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Leachate treatment using a novel sustainable fixed bed-based method

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ABSTRACT

Toxic and environmentally damaging leachate is the product of municipal solid waste disposal in landfill systems. Currently, 51% of landfill leachate (LFL) produced in Irish landfill sites is discharged directly into sewer mains with 48% being treated in increasingly overloaded regional wastewater treatment plants. These discharge and treatment options are inadequate and costly and pose risks for both public and environmental health. Unlike other European Union countries, onsite treatment of leachate in Ireland is uncommon (<1%), but could represent a viable and sustainable alternative to current practices. This study utilises a fixed bed column system to treat LFL. This system combines both bioremediation and adsorption into combined process. This research has shown that low-cost adsorption materials, such as oyster shells and pumice, are capable of reducing the concentration of ammonia, phosphate and nitrate from leachates. In addition, microbial isolates from leachate have demonstrated the ability to reduce toxic compounds, such as biological oxygen demand (BOD) and chemical oxygen demand (COD). This treatment has the ability to reduce landfill leachate (LFL) below the acceptable limits set by the Environmental Protection Agency (Ireland) for the discharge of leachate into receiving bodies. Ammonia, phosphate and nitrate were all treated to discharge limits and had a ≤94% overall removal of each compound, while BOD and COD had removals of 91% and 96% but exceeded the national discharge limits. These results demonstrate that leachate can be treated effectively by bioremediation and adsorption in a combined column system, which has the potential to implemented as a novel cost-effective onsite treatment method for LFL in Irish landfill. Further research is now required to test this system with larger volumes of LFL which vary in composition and concentration.

Keywords: Landfill leachate; Novel treatment; Wastewater; Bioremediation; Adsorption

1. Introduction

Landfill leachate (LFL) production and management are one of the greatest problems associated with municipal solid waste (MSW) landfills. The generation of MSW waste continues to grow due to population growth, industrial activities and lifestyle changes [1,2]. While there has been a decline in the number of landfills in the recent years, the generation of leachate is a legacy problem and its treatment is a major management issue for landfills operators within the European Union (EU) [3–5]. LFL is defined by McCarthy et al. [6] as 'liquid, which has percolated through the waste, picking up suspended and soluble materials that originate from or are products of the degradation of the waste'. As liquid penetrates through the solid matrix, it assists with biochemical, chemical and physical reactions, directly influencing the quality and quantity of the leachate produced [7]. Leachate, a chemical cocktail, is a major

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drawback of MSW landfills, as they continue to produce leachate for hundreds of years after the landfill is decommissioned [2,5,8]. The correct treatment of LFL is essential for the protection of the surrounding environments as uncontrolled discharge has the potential to impact negatively on ground and surface water resources.

Many methods are used to treat LFL; however, most are adapted from wastewater treatment methods. Usually, a combination of both biological and physiochemical methods is effective as it can be difficult to obtain satisfactory results with just one method due to diverse quality of LFL [9,10]. For example, LFL with a high organic content is best treated using biological methods, whereas LFL with a low organic content is best treated using physicochemical methods [11]. A number of treatment options have been successfully employed to treat LFL. A study carried out by Paskuliakova et al. [12] applied chlorophytes to reduce the total ammonia nitrogen and total organic nitrogen. Zayen et al. [13] combined processes of anaerobic digestion, lime precipitation microfiltration and reverse osmosis to treat LFL, while Kaur et al. [14] used cow dung ash as an adsorbent material to assess for the removal of organic material. Despite the success of these treatments, it is important to investigate other options, especially those that are low cost and can be implemented onsite in Irish landfills.

