

Nutrient removal from farm effluents

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Abstract

The objectives of the study were: (i) to examine the efficiency of nutrient removal during the treatment of dairy farm effluent in a two-pond system, and (ii) to produce an inexpensive but effective nutrient trap which could be recycled as a nutrient source or soil mulch. The concentration of chemical oxygen demand (COD), biological oxygen demand (BOD), nitrogen (N), phosphorus (P) and potassium (K) in a two-pond system used to treat dairy farm effluent was monitored over a period of 7 months. The retention of nutrients by two porous materials was examined both in the laboratory batch (zeolite and bark) and pilot-scale field (bark) experiments. The results indicated that biological treatment of farm effluents using the two-pond system was not effective in the removal of nutrients, which are likely to become pollutant when discharged to waterways. Both the bark and zeolite materials were effective in the removal of N, P and K from effluent. These materials can be placed in the second (i.e., aerobic) pond to treat effluents, which can then be discharged to streams with minimum impact on water quality. The nutrient-enriched porous materials can be recycled as a source of nutrients and soil conditioner.

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1. Introduction

Dairy and piggery farm effluents contain a large reserve of plant nutrients (Table 1). For example, in New Zealand, these effluents can supply enough nitrogen (N) annually to meet the requirements of 40 500 ha of corn or enough phosphorus (P) for 62 500 ha of pasture. World wide, such effluents can supply enough N for 6.7 million ha of corn or enough P for 10.5 million ha of pasture (Bolan, 2001).

In New Zealand, dairy and piggery farm waste is often treated biologically using a two-pond system. In a two-pond system, the first pond is anaerobic and the second pond, termed aerobic, is usually a facultative pond, with an aerobic top layer over an anaerobic base. The aerobic pond treatment is followed by discharge of the effluent to either land or stream. In New Zealand, with the introduction of the Resource Management Act

in 1991 discharge of effluents to surface waters is now a discretionary activity and requires resource consent, which demands the effluent nutrient concentration to be minimised before entering the surface waters. This can be achieved by land disposal of the effluent or nutrient stripping of the effluent by tertiary treatment (Selvarajah, 1999).

Regional Councils in New Zealand encourage land disposal of effluents as this practice is perceived as being less harmful to water quality than discharge directly to waterways. However, land disposal of farm effluents has some limitations: (i) possible only when the soil moisture and climatic conditions are favourable; (ii) requires greater pond storage facilities for holding the effluent when the soil moisture and climatic conditions are unfavourable for land application; (iii) difficult to manage and counter productive when land is waterlogged; (iv) can contaminate groundwater and surface water by leaching and runoff in some areas; and (v) the aerosols formed when spreading the effluent (e.g., piggery effluent) can result in odour problems.

Although the pond system is effective in the removal of suspended solids and carbon (i.e., biological oxygen

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Table 1

Mean concentration of biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), and nutrients in the pond effluent, and the percent removal of these components by the two-pond treatment system

Characteristic	Anaerobic pond inlet (g m^{-3})	Oxidation pond outlet (g m^{-3})	Percent removal (%)
TSS	320 (± 35) a	85 (± 22) b	74
COD	950 (± 152) a	453 (± 78) b	52
BOD	210 (± 23) a	91 (± 16) b	57
NH ₄ -N	115 (± 15) a	95 (± 12) a	8.3
NO ₃ -N	5 (± 1.8) a	15 (± 3.2) b	
Total P	28 (± 2.6) a	24 (± 2.1) a	14
Dissolved P	21 (± 2.3) a	18 (± 1.6) a	14
Total K	175 (± 24) a	168 (± 19) a	4.0

Percent removal = (anaerobic pond inlet – oxidation pond outlet)/anaerobic pond inlet.

± Standard deviation.

Averages within a row followed by same letters are not significantly different at $P \leq 0.05$ level, $n = 10$.

demand—BOD), there has been some debate about its efficiency in the removal of nutrients (Mason, 1997). These nutrients become pollutant when the farm wastes are discharged to waterways (Sharpley et al., 1998). Porous materials can be used to adsorb nutrients from effluents. For example, zeolite which is a naturally occurring, porous and electrically charged aluminosilicate mineral can be used to retain cations and anions from wastewater (Nguyen and Tanner, 1998). Similarly, bark has been found to be effective in the retention of nutrients (Lens et al., 1994). The contaminant-stripped effluents can then be discharged safely into waterways and the nutrient-enriched porous materials can be recycled as a soil conditioner or nutrient source.

The objectives of the study were: (i) to examine the efficiency of nutrient removal during the treatment of dairy farm effluent in a two-pond system, and (ii) to develop an inexpensive but effective nutrient trap which could be recycled as a nutrient source or soil amendment. The study was conducted in three phases: (i) monitoring dairy farm oxidation pond for carbon and nutrients; (ii) characterization of porous materials; and (iii) removal of nutrients from effluent.

