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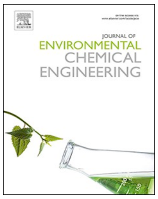

Immediate one-step lime precipitation and atmospheric carbonation as pre-treatment for low biodegradable and high nitrogen wastewaters: A case study of explosives industry

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ABSTRACT

The treatment of some industrial wastewaters is complex, since they usually contain complex non-biodegradable organic compounds or toxic compounds which are not easily treatable. These compounds are not removed by biological treatment in wastewater treatment plants and they may affect the removal of ammonium, nitrate, organic nitrogen by these treatment systems. Therefore, this research proposes a new and innovative low-cost and easy-to-apply pre-treatment to treat low biodegradable and high nitrogen wastewaters, using explosive wastewaters as case study. The pre-treatment is composed by immediate one-step lime precipitation (IOSLM) and atmospheric CO_2 carbonation (AC) processes. The novelty of the proposed pre-treatment is based firstly on the use of one reactant (hydrated lime) at high concentrations, added in one step, that produces immediately an abundant and insoluble precipitate able to sweep the organic matter and other contaminants from wastewater in a short time and ensure conditions (pH and Ca^{2+}) for the AC process. Secondly, the AC process uses the sludge produced in IOSLM to keep pH high for longer, allowing ammonia removal while simultaneously the pH is reduced by spontaneous reactions with atmospheric CO_2. IOSLM results showed 92.1 %, 98.2 % and 100 % of organic matter, oils and fats, and organic nitrogen removals, respectively, for the optimal hydrated lime dose ($7.76\ g\ L^{-1}$). In AC process 61 % of ammonium nitrogen was removed and pH reduced to 8.1 in 10 days.

1. Introduction

Industrial wastewaters usually contain complex non-biodegradable organic compounds or toxic compounds which are not easily treatable. Examples of these effluents can be found in textile industry due to the dyes and organic sizing agents used in the manufacturing process [1], in explosives industry as result of manufacture ammonium nitrate-fuel oil (ANFO), emulsion explosives, 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [2], in paper mills factories due to the amount of lignin, lignin derivatives and arsenic [3], and in tannery industry due to chemicals used in leather processing [4]. Furthermore, some of these industries discharge high amounts of wastewaters, especially when coming from large scale industrial parks, which may cause major environmental problems for the receiving water bodies. These compounds have high potential impact on human health and environment [2,5].

The treatment of these wastewaters is complex. Non-biodegradable compounds are not removed by the biological treatment of the wastewaters treatment plants (e.g., activated sludge) and they may affect the removal of ammonium, nitrate, organic nitrogen and organic matter in these treatment systems [6]. Therefore, a pre-treatment is required for these industrial wastewaters since, if not applied, the effectiveness of the biological treatment will be compromised. The pre-treatment of low biodegradable effluents has been a real challenge, especially when the effluent has specific features (as high concentrations of nitrogen) that could be removed biologically. In literature, some studies developed physical-chemical pre-treatment solutions to increase the

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biodegradability of the effluents, namely oxidation [7,8], electrochemical processes [9] and peroxi-coagulation [10], while other studies seek to remove non-biodegradable organic matter or toxic compounds of the effluents through membranes processes [11] or chemical precipitation and adsorption [12]. In chemical precipitation, the treatment of different industrial wastewaters with lime and hydrated lime has shown several benefits for the environment. Organic compounds present as suspended particles can be substantially removed by sweep coagulation phenomena caused by the formation and simultaneous precipitation of calcium carbonate. Moreover, dissolved compounds can also be removed, leading to significant reduction of several pollution parameters [13,14]. Georgiou et al. [13] used hydrated lime as a pre-treatment step for pH-raising and reduction of residual particulates of an anaerobic digestate generated in the treatment of animal manure. Hydrated lime was preferred because of its fast reaction and low cost, with effective clarification of the anaerobic digestate at high pH (≥11.5) [13]. These authors used air-stripping for ammonia removal, with removals ca. 100 % at 50 °C and 90 % at 30 °C (G/L = 2000) [13]. In Chen et al. [15], lime with fly ashes was preferred for the removal of heavy metals from industrial wastewater due to its relatively low cost. The application of carbonation improved the removal of heavy metals. Results showed that removals of Zn(II), Pb(II), Cu(II) and Cr(III) were enhanced between pH 7–11 and removals efficiencies as high as 99.37–99.69 % were obtained by the fly ash–lime-carbonation treatment [15]. A high arsenic acidic wastewater from a sulfuric acid factory was effectively treated in a combined process of pre-oxidation, lime and ferrous precipitation, ferric and manganese binary metal oxide (FMBO) adsorption and PACl coagulation [16]. A lime pre-treatment process, precipitation of lime by carbonation, for efficient bioethanol production from rice straw was developed without a solid–liquid-separation [17]. Carbonation was made using CO_2 gas bubbled into the treated slurry. This pre-treatment reveals very efficient [17]. These treatments were very efficient in removing the target compounds but some included several treatment processes and most were applied to remove heavy metals. In addition, some of these treatments have proven disadvantages, for example, air stripping presents high operating costs and often accumulates calcium carbonate on the walls of the stripping tower [17], and activated sludge is poorly tolerant to load and flow variations, and to toxic compounds [17]. Moreover, some treatments are expensive or produce sub-products which can be more harmful to the environment than the initial ones [18]. Therefore, it is necessary to find better alternatives for the treatment of these effluents. These alternatives should be technically feasible, low cost, less environmental impact and consider future reuses.

