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Article

Ozonation Pretreatment for Reduction of Landfill Leachate Fouling on Membranes: A Response Surface Methodology Analysis

Everton Gripa *[ID]**, Alyne M. Costa**[ID]**, Juacyara C. Campos** [ID] **and Fabiana V. da Fonseca**[ID]

Inorganic Processes Department, School of Chemistry, Federal University of Rio de Janeiro, Avenida Athos da Silveira Ramos, 149, E206, Rio de Janeiro 21941-909, Brazil; alyne.moraes.costa@gmail.com (A.M.C.); juacyara@eq.ufrj.br (J.C.C.); fabiana@eq.ufrj.br (F.V.d.F.)
* Correspondence: evertongripa@ufrj.br; Tel.: +55-21-98887-7237

Abstract: Batch ozonation was performed to assess its efficacy as a pretreatment for reverse osmosis (RO) membranes for treating leachate with high concentrations of recalcitrant organic compounds. Leachate samples from two different landfills were collected and characterized. The modified fouling index (MFI) was used to estimate the fouling potential of raw and ozonized leachates. A response surface experimental design was applied to optimize operational pH and ozone dose. The results demonstrate that the best operational conditions are 1.5 g/L of O_3 at pH 12.0 and 1.5 g/L of O_3 at pH 9.0 for Landfills 1 and 2, which reduce MFI by 96.22% and 94.08%, respectively. Additionally, they show toxicity factor decays of 98.44% for Landfill 1 and 93.75% for Landfill 2. These results, along with the similar behavior shown by leachate samples from distinct landfills, suggest that ozonation is a promising technology to fit this kind of wastewater into the requirements of RO membranes, enabling their use in such treatment.

Keywords: wastewater treatment; landfill leachate; membranes; fouling; ozone; response surface methodology

1. Introduction

Landfill is the most used technology for the treatment of municipal solid waste (MSW) worldwide [1]. However, the generation of by-products is inevitable during and after its operation. Landfill leachate is one of these undesirable by-products. It is a contaminant liquid that may cause serious environmental problems if not properly drained and treated. Such problems encompass the pollution of surface water and groundwater, which may directly affect the local population and biota [2–4]. It is generated from the microbiological degradation of organic matter contained in the solid waste and water that comes from both its natural moisture and rainwater that percolates the waste pile, infiltrating landfill inner layers [5,6].

Leachate composition depends on many factors and its characteristics vary over time and from one place to another. Therefore, the choice of the most appropriate treatment for such wastewater is a challenging task in its management [7,8]. As it is composed by both suspended/colloidal and dissolved matters in large amounts, a combination of separation and destruction mechanisms is recommended for the efficient treatment of this mixture [9]. Many studies using physical, chemical and biological processes to treat leachate from the most diverse origins can be found in literature.

Landfills' aging promotes the generation of leachates that are richer in recalcitrant organic matter [10]. Associated to the strict environmental regulations, this phenomenon creates a demand for methods to treat such wastewater other than the usual biological processes [11,12]. In this context,

the use of advanced technologies, such as membrane separation processes (MSP), particularly reverse osmosis (RO), has shown potential to fit leachate to the discharge parameters or even to its reuse [13–15].

According to Renou et al. [16], the RO membranes ability to retain both organic pollutants and inorganic salts makes this method able to properly treat complex wastewaters such as landfill leachate. However, Renou et al. [10] highlight that the greatest complication of MSP use is the decrease of permeate flux over operational time, which is attributed to concentration polarization and fouling. Whilst the first one is a reversible effect caused by the accumulation of solutes on membrane surface, fouling is a partially or totally irreversible effect caused by possible membrane alterations [17,18]. These phenomena may be responsible for permeate fluxes so diminished that the use of such membrane is not viable, especially with more restrictive membranes like RO [19]. The authors also describe that, to overcome such matter, the utilization of advanced pretreatments like advanced oxidation processes (AOP) is a possibility.

AOP represent a group of processes that nonselectively oxidize organic matter by the action of free hydroxyl radicals ($\bullet$OH). These radicals possess an elevated oxidative potential ($E^0 = 2.8$ V) and are produced inside the liquid during the process itself [20]. AOP differs from other wastewater treatments by presenting high efficiencies of recalcitrant organic matter degradation [21], which makes this method indicated for the treatment of leachates that may not be very susceptible to biological treatments.

Among AOP, one of the standouts is ozonation, which produces hydroxyl radicals by the action of a gas stream containing ozone that is fed to the wastewater [22]. The authors also describe that an advantage of ozonation is that ozone itself may directly oxidize organic matter, since it also presents a high oxidative potential ($E^0 = 2.07$ V). The direct oxidation of ozone is selective for unsaturated and aromatic organic compounds, which are very common in landfill leachate [14]. The mechanism of ozone oxidation (direct or indirect) is mainly guided by the pH of the sample, where an acidic environment favors the direct oxidation while an alkaline one favors the production of free radicals [14].

Ozonation has been effectively applied to reduce membrane fouling during surface and groundwater treatment. Brown et al. [23] used ozonation as pretreatment to improve the performance of a RO system used to treat synthetic surface water and observed that a 0.30 mg/L ozone dose caused increase in the RO permeate flux after 62.5 hours of operation when compared to raw water. Kim et al. [24] used a hybrid O_3/ultrafiltration (UF) system to treat natural waters and reported that the permeate flux decayed only 15% with the use of ozone while it decayed around 60% and 55% in the same UF conditions with no gas dispersion and with oxygen bubbles instead of ozone, respectively. Karnik et al. [25] evaluated the effects of an ozone dose around 0.05mg/L on the permeate flux of a nanocrystalline ceramic membrane used in the treatment of lake water, and observed that it decayed 11% with ozone, and 24% with just oxygen. Lee et al. [26] reported the use of an ozone dose of 0.1 mg of O_3 for each mg of suspended solid in the permeate flux of a microfiltration membrane used to treat sewage and observed slight improvements in the permeate flux over time.

In this scenario, the goal of this work is to evaluate the efficacy of the ozonation process to work as a single-step pretreatment to RO membranes in the treatment of recalcitrant landfill leachate. It was assessed by means of the direct impact of ozonation on the reduction of fouling potential of leachates from two distinct sanitary landfills located on the metropolitan region of Rio de Janeiro State (Brazil), both presenting an elevated amount of recalcitrant organic matter. Response surface methodology was used as a statistical tool to help guide the choice of the best conditions to ozonation application before RO step. The modified fouling index (MFI) was used to estimate the fouling potential of raw and pretreated leachates. Toxicity tests were also performed to evaluate the impact of this process on the local biota. The findings of this work are expected to generate relevant information concerning the viability of this treatment option for landfill leachate worldwide.