2. Methods

2.1. Monitoring dairy farm two-pond system

The performance of the Massey University No. 4 dairy farm two-pond treatment system was monitored over a period of 7 months. The objective of the study is to examine the efficiency of the two-pond system in reducing the concentration of nutrients and BOD. In a two-pond system, the first pond is anaerobic and the second pond is usually a facultative pond, with an aerobic top layer over an anaerobic base (Fig. 1). The two-pond system at the No. 4 dairy farm consists of an anaerobic pond (28 m length \times 22 m width \times 2 m depth) and an aerobic pond (40 m length \times 37 m width \times 1 m depth). The dairy shed effluent is first discharged to the

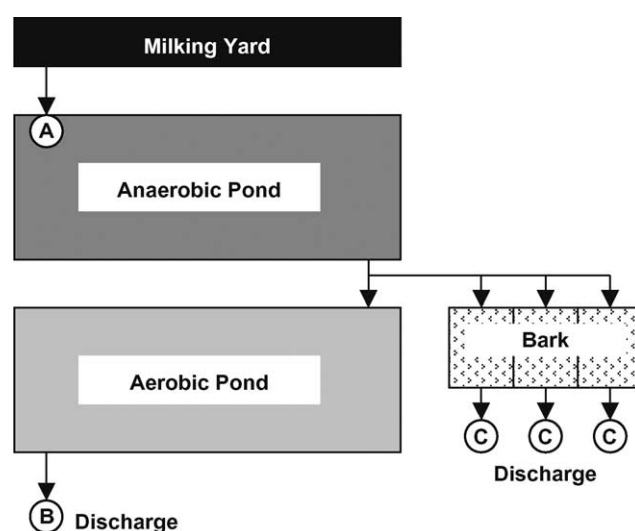


Fig. 1. Schematic representation of a two-pond treatment system. The pilot-scale bark treatment system is also shown. A, B and C are the sampling locations. A is the inlet point at the anaerobic pond (untreated effluent). B is outlet pipe at the aerobic pond without bark treatment (treated in the absence of bark). C is the outlet pipe at the aerobic pilot pond with bark treatment (treated in the presence of bark). (NB. Diagram is not drawn to scale.)

anaerobic pond and then to the aerobic pond. Depending on the concentration of BOD and nutrients, the effluent from the second pond is either spray irrigated to land or discharged to a stream. The No. 4 dairy farm milks around 400 cows for 270 days per annum. At the rate of 50 l of effluent production per day per cow it takes around 60 days to fill the first pond and another 75 days to fill the second pond. When both ponds are full the total retention time of the effluent in both ponds is estimated to be approximately 90 days. When we conducted the experiment both the ponds were full.

Effluent samples were collected from the inlet pipe in the first anaerobic pond (i.e., untreated effluent) and the outlet pipe in the second oxidation pond (i.e., treated effluent) at two monthly intervals (refer to Fig. 1 for the sampling locations). At each sampling period, 10 sam-

ples were collected over a period of 3 h during the milking period. The samples were analyzed for a range of parameters that include total suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD) and nutrients, N, P and K.

2.2. Characterization of porous materials

Pinus radiata bark and zeolite were used to remove the nutrients from effluent. The composted bark was obtained from New Zealand Bark Resource Ltd., Wellington, and a locally mined zeolite (clinoptilolite) sample was obtained from New Zealand Resource Refineries Ltd., Matamata. The bark was treated with an industrial waste product (i.e., slaked fluidized bed boiler ash—FBA) to enhance the cation and anion retention capacity of the original bark. The slaked FBA sample was obtained from the New Zealand Dairy Co-operation factory at Te Awamutu. It is an alkaline material (37.8% CaCO_3 equivalent; pH 12.2) and contains soluble gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and sparingly soluble ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$] (Wang et al., 1994). The bark and the FBA materials were mixed at a ratio of 1.0:0.10 (w/w) and incubated at 45% moisture content (w/w) for 4 weeks. The amount of FBA addition was based on the pH buffering capacity of the bark material (65 mmol OH^- or H^+ kg^{-1}). The particle size distribution and the cation exchange capacity (CEC) of zeolite and FBA-treated and untreated bark materials were measured (Blakemore et al., 1987).

2.3. Nutrient adsorption

The adsorption of ammonium (NH_4^+), phosphate (H_2PO_4^-) and potassium (K^+) ions by zeolite and bark was measured using a laboratory batch adsorption experiment. Adsorption was measured at various concentrations of these ions (0–500 g N m^{-3} ; 0–100 g P m^{-3} and 0–500 g K m^{-3}) using either NH_4Cl , KH_2PO_4 or KCl . The concentrations of these ions were based on the concentration in the dairy shed effluent. The porous materials were mixed with the nutrient solutions at a solid : solution ratio of 1:10 by shaking on an end-over-end shaker for 16 h at room temperature (20 °C). The amount adsorbed was calculated as the difference between the amount added and that remaining in solution after equilibration.

