



A circular approach for landfill leachate treatment: Chemical precipitation with biomass ash followed by bioremediation through microalgae

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ABSTRACT

The aim of this work was to study an integrated approach for landfill leachate remediation comprising chemical precipitation with biomass bottom ash as a pre-treatment to reduce color and turbidity followed by bioremediation through microalgae treatment for effluent disposal. Optimal pre-treatment conditions were determined through batch experiments and were found to be 160 g L⁻¹ ash dose, 96 h of contact time, overhead agitation at 15 rpm and ash particle size below 500 μm. These conditions led to removal efficiencies of 74.3% for chemical oxygen demand and 98.5% for color. Large quantities of sludge containing excess biomass ash and precipitated compounds were formed during the pre-treatment. To minimize solid disposal, this sludge was tested as a raw material for cementitious and aggregate substitute in mortar formulations. Following the pre-treatment, the leachate was inoculated with six different microalgae species to evaluate their ability to grow in such a recalcitrant effluent and remediate it. After a period of 27 days biomass concentration from 0.4 to 1.2 g L⁻¹ were achieved for the tested microalgae. Removal efficiencies were in the range of 18–62% for COD, 63–71% for N, and 15–100% for P. At the end of the treatment, algal biomass was characterized regarding protein, lipid, fatty acids, carbohydrate, and ash contents. This approach allows a low-cost remediation of these recalcitrant effluents when compared with the present options that include inverse osmosis, and the valorization of ash-rich precipitates and microalgae biomass improves the sustainability of the overall process.

1. Introduction

One of the most significant aspects in landfill management is the production of a highly complex leachate, that represents a very serious pollution problem affecting soils, water bodies and human health. Landfill leachate is an aqueous solution of organic and inorganic components produced by infiltration of rain water into the layers of waste deposits exposed to environmental conditions and subject to processes of aerobic and anaerobic decomposition by the local microbiome [1]. The composition of leachate is highly variable depending mostly on the type of waste in the landfill, landfill age, climate conditions and geochemical characteristics of the landfill site [2]. These complex

effluents are characterized by a dark color, bad odor and significant values of chemical oxygen demand (COD), ammonia-nitrogen and heavy metals [3]. Among the different leachate categories, the treatment of stabilized leachate is very difficult to achieve, largely due to the presence of refractory substances, such as humic and fulvic acids, which are not easily degraded [4,5]. To eliminate these refractory organic materials found in stabilized landfill leachate, it is necessary to use complementary remediation techniques, such as membrane technologies, ion exchange, adsorption by activated carbon, flocculation-coagulation, chemical oxidation or advanced oxidation processes [4,6]. The combination of different treatment processes has been proposed by several authors in order to achieve high treatment efficiencies and maximize the

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removal of organic and inorganic contaminants [1,7].

Chemical precipitation is a widely applied pre-treatment for wastewater treatment that aims to remove ammonia-nitrogen, heavy metals and other non-biodegradable organic compounds [8,9]. This process involves the combination of metal cations and some soluble anions to form insoluble species that precipitate and are subsequently removed by sedimentation or filtration. Several chemical precipitating agents can be used in this process, such as lime (CaO), hydrated lime (Ca(OH)₂) and combinations of magnesium oxide (MgO) and phosphates (PO₄³⁻) [10, 11].

Renou et al. [12] developed and optimized a treatment method for stabilized leachate by combining chemical precipitation using lime followed by filtration and reverse osmosis. This approach not only eliminated the brown color of the leachate, but also achieved 20–30% and 25–56% removal of COD and ammonia-nitrogen, respectively. In another study by the same authors, chemical precipitation with Ca(OH)₂ was investigated as a pre-treatment before ultrafiltration. The authors demonstrated that the chemical precipitation step allowed a 50% decrease in investment costs for the ultrafiltration unit and a 5–30% decrease in its operating costs [13].

The advantages of chemical precipitation when compared to other methods are its simplicity and low implementation costs. But the constant consumption of the chemical agent and the need to eliminate the generated sludge may increase operating costs, impairing economic viability [14]. As such, minimizing costs for this process entails finding low-cost precipitating agents, with suitable chemical characteristics and that are available in significant amounts. Biomass ash is an inorganic by-product of solid biofuels' combustion that is generated in large amounts in industrial boilers or thermal power plants. Usually, this by-product contains high concentrations of silicon, aluminum, iron, calcium, and magnesium oxides, and is known for its precipitating capacity [15]. There is an increasing number of thermal power plants operating on forestry biomass or biomass wastes worldwide, generating around 480 million tons of ash [16]. This ash may be used for soil amendment or incorporated in construction materials. However, new valorization processes should be proposed in order to manage such large quantities following environmentally friendly and sustainable criteria [15,17]. Chemical precipitation using fly or bottom ash is not very well documented in the literature and the works are mostly focused on the removal of metallic species from industrial wastewater [18]. Although chemical precipitation allows removal of several organic and inorganic contaminants, the process also involves extensive dissolution of ash components in the aqueous medium, namely calcium or magnesium cations, hydroxide ions or phosphates. Those soluble components yield high COD values and high pH values to the treated effluent. Consequently, the effluent must be acidified to return to neutrality and subjected to reverse osmosis or ion exchange processes to achieve regulated COD values [19].

Bioremediation with microalgae may also be used as a final step to reduce the concentration of dissolved components after chemical precipitation, due to the capacity of those microorganisms to absorb inorganic compounds [20]. Microalgae have been widely studied as biomass sources for several purposes, but also as bioremediation agents for treatment of wastewaters given their adaptability and few production requirements [21]. Previous works have established the ability of these microorganisms to remediate different contaminated effluents, such as dairy [22,23], urban [24,25], aquaculture [26], brewery [27,28], poultry [29] or power plant wastewaters [30]. There are also some studies on landfill leachate bioremediation using microalgae, but they are mostly performed with significant dilutions (between 1:5 and 1:10) to reduce color and allow the diffusion of light into the effluent [31] or using membrane reactors, where there is no direct contact between the microalgae and the leachate. This system allows for nutrient reclamation, such as nitrogen and phosphorus, but not a thorough removal of other leachate components [32]. The use of high dilution rates or membrane filtration also allows reducing the concentrations of

components with high toxicity for microalgae, and of the organic components that contribute to the opacity of the leachates. Nevertheless, large dilutions will require significant amounts of water and land space, making this solution less sustainable for large scale applications [33]. The association between leachate pre-treatment techniques and bioremediation with microalgae may be an alternative approach to overcome these limitations and achieve appropriate removal efficiencies. Nair et al. [33] used coagulation with aluminum sulphate and air-stripping to reduce the concentration of organic compounds, color and ammonia-nitrogen in a landfill leachate followed by bioremediation using *Chlorella pyrenoidosa*. This approach was intended to complete the removal of species contributing to the high COD value. The final concentration of microalgae biomass reached a value of 2.9 g L⁻¹ while consuming carbon dioxide at the rate of 0.26 g L⁻¹ d⁻¹ and achieving a COD removal of 74%.

The present work intends to study a sustainable approach to the treatment of a landfill leachate, by combining chemical precipitation with a low-cost precipitation agent (biomass ash), followed by bioremediation through microalgae. This combined approach involved the study of optimal precipitation conditions (concentration of precipitation agent, contact time and agitation type), followed by the evaluation of the bioremediation efficiency of different microalgae species (*Chlorella vulgaris*, *Chlorella protothecoides*, *Scenedesmus obliquus*, *Spirulina major*, *Isochrysis galbana* and *Nannochloropsis salina*). To the best of our knowledge, this is the first study where the pre-treatment with biomass ash is coupled with microalgae bioremediation to achieve adequate treatment conditions for highly loaded and poorly biodegradable landfill leachates. Moreover, potential applications for the obtained algal biomass were addressed, as well as possible pathways for the valorization of by-products formed during the chemical precipitation process. The evaluation of process by-products intends to assess the overall reduction in emissions whilst improving the sustainability of the global process.