2. Materials and Methods

2.1. Leachate Samples

For this work, leachate samples were collected from the equalization ponds of two landfills located at the metropolitan region of Rio de Janeiro State (Brazil), henceforth named Landfill 1 and Landfill 2. The samples were stored refrigerated at temperature lower than 10 °C.

2.2. Analytical Methodology

The characterizations of raw leachates from both landfills, as well as the ones pretreated by ozonation at their respective chosen best conditions, were made by the following parameters (along with their analytical methods, according to the American Public Health Association (APHA) [27], and their equipment): Absorbance at 254 nm—Abs_{254} (5910 B—Shimadzu UV mini 1240, Kyoto, Japan); total alkalinity (2320 B—Automatic Burette Tritette Class A, Weirtheim, Germany); conductivity (2510 B—MS Tecnopon Instrumentação, Piracicaba, SP, Brazil); true color (2120 C—Spectrophotometer DR2800 Hach, Loveland, CO, USA); biochemical oxygen demand—BOD_5 (5210 B—Oximeter YSI, Yellow Springs, OH, USA); chemical oxygen demand—COD (5220 D—Spectrophotometer DR2800, Loveland, CO, USA, and reactor Hach, Loveland, CO, USA); ammonia nitrogen—$N-NH_3$ (4500-NH_3 E—Orion 4 star Thermo pH ISE portable, Waltham, MA, USA); pH (4500-H^+ B—pHmeter microprocessor Quimis, Diadema, SP, Brazil); turbidity (2130 B—Turbidimeter: Poli Control-AP 2000, Diadema, SP, Brazil).

Acute ecotoxicity tests using *Allivibrio fischeri*, also known as *Vibrio fischeri* or *Photobacterium phosphoreum*, were also performed. As mentioned by Ghosh et al. [28], it is important to estimate the toxic potential before the discharge of any fluid on water bodies since some chemical compounds may, individually or in combination, be harmful to the biota even in small concentrations. Moreover, during AOP, the oxidation products generated can be even more toxic than the original contaminants [22], which makes such evaluation essential when this kind of treatment is applied to any wastewater.

For acute ecotoxicity tests, the methodology described in the Brazilian Standard NBR 15411-3 [29] in Microtox equipment (SDI, Analyzer model 500, Modern Water, New Castle, DE, USA) was used with a lyophilized strain from Biolux. Assays ran over 5 and 15 min and results were expressed in terms of EC50 (effective concentration of leachate in the dilution where a 50% reduction in luminescence is observed), toxicity units (TU = $100/EC50_{(15min)}$), ECNO (greatest effective concentration of leachate in a dilution where no statistically significant harmful effect is observed) and toxicity factor (TF = 100/ECNO).

As for the evaluation of ozonation efficacy, the modified fouling index (MFI) was used. MFI is an index that describes the fouling potential of a specific liquid sample during filtration processes. Although it is a mere indication of how fouling formation will behave during filtration in the actual membrane system, MFI allows the assessment of the fouling potential through the use of a very small liquid sample and disposable microfiltration membranes, which is good for the preservation of RO membrane since many permeation tests will be performed. It is verified in a pressurized system where the liquid sample percolates a 0.45 μm (Millipore) membrane with 47 mm in diameter at pressure of 30 psi (2.07 bar) and at room temperature (25 °C). Figure 1 illustrates an MFI unit scheme.

A chart of the inverse of filtration rate (t/V) as a function of permeate stream volume (V) is plotted. MFI is defined as the slope of the chart's straight region [30]. The steeper the slope, the bigger the capacity of the liquid to cause fouling. The establishment of fouling indexes, like MFI, is important for the design of treatment systems with membranes, mainly when dealing with nanofiltration (NF) or RO. Wastewaters that present excessive indexes may cause irreversible deposition on the membrane, reducing the permeate stream flux and harming the process performance.
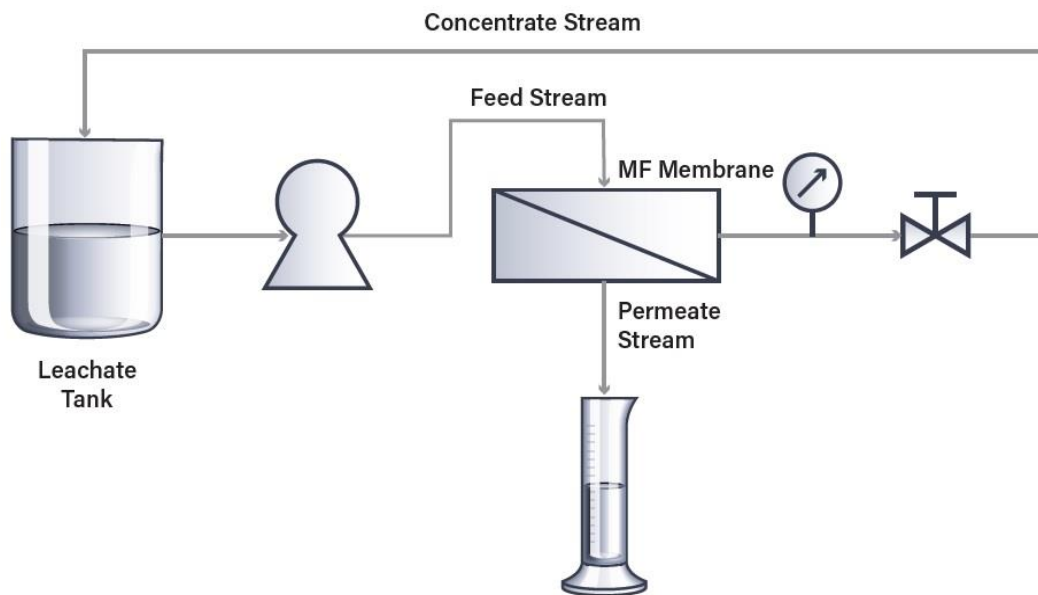
Figure 1. Scheme of the modified fouling index (MFI) unit used in this work.

2.3. Ozonation

Ozonation tests were all performed in an ozonation unit with some adaptations for this particular treatment. Its effectiveness was calculated as the percentage of MFI reduction that the leachate presented immediately after ozonation over the same index measured right before the ozonation process.

2.3.1. Ozonation Unit

The ozonation unit is composed of an O_3 generator, an analyzer of O_3 concentration on the gas stream, a semicontinuous reactor (where leachate is batch fed before the unit's start whilst gas stream is continuously fed), two O_3 destruction baths and an altered foam-collecting vessel, as well as all the hoses and manual valves necessary to ensure a proper gas flow through the unit. Figure 2 presents a scheme of such unit.