The Langmuir equation (Eq. (1)) was used to describe the batch adsorption data for the bark and zeolite samples.

$$S = bS_m C / (1 + bC) \quad (1)$$

where S is amount of solute adsorbed (g kg^{-1}), C is equilibrium solute concentration (g m^{-3}), and b and S_m are constants. The parameter b gives the binding constant (or affinity term) which reflects the relative rates of

adsorption and desorption at equilibrium and the parameter S_m gives the adsorption maximum.

2.4. Removal of nutrients from effluent

The removal of N, P and K from dairy farm effluent by the bark material was examined using a pilot-scale field experiment. It was decided to use only the untreated bark material for the pilot-scale field experiment because zeolite was very expensive and the treated bark contained high levels of toxic heavy metals such as cadmium. The untreated bark material was placed in three pilot-scale effluent ponds (1.0 m^3) adjacent to the two-pond system in No. 4 dairy farm. Each pond was filled with 450 kg of bark material (sufficient enough to retain N, P and K for 6 months) and the effluent from the anaerobic pond outlet was allowed to pass through the bark material. The effluent was added at the bottom of each pilot-scale pond using PVC tube and the flow rate in these ponds was maintained very low in order to achieve the retention period similar that in the big aerobic pond without bark addition.

In this pilot-scale field study there were two systems of effluent treatment. In the first system the effluent was anaerobically treated in the first pond and then aerobically treated in the second pond in the absence of the bark material. In the second system, the effluent was anaerobically treated in the first pond and then aerobically treated in the pilot-scale ponds in the presence of the bark material (Fig. 1). Effluent samples were collected from inlet pipe at the anaerobic pond (i.e., untreated effluent which was common for both systems) and the outlet pipes at the aerobic pond (i.e., treated effluent in the absence of the bark material) and the outlet pipes at the three pilot-scale ponds (i.e., treated effluent in the presence of the bark material). At each collection time 10 effluent samples were collected over a period of 3 h. The concentrations of TSS, BOD, COD, N, P and K in these samples were monitored at regular intervals over a 6-month period.

2.5. Chemical analysis

The effluent samples were analyzed for total N, $\text{NH}_4\text{-N}$, nitrate N ($\text{NO}_3\text{-N}$), total P, dissolved P, and total Ca, Mg, K and Na. Total N and P were analyzed after digesting the effluent samples using Kjeldahl mixture (concentrated sulfuric acid plus K_2SO_4 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and Se), and total cations were measured using separate effluent samples after digestion with concentrated nitric acid. The $\text{NO}_3\text{-N}$ concentration in the effluent was measured by following diazotization coupling reaction (Griess–Ilosvay reaction) method (Mahimairaja et al., 1990). The total N, $\text{NO}_3\text{-N}$ and total P were analyzed using the Technicon autoanalyser and the difference between total N and $\text{NO}_3\text{-N}$ concentrations gives the

concentration of $\text{NH}_4\text{-N}$. The dissolved orthophosphate in the effluent samples was measured by Murphy and Riley (1962) method. The concentrations of Ca, Mg, K and Na were measured using an atomic absorption/emission spectrophotometer (GBC, Melbourne). The TSS, BOD and COD contents were measured following the methods of APHA, AWWA, WPCF (1995) (Hach BOD apparatus, Biolab Corporation).

2.6. Statistical analysis

Four replications were used for particle size, CEC and nutrient retention measurements for the zeolite and bark materials. Ten effluent samples were collected at each sampling period. The data were analyzed using ANOVA procedure and comparison of means for particle size, CEC and nutrient retention measurements for the zeolite and bark materials, and TSS, BOD, COD and total nutrient concentrations in the effluents was undertaken by calculating standard deviation using Genstat 5 (second edition for Windows).

3. Results and discussion

3.1. Efficiency of two-pond system

The data on TSS, COD, BOD and nutrients in the effluent samples collected from the anaerobic inlet pipe (i.e., untreated effluent) and the oxidation pond outlet pipe (i.e., treated effluent) indicate that the pond treatment system achieved considerable reduction in the concentration of the first three components (Table 1; Fig. 2). However, there was no significant difference in the concentration of nutrients between the anaerobic pond inlet and the aerobic pond outlet (Fig. 2). Most of the N in the effluent was in $\text{NH}_4\text{-N}$ form and most of the P was present as dissolved reactive orthophosphate. There was a small reduction in the $\text{NH}_4\text{-N}$ in the oxidation pond outlet which is attributed to nitrification and/or ammonia volatilization (Table 1). The data indicate that the two-pond system was effective in removing suspended solids, COD and BOD but not with nutrient ions (Hickey et al., 1989).