2. Material and methods

2.1. Raw materials

Landfill leachate was collected at CITRI S.A., an industrial non-hazardous solid wastes landfill, located in Setúbal, Portugal. At the time of sample collection, the landfill was 6 years old, with a waste disposal rate of 100,000 ton year⁻¹. The average annual flow rate of leachate production is 3.4 m³ h⁻¹ [34,35]. Leachate was collected from the buffer pond in a 20 L plastic container and was stored at 4 °C to minimize chemical and biological changes.

The bottom ash used in these experiments was supplied by Prélis Cerâmicas Lda. and it is a by-product from the combustion of forestry biomass mixed with refuse derived fuel (RDF) in ceramic furnaces.

2.2. Landfill leachate characterization

The landfill leachate sample was characterized for its main physical-chemical properties. Color was evaluated by measuring the optical density at 600 nm (OD₆₀₀) as described by Ricordel & Djelal [36], using a spectrophotometer (Biocrome S4 Libra). Chemical oxygen demand (COD) was measured according to EPA 410.4 protocol using a HI83099 photometer (Hanna Instruments, USA). The values of pH and conductivity were determined using a pH meter (Crison MicropH 2001 meter) and a conductivity meter (Mettler Toledo MC226), respectively. Total solids, total suspended solids, total Kjeldahl nitrogen, total phosphorus and chlorine content were measured according to methods described in the Standard Methods for the Examination of Water and Wastewater [37]. Total phenolics were measured by the Folin-Ciocalteu method through an adaptation of the method described by Singleton et al. [38], using gallic acid as a calibration standard. Mineral composition (Al, B, Ba, Ca, Cr, Fe, K, Mg, Na, Ni and Zn) was determined by ICP-AES (Horiba

Jobin-Yvon Ultima). All the characterization analyses were conducted in triplicate, and the presented values correspond to average values (\pm standard deviation).

Detailed characterization of the landfill leachate is presented in Table 1.

2.3. Bottom ash characterization

The pH of the bottom ash was determined with a pH meter (Crison MicropH 2001 meter) in a water/ash suspension (10 L g⁻¹) after equilibrium for 24 h at room temperature [39]. Particle size distribution was determined by placing a known mass of bottom ash on a vibratory sieve shaker (Retsch) equipped with test sieves (Retsch) with dimensions of 500, 425, 250, 125, 100 and 50 μm . Screening was done for 10 min, after which the mass of sample collected in each sieve and the fraction smaller than 50 μm were weighed (Mettler Toledo AB204-S) [40]. Elemental analysis of the bottom ash was determined through X-Ray fluorescence spectrometry (Philips X Unique II spectrometer).

Detailed characterization of the bottom ash is presented in Table 2.

2.4. Chemical precipitation experiments

Chemical precipitation was carried out in batch experiments at room temperature in 100 mL flasks on an overhead shaker (Heidolph REAX top shaker) at 15 rpm to ensure uniform mixing. Optimization of operational conditions was done in a series of experiments varying the following parameters: ash particle size, contact time, agitation system and bottom ash dose. Effect of particle size was done by screening the bottom ash into different fractions of < 500 > 425 μm , < 425 > 250 μm , < 250 > 125 μm , < 125 > 100 μm , < 100 > 50 μm , < 500 μm (a mixture of all the fractions below 500 μm) and using the fractions in precipitation experiments. A fixed dose of each ash fraction was added to 50 mL of landfill leachate and the mixture was shaken for 2 h, in an overhead shaker at 15 rpm. Bottom ash without any treatment was also used for control. The effect of contact time was studied with an ash concentration of 120 g L⁻¹ leachate, in an overhead shaker at 15 rpm, for contact times of 2, 6, 24, 48, 72 and 96 h.

Agitation system experiments consisted of treating 50 mL of landfill leachate with a fixed amount of bottom ash with initial manual agitation

Table 1
Landfill leachate main characteristics.

Parameter	Units	Value
Color (OD _{600nm})	–	4.0 (\pm 0.1)
pH	–	8.1 (\pm 0.3)
Conductivity	mS cm ⁻¹	33.7 (\pm 0.9)
Total solids	mg L ⁻¹	33,658 (\pm 1103)
Total dissolved solids		31,908 (\pm 624)
Volatile solids		8368 (\pm 651)
Fixed solids		25,290 (\pm 719)
Total suspended solids		1750 (\pm 156)
COD	mg O ₂ L ⁻¹	9600 (\pm 571)
BOD ₅		1150 (\pm 70)
Total nitrogen	mg L ⁻¹	3295 (\pm 438)
Kjeldahl nitrogen		3266 (\pm 435)
Total phosphorus		22.9 (\pm 0.1)
Total phenolics	mg Gallic acid equivalents.L ⁻¹	742.2 (\pm 27.6)
Chlorine	mg L ⁻¹	10,497 (\pm 289)
Al		13.3 (\pm 1.7)
B		1.3 (\pm 0.2)
Ba		1.5 (\pm 0.5)
Ca		318.2 (\pm 30.4)
Cr		0.2 (\pm 0.1)
Fe		2.7 (\pm 0.4)
K		430.7 (\pm 40.8)
Mg		31.3 (\pm 6.9)
Na		624.4 (\pm 5.3)
Ni		0.1 (\pm 0.0)
Zn		1.5 (\pm 0.3)

Table 2
Bottom ash characterization.

Parameter	Value
<i>Particle size distribution (wt%)</i>	
> 500 μm	75.2 (\pm 0.2)
< 500 μm > 425 μm	6.6 (\pm 0.7)
< 425 μm > 250 μm	6.3 (\pm 1.3)
< 250 μm > 125 μm	6.5 (\pm 0.3)
< 125 μm > 100 μm	4.2 (\pm 0.1)
< 100 μm > 50 μm	1.1 (\pm 0.2)
pH	13.02 (\pm 0.03)
<i>Mineral composition (wt%)</i>	
Al ₂ O ₃	3.97 (\pm 0.04)
BaO	0.163 (\pm 0.002)
CaO	65.9 (\pm 0.2)
Cl	11.5 (\pm 0.04)
Cr ₂ O ₃	0.0679 (\pm 0.006)
CuO	0.0582 (\pm 0.003)
Fe ₂ O ₃	2.28 (\pm 0.03)
K ₂ O	1.180 (\pm 0.030)
MgO	3.16 (\pm 0.02)
MnO	0.17 (\pm 0.008)
Na ₂ O	0.556 (\pm 0.01)
P ₂ O ₅	0.765 (\pm 0.01)
SO ₃	0.915 (\pm 0.01)
SiO ₂	6.59 (\pm 0.06)
SrO	0.0855 (\pm 0.001)
TiO ₂	2.52 (\pm 0.06)
ZnO	0.0883 (\pm 0.001)

and leaving the flasks at rest during different contact times (6, 24, 48, 72 and 96 h). The same procedure was applied to flasks with the same experimental conditions using the overhead shaker at 15 rpm.

To determine the effect of bottom ash dose, ash concentrations of 80, 120 and 160 g L⁻¹ were evaluated for contact times of 6, 24, 48, 72 and 96 h. All the batch experiments were done in triplicate for each different parameter. After each experiment, the pre-treated leachates were filtered using technical filter paper to separate the formed sludges and treatment efficiency was monitored by measuring the filtrate color and COD, as described in Section 2.2.

Pre-treated landfill leachate produced under optimized conditions was further characterized regarding pH, conductivity, color, COD, BOD₅, Kjeldahl nitrogen, total phosphorus, total chlorine, total solids, total suspended solids, total phenolic content, and mineral composition as described in Section 2.2. All analysis were conducted in triplicate and the presented values correspond to average values (\pm standard deviation). Removal efficiency for each parameter was calculated using Eq. (1):

$$\text{Removal efficiency}(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f refer to initial and final concentration of a given characterization parameter.