Before O_3 generation starts, the semicontinuous reactor was fed with the leachate sample to be ozonated. The sample had its pH previously adjusted to the value specified for each experiment with the help of a 50% w/w NaOH solution or, eventually, with commercial HCl solution (purity of 37%). Such solutions were this concentrated in order to minimize dilution effects in the sample. During operation, the unit is continuously fed with a gas stream containing 99.5% of O_2 at the gauge pressure of 62 kPa (9 psi) and with a fixed flow rate of 5 L/min (following instructions of the O_3 generator manufacturer), which flows into the generator. There, a strong electrical discharge (known as corona discharge) produces O_3 from the O_2 molecules in the feeding gas stream.

Usually, the unit operates with valve A1 open and valves A2 and A3 closed, so that the generator's outlet gas stream, which contains O_2 and O_3, feeds the semicontinuous reactor at its bottom through a diffuser plate to divide it into small bubbles. To overcome reactor overflows caused by the foam generated during the contact of gas stream and leachate, a foam-collecting vessel was used. It was an adaptation of what was described by Salla et al. [31], who used a vessel to separate foam and gas. In this work, to avoid leachate loss, a recycle line was plugged at the bottom of the foam-collecting vessel through which the collected foam can be reintroduced to the reactor after its regeneration to the liquid form at regular time intervals. The unit operates in an intermittent mode between gas feeding and recycles. The recycle works by closing A1 valve, which stops the gas stream feeding to the reactor, and opening A2 and A3 valves, which makes the gas stream go through a by-pass line directly to the destruction baths and the regenerated foam be reintroduced to the reactor.

The O_3 analyzer is capable of continuously measuring O_3 concentrations in gas streams in terms of mg/L of gas by using small gas stream samples. In the unit, it is connected to the inlet line of the reactor and the outlet line of the foam-collecting vessel. Both connections are equipped with manual valves (B1 at the inlet and B2 at the outlet) to make the unit operate sending only one continuous gas stream sample at a time to the analyzer, subsequently enabling it to measure the amount of O_3 fed to the leachate or the amount not consumed by it. The dose of ozone is then calculated by the difference between these measurements, which represents the amount of ozone consumed by the leachate over the volume of leachate being treated.

The process stops by ceasing the gas stream feeding. Leachate volumes and test conditions are specified for each test ahead.
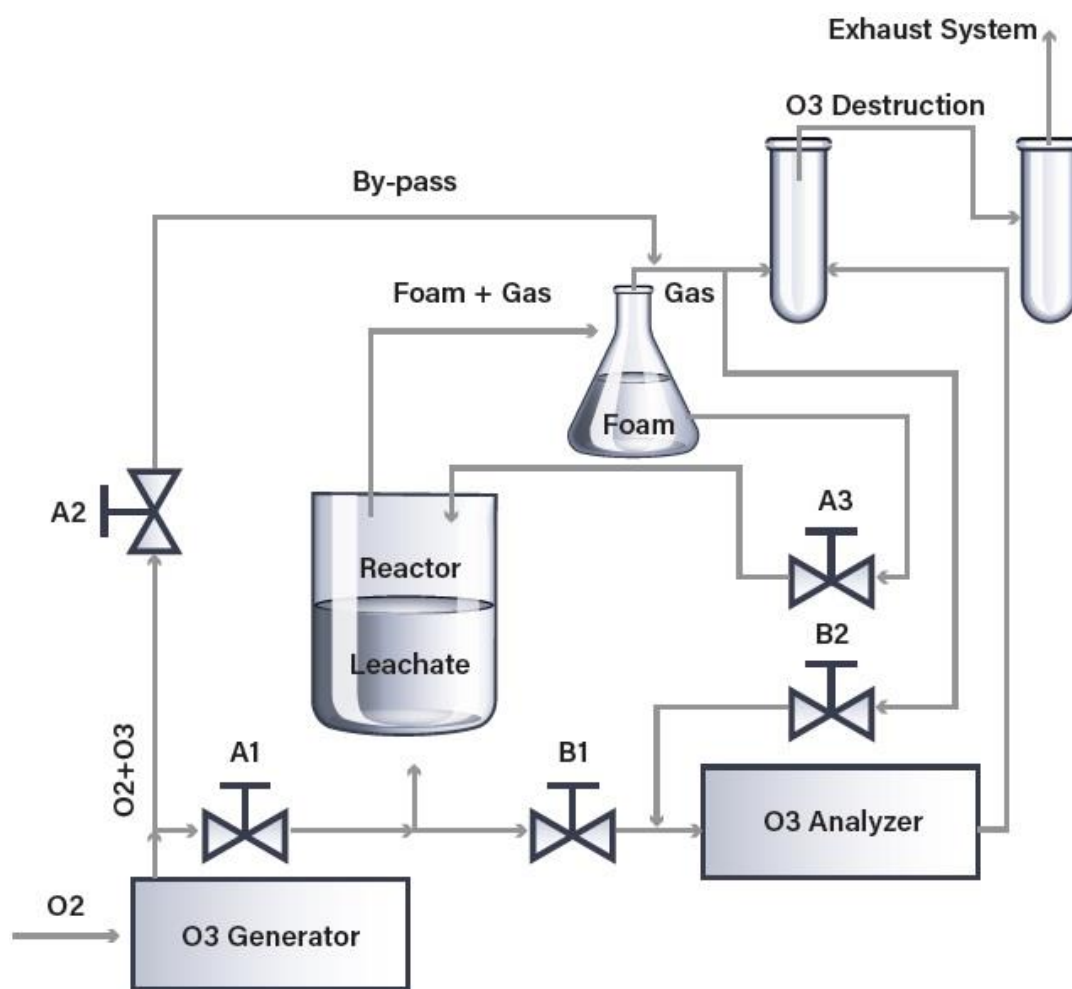

Figure 2. Scheme of the ozonation unit used in this work.

2.3.2. Response Surface Methodology of Ozonation

For each landfill leachate, an experimental design was made in order to produce a response surface. This design is a statistical tool to verify the influence of experimental parameters on an aimed response and also in which levels such parameters are better applied. It generates a mathematical model that suits the observed results in the best way possible and that expresses the expected response value of a test from the values applied for each evaluated parameter, making it possible to predict the response to be obtained [32]. The model is an equation that describes the regression of all experimental data to the surface that best fits them.