Currently, in Ireland, over 50 urban wastewater treatment plants (WWTPs) receive and treat MSW LFL, requiring transport and costly aerobic biological treatment. Volumes and composition of LFL collected at these sites vary greatly depending on the content, size and age of the specific landfill [6]. In 2013, there were approximately 1.1 million m^3 of LFL collected in Ireland, which was discharged directly either to sewers (51%) or transported to WWTPs (48%) for final treatment, with only 1% receiving any onsite treatment [15]. Out of the six current onsite treatments in Ireland, only three are directly discharged to receiving bodies. Treatment of leachate in WWTPs is not effective, as the systems employed in these treatment centres are often inadequate and do not effectively treat leachate to the discharge limits. Another drawback for WWTPs is the stringent emission limits. Noncompliance with ammonia and total nitrogen emission values in WWTPs has been attributed to leachate loading at these plants, resulting in the discontinuation of leachate acceptance by these facilities. This has resulted in a 30% decrease in the number of WWTPs treating leachate from 2010 to 2015 [4,6,15]. As such, it is of economic and environmental importance to investigate the best way to treat LFL, in order to develop a cost-effective, suitable treatment that will ultimately reduce LFL constituents to required discharged limits.

The main purpose of this study was to combine both biological, in terms of bioremediation, and the physicochemical treatment by adsorption, into a novel cost-effective system to treat LFL. This study utilised low-cost adsorption material and microorganisms isolated from leachate to treat LFL from an Irish landfill. Both treatment processes were combined into a continuous fixed bed system. The main objectives of the study were twofold: (1) to evaluate the effectiveness of the fixed bed system in terms of overall percentage removal efficiencies of ammonia, phosphate, nitrates, biological oxygen demand (BOD) and chemical oxygen demand (COD) and (2) to treat LFL to discharge limits set by Environmental Protection Agency (EPA), Ireland, for the discharge of wastewater to receiving bodies.

2. Materials and methods

2.1. Site description and sampling

LFL used in this study was sourced from Powerstown Landfill, Co. Carlow, Ireland (52°45′58.46″N, 6°57′20.13″W). The landfill is located 8 km south-east of Carlow town in a rural setting and has been operational since 1975. The site consists of three different phases: Phase 1 which operated from 1975 to 1990, Phase 2 which operated from 1991 to 2006 and Phase 3 opened in 2006 and is due close in late 2018. Phase 3 consists of four-lined cells, surface water settlement pond, leachate tank and green waste composting area. Leachate collection systems are in operation in both Phase 2 and Phase 3. It was decided to use LFL generated in Phase 3 as it is currently in operation and generates a more concentrated leachate than the other phases. LFL samples were collected in January and February 2017 from the leachate tank and stored at 4°C until use within 48 h.

2.2. Experimental setup

2.2.1. Continuous fixed bed system setup

Three sequential polyvinyl chloride columns (11 cm internal diameter, 30 cm height and IC 2,850 cm^3) were utilised in this study (Fig. 1). The first column (C1) was packed with c. 1 kg of soil (Westland Top soil) to a height of 20 cm. This soil was inoculated with a microbial master mix ($OD_{600} = 0.8$) that contains 18 previously isolated leachate degrading microorganisms (GenBank accession numbers: MG880063–MG880077) in nutrient broth (Lab M, United Kingdom). These organisms belong to the *Firmicutes*, *Actinobacteria* and *Proteobacteria* phylums, which were previously isolated from environmental sources. The soil/microbial isolate mixture was left to incubate for 48 h at room temperature (20°C) after which the excess liquid was allowed to drain off. The second column (C2) was packed with c. 1.3 kg of crushed oyster shells (particle size 5–10 mm) (Harty Oyster Farm, Dungarvan, Waterford, Ireland) to a height of 20 cm. The final column (C3) was packed with 0.65 kg of pumice stone (particle size 2–5 mm) (Lennox, Ireland) to a height of 20 cm. Both adsorption materials were prepared by triple washing with deionised water and dried at 100°C for 24 h [16,17]. Before commencement of the experiment, deionised water was washed through the column in a downflow direction to withdraw trapped air between the materials. Prior to this trial, batch studies were carried out using adsorbent materials, over a range of concentration, to determine whether both materials were suitable for adsorption [18–20].

2.2.2. Mathematical description of continuous fixed bed system

The performance of a packed bed is often described using the concept of a breakthrough curve (BTC). The time until the sorbed molecule is detected in the effluent and the shape of the BTC curve are very important characteristics for operation and process design of a biosorption column [21–23].