Thus, this study proposes a novel low-cost and easy-to-apply pre-treatment, composed by immediate one-step lime precipitation (IOSLM) followed by atmospheric CO_2 carbonation (AC) process, for low biodegradable organic matter and ammonium removal, using ANFO and emulsion explosives wastewaters as case study. This integrated pre-treatment is intended to improve the quality of these type of wastewaters to promote the viability of biological treatment or allow reuse within the factory processes. In addition, this environmental solution could mitigate the greenhouse gas production, boost the capture of ammonia to be reused in industries and recover the lime from the sludge produced through lime calcination processes. The research of the proposed integrated pre-treatment is based on the following assumption: (i) Hydrated lime is a low cost reagent [19] that can be easily acquired, and has been used efficiently to adjust pH and to remove hardness and impurities from water and wastewater [19–22]; (ii) Hydrated lime can be used as soil amendment for in situ remediation of explosives (RDX) and metals stabilization, as demonstrated by Martin et al. [23]; (iii) The effect of hydrated lime on the effluent biodegradability and on the removal of non-biodegradable organic compounds from ANFO and emulsion effluents have not been studied yet as far as the authors knowledge; (iv) Recent studies have shown that it is possible to reduce the pH by natural neutralization with atmospheric CO_2 (AC) at low-cost process [24,25]. However, no studies have referred the AC ability to remove ammonia or mentioned the effect of precipitated sludge (from chemical precipitation) in lowering the pH during the carbonation process.

2. Material and methods

2.1. Explosive wastewater (EW) characterization

EW was used as case study. EW was collected from an international industry that manufacture ANFO and emulsion explosives in Portugal. ANFO and emulsion explosives are used in mining industry quarrying and construction activities, and their demand has been increasing relative to other types of explosives due to their low manufacturing cost and risk of accidental ignition, and ease of handling [26,27]. ANFO explosives are composed of a mixture of ammonium nitrate (AN) with diesel fuel in the ratio of about 94 to 6% [28]. Emulsion explosives are composed of a dispersed phase (aqueous solution of inorganic oxidizing AN salt) surrounded by a continuous phase (emulsifying oil [29]). This wastewater (EW) is a mixture of effluents from leaks and spills in process areas, equipment washing operations, floor and auto-tank washing, and on-site wastewater pre-treatment. The on-site wastewater pre-treatment consists in breaking down residual emulsion by adding a liquid detergent, which results in the oil separation from the liquid phase. Table 1 summarizes the characteristics of the EW.

2.2. Experimental set-up

A scheme of the experimental unit used in this work is shown in Fig. 1.

2.2.1. Immediate one-step lime precipitation (IOSLM) tests

IOSLM experiments were conducted using 1000 mL of explosive wastewater where different doses (from 2 to 19 g L^{-1}) of hydrated lime (≥95 %, Spectrum® chemical) were added to raw water, under vigorous agitation (rotation speed of 3 Stirrer). Agitation was maintained until different precipitation pH were reached, from 9 to 12.5. Once

Table 1
Characteristics of the EW.

Parameters	Unit	Average ± standard deviation
COD	mg O_2 L^{-1}	5922 ± 1711
BOD_5	mg O_2 L^{-1}	50 ± 34
BOD_5 / COD	–	0.009 ± 0.006
TSS	mg L^{-1}	126 ± 3
Ammonium nitrogen	mg N-NH_4^+ L^{-1}	1553.9 ± 23.1
pH	Sorensen	7.63 ± 0.11
Redox Potential	mV	114.7 ± 74.3
Conductivity	mS cm^{-1}	12.21 ± 0.11
Nitrates	mg L^{-1}	7233 ± 47
Nitrites	mg N L^{-1}	10.96 ± 0.13
Chlorides	mg L^{-1}	290.0 ± 4.7
Dissolved oxygen	mg O_2 L^{-1}	6.505 ± 0.054
Calcium hardness	mg L^{-1} $CaCO_3$	203.4 ± 20.3
Calcium	mg L^{-1}	81.4 ± 8.1
Total hardness	mg L^{-1} $CaCO_3$	406.8 ± 20.3
Magnesium hardness	mg L^{-1} $CaCO_3$	203.4 ± 28.7
Magnesium	mg L^{-1}	49.4 ± 9.9
Phenolphthalein alkalinity	mg L^{-1} $CaCO_3$	47 ± 0.0
Total alkalinity	mg L^{-1} $CaCO_3$	560 ± 46.7
Bicarbonate	mg L^{-1} $CaCO_3$	558 ± 46.7
Carbonate	mg L^{-1} $CaCO_3$	2.2 ± 0.0
Kjeldahl-N	mg N-Kj. L^{-1}	1897.4 ± 0.0
Organic-N	mg N L^{-1}	343.5 ± 23.1
Oils and fats	mg L^{-1}	285.3
Total hydrocarbons	mg L^{-1}	46.0
Cadmium	mg Cd L^{-1}	< 0.025
Manganese	mg Mn L^{-1}	0.504 ± 2.51E-04

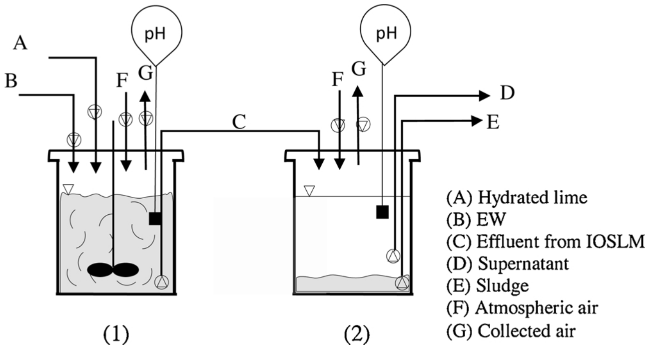


Fig. 1. Schematic diagram of the IOSLM (1) and AC (2) processes.

achieved, the agitation was kept for 1 min and then stopped. After the stirring period, the effluent was immediately transferred to normalized glass graduated cylinder (1 L, 37 cm height and 28 cm^2 of superficial area) and the sludge sedimentation operation started, so no agitation took place and solution rested during 46 min. Then, the type of sedimentation, the sedimented sludge volume and physicochemical characteristics of the pre-treated water (supernatant) were analysed.