2.5. Mortar formulations using residual sludge from landfill leachate pre-treatment

The sludge formed after landfill leachate pre-treatment (in optimized conditions) was air-dried for 24 h and tested as a replacement material for cement or aggregate in mortar formulations. For mortar production, the dried sludge was crushed and sieved in two fractions, < 63 μm and > 63 μm , corresponding to 46.6 wt% and 53.4 wt% of the total dried sludge mass, respectively. Two mortar formulations were produced: one as a cement substitute using the fraction < 63 μm (10 wt% substitution level) and the other as aggregate substitute using the fraction > 63 μm (10 wt% substitution level), according to the mortar mix design described in Table S1 (Supplementary Material). Mortar production and testing was executed according to NP EN 196-1:2006. The mortar mixture was poured under vibration into prismatic molds with

dimensions of $40 \times 40 \times 160 \text{ mm}^3$ which were covered with a plastic film in order to prevent water loss and stored for 24 h in a wet chamber (at approximately 87% relative humidity and $21 \text{ }^\circ\text{C}$ temperature). After 24 h, the mortars were demolded and cured in a water bath for 28 days. The workability of mortars was determined according to their spread diameter (expressed in mm). Compressive and flexural strength tests were performed at 28 days of curing age. The tests were conducted in triplicate and the produced mortars were compared with the reference mortar.

2.6. Bioremediation-based microalgae studies

2.6.1. Microalgae and growth media

The bioremediation of the pre-treated landfill leachate was evaluated using six microalgae species: *Chlorella vulgaris* - Cv (INETI 58, LNEG_UB, Portugal), *Chlorella protothecoides* - Cp (UTEX # 25 - INETI, LNEG_UB, Portugal), *Scenedesmus obliquus* - Sc (ACOI 204/07, Coimbra University Algotec, Portugal), *Isochrysis galbana* - Ig (CCAP 927/1, Scottish Marine Institute), *Nannochloropsis salina* - Ns (CCAP 849/2, Scottish Marine Institute) and *Spirulina major* - Sm (CCAP 1475/3, Scottish Marine Institute).

The experiments were conducted in 2 L graduated cylinders photo-bioreactors sealed with hydrophobic cotton, with a working volume of 820 mL and air bubbling agitation Stellar 380D, ($15.2 \text{ L L}^{-1} \text{ culture h}^{-1}$) to stir the culture and prevent cell sedimentation, to avoid stratification of nutrients and light, and to exchange O_2 and CO_2 . The microalgae grew at room temperature ($28 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$), under artificial lighting of $140 \mu\text{E m}^{-2} \text{ s}^{-1}$ (LED fluorescent lamps, digital luxmeter ROLINE, model RO 1332A) with cycles of 12 h light/12 h dark.

The trials were carried out using the pre-treated leachate diluted with deionized water (1:2) as a culture medium for the six microalgae species and with pre-treated landfill leachate without dilution for *Chlorella vulgaris* (designated as Cv-leachate). The inoculations were performed using approximately 20 mL of inoculum calculated in order to have an initial optical density (at 540 nm) between 0.2 and 0.4 [24]. Microalgae controls were grown in synthetic culture media, as follows: Cv and Cp were grown in *Chlorella* medium [41], Sc was grown in Bristol medium, Ig and Ns were grown in F/2 medium and Sm was grown in ASW:BG11 medium [42].

2.6.2. Microalgae growth monitorization

During the trials, samples were collected every 48 h from the bioreactors to evaluate pH (pH Tester pH108) and microalgae growth by measuring optical density at 540 nm (OD_{540}) using a spectrophotometer (Biochrom S4 Libra). Samples were also taken once a week to analyze Kjeldahl nitrogen, nitrates and total phosphorus according to the methods described in Standard Methods for the Examination of Water and Wastewater [37]. Microalgae dry weight was determined once a week by filtering the samples through a Whatman GF/C 47 mm filter [24]. When microalgae growth reached the stationary phase, the culture was harvested by centrifugation at 7000 rpm for 5 min (Sigma 4K15). The supernatant was analyzed for the parameters described in Section 2.2 and the algal biomass was dewatered and dried at $45 \text{ }^\circ\text{C}$ (Memmert oven) for 48 h for further characterization.

2.6.3. Biomass characterization

After drying, the collected algal biomass was ground for 4 min at a speed of 25 s^{-1} using a ball mill (Retsch, model MM400). Total nitrogen was determined by the modified Kjeldahl method [43] and total protein was calculated by multiplying the total nitrogen by the conventional conversion factor of 6.25 [44].

Total sugar content was determined after digestion using the method described by Miranda et al. [45] previously optimized for microalgae biomass. After digestion, total sugar content was determined by the phenol-sulfuric method [46]. Lipid content was determined after Soxhlet extraction with n-hexane and the lipid extracts were subjected to

transesterification by adding equal parts of sample and methanolic KOH (2N) [47]. Fatty acid composition of the extracts was determined by GC-MS (Focus GC, Polaris Q - Thermo), equipped with a DB-5 capillary column (30 m length, 0.25 mm inner diameter, and $0.25 \mu\text{m}$ film thickness). Samples were injected in splitless mode at $250 \text{ }^\circ\text{C}$ and the GC temperature was programmed as follows: initial temperature of $40 \text{ }^\circ\text{C}$, held for 1 min, increased to $150 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ and held for 15 min. Afterwards, temperature was increased to $250 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C min}^{-1}$ and lastly it was increased to $280 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$ and held for 10 min. The method used was an adaptation [48–51]. The transfer line and ion source temperatures were $250 \text{ }^\circ\text{C}$ and $230 \text{ }^\circ\text{C}$, respectively. The fatty acids were identified by comparing their mass spectra with those in NIST and WILEY databases and with the retention time and mass spectra of corresponding standards.

2.7. Statistical analysis

Experiments were performed in duplicate for microalgae growth and in triplicate for all the analysis, data were reported as mean \pm standard deviation (SD). The parameters such as removal efficiencies, productivities and biomass composition were compared using analysis of variance with one-way ANOVA, by IBM SPSS statistical 23 software. The mean values of individual samples, averages for culture medium and averages for each microalga were compared using the Tukey HSD test and correlation was considered statistically significant when $p < 0.05$.

3. Results and discussion

3.1. Landfill leachate and bottom ash characterization

The main characteristics of landfill leachate used in this work are described in Table 1.

This sample presented an alkaline pH (8.1) and a BOD_5 to COD ratio of 0.12, indicating that it could be categorized as a stabilized leachate. The COD value was relatively high which is generally associated with the presence of a refractory organic load, and may be related to the high concentrations of total dissolved solids and fixed solids showing a large contribution of inorganic soluble components [52]. The low BOD_5/COD ratios are typical of leachates obtained from industrial wastes that tend to contain a higher fraction of non-biodegradable compounds than leachates obtained from organic wastes. Factors such as leachate age and edaphoclimatic conditions also have an effect on the leachate's biodegradability. Leachate at an older age and under drier climates usually exhibit less biodegradability [13,53,54]. Also contributing to COD are some refractory organic compounds such as phenol derivatives whose concentration was $742 \text{ mg Gallic acid equivalents.L}^{-1}$. The high degree of leachate stabilization also limits treatment options, such as conventional biological methods that require considerable fractions of biodegradable organic material [55,56].

Conductivity was also relatively high, which can be explained by the high concentrations of anions and cations found in this landfill leachate sample. This observation is confirmed by the high concentrations of chlorides ($10,497 \text{ mg L}^{-1}$), calcium (318.2 mg L^{-1}), potassium (430.7 mg L^{-1}) and sodium (624.4 mg L^{-1}) detected in the leachate. Alkali and alkali-earth metals were the most abundant cations found in this leachate sample, indicating the presence of biomass-derived materials in the solid waste mix that originated the leachate [57].

Total dissolved solids also presented high concentrations, mainly due to the mineral component (fixed solids). Dissolved components were also related with the high color value measured as optical density at 600 nm, showing that the leachate sample presented light penetration limitations, thus affecting the ability to grow and develop bacteria or algae in the crude leachate. Kjeldahl nitrogen and total phosphorus contents were of 3266 mg L^{-1} and 22.9 mg L^{-1} , respectively, values that are comparable to those obtained for other stabilized leachate samples [58,59]. Unlike COD values and BOD_5/COD ratios, nitrogen

content tends to remain high as the landfill age increases. Apart from aluminum present at a concentration of 13.3 mg L^{-1} due to the presence of various aluminum wastes in the landfill, other metallic components were present in relatively low concentrations ($< 2.7 \text{ mg L}^{-1}$). This result may be explained by adsorption, precipitation and complexation reactions that occur in the landfill during the stabilization period in the storage pond [60].