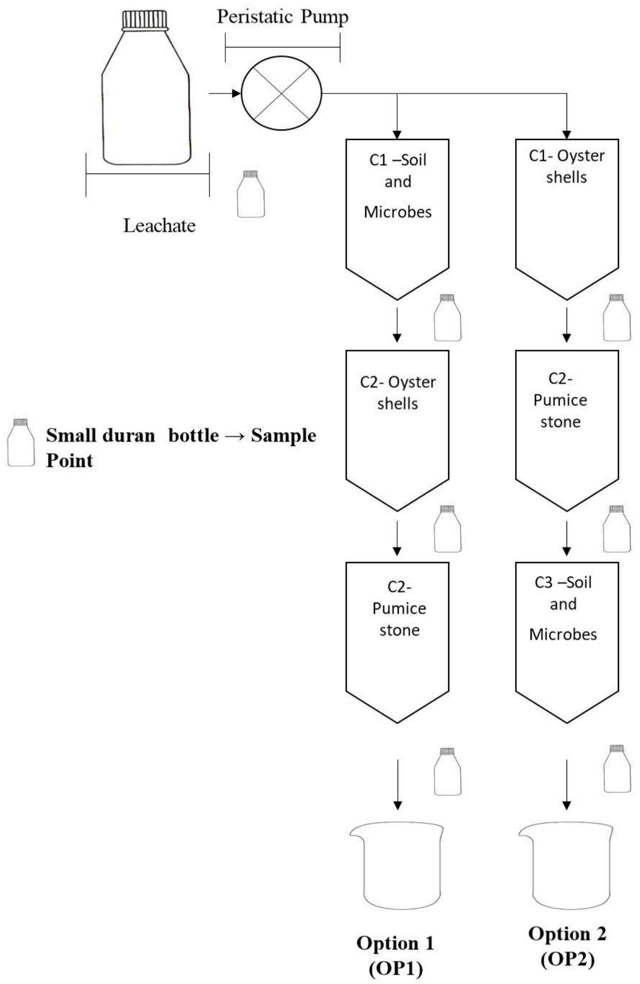

Fig. 1. Fixed bed system setup—with the different treatment options.

Experimental determination of these parameters is very dependent on column operating conditions, such as influent concentration and flow rate. A BTC is expressed as the influent/effluent (C/C_o against time (T)). The area (A) under the BTC can be obtained from this plot using trapezoidal rule. From this, we can then calculate the overall percentage removal of ammonia, phosphate, nitrates as well as BOD and COD using the following equations [23–25]:

The Q_{total} determines the total amount of pollutant adsorbed by the column:

$$Q_{\text{total}}\left(\text{mg}\right)=\frac{QA}{100}=\frac{Q}{1,000}\int_{t=0}^{t=T_{\text{total}}}C_{\text{ad}}dt \tag{1}$$

The total amount of ions delivered to the system (M_{total}) is determined by the following equation:

$$M_{\text{total}}\left(\text{mg}\right)-\frac{C_o.Q.T_{\text{total}}}{1,000} \tag{2}$$

In this equation, the Q and the T_{total} represent the flow rate (mL min^{-1}) and the total flow time (min), while C_o is the effluent concentration. Both equations are required to evaluate the removal efficiency of the column. Total percentage removal was calculated as follows:

$$\text{Total removal}\left(\%\right)=\frac{Q_{\text{total}}}{M_{\text{total}}}\times 100 \tag{3}$$

2.2.3. Optimisation and operation of column system

Optimisation of the fixed bed system was carried out by determining the best flow rate and order in which the columns should be placed. Two flow rates, 10 and 5 mL min^{-1}, were initially utilised in batch experiments to determine the optimum conditions for pollutant removal. The surface loading rate for each flow rate was 5.3 L h^{-1} m^{-2} for 10 mL min^{-1} and 2.65 L h^{-1} m^{-2} for 5 mL min^{-1}. The column was optimised further by changing the order in which the columns were placed. Option 1 (OP1) consisted of C1 – soil, followed by C2 – oyster shells, and a final C3 – pumice column (Fig. 1). Option 2 (OP2) consisted of C1 – oyster shells, followed by C2 – pumice, and a final C3 soil column (Fig. 1). Both trials were carried out over a 3 h period. For the purpose of optimising the fixed bed system and determining the effectiveness of each option, ammonia, phosphate and nitrate concentrations of effluent samples were analysed. Once the system was optimised, 5 L of LFL was actively pumped into the column at the determined optimal flow rate and allowed to filter via gravity into C1, C2 and C3 sequentially over a 16 h period. All trials were carried out at room temperature (20°C ± 2°C).