2.2.2. Atmospheric CO_2 carbonation (AC) tests

The AC tests consisted in keeping 5 L of EW treated by IOSLM in a 189 cm^2 of superficial area recipient at room temperature, without chemicals addition and agitation. Two set of experiments were made.

Firstly, AC process was tested for all the hydrated lime doses studied in ISOLM for sixteen days. In the first 14 days, the supernatant and the sludge were kept in the same recipient in contact with atmospheric air, at room temperature. After this time, the supernatant was separated from the sludge and it was exposed to air, for more two days. The influence of the sludge in the treated water characteristics was evaluated by pH and the Langelier Saturation Index.

In the second set of experiments, the AC process was made for the best hydrated lime dose found in ISOLM process (section 2.2.1) and the best condition found in the first AC set experiments. Process efficiency was monitored (section 2.3) over time. These experiments were maintained until a maximum removal of ammonia was observed and when the supernatant pH was close to 8.

2.3. Analytical methods

pH and redox potential measurements were performed in a WTW InoLab apparatus, using the electrodes SenTix 41 and WTW SenTix ORP, respectively. Electrical conductivity was evaluated in a Jenway 4510 m, using an electrode VWR CO 11. Chemical oxygen demand (COD) was determined by standard dichromate closed reflux method [30], using a digester WPA HC 6016 and quantified by Pharmacia Biotech Ultrospec 2000 UV/Visible spectrophotometer model 80-2106-00. Total suspended solids (TSS) were quantified by gravimetric method using filters Whatman™ 1001-110 [30]. Biological oxygen demand (BOD) was determined by Mohr method using system WTW's Oxitop® [30]. Chlorides were determined by Mohr method [30]. Oil and fats were measured gravimetrically after Soxhlet extraction [31]. Nitrate was determined by sodium salicylate method [32]. Ammonium nitrogen was measured by distillation method in BUCHI Distillation Unit B-316 and then by titration [30]. Kjeldahl nitrogen was determined by Kjeldahl method [30]. Nitrites and dissolved oxygen were determined by colorimetric and modifications of the Winkler methods, respectively [30]. Calcium and magnesium determinations were made by volumetric complexation with EDTA using eriochrome black T (calcium + magnesium) and calcon (calcium) indicators [30]. Phenolphthalein and total alkalinity were measured by neutralization titration [30]. Heavy metals were determined by flame atomic absorption spectrometry using Varian SpectraAA 220FS spectrometer [30]. Total hydrocarbons were measured by company “QUIMITESTE – Engenharia e Tecnologia, Lda”, using infrared spectrophotometry. The carbonates and bicarbonates were determined by APHA et al. [30]. Langelier Saturation Index was determined by saturation index [30]. Clarifying velocity was determined by Talmadge & Fitch method [33].

2.4. Statistical analysis

Experiments were made in triplicate for IOSLM and AC experiments as well as for parameter measurements, and their averages were calculated. The graphs were drawn by GraphPad Prism version 5.0 for Windows, GraphPad Software, La Jolla California USA. All data were submitted to one-way ANOVA using Tukey’s test at 95 % confidence level for distinction between averages, through the IBM SPSS Statistics for Windows, Version 20.0, Armonk, NY, IBM Corp. The correlation analysis was performed for IOSLM and AC experiments according to Pearson using RStudio™ software, version 1.2.1335, Inc., Boston, MA. All correlations were considered statistically significant at P values $<$ 0.05 or $<$ 0.001.

3. Results and discussion

3.1. EW characterization

Visually, EW is a homogeneous, turbid and whitish mixture. EW smells fuel, due to one of the raw materials used in the formation of ANFO and emulsion explosives.

As shown in Table 1, the EW pH is neutral (7.63 ± 0.11). The redox potential is positive (+114 ± 74 mV), which indicates that the effluent presents an oxidative environment. The conductivity is 12.21 ± 0.11 mS cm^{-1}, so the effluent has high mineralization. EW presents a high content of organic matter (5922 ± 1711 mg COD L^{-1}), which may be due to the presence of residual detergent used in the wastewater pre-treatment and/or additives used in the formation of explosives. The values of BOD_5 are low, about 50 ± 34 mg L^{-1}. This effluent is difficult to biodegrade because it has a very low biodegradability index (BOD_5/COD ratio = 0.009). The high concentrations of nitrate (7233 ± 47 mg L^{-1}) and ammonium (1554 ± 23 mg N-NH_4^+ L^{-1}) are characteristic of this type of effluent because they are part of the main raw materials used in the manufacture of explosives. Ghafari et al. [34] reported effluents from the explosives industry, with nitrate concentration above 1000 mg L^{-1} N-NO_3-. Nitrogenous organic matter is also high (344 ± 23 mg N L^{-1}) but nitrites concentration is insignificant (11.0 ± 0.1 mg N L^{-1}). The values of total suspended solids, oils and fats, and total hydrocarbons are 126 ± 3, 285.3 and 46.0 mg L^{-1}, respectively. According to the hardness classification presented by Sawyer et al. [31], EW is very hard with a total hardness of 406.8 ± 20 mg L^{-1} $CaCO_3$.

