diameter D, mm	0.008
Equivalent pore size,D_o, mm	0.009
Shape factor*, δ	21.5

Note: the value in parenthesis is the standard deviation. * calculated from the measured particle size distribution and the measured hydraulic conductivity (K) value.

decomposes with time (Barrington *et al.*, 1990). The 1.3 and 2.6% TS wastewater showed a steady seepage rate of 4.7 and 1.8×10^{-8} m s^{-1} from day 50 until day 57, the end of the experiment.

Treatment 4, also using the 1.3% TS wastewater, had a seepage rate of 2.0×10^{-8} m s^{-1}, from day 57 until day 165, the end of the experiment, except during the freezing period. Treatment 4 performed slightly better than the first three treatments because it was refilled with wastewater rather than its own seepage. Thus, the continuous addition of solid particles built a stronger physical seal.

Using the results of the first three treatments, the TS level of the wastewater was found to be exponentially related to the seepage rates measured after 57 days of experimentation:

$$S = 9.4 \times e^{-0.62(\mathrm{TS})} \tag{6}$$

where r = –0.99

For treatment 4, ammonium and organic N made up 48 and 50% of the seepage N, respectively, whereas nitrates made up 2%. An initial one day increase in seepage TN concentration was followed by a decrease from 236 to 103 mg L^{-1}, from day 2 to day 43 (Figure 4). This trend showed a TN loading rate below the environmentally accepted level of 600 mg m^{-2} d^{-1}, after 36 days of experimentation (Figure 5). During this period, the limestone cores accounted for little TN reduction in the seepage (Figure 6), since they retained only 0.02% of their mass in TN. Thus, the decrease in the TN loading rate resulted from bacterial activity and N volatilization. Conditions favoured bacterial activity as the seepage pH, ranging from 8.5 to 9.0, was still within that tolerated by most micro-organisms.

The freezing of the columns associated with treatment 4 occurred on day 45 and was followed by a thawing period from days 60 to 65. Freezing and thawing of the cores produced a twofold increase in seepage rate, from 2 to 4×10^{-8} m s^{-1} and a 7 fold increase in TN loading rate, from 250 to 1750 mg m^{-2} d^{-1}. As of day 95, the seepage and TN loading rates dropped to their levels before freezing. The fact that 20 days were required to reach normal TN loading rates is an indication of nitrifying activity. Nitrifying bacteria reproduce very slowly and are known to experience a lag period of at least 10 days (Loehr, 1974).

5. Summary

Compacted crushed limestone lined earth surfaces can limit seepage and TN loading rates of organic wastewater under 2×10^{-8} m s^{-1} and 600 mg m^{-2} d^{-1}, respectively, if the TS of the wastewater exceeds 1.3% and its TN level is under 1200 mg L^{-1}. The TS of the wastewater has a marked effect on the volume of liquid migrating through the limestone layer.

Ambient temperatures below 5 °C are conducive to high TN loading rates because nitrifying and denitrifying microbes actively reduce the wastewater TN as it migrates through the limestone.

Acknowledgement

The research was carried out with the financial contribution of the National Science and Engineering Research Council of Canada.

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