The central composite design (CCD), which is used in this work, is one type of response surface design, as it provides the possibility of suiting the observed data to a quadratic mathematical model to

predict the response. If so, an estimation of which experimental conditions may maximize or minimize the response could be conducted. The mathematical models generated may be illustrated in response surfaces to enable the visualization of response peaks. CCD methodology establishes that, for an evaluation of two parameters in two different levels, eight experiments are necessary (four from the factorial analysis and four from the axial points) plus the replicates of the central point (which are four in this work), totalizing twelve experiments for each design.

Both designs were made with the help of Design Expert software (6.0.4, StatEase Inc., Minneapolis, MN, USA, 2000) and featured as evaluated response the MFI reduction (in terms of percentage calculated over the MFI of raw leachate). In the software, the amount and order of experiments are organized according to the parameters and levels to be studied and, after the insertion of experimental results, a statistical analysis generates the mathematical models that describe the response surface. The experimental parameters evaluated on both designs are:

1. Leachate initial pH (from 8 to 12);
2. O_3 dose fed to the leachate (from 0.5 g/L to 1.5 g/L).

The decision for these intervals was guided by results observed in preliminary tests, which followed trial and error logic. The pH range was established to encompass the leachate's natural pH value (around 8) and more alkaline values. The O_3 dose range was established to encompass the minimum condition in which visual changes were observed in the leachate and an arbitrary 3-times-bigger condition.

3. Results and Discussion

3.1. Characterization of Leachate Samples

Table 1 presents the characterization of leachate samples from both landfills in this work.

Table 1. Characterization of leachate samples from both landfills.

Parameter	Units	Landfill 1	Landfill 2
pH	-	7.90 ± 0.01	7.95 ± 0.01
Total Alkalinity	mg $CaCO_3$/L	13,083 ± 325	14,015 ± 373
BOD_5 [1]	mg O_2/L	825 ± 6	1010 ± 16
COD [2]	mg O_2/L	3950 ± 60	4920 ± 40
BOD_5/COD	-	0.209	0.205
Abs_{254} [3]	-	35.4 ± 0.7	39.4 ± 1.0
$N-NH_3$ [4]	mg (NH_3-N)/L	2461 ± 34	2500 ± 50
True color	mg PtCo/L	9755 ± 25	7965 ± 33
Turbidity	NTU	134 ± 1	49.0 ± 0.1
Conductivity	mS/cm	26.36 ± 0.01	23.07 ± 0.01
MFI [5]	s/mL^2	10.32 ± 0.10	3.38 ± 0.15

[1] Biochemical Oxygen Demand; [2] Chemical Oxygen Demand; [3] Absorbance in 254 nanometers; [4] Ammonia nitrogen; [5] Modified fouling index.

First of all, it is important to observe that both leachates present similar and not very expressive BOD_5/COD ratios, which shows that, among their organic matter content, most chemical species are not biodegradable since they can be chemically oxidized but not biochemically oxidized. It indicates the presence of relevant concentrations of recalcitrant compounds among their organic loads, such as humic substances (humic and fulvic acids), which are commonly found in landfill leachate. Also, characterization results demonstrated that these samples possess similar compositions overall. Turbidity, however, is an exception, which is a parameter associated to the presence of suspended matter. Such difference reflects on the MFI values observed for both raw leachates, since MFI test takes place on a microfiltration membrane, which retains suspended matter, mainly. Therefore, it makes sense that the leachate that presents higher turbidity will also be the one to present higher MFI.

Despite the great difference observed between these values of MFI, they are both very elevated, especially if taking into account some reference MFI values for the application of RO in water treatment: from 0 to 2.0×10^{-6} s/mL^2 [33] or from 0 to 1.0×10^{-6} s/mL^2 [34]. Such intervals are not a consensus amongst scientific community and are mainly recommended for water treatment, there being several applications of RO membranes to treat wastewaters with MFI values above these intervals. However, wastewaters with MFI as high as the ones evaluated in this work will certainly cause accentuated decreases in permeate stream fluxes if applied directly to these membranes, making it essential to investigate pretreatments that reduce the fouling potential of these leachates.

3.2. Experimental Design

Table 2 presents the list of 12 experiments established for the CCD of Landfill 1 as well as the results observed for MFI in each test, expressed in terms of s/mL^2, its reduction calculated over the MFI of raw leachate (10.32 s/mL^2), expressed in terms of %, and the reductions predicted by the mathematical model, also expressed in terms of %.

Table 2. Central composite design results for the ozonation of Landfill 1 leachate.

#	pH	(A)	O$_3$ Dose (g/L)	(B)	MFI (s/mL^2)	Real (%)	Predicted (%)
1	8.0	−1	0.5	−1	3.20	68.95	69.73
2	8.0	−1	1.5	+1	1.91	81.52	78.81
3	12.0	+1	0.5	−1	1.07	89.64	90.63
4	12.0	+1	1.5	+1	0.39	96.18	99.71
5	7.2	$-\alpha$ [1.]	1.0	0	3.69	64.25	65.88
6	12.8	$+\alpha$ [1.]	1.0	0	0.17	98.38	95.44
7	10.0	0	0.3	$-\alpha$ [1.]	5.10	50.56	-
8	10.0	0	1.7	$+\alpha$ [1.]	0.56	94.53	95.20
9	10.0	0	1.0	0	0.98	90.50	88.78
10	10.0	0	1.0	0	1.20	88.37	88.78
11	10.0	0	1.0	0	1.18	88.57	88.78
12	10.0	0	1.0	0	1.08	89.55	88.78

[1.] where the numeric value of α is around 1.41 for CCD of two evaluated parameters.

The curves from which the slope was observed to extract MFI values for each experimental condition are illustrated on Appendix A (Figure A1). During the evaluation of results on the software, it was observed that test number 7, which corresponds to the minimum axial point for O$_3$ dose, was highlighted as an outlier, i.e., it was not in accordance with what was expected for it according to the results of the other experiments. A possible explanation is that the reduced mass of O$_3$ was not enough to properly start the degradation mechanisms. Test number 7 was then removed from the design, as it is recommended by the method in these cases, since, as an outlier, it would disturb the generation of the mathematical model that properly describes to results expected. The correct model to estimate MFI reduction as a function of the test parameters was then established and is demonstrated on Equation (1).

$$\text{ReductionL1 (\%)} = 88.78 + 10.45 \times A + 4.54 \times B - 4.06 \times A^2 \tag{1}$$

Equation (1) describes a model with the variables A (pH) and B (O$_3$ dose), where such variables must be transformed into their coded values, i.e., the variables must be converted, before the response estimation, in their proportional correspondent number in the interval (−1;+1) (which represents (8.0;12.0) for pH and (0.5;1.5) for O$_3$ dose) or (−1.41;+1.41), when taking the axial points into account. The R^2 factor credited to this model is equal to 0.9795, which says that this model is reliable to predict the MFI reduction percentages obtained in each test as long as both parameters are within the evaluated intervals.

