Coagulation/flocculation as a pretreatment of landfill leachate for minimizing fouling in membrane processes

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\textbf{ABSTRACT}

Several works in the literature indicate that the combination of physical-chemical treatment (coagulation/flocculation) and membrane separation process can be a promising alternative for landfill leachate treatment. The objective of the present work was to evaluate the fouling potential in membranes after pretreatment of raw leachate by coagulation/flocculation process. Samples of stabilized leachate from Gericinó controlled landfill (Rio de Janeiro City, Brazil) were used. FeCl\textsubscript{3} and Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} were applied as coagulating agents. The pH and coagulant dosage were evaluated. Modified fouling index (MFI) and silt density index (SDI) were used to estimate the formation of deposits in the nanofiltration (NF) or reverse osmosis (RO) membranes for leachate treatment. SDI was not significantly reduced despite the great removal of suspended matter by the pretreatment. The MFI of leachate pretreated with FeCl\textsubscript{3} was 100 times lower than the MFI of leachate pretreated with Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} and about 10,000 times lower than the raw leachate. This can be attributed to the influence that the organic matter exerts on the MFI. Therefore, the results showed coagulation/flocculation would be a good pretreatment for NF or RO treatment of landfill leachate.

Keywords: Fouling; Membrane; Modified fouling index; Silt density index

1. Introduction

Minimizing the environmental impacts associated with generation of solid waste is a worldwide need [1]. Over one billion tons of waste are produced globally and this volume is expected to increase to 2.2 billion tons by 2025 [2]. Disposal in sanitary landfill is the most widely used method of waste management [3–5]. This method is considered a safe solution for the treatment of solid waste, in spite of generating leachate and biogas [6]. The leachate is a liquid that is highly polluting to the aquatic environment, therefore, it needs to be treated before the discharge into water bodies [7].

Among the most ordinary treatments to reduce the leachate’s contaminant load, there are the biological processes [4,8,9]. However, in the case of mature landfills, biological treatment is normally not enough to reach the required maximum level of pollutants to discharge in receiving bodies, especially in the cases of leachate with recalcitrant compounds [4,8]. Therefore, the presence of non-biodegradable organic matter makes it necessary to apply for other treatment techniques, otherwise the final effluent cannot meet the strict discharge regulations required [4].

Membrane processes such as nanofiltration (NF) and reverse osmosis (RO) are able to remove dissolved...
substances in aqueous wastewaters, such as inorganic salts and organic compounds, as well as retaining the smaller particulate matter that the coagulation/flocculation process does not have the potential to do [4,10]. The use of membrane filtration in landfill leachate treatment has shown the capacity of achieving the necessary standards for discharge [4,11]. However, membrane technology is not suitable as a single step in leachate treatment due to the occurrence of serious fouling [12].

The successful application of NF technology requires efficient control of membrane fouling and in particular, organic matter is the main originator of membrane fouling [4]. Landfill leachate RO feasibility is highly conditioned by the control of concentrate treatment costs and the choice of the feed pretreatment mode in order to reduce membrane fouling [4,11]. For this, coagulation-flocculation processes can be used to remove suspended solids as pretreatment [12,13]. In this context, the combination of this physical-chemical treatment with a membrane separation process can be a promising alternative for the treatment of leachate [8,9,13].

The coagulation-flocculation process can be an effective pretreatment option for landfill leachate [3,14]. Applying this technique, it is possible to reduce the chemical oxygen demand (COD), turbidity, color, suspended solids and metals with high efficiencies [15], however, its performance depends on coagulant type and dose, pH, velocity gradient of mixing, rapid mixing time, slow mixing time and sedimentation time [16]. Several researches have shown that cationic coagulants such as aluminum or iron salts led to better treatment efficiency as they help in agglomeration of slow-settling microflocs into larger and denser flocs [8,10,13].