3.2. Immediate one-step lime precipitation (IOSLM) process

The results of IOSLM bench tests are different from the typical lime precipitation (tested by Zayen et al. [21] and Renou et al. [22]), because a high concentred lime solution is added in excess, at once, to the water under vigorous agitation (rotation speed of 3 Stirrer). This produces an instantaneous and intense precipitate followed by the "sweeping" phenomenon of particles, in a short time. In this process, the flocculation step did not take place because agitation would reduce the "sweeping" effect. In addition, hydrated lime is used in high concentrations because it is important for the next process (AC), since the presence of calcium ions in excess will promote reactions with atmospheric CO_2 and the pH decrease. This is a new technology that has presented recently [35].

Fig. 2A describes in detail the effect of hydrated lime dose on pH, phenolphthalein alkalinity and total alkalinity of the EW. Results

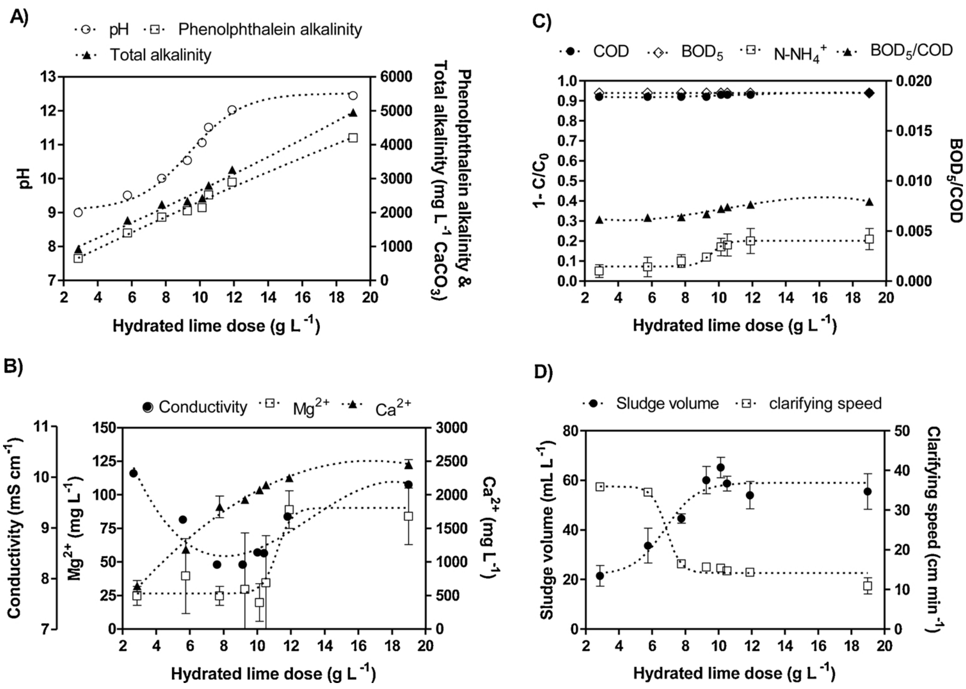
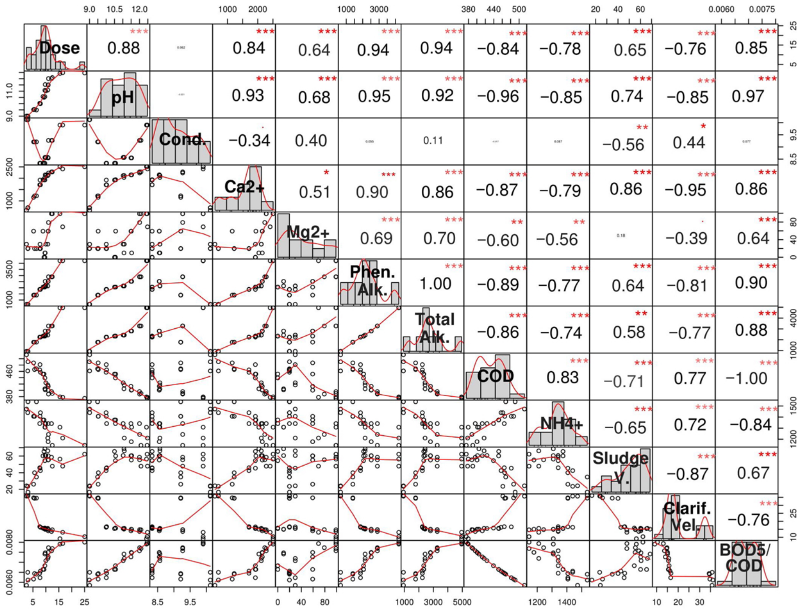


Fig. 2. Effect of the hydrated lime dose on the: **A)** pH, phenolphthalein alkalinity and total alkalinity; **B)** electrical conductivity, magnesium and calcium concentration; **C)** COD, BOD_5 and ammonium removals and biodegradability index, and **D)** sludge volume produced and his clarifying speed.

Table 2

Correlation matrix between parameters determined in immediate one-step lime precipitation tests.