2.3. Influent and effluent analysis

Influent (LFL) and effluent samples were analysed before and after each sampling point as indicated in Fig. 1. All reagents used were of analytical grade and supplied by Sigma-Aldrich, Ireland unless otherwise stated. Ammonia (NH_3–N) was analysed using the phenate method [26] and analysed on Shimadzu UV1800 Spectrophotometer BOD was tested over 5 d (BOD_5) using a Hanna dissolved oxygen meter [26]. COD was analysed using HACH Lange COD vials. Phosphate (PO_3) was analysed using molybdovanadate reagent (HACH Lange Ireland), and nitrate (NO_3–) analysis was carried out using NitraVer® 5 reagent powder pillows (HACH Lange Ireland). All HACH products were used according to manufactures instruction and measured on HACH DR 6000 UV Spectrophotometer.

3. Results and discussion

3.1. Leachate composition and characterisation

The chemical composition of leachate used in this study was analysed and compared with known readings from Powerstown Landfill, supplied by Carlow Co. Council, Ireland, during the period 2009–2016 (Table 1). There are various factors that affect the parameters of leachate including age, precipitation, seasonal weather variation, waste type and composition [7,27–29]. LFL was analysed before treatment to access the stage of waste degradation that had occurred in the landfill in order to determine the best treatment option. It is known that a landfill has different phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis, and leachate composition differs at each phase [30–32]. During each phase, the characteristic of the leachate changes significantly; leachate in the hydrolysis–acetogenesis phase (landfill < 10 years old) is known for having pH of ≤6.5 and having high concentrations of BOD and COD, as well as a BOD_5/COD ratio of <0.6. While older landfill (10+ years) in the methanogenic phase are known for having COD < 4,000 mg L^{-1} O_2, high level of ammonia–nitrogen >400 mg L^{-1} and a low BOD_5/COD ratio of <0.01 [7,28,33,34]. BOD_5 from Powerstown varies from 46 to 180 mg L^{-1} O_2, and the current EPA limit for BOD_5 is set at 5 mg L^{-1} O_2 (Table 1). COD ranges from 450 to 650 mg L^{-1} O_2, with EPA limits set at 40 mg L^{-1} O_2. According to Christensen et al. [34] and Jokela et al. [35], this leachate would classify the landfill being in the methanogenic phase, which is determined by a COD range of 500–4,500 mg L^{-1}. The BOD_5/COD ratio is good at determining the organic composition of leachate, and it is a good representation of waste stabilization, the transition from early acetogenic phase to the mature methanogenic phase. In young landfills, this ratio is high and falls in mature landfills. Ratios between 0.4 and 0.6 are an indicator that the organic matter in the leachate is biodegradable. In mature landfills, this ratio is often in the range of 0.05–0.2, and this ratio drops because leachate from mature landfills typically contains humic and fulvic acids, as well as recalcitrant organic compounds, which are not biodegradable [34,36–38]. The BOD_5/COD ratio ranges from 0.18 to 0.26 indicating that leachate is stable and could be difficult to treat biologically but should respond well to physicochemical treatments.

Leachate is known for having a high concentration of ammonia, and this is a critical problem as it promotes algae growth, accelerates eutrophication and decreases the effectiveness of biological treatments [39,40]. In addition, ammonia can continue to leach from landfills for up to 50 years after their decommission and can be difficult to treat in WWTPs [5,41]. The ammonia levels in the Powerstown leachate used in this study ranged from 790 to 1,010 mg L^{-1} (Table 1), and these high levels correspond to methanogenic phase [7,33,42]. High levels of ammonia are one of the main factors contributing to the 30% decrease in WWTPs accepting leachate from 2010 to 2014 within Ireland [43]. It is therefore essential to use a treatment option, be it biological or physicochemical, that can reduce ammonia level to discharge limits.