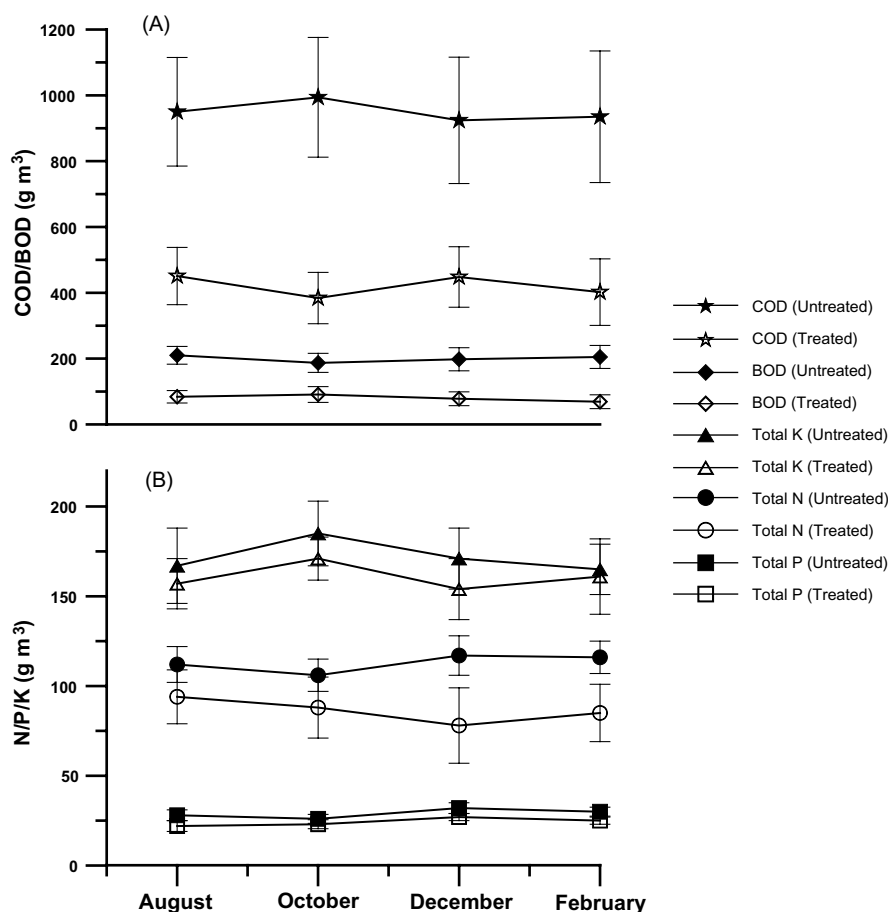


Fig. 2. (A) Concentration of chemical oxygen demand (COD: ★, ☆) and biochemical oxygen demand (BOD: ◆, ◇), and (B) nitrogen (●, ○), phosphorus (■, □) and potassium (▲, △) in the dairy farm anaerobic pond inlet (i.e., untreated—closed symbols) and the oxidation pond outlet (i.e., treated—open symbols) in a two-pond treating system.

It has often been observed that two-pond systems are very efficient in removing suspended solid and organic carbon. For example, depending on the age of the two-pond system, Warburton (1983) and Mason (1997) obtained 75–85%, 53–65% and 65–78% removal of TSS, BOD and COD, respectively. The suspended solid is removed by both gravity sedimentation, and the breakdown of the carbon constituents is achieved by active buildup in the microbial population in the anaerobic pond. The detention time for the effluent in the pond was approximately 90 days which was considered sufficient to cause gravity sedimentation of suspended particulate materials with a particle size $>60\text{ }\mu\text{m}$ in diameter. The removal of soluble organic carbon (i.e., BOD) from liquid waste is achieved by complete degradation (oxidation) yielding energy (i.e., microbial respiration), which is subsequently used to synthesize microbial biomass (i.e., sludge) (Ciaccio, 1971).

Most farm effluents are expected to be enriched with nutrients even after biological treatment using pond systems (Hickey et al., 1989; Longhurst et al., 2000). A major reason for insignificant removal of N can be attributed to poor nitrification of $\text{NH}_4\text{-N}$ in the oxidation pond, as a result of sludge buildup in the pond bottom. Accumulation of sludge is likely to reduce the oxygen content in the second pond, thereby decreasing the rate of oxidation of $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ (Mason, 1997). One of the major pathways of N removal in effluent ponds is biological denitrification, leading to the emission of nitrous oxide and dinitrogen gas (Lowrance and Hubbard, 2001; Groffman and Crawford, 2003). However, unless the $\text{NH}_4\text{-N}$ is oxidized to $\text{NO}_3\text{-N}$, the subsequent denitrification of $\text{NO}_3\text{-N}$ is unlikely to occur. Thus, regular removal of sludge from the oxidation pond is necessary to improve the removal of N during effluent treatment. Removal of P in pond effluent is enhanced through chemical precipitation using calcium, iron, aluminum and magnesium compounds (Weaver and Ritchie, 1994). Most of the K in effluent remained in ionic form in solution and the poor removal of K is attributed to its low demand for microbial growth (Alexander, 1977).