Dolar et al. [13] studied the effectiveness in laboratory-scale experiments of coagulation/ultrafiltration and adsorption/ultrafiltration as pretreatment options for treating stabilized landfill leachate using NF and RO. The results indicated that coagulation with FeCl₃ showed better reduction of COD (65%), total organic carbon (86%) and turbidity (87%) than the adsorption process (32%, −132% and 7%, respectively) [13]. Assou et al. [14] investigated the use of aluminum and iron salts as coagulating agents to reduce pollutant concentrations in leachate. The results indicated that coagulation/flocculation with FeCl₃ and Al₂(SO₄)₃ are, both, effective in the reduction of COD (67% and 60%, respectively) [14]. Ishak et al. [12] evaluated the feasibility of coagulation/flocculation coupled with UV-based sulfate radical oxidation process in the removal of COD of stabilized landfill leachate. For coagulation/flocculation, ferric chloride was used and it effectively removed 76.9% of COD at pH 6 [12]. Shu et al. [8] treated the composting leachate using a hybrid coagulation-nanofiltration process. The COD and turbidity removal efficiency reached 62.8% and 75.3%, respectively, at an optimum dosage of poly ferric sulfate (PFS), used as coagulant, and 89.7% of COD was reduced downstream the NF process [8].

To assess the treatability of a given wastewater with NF and RO membranes, a variety of fouling indexes have been developed over the years, among them, the three principal indexes are the silt density index (SDI), the modified fouling index (MFI) and the mini plugging factor index (MPFI) [17]. These indexes are determined from simple membrane tests.

The objective of the present work was to evaluate the fouling potential in membranes after pretreatment of raw leachate by coagulation/flocculation process. Since the successful application of membrane technology requires efficient control of membrane fouling, in this work, the MFI and SDI parameters were used to evaluate fouling potential.

2. Materials and methods

2.1. Landfill leachate samples

Samples of leachate were collected from the stabilization ponds located in Gericinó Landfill (Rio de Janeiro City, Brazil). Gericinó Landfill began its operations in 1987 and, at the time of sampling, it was in the process of closure. This landfill received only municipal waste (2,000 t per day), generating 500 m³ a day of leachate, which was stored in the accumulation pond [18]. Three samples were collected in the period of October 2016 to August 2017 (samples I, II and III). The characterization of such leachate was based on the following parameters and methods [19]: absorbance at 254 nm (5910-B), which provides an indication of the aromatic organic matter contents, true color (2120-C), total alkalinity (2320-B), chloride (4500 Cl⁻-B), ammonia nitrogen (4500 NH₃-N), chemical oxygen demand – COD (5220-D), pH, total organic carbon–TOC (5310-C) and humic substances concentration. The concentration of humic substances was determined by the modified spectrophotometric/colorimetric method based on the binding between toluidine blue dye (TB) and humic acid molecules to produce a dye-humic acids complex that causes a decrease in absorbance at 603 nm [20,21].

Several authors point out that the main cause of fouling in leachate filtration in membranes is the organic matter [4,18,20]. Because of this, the parameters related to organic matter (COD and TOC) were systematically measured in all experiments. The parameter color is closely correlated to the concentration of HS since the dark color in the leachates is due to the presence of HS [18]. In addition, the feed leachate samples and the best results for coagulation/flocculation treatment obtained, the humic substance concentration was measured.

2.2. Leachate treatment

A coagulation/flocculation procedure was conducted to evaluate its efficiency in the removal of organic matter. The coagulants used were FeCl₃ and Al₂(SO₄)₃. The coagulation/flocculation process was conducted in a jar test apparatus, reaction volume was 1 L, rapid mixing was carried out for 2 min at 150 rpm and slow mixing, for 20 min at 60 rpm. Following that, the leachate was decanted over a period of 60 min. The pH was adjusted using sulfuric acid (98%).

The protocol of the coagulation/flocculation experiments followed this sequence:

- Determination of the most appropriate value of pH: dosage of coagulant was fixed at the 4,000 mg FeCl₃ or Al₂(SO₄)₃ per liter and the pH varied in the range of 4.0–6.5 and the natural leachate pH;
- Determination of the most appropriate dosage of coagulant: the pH in all jars was fixed at value obtained
in previous step and the dosage of the coagulant varied in the ranges: 250 – 4,200 mg FeCl$_3$/L and 500–4,800 mg Al$_2$(SO$_4$)$_3$/L.

Due to the limitations of great volume of leachate collection, different samples were used in the experiments: sample I for the ferric chloride tests, sample II for the aluminum sulfate coagulant tests and the sample III for the fouling potential parameters tests (described in section 2.3). At the end of procedure, the clarified phase was collected, and the COD, true color and TOC values of such phase were measured. Besides, in order to minimize the existing differences due to the use of different samples, the efficiency of removal (eq. (1)) was calculated, which is a parameter that provides a result relative to the feed leachate used.

$$E(\%) = \frac{(C_f - C_r)}{C_f} \times 100$$

where $E(\%)$ is the removal efficiency (%); $C_f$ is the concentration in feed leachate; $C_r$ is the concentration in treated leachate.