The characteristics of this leachate determine the need for a pre-treatment step to reduce color, total solids and COD before any kind of bioremediation process can be evaluated.

The bottom ash used in the coagulation experiments was evaluated for granulometric distribution and mineral components, two key parameters for its application as coagulation agent (Table 2).

The ash sample is mainly composed by particles with diameter $> 500 \mu\text{m}$ but it is the fraction with diameter $< 500 \mu\text{m}$, corresponding to only 24.7% (wt%) of the total ash sample, that is expected to have a greater influence in the coagulation process given its higher surface area.

The partial dissolution of ash mineral components in the landfill leachate contributes to a pH increase, important to promote deprotonation of anionic species and facilitate its complexation by divalent and trivalent ions and subsequent precipitation [61]. The ash sample contains various mineral components, such as CaO (65.9%), Al_2O_3 (3.97%), Fe_2O_3 (2.28%) or MgO (3.16%), that may be a source of these cationic species that are necessary for the complexation processes.

3.2. Chemical precipitation experiments

COD and $\text{OD}_{600\text{nm}}$ were used as critical parameters to monitor the effectiveness of the chemical precipitation pre-treatment. These parameters were chosen because COD is a measure of the oxygen needed in the chemical oxidation of inorganic and organic matter in the leachate and $\text{OD}_{600\text{nm}}$ reflects its color evolution.

Throughout the batch experiments pH and conductivity of the leachate increased with the ash treatment to values of 11.8–12.4 and 44–54 mS cm^{-1} , respectively. This is expectable since hydroxides and other ash mineral components are partially soluble in water at room temperature, thus they will dissolve in the leachate, increasing the concentration of OH^- ions and other anions and cations in general.

The effect of the particle size distribution in the chemical precipitation efficiency was studied by performing independent precipitation tests using different fractions of the bottom ash (50–100 μm , 100–125 μm , 125–250 μm , 250–425 μm , 425–500 μm and $< 500 \mu\text{m}$ - a mixture of all particle sizes below 500 μm), as well as the bottom ash, as received. The highest removal efficiencies for both $\text{OD}_{600\text{nm}}$ (90.4–91.6%) and COD (59.7–61.1%) were obtained with the two smaller ash particle sizes (Fig. 1).

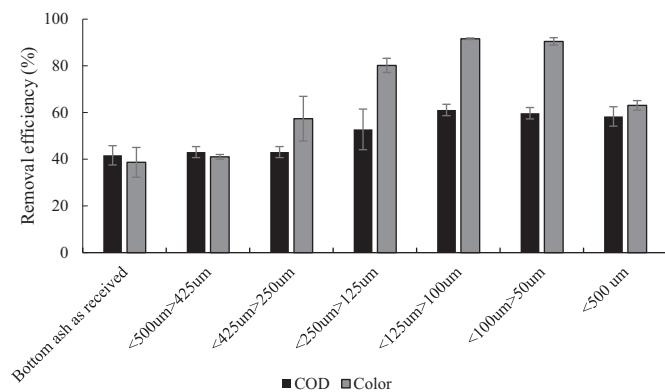


Fig. 1. Effect of bottom ash particle size distribution on landfill leachate COD and color removal ($\text{OD}_{600\text{nm}}$) efficiencies (Contact time = 2 h; Ash dose = 120 g L^{-1} ; Overhead agitation).

With the increase of particle size, the removal efficiencies decreased, possibly due to smaller surface area of larger particles or external mass transfer limitations. For the ash fractions with particle size larger than 250 μm , COD removal was less than 50% and $\text{OD}_{600\text{nm}}$ removal was less than 70%. Nevertheless, the tests held with the particle size fraction of $< 500 \mu\text{m}$ had COD and $\text{OD}_{600\text{nm}}$ removal values of 58.3% and 63.0%, respectively, representing an improvement compared to the behavior of the bottom ash as received.

The ash dose and the type of agitation used in this work showed significant influence in $\text{OD}_{600\text{nm}}$ and COD values (Fig. 2).

Without agitation, COD removal efficiencies higher than 50% were reached after 48 h and $\text{OD}_{600\text{nm}}$ removal efficiencies higher than 80% were obtained after 72 h. When using overhead agitation, comparable removal efficiencies were achieved for COD and $\text{OD}_{600\text{nm}}$, after 6 h and 24 h, respectively, showing that agitation accelerates the dissolution of ash components in the effluent, thus reaching equilibrium values in shorter times.

The ash dose was also varied from 80 to 160 g L^{-1} of leachate (Fig. 2c and 2d), and the best removal efficiencies were obtained for the highest ash dose (160 g L^{-1}) both for COD (60.1–87.6%) and $\text{OD}_{600\text{nm}}$ (96.3–98.2%). Nevertheless, as leachate color was more sensitive to this chemical precipitation treatment than COD, even with the lowest ash dose (80 g L^{-1}) removal efficiencies for $\text{OD}_{600\text{nm}}$ were higher than 70%, for all contact times.

COD removal can be related with the removal of highly recalcitrant organic compounds, such as humic and fulvic acids, which are also responsible for the dark brown color of the leachate. In alkaline conditions, this heavy organic fraction suffers deprotonation of its hydroxyl and carboxylic groups, increasing their tendency to form bonds with cationic species [62,63]. The large variety of polyvalent cations present in the bottom ash sample, as well as its alkaline nature (Table 2), favors complexation reactions of these humic substances. These results are in accordance with other works that used lime as a precipitating agent [13].

Considering the results obtained in the chemical precipitation experiments, a larger volume of landfill leachate was treated in selected conditions (ash dose of 160 g L^{-1} , contact time of 96 h, ash particle size $< 500 \mu\text{m}$ and overhead agitation) for further bioremediation studies. This bottom ash sample corresponds to wastes from industrial processes that would otherwise be landfilled. As such, bottom ash may be used in high concentrations without affecting the economic viability of the process. The treated leachate was characterized for a better description of the chemical precipitation effects and to define the leachate characteristics in the beginning of the bioremediation experiments (Table 3).

After the chemical precipitation treatment, $\text{OD}_{600\text{nm}}$ was reduced by 98.5%, turning the leachate's dark brown color into a light translucent yellow that enables light penetration, a necessary condition for microalgae growth (Fig. S1 Supplementary Material). Moreover, the COD and BDO_5 values of the treated leachate decreased by 81.1% and 92.0%, representing the removal of a significant fraction of the oxidizable compounds present in the original leachate. Nevertheless, it should be noted that the biodegradability of the leachate was not improved by the precipitation process. The process caused a decrease in BDO_5/COD ratio from 0.12 to 0.05, indicating that a large fraction of the precipitated species were biodegradable while more recalcitrant species remained in the treated leachate.

Total dissolved solids and fixed solids of the treated leachate increased by 23.1% and 49.5%, because of the partial dissolution of ash components. This ash dissolution effect is also reflected by the increase of pH, conductivity, and concentration of some inorganic components, such as chlorine, aluminum, barium, calcium, potassium, and sodium. Nevertheless, total suspended solids, Kjeldahl nitrogen, total phosphorus and total phenolics suffered considerable reductions (61.0%, 33.1%, 45.4% and 89.7%, respectively) following the pre-treatment, achieving values that are more adequate for the subsequent remediation step. B, Cr, Fe and Mg were also removed, indicating that these