3.2. Characteristics of porous materials

The data on particle size and CEC of the porous materials indicate that zeolite contained more fine particles than the bark (Table 2). Approximately 50% of the particles in the zeolite sample were $<0.2\text{ mm}$ in diameter, whereas in the bark only 15% was $<0.2\text{ mm}$. Since the presence of fine material in zeolite was likely to cause clogging it was decided to use bark only in the pilot-scale pond experiment. As expected, the zeolite sample had a higher CEC value than the bark, indicating that bark is less effective in the retention of cations such as NH_4^+ and K^+ in the effluent. However, treatment of the bark with FBA increased its CEC. FBA contained slaked lime $[\text{Ca}(\text{OH})_2]$ which increased the pH of the bark. The elevation in pH increased the CEC of the bark mainly due to dissociation of H^+ from weakly acidic functional groups of organic matter (Thomas and Hargrove, 1984). The pH-induced increase in CEC ($176\text{ mmol kg}^{-1}\text{ pH}^{-1}$) of the bark material was less than that estimated for soil organic matter ($300\text{ mmol kg}^{-1}\text{ pH}^{-1}$) (Helling et al., 1964), which is attributed to the difference in the nature and amount of functional groups.

3.3. Nutrient adsorption

The batch adsorption data for the bark and zeolite samples were adequately described by the Langmuir equation (Eq. (1)) (Table 3). The parameter S_m indicates that zeolite retained greater amounts of NH_4^+ and K^+ than the untreated bark with less difference in H_2PO_4^- retention between the porous materials. Greater retention of NH_4^+ , K^+ and H_2PO_4^- ions was obtained for the FBA-treated bark than for the untreated bark. From the CEC values it was estimated that the maximum adsorption for NH_4^+ by the untreated bark, treated bark, and zeolite were 13.4, 18.8 and 21.8 g kg^{-1} , respectively. The respective values for K^+ retention were 37.4, 52.5 and 60.8 g kg^{-1} . In the case of zeolite, the adsorption maxima for NH_4^+ and K^+ ions calculated from Eq. (1) were close to its CEC indicating that the adsorption obeyed a simple ion-exchange process (Nguyen and

Table 2
Particle size analysis (PSA), pH and cation exchange capacity (CEC) characteristics of bark and zeolite

Characteristic	Bark		Zeolite
	Untreated	Treated	
pH	5.65 (± 0.34) a	7.82 (± 0.24) b	6.2 (± 0.34) a
PSA (g kg^{-1})			
2.0–4.0 mm	271 (± 11) a	256 (± 14) a	45 (± 3.5) b
0.2–2.0 mm	586 (± 14) a	486 (± 18) b	453 (± 12) c
$<0.2\text{ mm}$	152 (± 12) a	258 (± 16) b	502 (± 14) c
CEC (mmol kg^{-1})	958 (± 22) a	1346 (± 43) b	1558 (± 16) c

\pm Standard deviation.

Averages within a row followed by same letters are not significantly different at $P \leq 0.05$ level, $n = 4$.

Table 3

Parameters of Langmuir equation (Eq. (1)) describing the adsorption of NH_4^+ , H_2PO_4^- , and K^+ ions by the bark and zeolite, and percent saturation of CEC by NH_4^+ and K^+ ions

Nutrient ion	Parameter	Bark		Zeolite
		Untreated	Treated	
NH_4^+	S_m	14.52 (± 2.65) a	21.36 (± 3.51) b	20.35 (± 2.84) b
	b	0.526 (± 0.082) a	0.487 (± 0.12) a	0.453 (± 0.075) a
	R^2	0.724	0.632	0.876
	Saturation (%)	108.3	113.3	93.3
H_2PO_4^-	S_m	3.56 (± 0.84) a	16.52 (± 4.21) b	2.17 (± 0.52) c
	b	0.672 (± 0.143) a	0.764 (± 0.241) a	0.452 (± 0.089) a
	R^2	0.564	0.435	0.663
K^+	S_m	33.69 (± 5.62) a	49.53 (± 6.25) b	58.52 (± 4.25) c
	b	0.421 (± 0.085) a	0.462 (± 0.12) a	0.382 (± 0.15) a
	R^2	0.673	0.583	0.865
	Saturation (%)	90.1	94.4	96.3

\pm Standard deviation.