	Dose	pH	Cond.	Ca2+	Mg2+	Phen. Alk.	Total Alk.	COD	NH4+	Sludge V.	Clarif. Vel.	BOD5/COD
Dose	Dose	0.88 ***	0.062	0.84 ***	0.64 ***	0.94 ***	0.94 ***	−0.84 ***	−0.78 ***	0.65 ***	−0.76 ***	0.85 ***
pH		pH	[illegible]	0.93 ***	0.68 ***	0.95 ***	0.92 ***	−0.96 ***	−0.85 ***	0.74 ***	−0.85 ***	0.97 ***
Cond.			Cond.	−0.34 .	0.40	0.055	0.11	[illegible]	0.087	−0.56 **	0.44 *	0.077
Ca2+				Ca2+	0.51 *	0.90 ***	0.86 ***	−0.87 ***	−0.79 ***	0.86 ***	−0.95 ***	0.86 ***
Mg2+					Mg2+	0.69 ***	0.70 ***	−0.60 **	−0.56 **	0.18	−0.39 .	0.64 ***
Phen. Alk.						Phen. Alk.	1.00 ***	−0.89 ***	−0.77 ***	0.64 ***	−0.81 ***	0.90 ***
Total Alk.							Total Alk.	−0.86 ***	−0.74 ***	0.58 **	−0.77 ***	0.88 ***
COD								COD	0.83 ***	−0.71 ***	0.77 ***	−1.00 ***
NH4+									NH4+	−0.65 ***	0.72 ***	−0.84 ***
Sludge V.										Sludge V.	−0.87 ***	0.67 ***
Clarif. Vel.											Clarif. Vel.	−0.76 ***
BOD5/COD												BOD5/COD

Notes: 1) Where it is written: "cond.", "Phen. Alk", "Total Alk", "Sludge V." and "Clarif. Vel." means conductivity, Phenolphthalein Alkalinity, Total Alkalinity, Sludge volume and clarifying velocity, respectively; 2) The distribution of each variable is shown on the diagonal. On the bottom of the diagonal: the bivariate scatter plots with a fitted line are displayed. On the top of the diagonal: the value of the correlation plus the significance level as stars. Each significance level is associated to a symbol : p-values(0, 0.001, 0.01, 0.05, 0.1, 1) < = > symbols("***", "**", "*", ".", " ").

presented in Table 2 indicate that hydrated lime dose has a significant positive correlation with pH (r = 0.88, $P < 0.001$), phenolphthalein alkalinity (r = 0.94, $P < 0.001$) and total alkalinity (r = 0.94, $P < 0.001$). Hydrated lime dose added (2–18.98 g L^{-1}) increases the pH from 9 to 12.45 due to the addition of OH- to the solution. Experimental tests have shown that it is not possible to increase the pH beyond 12.45 even if higher dose of lime is added. Zayen et al. [21] also observed this behaviour in neutralization of a landfill leachate with lime. Between 2 and 10.5 g L^{-1} of hydrated lime added, the pH increase is proportional to the lime dose applied (Fig. 2A). However, from 10.5

to 18.98 g L^{-1} of lime doses added, this behaviour is not observed. Thus, a minimal dose of the hydrated lime applied may cause a significant increase in pH ($P < 0.05$). Theoretically, at 10 g L^{-1} of hydrated lime (corresponding to a pH between 10.5–11) all the ammonium ions are converted to ammonia by consumption of OH- ions [36,37] according to Eq.(1), which justifies the pH suddenly increase at this dose (Fig. 2A).

$$NH_{3\,(g)} + H_2O_{\,(l)} \leftrightarrow NH_4^{+}{}_{(aq)} + OH^-_{(aq)}\ pK_a = 9.25\ (25\,^{\circ}C) \tag{1}$$

Renou et al. [22] studied the pre-treatment of three different raw landfill leachates, using chemical precipitation with lime followed by flocculation. They dosed about 1.8, 3 and 4 g L^{-1} of $Ca(OH)_2$ to achieve a pH 10, while in this work, about 8 g L^{-1} of hydrated lime was added to get the same pH. This difference in the lime dose consumed may be due to some differences in the physicochemical characteristics of the wastewater used, namely the initial pH (8.35, 8.55 and 8.60, respectively for the doses applied 1.8, 3 and 4 g L^{-1}), alkalinity (175, 285 and 495 mg L^{-1} $CaCO_3$) or the initial concentration of the ammonium ion (370, 468 and 730 mg L^{-1}) [22]. The highest the ammonium ion concentration in the effluent, the highest hydrated lime will be needed. The phenolphthalein and total alkalinities mean values increase from 654 to 4203 mg L^{-1} $CaCO_3$ and from 934 to 4950 mg L^{-1} $CaCO_3$, respectively, for the hydrated lime doses tested (Fig. 2A). This increase is related to the increase in hydroxide and carbonate content. Since the concentration of ammonium ion in EW is high, it may be possible that the ammonia contributes to alkalinity [31] at all lime doses applied, but mainly for doses whose pH is greater than 9.25. Rounds [38] mentioned that high quantities of titrant acid were need to reach the first equivalence point (pH ≈ 8.3) which would otherwise be represented by carbonate and hydroxide, since ammonia (NH_3) will react with hydrogen ions from the titrant to produce ammonium ion (NH_4^+).