The model is quadratic for variable A with a negative coefficient (−4.06), therefore, it suggests that there is a maximum MFI reduction at pH 12.6. However, this pH value is not within the evaluated

pH interval and thus it is only possible to conclude that, within the evaluated interval, MFI reduction will be maximized at pH 12.0. Also, the model is linear for variable B with a positive coefficient (+4.54), i.e., within the evaluated interval, the bigger the O_3 dose fed to the leachate (1.5 g/L), the greater MFI reduction will be. At these test conditions, a 99.71% reduction in MFI is expected, which makes it possible to declare that the ozonation process shows great potential to reduce membrane fouling of this leachate. Figure 3 illustrates the response surface obtained from such model.
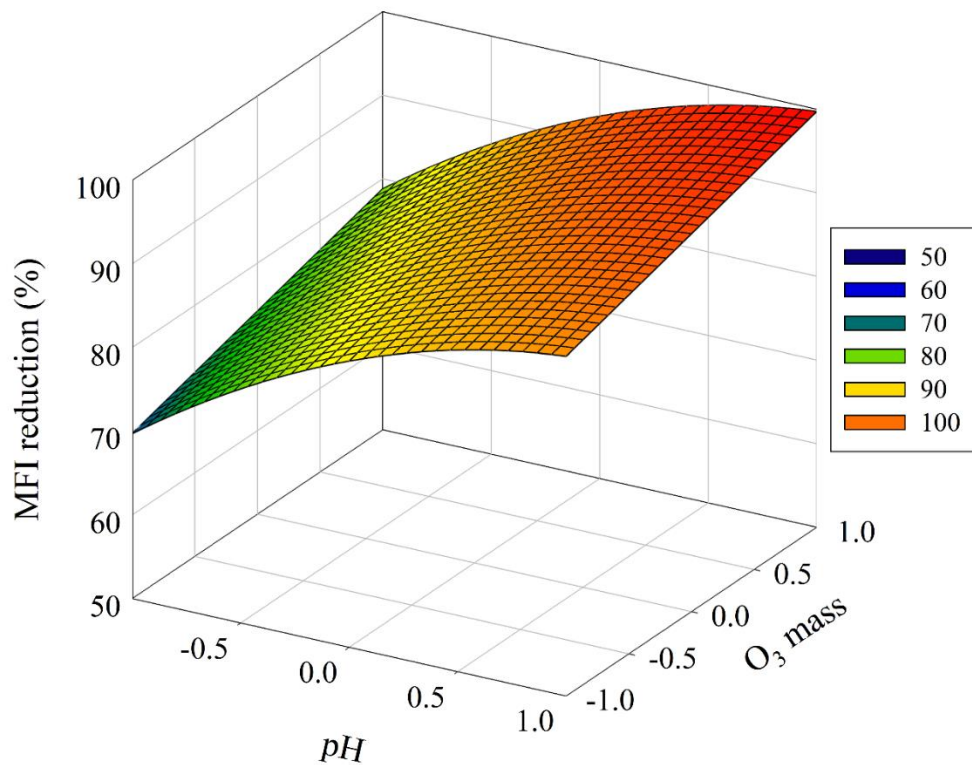

Figure 3. Response surface generated from the mathematical model that describes MFI reduction for Landfill 1.

Table 3 presents the list of 12 experiments established for the CCD of Landfill 2 in the same structure as Table 2. MFI reduction percentage was calculated over the one from Landfill 2 raw leachate (3.38 s/mL^2).

Table 3. Central composite design results for the ozonation of Landfill 2 leachate.

#	pH	(A)	O_3 dose (g/L)	(B)	MFI (s/mL^2)	Real (%)	Predicted (%)
1	8.0	−1	0.5	−1	0.92	72.81	77.38
2	8.0	−1	1.5	1	0.31	90.81	91.82
3	12.0	1	0.5	−1	1.64	51.54	53.62
4	12.0	1	1.5	1	1.03	69.69	68.06
5	7.2	$-\alpha$ [1.]	1.0	0	0.71	78.96	77.30
6	12.8	$+\alpha$ [1.]	1.0	0	1.91	43.51	43.80
7	10.0	0	0.3	$-\alpha$ [1.]	0.73	78.54	74.86
8	10.0	0	1.7	$+\alpha$ [1.]	0.21	93.85	95.22
9	10.0	0	1.0	0	0.55	83.62	85.04
10	10.0	0	1.0	0	0.33	90.15	85.04
11	10.0	0	1.0	0	0.67	80.29	85.04
12	10.0	0	1.0	0	0.41	87.93	85.04

[1.] where the numeric value of α is around 1.41 for CCD of two evaluated parameters.

The curves from which the slope was observed to extract MFI values for each experimental condition are illustrated on Appendix A (Figure A2). The mathematical model that describes MFI reduction percentage as a function of the evaluated variables for Landfill 2 is presented in Equation (2).

$$\text{ReductionL2 (\%)} = 85.04 - 11.88 \times A + 7.22 \times B - 12.32 \times A^2 \tag{2}$$

Equation (2) also describes a model with the variables A (pH) and B (O_3 dose), where such variables must be transformed into their coded values, (−1;+1) or (−1.41;+1.41), when taking the axial points into account. The R^2 factor credited to this model is equal to 0.9608, which says that this model is also reliable to predict the MFI reduction percentages obtained in each test, as long as both parameters are within the evaluated intervals.