Averages within a row followed by same letters are not significantly different a $P \leq 0.05$ level, $n = 4$.

Tanner, 1998; Green et al., 1996). Whereas in the case of bark, although the maximum adsorption for K^+ was close to its CEC, adsorption of NH_4^+ exceeded the CEC, indicating that some NH_4^+ ions were immobilized to organic N, which was more pronounced in the pilot-scale experiment.

The strong affinity of zeolite for cation retention, attributed mainly to its high CEC has been demonstrated (Nguyen and Tanner, 1998). The cation adsorption capacity varied with the crystalline nature and particle size of zeolite, and the ionic composition of the aqueous medium. For example, Nguyen and Tanner (1998) obtained maximum NH_4^+ adsorption values of 5.77 and 8.28 g kg^{-1} for clinoptilolite and mordenite, respectively, which varied in CEC. Similarly, Bernal and Lopez-real (1993) obtained a range in NH_4^+ adsorption (8.15–15.17 g N kg^{-1}) for a number of zeolite samples that varied in particle size. Booker et al. (1996) observed that the amount of NH_4^+ adsorbed (4.5 g kg^{-1}) from sewage water by an Australian zeolite was less than its CEC value, which was attributed to the competition for adsorption sites by other ions.

The increases in the retention of NH_4^+ , K^+ and H_2PO_4^- ions by the FBA-treated bark is due to the increase in the CEC of the material and the precipitation of H_2PO_4^- ion. FBA contained Ca and Mg oxides which enhanced the precipitation of H_2PO_4^- as Ca and Mg phosphates. Precipitation as magnesium and ammonium phosphate [struvite— $\text{Mg}(\text{K}, \text{NH}_4)(\text{PO}_4) \cdot 6\text{H}_2\text{O}$] is a common process of H_2PO_4^- removal from wastewater rich in NH_4^+ and H_2PO_4^- ions. For example, Webb and Ho (1992) and Weaver and Ritchie (1994) observed that the treatment of piggery effluent with liming materials such as dolomite reduced the concentration of P in solution through precipitation as calcium phosphate and struvite formation.

3.4. Removal of nutrients from effluent

The results from the pilot-scale field experiment showed that bark treatment achieved a considerable reduction in the concentration of N (Fig. 3). The mean concentrations of N in the untreated effluent, treated effluent in the absence of bark and the treated effluent in the presence of bark were 145.4, 95.4 and 18.7 g m^{-3} , respectively. The N concentrations in the bark treated effluent were much less than the estimated maximum permissible level (MPL) value (75 g m^{-3}) for the direct discharge of the effluent to the waterway and reached close to the recommended MPL value (0.22 g m^{-3}) in stream water (Hickey and Vickers, 1994). Bark treatment achieved a significant reduction in the concentration of P in the effluent. The P concentrations approached the estimated MPL value (3 g m^{-3}) for the direct discharge of the effluent, but were still higher than the recommended MPL value (0.02 g m^{-3}) in stream water. There was only a small reduction in the concentration of K by bark treatment. There is no guideline for MPL for K concentration in stream water as it is not considered a significant water pollutant. Treatment with bark caused a considerable reduction in the concentration of TSS, BOD and COD in the effluent (Table 4). The BOD values in the bark treated effluent were much less than the estimated MPL value (100 g m^{-3}) for effluent discharge to the waterway but were still higher than the recommended MPL value (5.0 g m^{-3}) in stream water. Bark treatment achieved almost complete removal of TSS, indicating that the bark materials was an effective filtering medium for suspended solid and there was no indication of the breakdown of the bark material within the 6 months of period of the pilot-scale study.

The MPL value in the stream water gives the concentration above which the BOD and the N and P