Fig. 2B presents the variation of conductivity, magnesium and calcium concentrations with hydrated lime dose added. According to Table 2, the hydrated lime dose shows significant positive correlations with magnesium ($r = 0.64$, $P < 0.001$) and calcium ($r = 0.84$, $P < 0.001$) concentrations, while no significant correlation is observed with conductivity. Conductivity concentration decreases and reaches the minimum of 8.3 mS cm^{-1} (corresponding to the maximum conductivity removal of 32 %) between 7.76 and 9.26 g L^{-1} of hydrated lime (at pH 10 and 10.5, respectively). After 9.26 g L^{-1} of hydrated lime added, conductivity starts to rise (Fig. 2B). Usually, the conductivity reduction is due to the chemical precipitation of organic and inorganic (e.g. calcium and magnesium) salts in the form of hydroxides or carbonates, as explained below [22]. Magnesium present in EW may precipitate as magnesium carbonates or magnesium hydroxide according to Eq.(2) and Eq.(3) [25,39].

$$Ca(OH)_2 + Mg(HCO_3)_2 \leftrightarrow MgCO_3 + CaCO_3\ (s) + 2H_2O \tag{2}$$

$$Ca(OH)_2 + MgCO_3 \leftrightarrow Mg(OH)_2\ (s) + CaCO_3\ (s) \tag{3}$$

The conductivity demonstrates weak and insignificant correlation with calcium ($r = -0.34$, $P > 0.05$) and magnesium ($r = 0.40$, $P > 0.05$) for the range of hydrated lime dose studied; however, a significant positive correlation is observed between conductivity and calcium ($r = 0.95$, $P < 0.001$) or magnesium ($r = 0.78$, $P < 0.001$) from 9.26 g L^{-1} of hydrated lime added. Anyway, the conductivity never exceeds the initial value whatever the lime dose added. In addition, other metallic substances (such as zinc, nickel or manganese) may be present in wastewater, since they are part of the raw fuel oil material and tend to precipitate in the form of hydroxides and/or carbonates contributing in this way to the conductivity variation. Furthermore, this wastewater has high concentrations of sodium, nitrates and chlorides, which may be also responsible for the high conductivity. The magnesium concentration increases after 10.5 g L^{-1} of hydrated lime added (reaching ca. 80 g L^{-1}, Fig. 2B). This increase may be due to the prevalence of other metals that precipitate first in relation to magnesium or magnesium contamination from the reagent.

For calcium, concentration increases from 642.8 to 2457.1 mg L^{-1} with hydrated lime doses (the initial calcium effluent concentration was 81.4 mg L^{-1}). This increase contrasts with conventional softening behaviour, because above pH 9.5 the calcium added and the existing in solution (EW) should precipitate in the form of calcium carbonate, according to Eq.(4) and Eq.(5) [25,39]. The reason for the observed behaviour is the fact that hydrated lime doses applied are, stoichiometric, too high for the bicarbonate in the solution, making bicarbonate a limiting reagent, even for the lowest lime dose applied. Thus, since the hydrated lime is poorly soluble, lime will contribute to sludge but also will be dissociated in calcium cations (Ca^{2+}) and hydroxide anions (OH-) (Eq. (6)), increasing the concentrations of these ions in solution at the studied doses. However, when the maximum solubility of $Ca(OH)_2$ is reached, at ca. pH 12 and 11.89 g L^{-1} of lime dose added (Fig. 2B), calcium tends to remain constant even though more calcium hydroxide is added.

$$Ca(OH)_2 + H_2CO_3 \leftrightarrow CaCO_3\ (s) + 2H_2O \tag{4}$$

$$Ca(OH)_2 + Ca(HCO_3)_2 \leftrightarrow 2CaCO_3\ (s) + 2H_2O \tag{5}$$

$$Ca(OH)_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2\ OH^-_{(aq)} \tag{6}$$

Fig. 2C shows the variation of COD, BOD_5, ammoniacal nitrogen and biodegradability index as a function of the hydrated lime dose added. Hydrated lime dose shows significant negative correlations with COD ($r = -0.84$, $P < 0.001$) and NH_4^+ ($r = -0.78$, $P < 0.001$) concentrations, while a significant positive correlation with biodegradability index ($r = 0.85$, $P < 0.001$) is observed. No correlation between hydrated lime dose and BOD_5 is found because its removal was constant at 94 %, independently of the dose applied. COD removals vary between 92 and 94 %, for the lime doses applied. Biodegradability index is 0.0069 ± 0.0007 for all the doses applied so no significant changes were observed from the initial effluent value (Table 1). IOSLM process removed proportionally both biodegradable and non-biodegradable organic matter for all the lime doses tested. The removal of organic matter is related with the addition of calcium hydroxide in excess and its subsequent drag during sedimentation [25,39]. In fact, when appreciable amount of hydrated lime is added, the calcium carbonate and calcium hydroxide produced act as coagulating agents. Thus, they improve the drag of the organic matter and the "sweeping effect" occurs [40,41]. Other contaminants like heavy metals, hydrocarbons, oils and fats and other organic substances, at this pH, become prone to drag from the solution, helped by the produced precipitate. So, a sedimentation in mantle occurs and consequently a liquid-solid interface is formed, which results in a clarified supernatant (without the flocculation step) and consolidated sludge. Martin et al. [23] evaluated the potential of hydrated lime for metal immobilization and explosives transformation in soil. These authors concluded that hydrated lime reduced the RDX and zinc metal in leachates and runoff water about 26–92 % and 66–83 %, respectively, and gave conditions for optimum explosives decomposition. In our study, hydrocarbons removals are ca. 96, 91 and 90 % for the lime doses of 10.13, 11.89 and 18.98 g L^{-1}, respectively.