Table 1
Composition of leachate from Powerstown landfill from 2009 to 2015, leachates used in this study and the discharge limits set by the EPA

Compound	Powerstown leachate 2009–2016[a]	Leachate used in this study	EPA limits (mg L^{-1})
Ammonia (mg L^{-1} N)	360–960	790–1,040	≤4
BOD (mg L^{-1} O_2)	46–1,322	112–170	≤5
COD (mg L^{-1} O_2)	539–3,005	450–650	≤40
Nitrate (mg L^{-1} N)	NM[b]	89–120	≤50
Phosphate (mg L^{-1} P)	1.2–7.4	3.6–7.25	≤0.4

[a]Sampling did not occur in 2010 or 2013. [b]NM = Not measured.

3.2. Optimisation of fixed bed system

Prior to running this trial, adsorption material was subject to batch studies for adsorption isotherm. Both adsorption materials followed the Langmuir model, giving adsorption capacity for ammonia of 1.03 mg L^{-1} N for Oyster shells and 1.19 mg L^{-1} for pumice.

3.2.1. Effects of flow rate

It was the hypothesis that slower flow rates with a higher retention time (RT) could result in a greater percentage removal of each compound analysed. In this study, two flow rates were examined, 5 and 10 mL min^{-1}, for which the RT was 150 and 110 min, respectively. For all three compounds examined, there was a higher percentage removal achieved at 5 mL min^{-1} for phosphate and nitrate, while ammonia did not show a large deviation. There was a difference between the two flow rates for ammonia of 0.3% and nitrate of 1.26%, respectively (Fig. 2). The mean effluent concentration of ammonia at 5 mL min^{-1} was 4.2 ± 0.5 mg L^{-1} N, which is slightly above the EPA limit of 4 mg L^{-1}, while for the 10 mL min^{-1} flow rate, the mean effluent value was 7.14 ± 1.48 mg L^{-1} N. The mean concentration for nitrate, at both flow rates, was below the EPA limit of 50 mg L^{-1} N (Fig. 2). Phosphate showed the largest difference in percentage removal of 5.5% between each flow rate. Similar to ammonia, the mean effluent concentration was below the EPA limits for 5 mL min^{-1} at 0.287 mg L^{-1} P, while 10 mL min^{-1} final effluent was above the EPA guidelines. Overall, the 5 mL min^{-1} flow rate showed the greatest removal for the three compounds tested, possibly due to the longer RT, and as such was used in the subsequent LFL trial.

3.2.2. Effects of column position

In order to optimise the fixed bed system further, it was essential to look at the different order in which treatment could occur. The order of the columns was based on a two-step treatment process: (1) bioremediation and (2) adsorption (Fig. 3). Option 1 (OP1) looked at bioremediation first followed by adsorption. The order of the column was as follows: C1 – soil and microbial isolates, C2 – oyster shells, and C3 – pumice. Option 2 (OP2) placed adsorption first

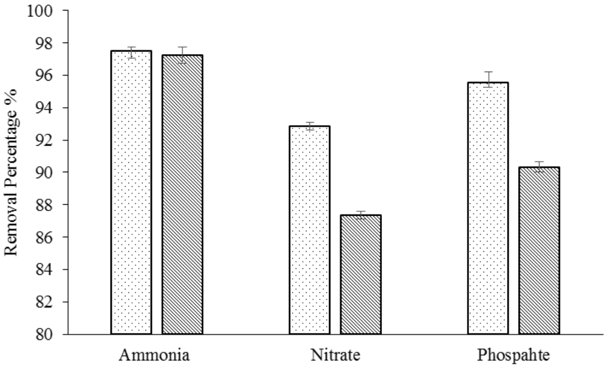

Fig. 2. Removal percentage efficiencies of compounds tested at 5 mL min^{-1} (□) and 10 mL min^{-1} (▨) flow rates.