All experiments were performed in triplicate and at 25°C. The results presented correspond to the average values.

### 2.3. Determination of fouling potential on membrane processes

SDI and MFI parameters were used to estimate the formation of deposits and scaling that may cause fouling on membranes. For this purpose, a pressurized flat membrane system was used in which raw and pretreated samples of leachate pass through a 47 mm diameter microfiltration membrane (cellulose nitrate membrane with 0.45 μm pores from Sartorius Stedim Biotech, Goettingen, Germany), at a fixed pressure according to ASTM D4189-07 [22], ASTM D8002-15 [23] and Tchobanoglous et al. [17]. The tests were performed in duplicate. The permeate is collected in graduated test tubes, allowing the measurement of permeate volume over time.

For SDI tests, the operating conditions were fixed at the pressure of 200 kPa (2 bar) and at room temperature (25°C). The time required to collect a fixed volume (20 mL in this study) of permeate is observed. The interval between the end of the first collection and the beginning of the second one was 5 min. After interval time, the time required to collect another 20 mL of permeate is observed. SDI is, then, calculated according to Eq. (2).

$$SDI = 100 \times \frac{[1 - (t/t_f)]/t}{t_f}$$

where $t_f$ is the initial permeate volume $V$ (20 mL) collection time (min); $t_f$ is the final permeate volume $V$ (20 mL) collection time (min) and $t$ is the time interval between $t_f$ and $t_f$ (min).

For MFI tests, it was observed the time required to collect portions of 50 mL of permeate until a total amount of, at least, 500 mL at operating pressure fixed at 200 kPa (1.406 bar) and room temperature (25°C). Then, these 10 or more observed points allow the construction of a curve in which the inverse of the volumetric flow rate ($t/V$) is a function of the filtered volume ($V$). The MFI is the slope of this curve, illustrated in Eq. (3).

$$t/V = MFI \times V + a$$

where $t$ is the time of permeate collection (s); $V$ is the permeate volume (L); and $a$ is the linear coefficient.

### 3. Results and discussion

Table 1 presents the results of characterization of 3 different samples collected in Gericinó Landfill and used in this work. The composition of the leachate from Gericinó Landfill corresponds to the phase of methanogenic decomposition (age over 10 years), which can be verified mainly by the basic pH. This is in accordance to what is expected for Gericinó Landfill, which is 30 year-old landfill [18,24]. Leachate recirculation to the landfill [18] may be one of the causes of such high concentrations of salts and ammonia in the leachate. In the present work, most of the characterization’s parameters are within the range showed by Lima et al. [18], that characterized this same leachate in the period of 2014–2016: COD between 978 and 1,813 mg/L; TOC between 437 and 648 mg/L; absorbance at 254 nm between 11 and 21; true color between 4,977 and 5,679 mg/L; pH between 7.7 and 8.6 and humic substances between 796 and 1,132 mg/L. It should be considered that the differences in all these concentrations may be associated to leachate’s sampling conditions, which were done in different moments and under different weather circumstances.

#### 3.1. Leachate treatment

Figs. 1 and 2 show the results of coagulation/flocculation experiments for choosing the best conditions of pH and coagulant dosage for both ferric chloride and aluminum sulfate.

According to Fig. 1, for both coagulants, the pH that generated the greatest removal efficiencies COD, TOC and true color was 6.0. From Fig. 2, the best removal efficiencies of COD, TOC and true color can be observed at 4,200 mg FeCl$_3$/L (84%, 72% and 89%, respectively) and at 4,500 mg Al$_2$(SO$_4$)$_3$/L (61%, 33% and 89%, respectively). Table 2 shows