Ammoniacal nitrogen removals vary between 5 and 12 % until 9 g L^{-1} of hydrated lime added and increases to 21 % after the addition of 10.13 g L^{-1} of hydrated lime (Fig. 2C). This increase in ammonia removal is related with the increase availability of ammonia to be volatilized [20] as a result of the displacement of the chemical equilibrium (Eq. 1) (conversion of ammonium ion to ammonia) due to increased pH [36]. Thus, a significant negative correlation with NH_4^+ concentration and pH ($r = -0.85$, $P < 0.001$) is observed in Table 2. Berge et al. [42] and Wang et al. [37] reported that pH is normally adjusted above 10.5–11.5 to convert all the ammoniacal nitrogen into ammonia. From the applied dose 10.13 g L^{-1} (pH = 11.06), ammonia removal remained constant at around 21 %. Renou et al. [22,41] obtained higher percentages of ammonia removals (25–56%) by applying lime precipitation to a leachate. These higher removals are related with the operational conditions used in the processes. Renou et al. [22,41] applied rapid mixing at 300 rpm for 5 min followed by slow mixing at 30 rpm for 30 min and sedimentation during 30 min, while in this work a rapid mixing for 1 min and a sedimentation for 46 min was applied. In fact, higher time of operation contributes to higher ammonia removal. However, for the same time of operation, agitation step promotes the release of ammonia to atmosphere when compared to sedimentation step. Water and ammonia are polar molecules, so the ammonia has some capacity to remain in solution unless there is turbulence (i.e., greater contact between water and air, as occurs in the agitation operation). Therefore, IOSLM should be coupled to an ammonia capture system, not only to recover and reuse ammonia (e.g. in the explosives industry since ammonia is one of the ingredients used), but also to avoid air pollution. As expected, no removal of nitrates is observed in the tested conditions, because nitrates are soluble ionic compounds in water [43].

Fig. 2D shows the variation of sludge volume produced and the clarifying velocity as a function of the hydrated lime dose. Sludge volume shows significant positive correlation with hydrated lime dose ($r = 0.65$, $P < 0001$, but the sludge volume only increases linearly $r=0.99$ up to the dose of 9.26 g L^{-1} of hydrated lime, reaching a maximum value of ca. 60 mL L^{-1}. After 9.26 g L^{-1} of lime added, the sludge volume tends to remain constant even doubling the lime dose added, because of the sludge compaction caused by its own weight. Clarifying velocity shows significant negative correlation with hydrated lime dose ($r=-0.76$, $P < 0.001$) and sludge volume ($r=-0.87$, $P < 0.001$). The latter high correlation was expected since the high quantities of sludge produced imply the increase of collisions between particles, causing retardation of sedimentation and, therefore, a slower clarifying velocity.

The optimal hydrated lime dose is 7.76 g L^{-1} for this EW and tested conditions. This dose was selected based on the supernatant quality (COD and conductivity removals), volume of the sludge produced associated with the needs of the hydrated lime and characteristics that may contribute to the success of the next treatment (ammonia removal), such as pH. This dose removes 98.2 % of oils and fats, 100 % of organic nitrogen, 92.1 % of COD and 10.2 % of ammonium ion. Since hydrated lime can globally cost around US$110-125/ton, approximately US$0.97/$m^3$ will be spent with hydrated lime to treat this EW for the optimal dose in the IOSLM process [44,45]. This cost can be reduced if the sludges are reused by calcination process and if this effluent is properly treated and reused in industry processes operation. Some possibilities for lime sludge valorisation are application in building construction materials [46], or biofuel [47] and bioethanol production [48].

Table 2.

3.3. Atmospheric CO_2 carbonation (AC) process

3.3.1. Influence of sludge on the atmospheric CO_2 carbonation process

The influence of the IOSLM sludge on the AC supernatant was evaluated through pH (Fig. 3A) and Langelier Saturation Index (Fig. 3B) and for all the hydrated lime doses applied. Fig. 3A demonstrates that pH decreases during the atmospheric CO_2 carbonation with IOSLM sludge (between 0 and 14th days) for all the hydrated lime doses applied. This decrease is less evident for the highest dose (18.96 g L^{-1}) because supernatant was buffered in IOSLM. After removal of the sludge from the AC process (between 14th and 16th days), a higher decrease in the supernatant pH is observed, for all the lime doses applied, when compared with the previous situation. Thus, the contact between the sludge and the supernatant slows down the pH decrease of the supernatant. This observation can be an advantage for ammoniacal nitrogen removal, since the sludge avoids a sudden drop in pH and consequently ammoniacal nitrogen will be in the form of ammonia for longer time. As a result, ammonia can be captured in a separate process and reused in the explosives industry, for example. According with equation (1), the AC process must be applied for pH between 9.2 and 11, as proposed in ISOLM, where about 100 % of the ammoniacal nitrogen is in the form of ammonia. However, after the removal of ammonia, sludge should be removed from the AC process because a rapid drop in pH is observed (Fig. 3A). The pH range obtained ($6 < pH < 7.5$, Fig. 3A) is considered optimal for some plants used in phytoremediation, as well as for soil microorganisms responsible by nitrification (pH 6.6–8.0) and denitrification (pH 6.0–8.0) processes [49]. In literature, no studies were found on the use of AC with sludge in wastewater treatment, so a new solution for ammonia recovery is presented. These results demonstrate that there are chemicals equilibriums between sludge and supernatant, and between supernatant and atmospheric air during AC process. However, even if a physical separation of these two phases (sludge and supernatant) is done and the supernatant is exposed again to the AC process, new residuals sludge could be formed or residual calcium carbonate in the supernatant could be dissolved, due to the chemical equilibrium with the atmosphere, and so a new chemical equilibrium between the supernatant and the new sludge will be restored, as can be seen in Fig. 3B, particularly for lime doses of 2.86, 5.75 and 11.89 g L^{-1}, whose Langelier saturation index varied greatly on 16th day.