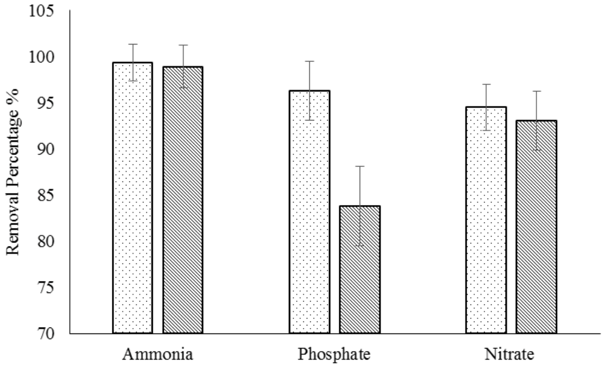

Fig. 3. Removal percentage, for the effects of column position for both option 1 (░) and option 2 (▒).

followed by bioremediation: C1 – oyster shells, C2 – pumice, and C3 – soil and microbial isolates. Overall, the phosphate was the only compound that shows a major difference in percentage removal (Fig. 3). There was a difference of 12%, in both options for phosphate. Both ammonia and nitrate show deviation between the two options of 0.3% and 1.4% (Fig. 3), respectively. Overall, OP1 showed the greater percentage removal for each compound tested; therefore, this will be used in further studies.

3.3. Optimised column study

The system was operated using the OP1 (Fig. 2) configuration with a 5 mL min^{-1} flow rate. The system's influent and effluent were analysed routinely after each column and analysed as described earlier to determine the percentage removal rates of COD, BOD, ammonia, nitrate and phosphate.

3.3.1. C1 – bioremediation

The results from C1 indicated that ammonia, phosphate and nitrate % removal efficiencies were 74%, 47% and 56%, respectively (Table 2). Despite this reduction, specifically for ammonia, none of the parameters measured reached the EPA discharge limits after treatment in C1, with final effluent concentrations of 108 mg L^{-1} N of ammonia, 2.75 mg L^{-1} P of phosphate and 82 mg L^{-1} N of nitrates (Table 2). However, it should be noted that the RT of C1 was 90 min and percentage removal efficiencies may be improved by increasing this to allow more contact time between the microorganisms and the influent. In addition, the application of effluent recycling within C1 could further improve bioremediation of these constituents. Interestingly, both BOD and COD showed reductions >80%. This was unexpected, as previously described (Section 3.1) as leachate from Powerstown is of a mature nature, which should not respond well to biological treatment.

Table 2
Influent and effluent concentrations and total percentage removal of compounds tested for Column 1 containing soil and microbial isolates

	Influent concentration[a] (mg L^{-1})	Effluent concentration[a] (mg L^{-1})	Removal efficiency (%)
Ammonia (mg L^{-1} N)	428 ± 2.5	108 ± 2.1	74.7
Phosphate (mg L^{-1} P)	5.2 ± 0.6	2.7 ± 0.6	47.7
Nitrate (mg L^{-1} N)	187.3 ± 1.2	82 ± 1.6	56.2
BOD (mg L^{-1} O_2)	150 ± 1.5	15.2 ± 1.5	89.8
COD (mg L^{-1} O_2)	650 ± 2.3	125.3 ± 2.4	80.7

[a] All results for influent and effluent concentration are presented as mg L^{-1} ± standard deviation.

Table 3
Influent and effluent concentrations and total percentage removal of compounds tested for Column 2 containing oyster shells

	Influent concentration[a] (mg L^{-1})	Effluent concentration[a] (mg L^{-1})	Removal efficiency (%)
Ammonia (mg L N)	108 ± 2.1	24.6 ± 1.4	77.1
Phosphate (mg L P)	2.8 ± 0.6	1.1 ± 0.2	57.0
Nitrate (mg L N)	82 ± 1.6	52.2 ± 1.9	36.3
BOD (mg L O_2)	15.3 ± 1.5	7.5 ± 1.4	50.1
COD (mg L O_2)	125.4 ± 2.3	94 ± 1.3	24.8

[a] All results for influent and effluent concentration are presented as mg L^{-1} ± standard deviation.

3.3.2. C2 – adsorption 1 – oyster shells

Oyster shells, a readily available waste product of the aqua industry within Ireland, were chosen as the adsorption material of C2. Results for C2 showed it was particularly effective in reducing ammonia with a ≥77% removal efficiency recorded (Table 3) from the previous effluent concentration (C1). Results also indicated C2 was effective in reducing phosphate and nitrates (Table 3). However, neither were reduced below discharge limits after this treatment with effluent levels at 1.18 mg L^{-1} P and 52.23 mg L^{-1} N (Table 3). Similarly, BOD and COD were reduced by 51% and 24%, respectively (Table 3), but did not meet the discharge limits (Table 3). Low percentage removal was expected as physiochemical treatment is not known for reducing the level of organic matter. Overall, the results for C2 have indicated that physicochemical treatment is an effective option for the treatment of mature leachate.