Once again, the model is quadratic for variable A with a negative coefficient (−12.32), therefore, it suggests that there is a maximum MFI reduction at pH 9.0. Also, the model is linear for variable B with a positive coefficient (+7.22), i.e., within the evaluated interval, the bigger the O_3 dose fed to the leachate (1.5 g/L), the greater MFI reduction will be. At these test conditions, a 95.12% reduction in MFI is expected, which makes it possible to declare that the ozonation process shows great potential to reduce membrane fouling of this leachate, too. Figure 4 illustrates the response surface obtained from such model.
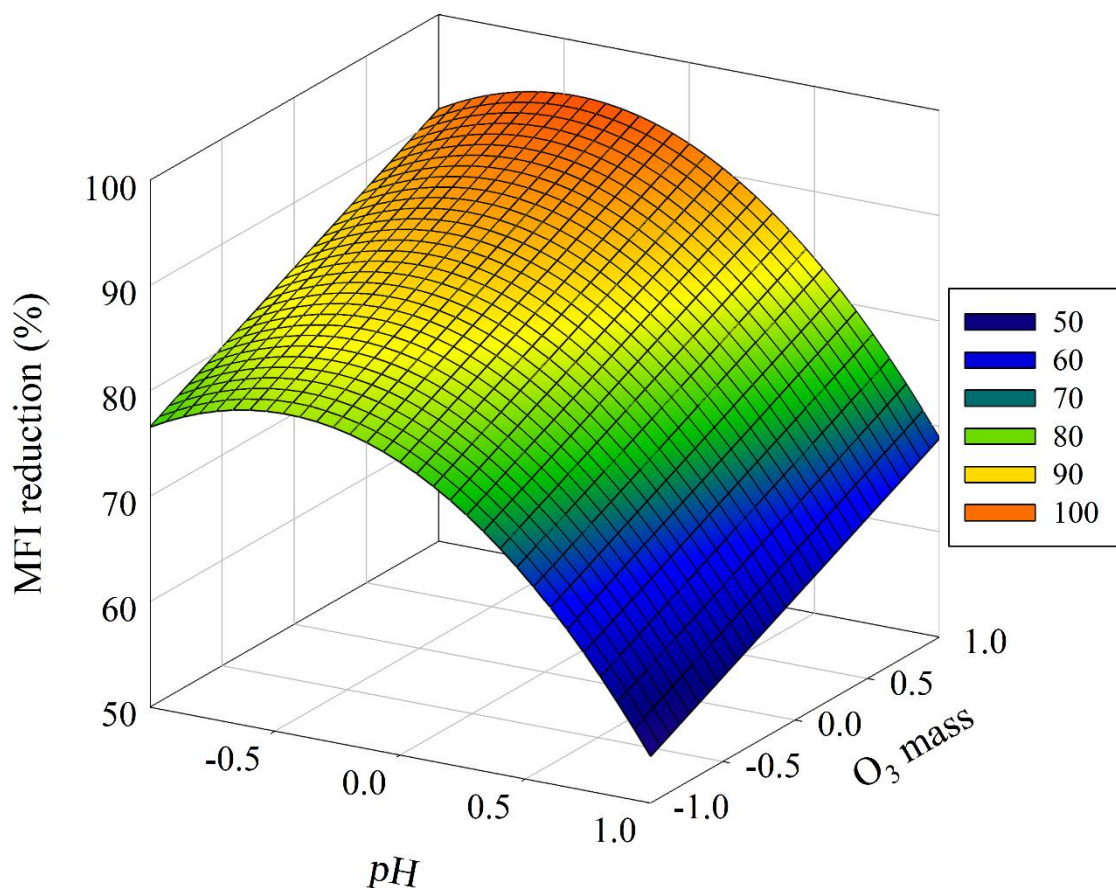

Figure 4. Response surface generated from the mathematical model that describes MFI reduction for Landfill 2.

Comparing Equations (1) and (2), it is possible to observe that both mathematical models follow similar structures: linear with a positive coefficient for O_3 dose and quadratic with a negative coefficient for pH. The biggest difference between them is the pH value in which MFI reduction is maximized (12.6 for Landfill 1 and 9.0 for Landfill 2). Both values of pH correspond to an alkaline environment,

where O_3 acts predominantly generating hydroxyl radicals. However, in less alkaline conditions, like pH 9.0, it is admitted that O_3 direct oxidation may also be a part of organic matter degradation, even if it happens in a smaller scale [35].

Although a 99.71% reduction on the MFI of Landfill 1 leachate is expected on the best evaluated ozonation conditions (pH = 12.0 and O_3 dose = 1.5 g/L), such process actually produced a pretreated leachate whose MFI was 0.39 s/mL^2, only 96.22% lower than the one from raw leachate (10.32 s/mL^2). Similarly, for Landfill 2, despite the expected 95.12% reduction on the best evaluated ozonation conditions (pH = 9.0 and O_3 dose = 1.5 g/L), such process actually produced a pretreated leachate whose MFI is 0.20 s/mL^2, 94.08% lower than the one from raw leachate (3.38 s/mL^2).

First, the great ability of ozonation to act in the reduction of fouling potential is clear, since all reductions, predicted or real, are above 90%. In addition, despite the mathematical models suggesting that MFI would be more intensively reduced in Landfill 1 leachate, in practice, a smaller difference between the MFI reductions is observed.

Although all reduction efficiencies are considerably high, MFI final values are still far above those indicated intervals for the direct application in RO membranes when treating water. This points to the conclusion that the ozonation process is not sufficient to be used as a single-step pretreatment. Possibly, the association between ozonation and other treatment techniques would provide a pretreated leachate with even lower MFI values. Torres [36], for example, verified that the isolated use of the Fenton reaction, another AOP method, was not enough to reduce the MFI of the studied leachate to a point where it would be suitable for direct application on RO membranes, but when the Fenton reaction was associated with a submerged microfiltration step, the author judged that the resulting water was sufficient for such application. The work of Torres supports the idea of associating the ozonation process to a microfiltration step to improve this pretreatment efficiency.

3.3. Characterization of Samples Pretreated with O_3

Table 4 presents the characterization of raw leachate samples and pretreated leachate samples in their respective best conditions of ozonation for both evaluated landfills.

Table 4. Characterization of raw and pretreated samples of leachate (pH = 12.0 and O_3 dose = 1.5 g/L for Landfill 1; pH = 9.0 and O_3 dose = 1.5 g/L for Landfill 2).