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Leachate Samples</th>
<th>COD (mg/L)</th>
<th>TOC (mg/L)</th>
<th>ABS 254</th>
<th>True color (mg Pt-Co/L)</th>
<th>Total alkalinity (mg CaCO$_3$/L)</th>
<th>NH$_3$-N (mg/L)</th>
<th>Chloride (mg/L)</th>
<th>pH</th>
<th>HS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>2,113</td>
<td>1,657</td>
<td>1,460</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>TOC (mg/L)</td>
<td>413</td>
<td>505</td>
<td>460</td>
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<td></td>
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<tr>
<td>ABS 254</td>
<td>19.3</td>
<td>18.6</td>
<td>24.7</td>
<td></td>
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<tr>
<td>True color (mg Pt-Co/L)</td>
<td>5,106</td>
<td>3,320</td>
<td>3,295</td>
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<td></td>
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<tr>
<td>Total alkalinity (mg CaCO$_3$/L)</td>
<td>3,900</td>
<td>3,377</td>
<td>5,843</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>NH$_3$-N (mg/L)</td>
<td>623</td>
<td>816</td>
<td>1,083</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>1,917</td>
<td>1,673</td>
<td>2,703</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>pH</td>
<td>7.9</td>
<td>8.2</td>
<td>8.2</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>HS (mg/L)</td>
<td>572</td>
<td>543</td>
<td>560</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
the pretreated landfill leachate’s characterization results for the best conditions in coagulation/flocculation experiments with both coagulants and their respective raw leachate sample’s characterizations. In general, for parameters that represent organic matter (COD, TOC, ABS254 and color), the coagulant FeCl₃ obtained best results of removal, except for humic substances.

The predominant mechanism of action of these coagulating agents is the sweep coagulation, in which, depending on the metal salt concentration, the pH value of the mixture, the rapid mixing rate and the nature and distribution of particle sizes, precipitate formation may occur (Al(OH)₃ and Fe(OH)₃) [25].

The removal of organic matter was more effective at pH 6.0, that may be due to the fact that ferric and aluminum ions can hydrolyze and form polynuclear cations and other...
chemical species with positive charges [25]. The pH 6.0 was also found as optimal point for pH by Shu et al. [8] to pre-
treat leachate, but the FeCl₃ dosage considered as optimal
was lower, 1,200 mg FeCl₃/L. Other authors [26,27] found an
optimal dose of FeCl₃ of, approximately, 4,500 mg FeCl₃/L,
the same of this work, but their pH optimal values were
around 8.0.

The use of aluminum sulfate as coagulant for leachate treatment in Portugal showed the pH 6.0 as the
best operational condition, but using a lower dosage of coagulant (1,027 mg Al(SO₄)₃/L) and, for greater coagulant
concentration, there was no increase in the removal of COD
(maximum removal of 39%) [28]. This phenomenon was
attributed to the stabilization of the colloidal particles in
positive form [29]. The removal percentage of organic mat-
ter obtained applying a coagulation/flocculation process is
usually around 10%–25% for non-stabilized landfills and
50%–65% for stabilized landfills [30].

As expected, the ammonia nitrogen was not removed
during the coagulation/flocculation process. Although, not
indicated in the literature as a main fouling membrane agent,
the ammonia nitrogen can be removed from the landfill
leachate in a preliminary step of treatment using ammonia
stripping [31].

Lima et al. [18] evaluated the leachate generated in the
same landfill (Gericinó Landfill) and, for samples collected
in 2014, the best conditions for coagulation/flocculation
using ferric chloride was pH 4.0 and coagulant concentration
around 2,000 mg FeCl₃/L, reaching removal efficiencies of
93% of color, 71% of TOC, 69% of COD and 76% of HS. It
is important to note that the COD and ABS254 of samples
collected in [18] were lower and HS were higher than the
samples of the present work.

The variability of results for pH and coagulant
concentration conditions for landfill leachate’s coagulation/
flocculation shows that the optimal treatment conditions
will depend on the concentration and the quality of organic
matter of each specific sample of leachate, which is very
unpredictable even if they are generated in the same landfill.
Due to this, an adequate monitoring of the quality of the
leachate generated to adjust the best coagulation/flocculation
conditions to minimize fouling in the membrane processes
is required.

3.2. Determination of fouling potential on NF and RO membranes

For each coagulant, three samples of effluents pretreated
at pH 6.0 and with different dosages were chosen for the
determination of SDI and MFI to verify if the ferric and
aluminum ions added during the pretreatment would
influence the fouling formation on membrane: a lower,
intermediate and a greater concentration. The last one was
the concentration that provided the best results for organic
matter removal. For FeCl₃, the concentrations evaluated were
500, 3,000 and 4,200 mg/L and for Al(SO₄)₃ 545, 2,182 and
4,500 mg/L. The results of SDI and MFI are shown in Table 3
and profiles of MFI are shown in Fig. 3.