3.3.3. C3 – adsorption 2 – pumice stone

Pumice, a volcanic stone, was used as the final low-cost adsorbent material. A study by Çifçic et al. [44] highlights that pumice is known for its ability to remove contaminants from wastewaters, such as heavy metals, ammonia and phosphorus. The aim of this column was to act as a fine filter for the removal of the remaining compounds analysed. Results of the effluent analysis of C3 indicate that over a 10 h period, ammonia, phosphate and nitrates were treated to discharge limits. Despite this, C3 proved to be ineffective for the removal of COD and BOD with percentage removal less than <42% and 26%, respectively (Table 4).

Table 4
Influent and effluent concentrations and total percentage removal of compounds tested for Column 3 containing pumice stone

	Influent concentration[a] (mg L^{-1})	Effluent concentration[a] (mg L^{-1})	Removal efficiency (%)
Ammonia (mg L N)	24.6 ± 1.4	2.3 ± 1.1	90.6
Phosphate (mg L P)	1.1 ± 0.2	0.2 ± 0.1	76.2
Nitrate (mg L N)	52.2 ± 1.9	4.2 ± 1.3	91.9
BOD (mg L O_2)	7.5 ± 1.4	5.5 ± 0.9	26.2
COD (mg L O_2)	94 ± 1.3	55 ± 1.8	41.4

[a]All results for influent and effluent concentration are presented as mg L^{-1} ± standard deviation.

3.3.4. Overall system

In general, results of the combined system were encouraging with the discharge limits set by the EPA for the compounds investigated being reached in the final effluent over a 10 h period (Table 5).

Overall, 99% of ammonia was removed (Table 5) from the system in a relatively short time frame with the final effluent concentration of 2.3 mg L^{-1} N well below the EPA guidelines for discharge to receiving bodies [45]. This is a positive result, as currently in Ireland over 30% of WWTPs are refusing to treat leachate due to the high ammonia concentration and being unable to reach this limit on a regular basis. These stringent emission limits represent a significant threat to the sustainability of cotreatment of leachate with municipal wastewater in WWTPs. The variation in ammonia concentration within leachate also poses a risk to the effective treatment of other wastewaters in WWTPs, due to the ammonia levels within leachate not being disclosed upon acceptance at WWTPs. The ammonia level within leachate can cause WWTPs hitting maximum hydraulic loading for leachate, causing a backlog and storing of leachate onsite [4–6,43]. The combined system shows promise for the removal of ammonia and should show comparable results with a different concentration of ammonia in leachate.

Phosphate contamination of water bodies is a major environmental issue as it can result in algae blooms and eutrophication of ground and surface water. Phosphate levels in leachate from Powerstown show little variation ranging from 3.6 to 7.25 mg L^{-1} P (Table 1). The bioremediation of phosphate (C1) showed promising results, with a reduction of 41% observed after this treatment step (Table 2). Furthermore, treatment with both of the adsorption materials brought the removal of phosphate to 0.28 mg L^{-1} P (Table 4), within the EPA discharge limit of 0.4 mg L^{-1} P. Overall, the combined system affected a 95% removal of phosphate (Table 5), with the greatest removal rate occurring in the adsorption columns at a combined 54%.

Similar to phosphates, nitrate pollution can cause eutrophication in rivers and lakes [46]. Furthermore, if nitrates contaminate potable water supplies, they have the potential to cause methemoglobinaemia, blue baby syndrome, in infants [47]. Ammonia broken down is reduced to nitrite and then to nitrate during the nitrification process. This process is generally carried out by *Nitrosomonas* spp., but other groups of heterotrophic bacteria and fungi can also carry out nitrification, although at a slower rate [48]. Nitrate levels within leachate used in this study did not vary greatly, 89–120 mg L^{-1} N but were all above the EPA limits (Table 1). Results recorded for C1 effluent analysis indicated a low reduction rate of nitrate (56.2%; Table 2), and this may be due to bacteria nitrifying ammonia to nitrate. The Oyster shells column effected a 36.6% removal of nitrate but discharge limit of 50 mg L^{-1} N was not achieved at this stage (Table 3). Finally, in C3, there was a 91% removal of nitrate (Table 4) with the effluent reading below discharge limit of 50 mg L N. Overall, a reduction of nitrate to 4.2 mg L^{-1} N was recorded (Table 5), which is substantially below the discharge limit of 50 mg L^{-1} N, representing a 97% reduction rate.