Param.	Units	Landfill 1			Landfill 2		
		Raw	Treat.	Red. (%)	Raw	Treat.	Red. (%)
pH	-	7.90 ± 0.01	10.80 ± 0.01	-	7.95 ± 0.01	8.60 ± 0.01	-
Alkalinity	mg CaCO$_3$/L	13,083 ± 325	23,570 ± 514	−80.16	14,015 ± 373	3799 ± 264	72.89
BOD$_5$	mg O$_2$/L	825 ± 6	483 ± 5	41.45	1010 ± 16	457 ± 5	54.75
COD	mg O$_2$/L	3950 ± 60	2740 ± 50	30.63	4920 ± 40	2510 ± 50	49.09
BOD$_5$/COD	-	0.209	0.176	15.60	0.205	0.182	11.13
Abs$_{254}$	-	35.4 ± 0.7	14.6 ± 0.4	58.76	39.4 ± 1.0	15.5 ± 0.5	60.66
N-NH$_3$	mg (NH$_3$-N)/L	2461 ± 34	1404 ± 22	42.95	2500 ± 50	1995 ± 23	20.20
True color	mg PtCo/L	9755 ± 25	701 ± 4	92.82	7965 ± 33	524 ± 5	93.43
Turbidity	NTU	134 ± 1	39.7 ± 0.1	70.42	49.0 ± 0.1	11.0 ± 0.1	77.55
Conductivity	mS/cm	26.36 ± 0.01	22.27 ± 0.01	15.52	23.07 ± 0.01	19.70 ± 0.01	14.61
MFI	s/mL^2	10.32 ± 0.10	0.39 ± 0.02	96.22	3.38 ± 0.15	0.20 ± 0.01	94.08

Firstly, pH in both leachates is higher after ozonation, which is easily explained by the pH adjustment prior to the process. Such elevation shows influence on the leachate alkalinity, as it may be observed on Landfill 1, where pretreated leachate alkalinity is higher than the raw leachate one, since the excessive free hydroxyls elevate the alkalinity measurement. As for Landfill 2, whose operational pH is lower than the one for Landfill 1 and that, therefore, possesses less free hydroxyls at the end of ozonation, alkalinity is considerably lower in the pretreated leachate than it is in the raw leachate (72.89% lower), even with pH increasing from 7.95 to 8.60, which indicates that ozonation is capable of reducing leachate concentrations of carbonates and bicarbonates.

The differences in operational pH caused a variance in the efficiency of ammonia nitrogen removal as well (42.95% removal for Landfill 1 and 20.20% removal for Landfill 2), despite the similarity of ammonia nitrogen concentrations in the raw leachates. It is known that ammonia can be removed from leachate through air stripping, a process based on mass transfer of a gas dissolved in a liquid phase to a gaseous stream, a phenomenon called desorption [34]. The concentration of ammonia nitrogen encompasses the ionized (NH_4^+) and nonionized (NH_3) portions of ammonia. These two species present themselves in a chemical balance that depends on the pH given that, at alkaline conditions, the available OH^- ions shift the balance to the formation of nonionized ammonia [34]. Such balance is demonstrated in Equation (3).

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \tag{3}$$

As the gaseous stream in air stripping is not capable of desorbing the ionic ammonia, usually, this process depends on the wastewater pH elevation to values close to 12.0 to force the generation of the nonionic form so that it can be carried by the bubbles [34]. Thus, it is believed that the ozonation process applied to Landfill 1 leachate, which happened at pH 12.0, was able to desorb ammonia to its gaseous stream in a more effective way than the process applied to Landfill 2, at pH 9.0.

The evaluation of organic matter content demonstrated that ozonation had just a modest efficiency on its reduction. However, it is curious to notice that, for both leachates, there were reductions in BOD_5/COD ratios, which indicates that the pretreated samples are even less susceptible to biological treatments than the raw ones. This behavior does not follow what is likely to happen for wastewaters that undergo AOP processes, which are frequently used for increasing the biodegradability of organic loads [22,37].

As expected, the ozonation process showed low efficiencies in reducing conductivity. Nevertheless, as described by Gottschalk et al. [35], high concentrations of inorganic salts in wastewaters make the coalescence of ozone bubbles decrease, which expands the liquid–gas interface, and, therefore, favors the O_3 mass transfer from the gaseous to the liquid phase. It is anticipated that the leachate conductivity will be reduced by RO membranes in a future treatment step.

The process was greatly efficient in reducing leachate turbidity and color, the last one achieving reductions over 90%. It is known that the dark color of leachate is mainly caused by humic substances, which are also responsible for the great recalcitrance of this effluent [38]. Thus, it seems that ozonation was particularly effective in transforming such substances.

Chen et al. [13] observed reductions of 41.32%, 68.82% and 83.50% for COD, Abs_{254} and color, respectively, when applying around 1.6 g of O_3 to treat 2 L of leachate's concentrate that was previously submitted to a coagulation step. Singh et al. [14] reported reductions in Abs_{254} of 65%, 78% and 78% and in the dissolved organic carbon (DOC) of 13%, 15% and 17% for the leachate of three stabilized landfills evaluated in their work. The authors applied around 7 g of ozone to treat 1 L of each leachate. As for Amaral-Silva et al. [39], the authors reported COD reduction of 34% and color reduction of 95% when treating 500 mL of recalcitrant leachate with 1.8 g of O_3 at pH 9.0. All these reduction percentages are similar to what is observed on this work, being high for color, moderate for Abs_{254} and low for organic matter content.

3.4. Toxicity

Table 5 presents the results of acute ecotoxicity for the raw leachate from both landfills and their respective pretreated effluents at the best ozonation conditions.

Although both pretreated samples do not present toxicity levels that fit the standards of Rio de Janeiro State for discharge in water bodies (TF < 8) [40], it is clear that the ozonation process was able to reduce the leachates toxicity to a great extent (98.44% of TF reduction for Landfill 1 and 93.75% for Landfill 2). This shows that ozonation did not produce intermediate oxidation products that are more toxic than the original ones in relevant concentrations, which is a phenomenon that was observed by Urbano et al. [22]. The authors used an ozonation process to degrade sulfaquinoxaline molecules in

low concentrations and noticed that the solution's acute ecotoxicity increased (up to 85% of luminosity inhibition in *Vibrio fischeri* tests) when ozonation happened in alkaline pH.

Table 5. Acute ecotoxicity for raw leachate from Landfills 1 and 2 and pretreated leachates in their respective best ozonation conditions (pH = 12.0 and O_3 dose = 1.5 g/L for Landfill 1; pH = 9.0 and O_3 dose = 1.5 g/L for Landfill 2).

Sample	EC50$_{15min}$	TU (100/EC50)	ECNO	TF (100/ECNO)
RL1 [1.]	0.77%	129.90	0.16%	625.00
PL1 [2.]	31.87%	3.14	10.24%	9.77
RL2 [3.]	1.62%	61.92	0.32%	312.50
PL2 [4.]	35.25%	2.84	5.12%	19.53

[1.] raw leachate from Landfill 1; [2.] pretreated leachate from Landfill 1; [3.] raw leachate from Landfill 2; [4.] pretreated leachate from Landfill 2.

The results presented throughout this work attest that ozonation has great capacity to reduce the fouling potential of leachate. They suggest, therefore, that this technology can be applied as an effective pretreatment prior to a RO step, given the operational and efficiency difficulties of RO membranes when applied to leachate treatment. The possibility to reduce membrane fouling by applying a prior ozone treatment step is a promising alternative to make RO membranes a viable and efficient treatment option.