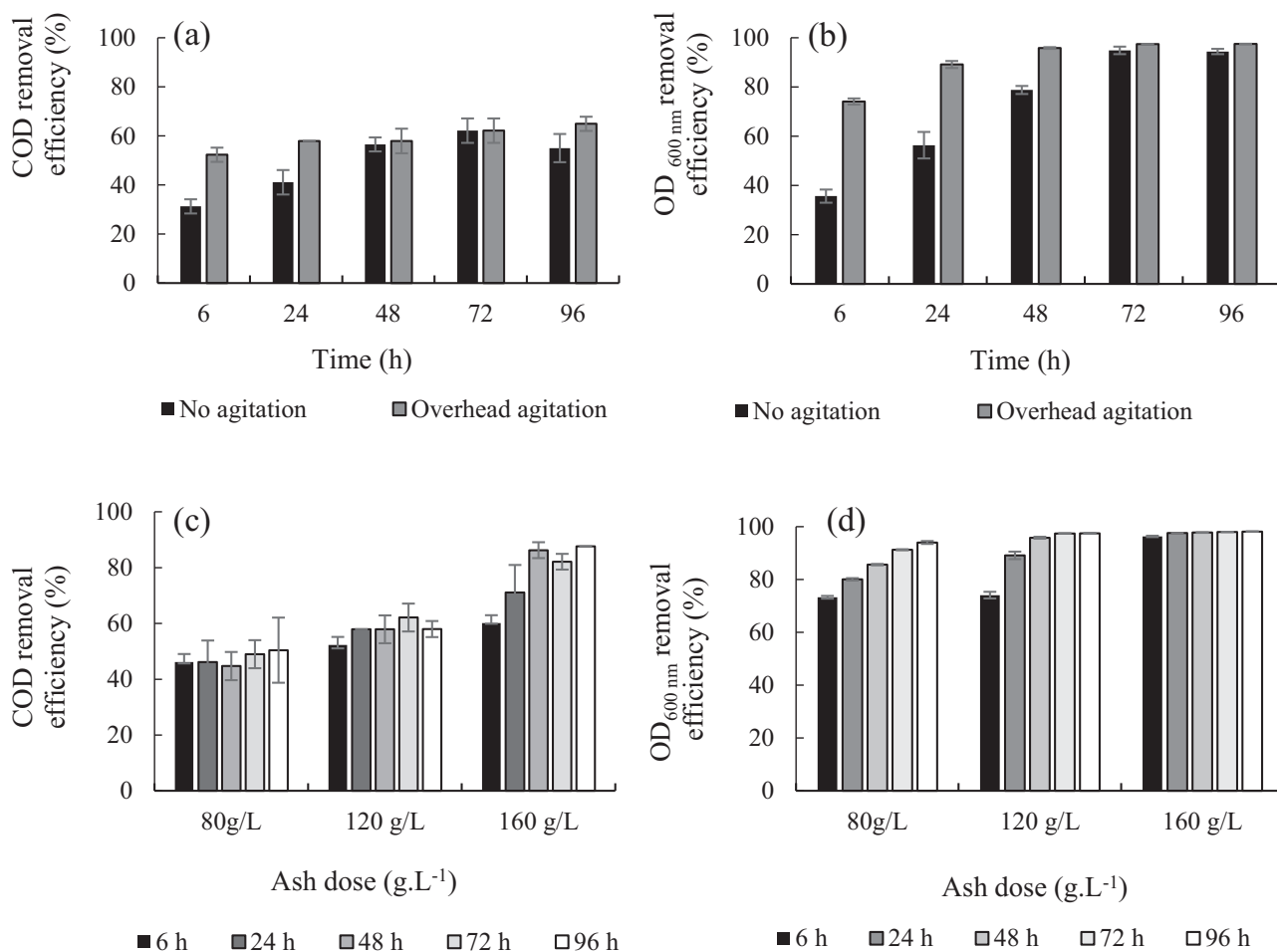


Fig. 2. Effect of agitation system and contact time on landfill leachate: (a) COD removal efficiency and (b) OD_{600nm} removal efficiency (Ash dose = 120 g L⁻¹; Particle size < 500 μm); Effect of bottom ash dose and contact time on landfill leachate: (c) COD removal efficiency and (d) OD_{600nm} removal efficiency (Overhead agitation; Particle size < 500 μm).

elements were not significantly dissolved during the ash treatment [64, 65]. Removal of mineral components is an important contribution of the bioremediation step. The pre-treatment process efficiently removes organic contaminants that contribute to the leachate color, but it is also a source of additional inorganic compounds that are transferred from the biomass ash into the leachate. Some components that were absent in the original leachate (Mn, Cu, Cd, Pb or Cr) were also not detected in the treated leachate, confirming that these components were not dissolved by contact with the biomass ash. However, these metals were virtually non-existent in the original leachate. Overall, biomass bottom ash showed the ability to act as a precipitating agent with significant improvements, particularly regarding color, total suspended solids, and COD, which were limiting factors for microalgae growth [66]. As such, this mineral waste has the potential to be used as an efficient, sustainable, and cost-effective alternative to the commonly applied precipitating agents in landfill leachate pre-treatment.

3.3. Microalgae bioremediation

Batch growth experiments were performed using the pre-treated leachate, as is or after dilution with distilled water (1:2), to evaluate the behavior of different microalgae (*Chlorella vulgaris*, *Chlorella protothecoides*, *Scenedesmus obliquus*, *Spirulina major*, *Nannochloropsis salina*, *Isochrysis galbana*) in this effluent when compared to a synthetic growth medium.

The batch growth experiments ended after 27 days, corresponding to

the achievement of COD levels below the legal discharge limits: 150 mg O₂ L⁻¹ [67]. Microalgae took a long time to develop in this effluent due to its characteristics (low degradability, chlorine, and phenolic content). The biomass concentration in these 27 days, expressed as the final concentration in the culture medium is presented in Fig. 3.

The obtained results indicate that Cv were able to grow in the pre-treated undiluted landfill leachate. The other tested microalgae were also able to grow in the pre-treated landfill leachate with dilution (1:2) achieving biomass concentrations that varied from 0.43 ± 0.16 g L⁻¹ (Ns) to 1.13 ± 0.00 (Sc), corresponding to 29.5–79.8% of the values obtained with the synthetic culture medium, respectively. These differences may be due to the low phosphorus concentration in the pre-treated leachate (12.5 mg L⁻¹) and the presence of some inorganic components that may present some toxicity, namely chlorine (22.8 g L⁻¹) or aluminum (23.6 mg L⁻¹).

Sc (1.13 ± 0.00 g L⁻¹), Cv (1.08 ± 0.05 g L⁻¹) and Cp (0.88 ± 0.04 g L⁻¹) stood out in terms of biomass concentration in the diluted leachate (Fig. 3). For these three microalgae, growth in the diluted leachate was not significantly different from growth in culture medium. The higher value of biomass concentration (1.23 ± 0.11 g L⁻¹) was obtained with Cv grown in the undiluted leachate, which may indicate that the diluted effluent contained insufficient nutrients. However, in preliminary tests using lower volumes of pre-treated undiluted leachate Sm, Ns and Ig microalgae cultures did not develop. These were the microalgae chosen for the preliminary tests because they

Table 3

Composition and properties of landfill leachate after the pre-treatment with bottom ash and corresponding removal efficiency (Pre-treatment conditions: 160 g L⁻¹ Ash dose; Overhead agitation; 96 h Contact time).

Parameter	Units	Value	Removal efficiency (%)
Color (OD _{600nm})	–	0.06 (± 0.00)	98.5
pH	–	12.7 (± 0.1)	–
Conductivity	mS cm ⁻¹	53.8 (± 0.3)	– 59.6
Total solids	mg L ⁻¹	39,960.3 (± 270)	– 18.7
Total dissolved solids		39,278.1 (± 1001)	– 23.1
Volatile solids		2146.7 (± 57.0)	74.3
Fixed solids		37,813.3 (± 579.6)	– 49.5
Total suspended solids		681.9 (± 70.5)	61.0
COD	mg O ₂ L ⁻¹	1818.2 (± 285.70)	81.1
BOD ₅		92.1 (± 13.9)	92.0
Total nitrogen	mg L ⁻¹	2204.6 (± 63.44)	33.1
Kjeldahl nitrogen		2184.0 (± 39.97)	33.1
Total phosphorus		12.5 (± 2.35)	45.4
Total phenolics	mg Gallic acid equivalents L ⁻¹	76.61 (± 7.4)	89.7
Chlorine	mg L ⁻¹	22,749.2 (± 1036.5)	– 116.7
Al		23.6 (± 0.13)	– 77.4
B		0.1 (± 0.0)	92.3
Ba		6.5 (± 4.9)	– 333.3
Ca		621.7 (± 77.1)	– 95.4
Cr		0.1 (± 0.0)	50.0
Fe		1.6 (± 0.4)	40.7
K		640.1 (± 34.7)	– 48.6
Mg		12.8 (± 0.92)	59.1
Na		660.5 (± 26.7)	– 5.8
Ni		0.1 (± 0.0)	0.0
Zn		1.8 (± 0.82)	– 20.0

Bold values represents the most significant removal efficiency reductions.

are theoretically the most adapted to media with high salt content [68–70].