Unfortunately, BOD and COD discharge limits were not achieved by this system. COD concentrations in the final effluent were 55 mg L^{-1} O_2 which did not reach the EPA discharge limits of 40 mg L^{-1} O_2 (Table 5). Similarly, BOD concentrations in the final effluent were 5.5 mg L O_2, just above the EPA discharge limit of 5 mg L^{-1} O_2. Nevertheless, it is important to note that high percentage removal rates were achieved for both BOD and COD, of 96% and 91%, respectively, using this novel treatment system. These results are positive, and it is believed further optimisation of the system could further improve these effluent removal rates. For example, increasing the RT in C1 or effluent recycling throughout the column, to give more contact time between the microorganisms and the liquor.

4. Conclusion

In conclusion, these results demonstrate that leachate can be treated effectively by bioremediation and adsorption in a

Table 5
Initial influent and final effluent concentration, EPA discharge limit to receiving bodies and overall removal efficiency (%) of combined system

	Influent concentration[a] (mg L^{-1})	Effluent concentration[a] (mg L^{-1})	EPA limits (mg L^{-1})	Removal efficiency (%)
Ammonia (mg L N)	428 ± 2.5	2.3 ± 1.1	≤4	99.4
Phosphate (mg L P)	5.26 ± 0.6	0.28 ± 0.1	≤0.4	94.6
Nitrate (mg L N)	187.33 ± 1.2	4.2 ± 1.3	≤50	97.7
BOD (mg L O_2)	150 ± 1.5	5.53 ± 0.9	≤5	96.3
COD (mg L O_2)	650 ± 2.3	55 ± 1.8	≤40	91.5

[a]All results for influent and effluent concentration are presented as mg L^{-1} ± standard deviation.

combined column system. LFL represents a major problem for MSW landfills; however, this treatment system may represent a cost-effective, novel treatment option within Ireland. The main findings of this study are highlighted below:

- Bioremediation was successful at treating LFL, specifically ammonia which achieved a removal efficiency of ≥99%. It was also the most suitable treatment for BOD and COD, with percentage removals of 89% and 80%.
- Adsorption, using the low-cost material, such as pumice and oyster shells both can reduce ammonia, phosphate and nitrate levels in LFL.
- As a whole, the system employed in this study effectively achieved discharge limits for ammonia, phosphate and nitrate.
- BOD and COD discharge limit were not reached by this system, but may be achieved through leachate recirculation or by increasing the RT in C1, but further studies are needed.

Further research is now required to determine the potential of using this system on larger volumes of LFL which vary in composition and concentration. This system has the potential to be a novel cost-effective treatment method for LFL. Additional research is ongoing to develop and optimise a large-scale on-site treatment system using larger volumes and different concentrations of leachate.

Abbreviation list

LFL	—	Landfill leachate
MSW	—	Municipal solid waste
EU	—	European Union
WWTPs	—	Wastewater treatment plants
EPA	—	Environmental Protection Agency
BOD	—	Biological oxygen demand
COD	—	Chemical oxygen demand
C1	—	Column 1
C2	—	Column 2
C3	—	Column 3
RT	—	Retention time
BTC	—	Breakthrough curve
OP1	—	Option 1
OP2	—	Option 2

List of symbols

C	—	Influent, mg L^{-1}
C_o	—	Effluent, mg L^{-1}
A	—	Area
Q	—	Flow rate, mL min^{-1}
Q_{total}	—	Total amount of pollutant adsorbed by the column, mg
T_{total}	—	Total flow time, min
T	—	Time, min
M_{total}	—	Total amount of ions delivered to the system, mg

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