4. Conclusions

The results demonstrated ozonation's great capacity to reduce the fouling potential of both leachates, with real MFI reductions of 96.22% for Landfill 1 and 94.08% for Landfill 2. Also, a similar behavior was observed for these two landfills in the reduction of many evaluated parameters, which indicates that this technology is capable of fitting this kind of wastewater to proper conditions for the application on RO membranes.

However, it is noteworthy that the optimum operational pH varied considerably from one landfill to the other (12.0 for Landfill 1 and 9.0 for Landfill 2), which provoked differences in the removal efficiencies of some parameters, such as alkalinity and ammonia nitrogen, and points to the need of an evaluation of the best operational pH on a case by case basis. It is worth mentioning that, despite the technical efficacy presented in this study by such method, pH 12.0 is very high and possibly very expensive for practical applications, which is also valid for the O_3 dose applied to both samples. An economic evaluation is required before applying ozonation on this type of treatment.

The reductions in BOD_5/COD ratios for both samples go against what is likely to happen for wastewaters that undergo AOP processes, frequently used for increasing the biodegradability of organic loads. It was also worth noticing that ozonation significantly reduced leachate toxicity in both cases, since toxicity factor decayed from 625.00 to 9.77 for Landfill 1 and from 312.50 to 19.53 for Landfill 2.

Nonetheless, the best operational conditions for both effluents and their final MFI values suggest that ozonation would be insufficient as a single-step pretreatment and that it would be useful to apply a treatment step like microfiltration along with the ozonation step in order to minimize the O_3 demand and to reduce even more the fouling potential of this wastewater. Such association is expected to provide further improvements on this pretreatment, making it possible to build a treatment plant where ozonation and membrane processes can effectively treat recalcitrant leachates.

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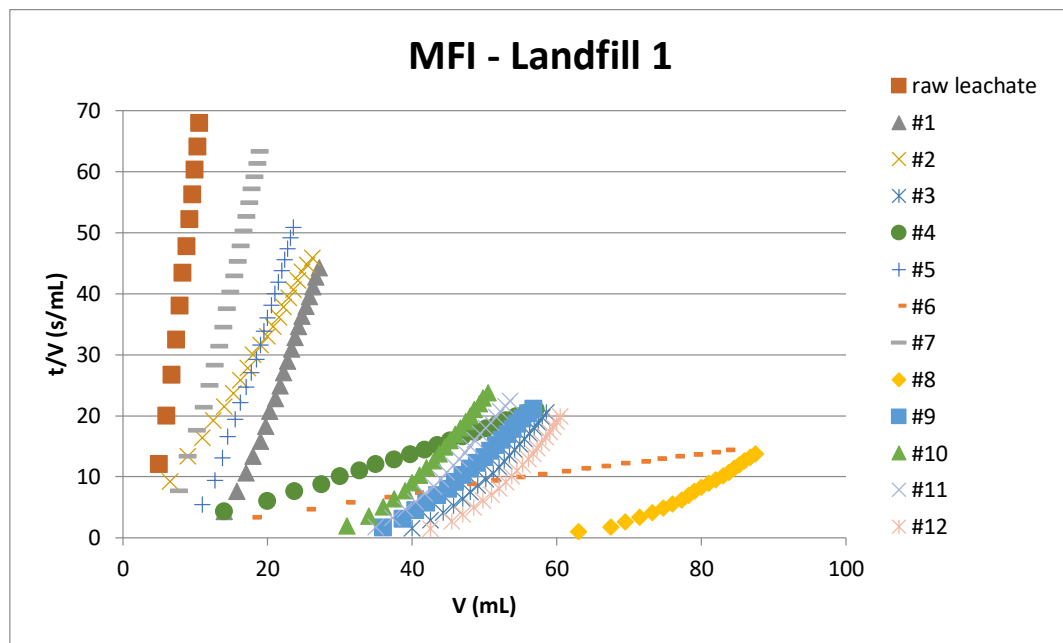
Appendix A

Figure A1. MFI curves for the Landfill 1's raw leachate and for the pretreated leachate in each experimental condition. The best ozonation condition (pH = 12.0 and O_3 dose = 1.5 g/L) corresponds to experiment #4.
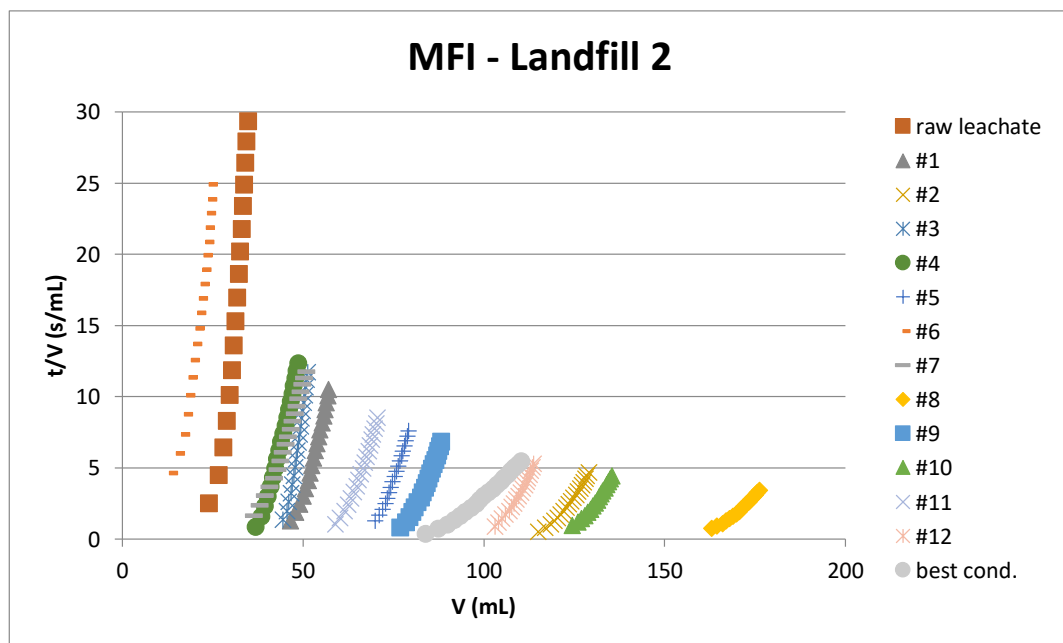

Figure A2. MFI curves for the Landfill 2's raw leachate, for the pretreated leachate in each experimental condition and for the best ozonation condition (pH = 9.0 and O_3 dose = 1.5 g/L).

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