The bioremediation efficiency for several critical parameters is presented in Table 4 for these seven batch growth experiments.

Removal of total nitrogen in the leachate was similar among the 6 microalgae, between 52.5 (for Ns-leachate 1:2) and 62.9% (for Cv-leachate). Phosphorus was completely or almost completely removed

by Sc, Sm, Ig and Cv-leachate. In contrast Cv-leachate (1:2) and Cp-leachate (1:2) practically did not remediate phosphorus. Since phosphorus concentration was already low in the original leachate (22.9 mg L⁻¹) and this component was widely removed during the pre-treatment step, the final concentration in the treated leachate was only 12.5 mg L⁻¹, constituting a limiting nutrient for microalgae growth. In these conditions, the low phosphorus removal efficiency observed for Cp and Cv-leachate (1:2) should correspond to some release of this element to the leachate by microalgae, since their cultures reached the onset of the death phase. Regarding COD, the removal efficiency in the leachate were between 64.8% (for Sc) and 85.7% (for Ns). COD removal obtained in the present study would allow to discharge the effluent treated by the Ns and Ig algae. These removal efficiencies are in line with the work of Quan et al. [71] with *Scenedesmus obliquus* microalga in landfill leachate. The removal efficiency of BOD₅ was higher than 67% for all microalgae, with Ns reaching 100%, which is a very promising result. All microalgae remediated around 52.2% and 58.5% of phenols, with Cv-leachate reaching the highest removal efficiency (70.4%). Removal of fixed solids varied between 31.8% and 55.7%, for the pre-treated diluted leachate (1:2). For the pre-treated leachate without dilution, fixed solids removal reached a value of 82.2% (with Cv microalga). Sodium, potassium, magnesium, and calcium are quite common metals in leachate, remaining in high concentrations even after pre-treatment, but did not interfere with microalgae growth.

3.4. Microalgae valorization

The produced algal biomass was evaluated by quantifying the protein, carbohydrates, lipids, and ash content at the end of the experiment, to evaluate the influence of the growth medium in the physiological state of the microalgae (Fig. 4).

The most notorious effect of the use of landfill leachate was the increase in the ash content of the microalgae, reflecting the capacity of these microorganisms to remove mineral components that are abundant in the treated leachate. All microalgae contained a higher amount of ash when grown in the leachate when compared to the same algae grown in control medium. In particular, the ash content of Cv grown in the treated leachate (CV-leachate) was higher than that of the same microalgae grown in the diluted leachate, (Cv-leachate, 1:2), suggesting that adsorption of mineral components from the culture medium was concentration dependent. The microalgae with the highest protein content were Sm (48.3 ± 1.2%), Cv (37.5 ± 1.6%) and Cp (37.1 ± 1.1%) controls followed by Sm, Cp and Cv-leachate (1:2) with 35.8 ± 2.4%, 33.8 ± 1.8% and 33.2 ± 3.1%, respectively. These results indicate that the treated leachate had a minimum of nutrients adequate for a protein

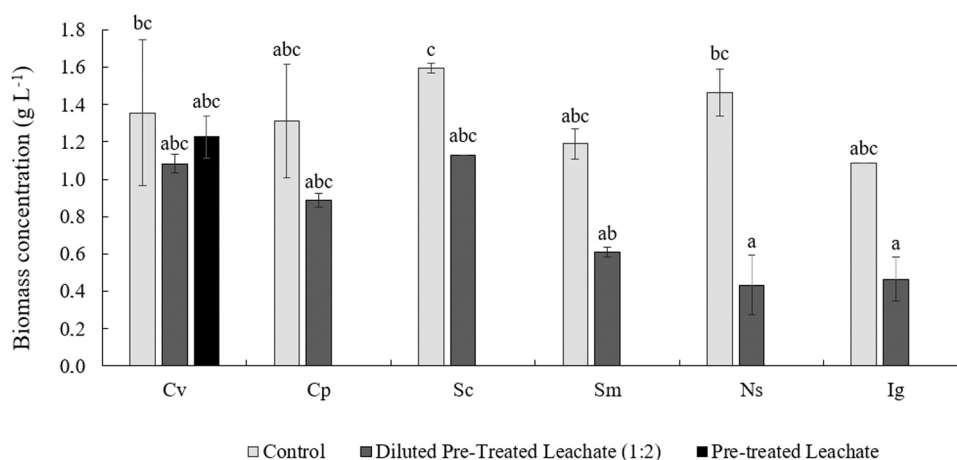


Fig. 3. Biomass concentration of the six microalgae in pre-treated landfill leachate and control after 27 days of culturing (mean ± SD, n = 2). Cv – *Chlorella vulgaris*; Cp – *Chlorella protothecoides*; Sc – *Scenedesmus obliquus*; Sm – *Spirulina major*; Ns – *Nannochloropsis salina*; Ig – *Isochrysis galbana*. Values with different index letters show significant differences with p < 0.05.

Table 4

Removal efficiency for bioremediated leachate with the six microalgae (Cv – *Chlorella vulgaris*; Cp – *Chlorella protothecoides*; Sc – *Scenedesmus obliquus*; Sm – *Spirulina major*; Ns – *Nannochloropsis salina*; Ig – *Isochrysis galbana*).

Sample	Removal efficiency (%)					
	Total nitrogen	Total phosphorus	COD	BOD ₅	Total phenolic compounds	Fixed solids
Cv - leachate (1:2)	59.2 ^a	16.9 ^a	70.3 ^{ab}	67.4 ^a	56.1 ^a	41.4 ^{ab}
Cv - leachate	62.9 ^a	96.0 ^b	79.7 ^{cd}	78.3 ^{ab}	70.4 ^b	82.2 ^c
Cp - leachate (1:2)	53.3 ^a	15.3 ^a	71.4 ^{ab}	78.3 ^{ab}	58.5 ^a	42.0 ^{ab}
Sc - leachate (1:2)	60.7 ^a	100 ^b	64.8 ^a	79.3 ^{ab}	56.7 ^a	55.7 ^b
Sm - leachate (1:2)	60.3 ^a	100 ^b	72.5 ^{bc}	89.1 ^{ab}	56.2 ^a	51.4 ^b
Ns - leachate (1:2)	52.5 ^a	88.3 ^b	85.7 ^d	100 ^b	58.4 ^a	31.8 ^a
Ig - leachate (1:2)	58.9 ^a	100 ^b	84.6 ^d	89.1 ^{ab}	55.3 ^a	43.8 ^{ab}

Note: Values with different index letters show significant differences with $p < 0.05$.

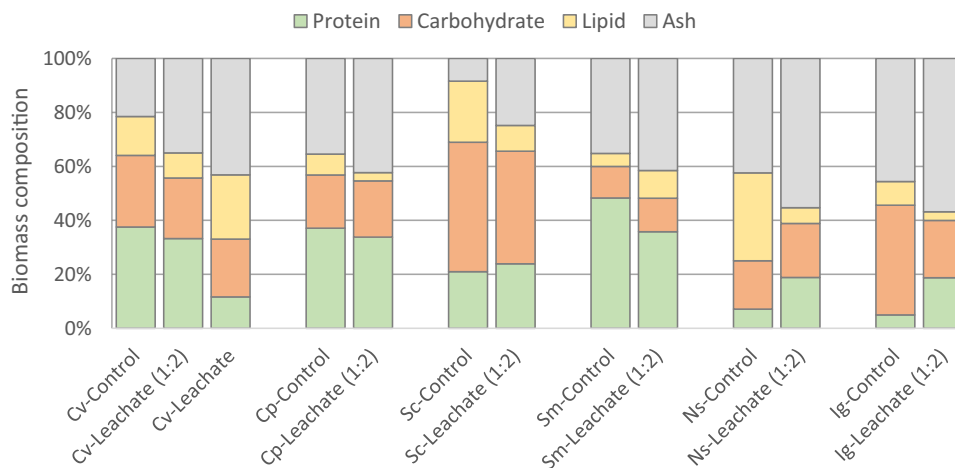


Fig. 4. Biomass composition (in % dry weight) for the six microalgae in pre-treated leachate and control medium (mean, $n = 3$). Cv – *Chlorella vulgaris*; Cp – *Chlorella protothecoides*; Sc – *Scenedesmus obliquus*; Sm – *Spirulina major*; Ns – *Nannochloropsis salina*; Ig – *Isochrysis galbana*.