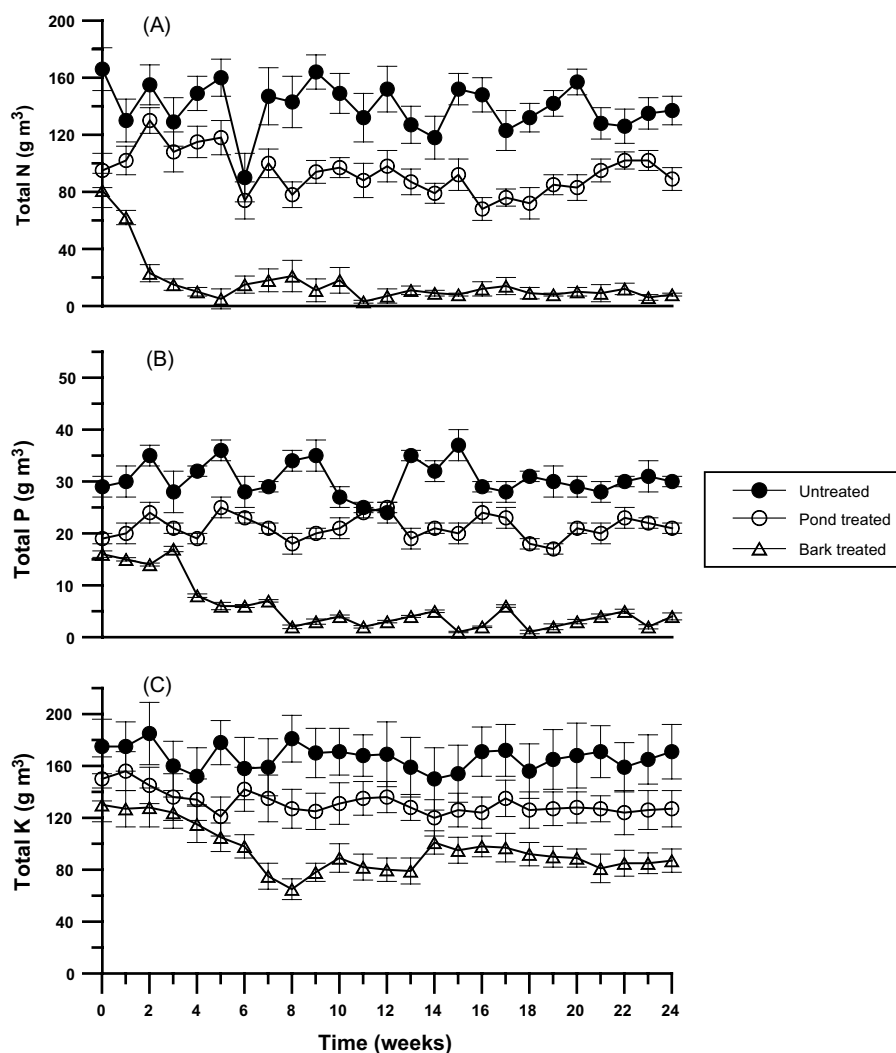


Fig. 3. The effect of bark treatment on the concentration of (A) nitrogen, (B) phosphate and (C) potassium in the pond effluent in the pilot-scale experiment ((●) untreated, (○) pond treated and (△) bark treated).

Table 4

Concentration of biological oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solids (TSS) at different stages of bark treatment

Characteristic	Time (weeks)	Concentration (g m^{-3})			Percent removal	
		Anaerobic inlet	Aerobic outlet		Without bark	With bark
			Without bark	With bark		
BOD	1	235 (± 28) a	95 (± 18) b	85 (± 20) b	59.0	63.8
	12	210 (± 25) a	110 (± 15) b	62 (± 12) c	47.6	70.4
	24	195 (± 21) a	105 (± 12) b	55 (± 8) c	46.2	71.4
COD	1	855 (± 124) a	420 (± 62) b	320 (± 41) c	50.8	62.6
	12	910 (± 102) a	452 (± 51) b	215 (± 18) c	50.3	76.4
	24	780 (± 89) a	395 (± 62) b	185 (± 21) c	49.4	76.2
TSS	1	380 (± 41) a	120 (± 18) b	68 (± 21) c	68.4	68.4
	12	410 (± 35) a	95 (± 22) b	32 (± 11) c	76.8	92.1
	24	350 (± 51) a	105 (± 21) b	25 (± 9) c	70.0	92.8

Percent removal was calculated as shown in Table 1.

\pm Standard deviation.

Averages within a row followed by same letters are not significantly different a $P \leq 0.05$ level, $n = 10$.

Table 5

Loading of nutrients, nutrient retention capacity of the bark and the amount of bark required to retain the nutrients in the effluent

Nutrient	Deposited (g cow ⁻¹) ^a	Retention capacity ^b (g kg ⁻¹ bark)	Amount of bark required	
			(kg cow ⁻¹ day ⁻¹)	(m ³ farm ⁻¹ yr ⁻¹) ^c
Nitrogen	10.42	25.52	0.41	115
Phosphorus	1.76	8.56	0.21	59.6
Potassium	8.72	23.4	0.38	104

^a Calculated for a 500 kg cow spending a total of 180 min per day at the milking shed and holding yards.^b Obtained from the pilot-scale experiment.^c Calculated for a herd of 250 cows for a milking period of 270 days (August–April); the bulk density of the bark is 0.24 Mg m⁻³.

nutrients affect the water quality mainly by enhancing algal growth. Whereas the estimated MPL value in the effluent gives the concentration above which the BOD and the N and P nutrients in the effluent increases the concentration of these contaminants above MPL in the stream water when the effluent is discharged. It is important to point out that the MPL values for the direct discharge of the effluent to the waterway were estimated on the basis of dilution, which depends on the flow rate in the waterway and the volume of the effluent produced.