The values of SDI and MFI recommended by Tchobanoglous et al. [17] and the membrane manufacturers,
for water treatment by NF or RO processes, are SDI < 3.0/min and SDI < 2.0/min, respectively, and MFI < 1.0 × 10⁻³ s/mL² and MFI < 2.0 × 10⁻⁴ s/mL², respectively. These values are typically applied to process water with
low scale potential [32,33]. Therefore, the filtration profile
(inverse of the filterability, in MFI graph) during the MFI
test was preferably used to evaluate the performance of the
couagulants, in present work.

SDI did not present a significant difference in comparison
among the pretreated leachates and the raw leachate. Since
SDI measures suspended solids, mainly colloidal material,
derived from silicates of aluminum or iron and organic

Table 3
Results of SDI and MFI for raw leachate and leachate after
couagulation/flocculation processes. Raw leachate = sample III

<table>
<thead>
<tr>
<th>Sample</th>
<th>SDI (min⁻¹)</th>
<th>MFI (s/mL²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw leachate</td>
<td>19.6 ± 0.2</td>
<td>1.64 ± 0.04</td>
</tr>
<tr>
<td>Pretreated leachate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 6.0 and 500 mg FeCl₃/L</td>
<td>18.9 ± 0.5</td>
<td>0.63 ± 0.02</td>
</tr>
<tr>
<td>pH 6.0 and 3,000 mg FeCl₃/L</td>
<td>16.6 ± 0.2</td>
<td>(6.0 ± 0.2) × 10⁻⁴</td>
</tr>
<tr>
<td>pH 6.0 and 4,200 mg FeCl₃/L</td>
<td>17.1 ± 0.1</td>
<td>(2.8 ± 0.1) × 10⁻³</td>
</tr>
<tr>
<td>pH 6.0 and 545 mg Al(SO₄)₃/L</td>
<td>17.2 ± 0.6</td>
<td>0.92 ± 0.03</td>
</tr>
<tr>
<td>pH 6.0 and 2,182 mg Al(SO₄)₃/L</td>
<td>17.2 ± 0.6</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>pH 6.0 and 4, 500 mg Al(SO₄)₃/L</td>
<td>18.4 ± 0.8</td>
<td>(3.58 ± 0.15) × 10⁻²</td>
</tr>
</tbody>
</table>

Table 2
Characterization of leachate samples after pretreating with coagulation/flocculation processes

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Coagulant: FeCl₃</th>
<th>Coagulant: Al(SO₄)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw leachate</td>
<td>Pretreated leachate</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>Sample I</td>
<td>Sample II</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>2,113</td>
<td>340</td>
</tr>
<tr>
<td>Color (mg PtCo/L)</td>
<td>5,106</td>
<td>966</td>
</tr>
<tr>
<td>ABS254</td>
<td>19.3</td>
<td>3.6</td>
</tr>
<tr>
<td>NH₄-N (mg/L)</td>
<td>623</td>
<td>620</td>
</tr>
<tr>
<td>HS (mg/L)</td>
<td>572</td>
<td>250</td>
</tr>
</tbody>
</table>
concentration.

pretreated landfill leachates with other techniques than above that recommended in the scientific literature for high residual Fe coagulant (pH 6.0 and 3,000 mg FeCl₃/L), probably due to high residual Fe⁺ concentration.

Other researches also obtained values of SDI and MFI for the different samples analyzed.

4. Conclusion

The characterization of this leachate revealed a high concentration of organic matter, being compatible with data from the scientific literature for stabilized leachate originated in landfills over 30 years old.

The coagulation/flocculation process, using FeCl₃ and Al₂(SO₄)₃ as coagulating agents, was satisfactory as a preliminary treatment of Gericinó leachate, reducing significantly the sample’s concentration of organic matter and true color. However, FeCl₃ showed better performance in removing organic matter from leachate as well as in reducing fouling potential for membrane processes. Considering both aspects, the best conditions for applying this pretreatment were pH 6.0 and 3,000 mg FeCl₃/L, which lead to a reduction of 56% of absorbance at 254 nm, removal efficiency of 82% of true color, 40% of TOC and more than 69% of COD.

Finally, it should be noted that the SDI parameter was not the most adequate to evaluate the fouling potential for this type of sample, since it did not show the required sensitivity for the different samples analyzed.

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References