production almost equivalent to the control medium. Nevertheless, the remaining microalgae grown in the leachate originated higher protein content than the ones grown in the control. For carbohydrates, Sc grown in control medium had a concentration of $48.0 \pm 3.8\%$, followed by Sc-leachate with $41.7 \pm 2.2\%$ and by Ig-control ($40.7 \pm 1.3\%$). The remaining microalgae had a value of $19.4 \pm 4.2\%$ for this parameter. Accumulation of carbohydrates in algal biomass is generally related to nutrient restriction namely during feast and famine cycles [72]. Nevertheless, the carbohydrate levels of the microalgae grown in the

treated leachate with or without dilution were comparable or lower than the same microalgae grown in control medium, indicating that nutrient availability was not a relevant stress factor during these experiments. Concerning lipid concentration, Ns-control presented a value of $32.6 \pm 1.9\%$, Cv-leachate had $23.8 \pm 0.8\%$ and Sc-control had $22.6 \pm 1.4\%$ while other microalgae showed a value of $7.7 \pm 3.3\%$.

According to the literature, the composition of microalgae varies depending on several factors, especially microalgae strain, light (intensity and period), temperature, pH, culture medium, and aeration

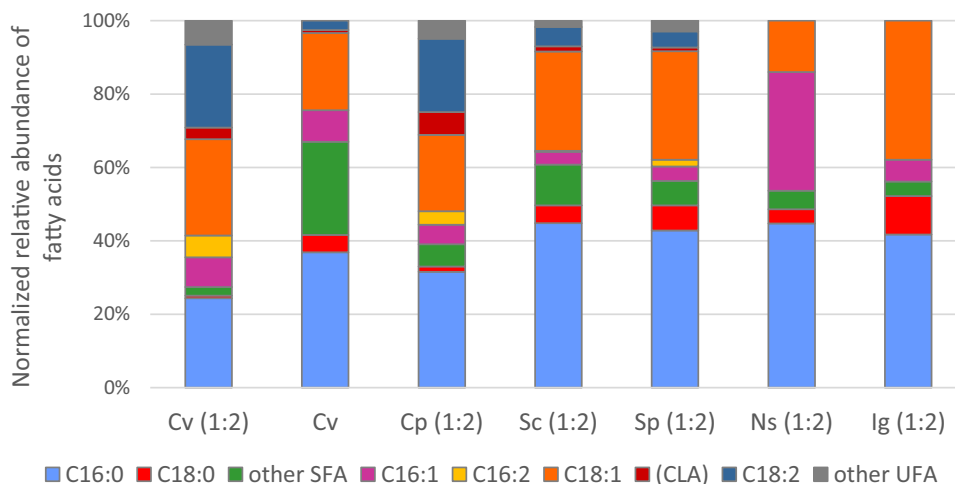


Fig. 5. Composition in fatty acids of microalgae grown in landfill leachate (Cv – *Chlorella vulgaris*; Cp – *Chlorella protothecoides*; Sc – *Scenedesmus obliquus*; Sm – *Spirulina major*; Ns – *Nannochloropsis salina*; Ig – *Isochrysis galbana*).

conditions [66]. However, the composition of the studied algae is within the average observed by other authors [22,73,74].

Regarding the fatty acid composition of the analyzed microalgae biomass, there is a predominant mixture of unsaturated fatty acids including palmitoleic (C16:1), hexadecadienoic (C16:2), oleic (C18:1), linoleic (C18:2), linolenic (C18:3) and conjugated linoleic acid (CLA). It also includes saturated fatty acids such as palmitic (C16:0), stearic (C18:0), behenic (C22:0) and lignoceric (C24:0). Fig. 5 shows the fatty acid profile found in the studied microalgae.

The tested microalgae did not develop the same proportions of fatty acids. Nonetheless, all microalgae have the highest relative abundance for palmitic acid (except for Cv (1:2) that has a higher abundance of oleic acid), followed by oleic acid (except Ns). Chang et al. [75] also investigated the development of *Chlorella vulgaris* in landfill leachate without direct contact with the leachate and concluded that the most abundant fatty acids were saturated, unsaturated and polyunsaturated, namely C16:0, C16:1, C16:2, C18:1 and C18:3. Other authors who analyzed *Chlorella* sp. and *Scenedesmus* sp. also concluded that the main fatty acids in these algae were C16:0, C18:2 and C18:1 [73,76]. Mitra & Mishra [77] studied the microalga *Nannochloropsis salina* and found the same proportion of fatty acids found in the present study. An experiment with *Isochrysis galbana* grown in medium with nitrogen starvation also concluded that the main fatty acids found in this microalga were C16:0 and C18:1 [78].

The obtained algal biomass could be used to produce biofuels, such as bioethanol, by alcoholic fermentation and/or biohydrogen, by dark fermentation, once Sc has about 41% of sugars in its composition. It could also be used to produce animal feed, since Cv and Sm have a balanced composition and a considerable amount of protein. And lastly, pigment extraction can also be an alternative, because pigments are very interesting high added-value products.

3.5. Mortar production

One of the main drawbacks of chemical precipitation includes the high dose of precipitant that is required, as seen in the previous section. These very significant amounts of precipitating agent generate sludge (ash + precipitated material), which needs further management or valorization. For that purpose, preliminary tests of mortar production were done, incorporating the sludge produced after chemical precipitation of landfill leachate. Mineral composition of the dried sludge is represented in Table 5.

This dried sludge sample mainly contains CaO (66.1%), possibly because the biomass material that was burnt consisted mainly of oxalates and carbonates [79,80]. This sample shows similarities with other biomass ash samples described in the literature, namely beech wood

chips [81], agave [82] or eucalyptus, maple or birch bark [83]. Chlorine concentration decreased when compared to the initial ash composition, mostly because this element was dissolved in the landfill leachate during precipitation, which can also be assessed in the characterization of the pre-treated landfill leachate (Table 3). The presence of chlorine in the bottom ash sample is related with the plastic component of the fuel that was used, since it also comprised RDF.

Characterization results for the produced mortars are detailed in Table 6 and the visual aspect of the dried sludge and produced mortars can be seen in Fig. S2 (Supplementary Material).

Differences on the average apparent density are small and according to Modolo et al. [85] ash-containing formulations tend to be slightly more compact. This is not the case with these samples, possibly because of their organic component resulting from the precipitation process. Since ash particles are small, the produced mixes are thicker, which reflects on the spread value. Nevertheless, only the 10% cement replacement sample showed a spread value below specification limits (140 and 170 mm). As seen in Table 6, the application of dried sludge both as a cementitious and aggregate replacement implies a decline in mechanical behavior. Both substitutions showed lower compressive strength values when compared to the reference mortar, although the decline was more expressive when using the dried sludge as an aggregate replacement.

Regarding flexural strength, both mortars with sludge incorporation showed lower values than the reference, although this reduction was in smaller extent when compared to the compressive strength. Other works using biomass ash as a cement replacement found flexural strength values similar to the reference mortar [86,87], whereas in the work of Rajamma et al. [88] this parameter also decreases. Overall, the mechanical properties measured in the produced mortars are lower than several literature reports using biomass ash in mortars [82,89]. The observed differences are probably due to the presence of a significant organic fraction in this dried sludge sample, corresponding to components such as humic and fulvic acids, typically present in the landfill leachates and removed by precipitation during the pre-treatment [90]. Nevertheless, the compressive strengths of the prepared mortars with incorporation of dried sludge were above 3,5 MPa, therefore obeying the criteria for CS III mortars, according to EN 998-1:2003 [91]. Also, the application of this sludge in construction materials could be further studied by testing other incorporation levels, allowing a useful valorization of this by-product as replacement of mineral resources.