At the end of the trial the bark samples were analyzed for total N, P and K (Table 5). The results from the pilot-scale study showed that the bark materials retained higher levels of N and P than that predicted from the batch adsorption study. In the batch adsorption study, the adsorption of N and P was achieved mainly through physico-chemical adsorption onto cation and anion exchange sites and the maximum adsorption values were 14.52 gN kg⁻¹ and 3.56 gP kg⁻¹. Whereas in the pilot-scale study the adsorption values were 25.52 gN kg⁻¹ and 8.56 gP kg⁻¹. This indicates that in the case of the later experiment, microbial immobilization of N and P played an important role in the retention of these nutrients. The composted bark material used in the pilot-scale study provided a good carbon source for microbial growth.

Mass balance calculation indicated that, although most of the P and K (98–105%) added through effluent application was recovered in the bark and the leachates, only 68% of the added N was recovered. This indicates that some of the N was lost through ammonia (NH₃) volatilization and/or denitrification. Since the pH of the bark medium (6.2) was less than the pK_a value (7.6) for the dissociation of NH₄⁺ ion to NH₃ and H⁺ ions, NH₃ volatilization may not be a major process. A number of workers have shown that carbon-rich materials, such as sawdust and bark are effective in the removal of NO₃-N from wastewater and drainage effluents through denitrification process (Blowes et al., 1994; Schipper and Vojvodic-Vukovic, 2000).

While a number of studies have examined the potential value of zeolite to trap nutrients from wastewater, only limited work has been conducted on the value of bark. Cintoli et al. (1995) observed that treating

prescreened piggery wastewater using zeolite reduced NH₄⁺ concentration from 1500 to 400 mg l⁻¹. The ion-exchange pretreatment by zeolite led to a reduction in the toxicity of wastewater to the anaerobic microbial population, thereby improving the subsequent anaerobic treatment. Green et al. (1996) observed that zeolite was effective in NH₄⁺ retention by the process of ion-exchange and the subsequent release of the adsorbed NH₄⁺ was induced through nitrification by active biomass co-immobilized onto zeolite (Yang, 1997).

Lens et al. (1994) observed that pine bark achieved a reduction of 72% TSS, 63% COD, 97% BOD, 64% NH₄⁺-N, and 35% total N from wastewater. Composted bark has been found to be efficient in the removal of Cu (Reddy et al., 1997) and Cr (Gaballah et al., 1994) from aqueous solutions through the process of ion-exchange/complexation. Pine bark has often been found to be an effective growing medium due to its ability to retain both nutrients and water (Handreck, 1993; Chong et al., 1994; Spiers and Fietje, 2000). Bark is commonly used as a biofilter medium to remove odour from a number of industries (Andreoni et al., 1997; Luo and van Oostrom, 1997).

Based on the nutrient retention capacity of the bark measured from the pilot-scale experiment, the quantity of bark required to remove the nutrients in the dairy farm effluents was calculated (Table 5). Currently there are approximately 14 700 dairy farms in New Zealand with an average herd size of 200. At a preliminary estimate of 115 m³ bark per dairy unit, approximately 1.69 million m³ bark is required annually to remove the nutrients from the dairy farm waste water. Annually the timber industry in New Zealand produces about 2.5 million m³ bark most of which is land-filled. The fertilizer value of the nutrients (N, P and K) retained in this bark is approximately equivalent to 390 000 tons urea (460 gN kg⁻¹), 602 000 tons of single superphosphate (95 gP kg⁻¹) and 329 000 tons of muriate of potash (500 gK kg⁻¹).

4. Conclusions

The study indicated that biological treatment of farm effluents using a two-pond system was not effective in

the removal of nutrients and these nutrients become pollutant when discharged to waterways. However, when the pond treatment was improved with the use of porous bark and zeolite materials the N, P and K removal from the effluent was effective. These materials can be placed in the second (aerobic) pond to treat effluent, which then can be discharged to streams with minimum impact on water quality.

The effluent treated porous materials can be used as a source of nutrients that can be spread onto the farm and also as a mulching material to conserve soil moisture and as a bedding material for vermicomposting. The nutrient-enriched bark materials can be used as a slow release source of nutrients, especially for organic production. The C:N ratio of the nutrient-enriched bark material was much less than (19.1:1) than that of the original bark (115:1), indicating that the incorporation of the enriched material is likely to result in the release of nutrients (mineralization) for plants uptake.

Large quantities of bark are produced as a waste by-product from the timber industry in New Zealand. The bark-filter system is a low-input technology that can be used not only to remove nutrients from farm effluent but also pollutants from domestic and industrial wastewaters.

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