3.6. Scale-up potential

Fig. 6 shows an annual diagram of the treatment of landfill leachate with the production of algal biomass and other by-products, with the inflows and outflows, under the same conditions as in the present study, but on an industrial scale. For this analysis, the amount of landfill leachate produced by CITRI, S.A. (in an annual basis), was considered. Data was collected according to their environmental license LA no. 20/2007 [35]. Considering only 6 months of leachate production at the

Table 5
Mineral composition of the sludge formed after landfill leachate pre-treatment.

Parameter	Value (wt%)
Al ₂ O ₃	4.03 (± 0.04)
BaO	0.142 (± 0.001)
CaO	66.1 (± 0.2)
Cl	7.78 (± 0.04)
Cr ₂ O ₃	0.0229 (± 0.003)
CuO	0.0457 (± 0.003)
Fe ₂ O ₃	2.42 (± 0.03)
K ₂ O	0.901 (± 0.02)
MgO	3.74 (± 0.02)
MnO	0.186 (± 0.000)
Na ₂ O	2.52 (± 0.03)
P ₂ O ₅	0.708 (± 0.01)
SO ₃	1.18 (± 0.02)
SiO ₂	7.4 (± 0.06)
SrO	0.0677 (± 0.001)
TiO ₂	2.67 (± 0.06)
ZnO	0.102 (± 0.002)

Table 6
Spread value, apparent density, compressive and flexural strength of the produced mortars.

Properties	Samples		
	Reference	10% cement replacement	10% aggregate replacement
Spread value (mm)	140.00 (± 0.00)	139.50 (± 0.71)	151.00 (± 1.41)
Apparent density (g cm ⁻³)	2133.20 (± 1.46)	2114.84 (± 5.10)	2038.41 (± 6.46)
Compressive strength (MPa)	22.70 (± 0.17)	14.60 (± 0.53)	13.60 (± 0.36)
Flexural strength (MPa)	6.16 (± 0.15)	4.92 (± 0.07)	4.92 (± 0.17)

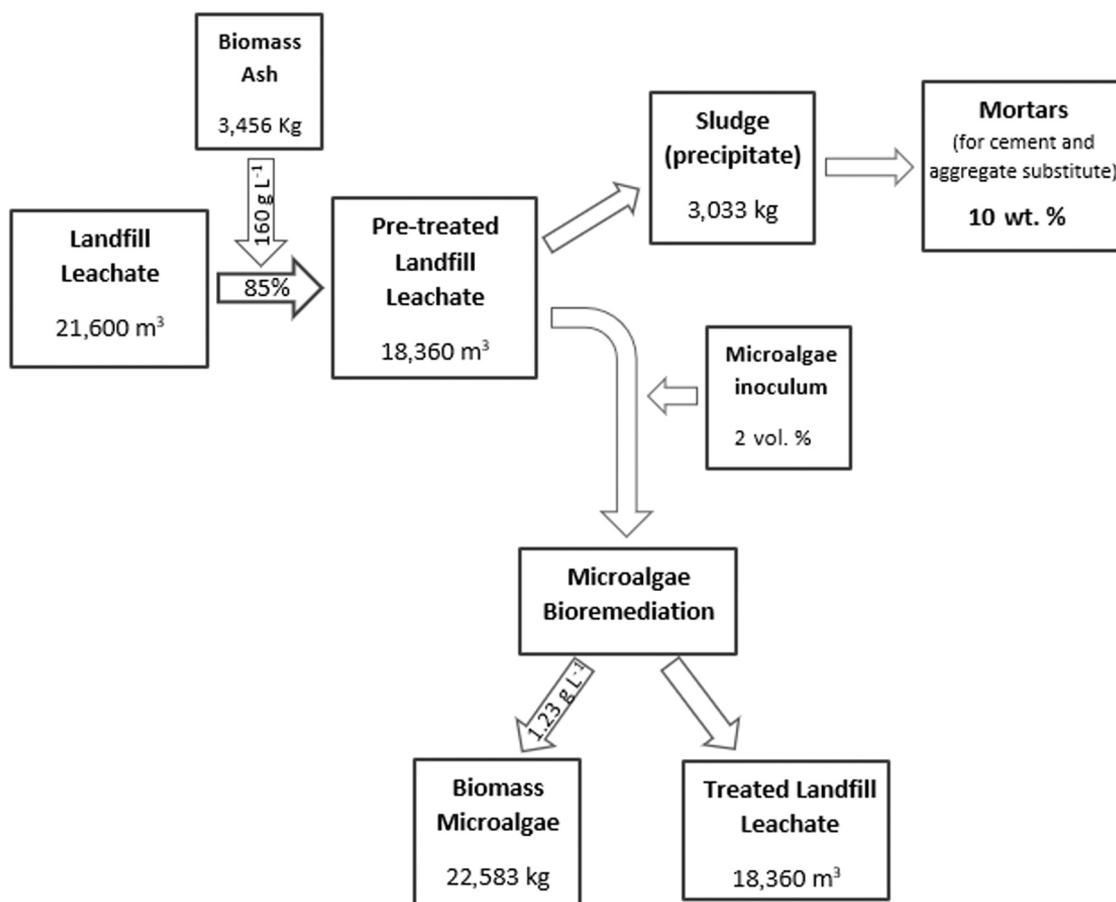


Fig. 6. Annual diagram of the potential for bioremediation of landfill leachate by microalgae on an industrial scale (based on the present study).

landfill and taking into account the reduced rainfall during the Spring / Summer period, it is possible to obtain a maximum leachate volume of $21.6 \times 10^6 \text{ L year}^{-1}$.

Applying a chemical pre-treatment with biomass ash (waste), with a yield of 85%, results in a pre-treated leachate volume of $18,360 \text{ m}^3$. This volume is sent to reactors where a bioremediation process with microalgae occurs. Considering a biomass concentration of 1.23 g L^{-1} in this leachate, it would be possible to obtain 22.6 tons of microalgal biomass.

4. Conclusions

The use of bottom ash in the pre-treatment of landfill leachate has been evaluated and optimal operational conditions were found to be an ash dose of 160 g L^{-1} , 96 h of contact time, using overhead agitation at 15 rpm and an ash particle size below $500 \mu\text{m}$. This pre-treatment strongly reduces color ($\text{OD}_{600\text{nm}}$) and COD by precipitation of recalcitrant organic matter that otherwise would impair the efficiency of other remediation processes. Nevertheless, ash dissolution contributes to the increase of pH and conductivity of the treated effluent and therefore further remediation steps must be applied to decrease critical discharge parameters.

The tested microalgae were able to reduce the levels of COD, total nitrogen, and phosphorus, but only *Isochrysis galbana* and *Nannochloropsis salina* reduce COD below the values permitted by law for discharge. The highest biomass concentration was obtained for *Chlorella vulgaris* grown in undiluted leachate (1.23 g L^{-1}), however *Isochrysis galbana* showed the best remediation efficiency (58.9% for total nitrogen, 100% for total phosphorus, 84.6% for COD and 89.1% for BOD_5). The obtained algal biomass shows potential to be used for biofuel production (bioethanol, by alcoholic fermentation or biohydrogen, by dark-

fermentation due to its high sugar content) and/or animal feed (according to protein content and PUFAs type), but also for pigment extraction, to be used as animal supplement.

Mortar production was assessed as a valorization pathway for the sludges produced by the chemical pre-treatment of the landfill leachate. The results showed that sludge incorporation had no significant effect in the mortars spread values or apparent density. But, the mechanical properties of the mortars worsened, indicating that this incorporation should be lower than 10 wt% or limited to material applications without stringent mechanical requirements.

Globally, this process enables an extensive removal of organic and inorganic components from landfill leachate, using approaches with low energy intensity and low operational costs and producing two tradable by-products, the microalgae biomass and the dry sludge that may be used in material applications.

CRediT authorship contribution statement

Catarina Viegas: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Writing - review & editing; **Catarina Nobre:** Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Writing - review & editing; **André Mota:** Investigation; **Cândida Vilarinho:** Resources, Writing - review & editing; **Luísa Gouveia:** Writing - review & editing, Funding acquisition; **Margarida Gonçalves:** Conceptualization, Resources, Supervision, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2021.105187](https://doi.org/10.1016/j.jece.2021.105187).

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