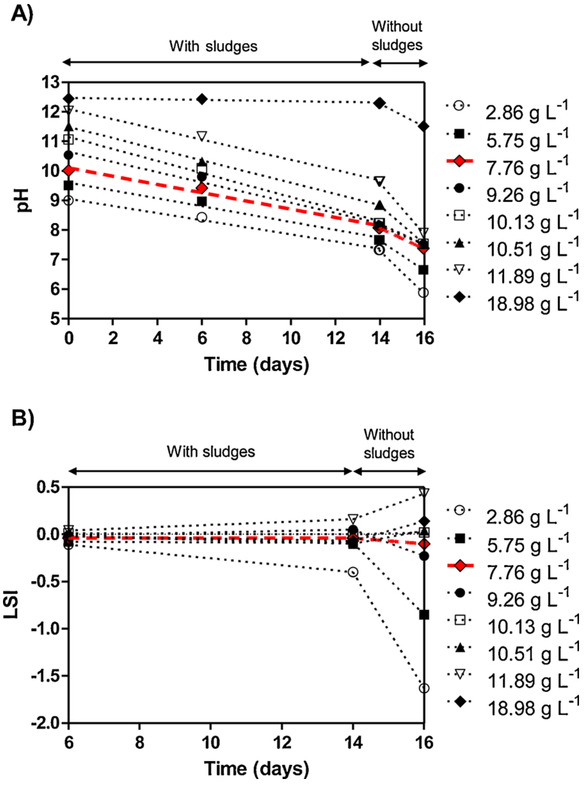


Fig. 3. Evolution of supernatant characteristics, in terms of: **A)** pH and **B)** Langelier Saturation Index, for atmospheric CO_2 carbonation process, with and without sludges for different hydrated lime doses applied.

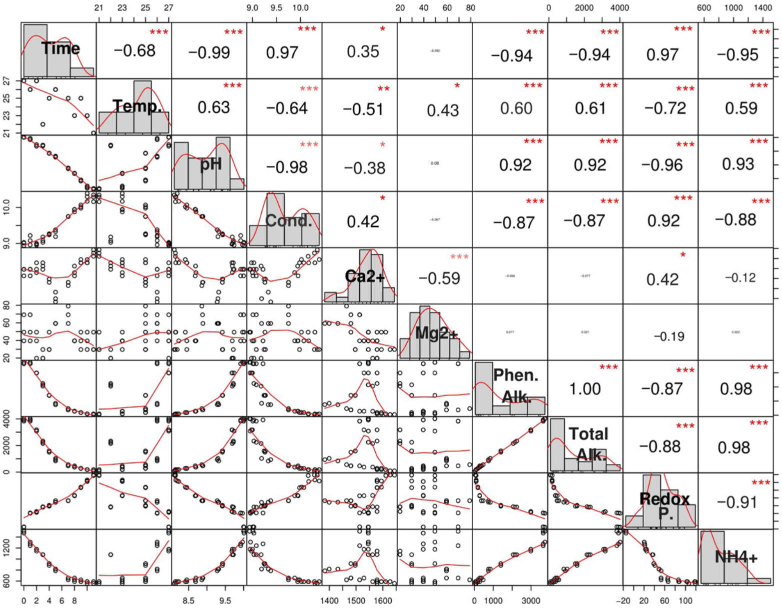
3.3.2. Optimised solution

The optimised integrated pre-treated solution was studied to guarantee the pH reduction and the removal of ammoniacal nitrogen and ammonia recover of the low biodegradable wastewaters, which includes the best conditions obtained in ISOLM and in AC processes. Thus, the optimal hydrated lime dose (7.76 g L^{-1}) from IOSLM and the 11 days of AC with the supernatant in contact with the sludge were tested.

According to Table 3, the AC time shows significant negative

Table 3

Correlation matrix between parameters determined in atmospheric CO_2 carbonation process tests.



Notes: 1) Where it is written: "Temp", "cond.", "Phen. Alk", "Total Alk" and "Redox P." means temperature, conductivity, Phenolphthalein Alkalinity, Total Alkalinity and Redox Potential, respectively; 2) The distribution of each variable is shown on the diagonal. On the bottom of the diagonal: the bivariate scatter plots with a fitted line are displayed. On the top of the diagonal: the value of the correlation plus the significance level as stars. Each significance level is associated to a symbol : p-values(0, 0.001, 0.01, 0.05, 0.1, 1) < = > symbols("***", "**", "*", ".", " ").

correlation with pH ($r = -0.99$, $P < 0.001$) and significant positive correlation with redox potential ($r = 0.97$, $P < 0.001$). Fig. 4A shows a pH decrease from 10 to 8.1, while the redox potential increases from -14.8 to 118.5 mV, during experimental time. The observed decrease in pH over time is justified by the following reactions (Eqs. (7) to (10)).

$$CO_2\ (g) \leftrightarrow CO_2\ (aq) \tag{7}$$

$$CO_2\ (aq) + H_2O\ (l) \leftrightarrow H_2CO_3\ (aq) \tag{8}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{9}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{10}$$

The carbonic acid present in EW is totally consumed during the IOSLM to produce calcium carbonate (Eq.4), causing a chemical disequilibrium of CO_2 between the supernatant and the atmosphere. As a way of counteracting this disequilibrium, the CO_2 present in the atmosphere has the tendency to dissolve in the water through the water-air interface until reaching equilibrium (Eq.7). During this phase, CO_2 dissolves in the effluent by combining with water molecules to form carbonic acid (Eq.8), and then decomposes naturally into molecules of bicarbonate (Eq.9) and carbonate (Eq.10) producing hydrogen ions (H^+) and leading the pH decrease in the supernatant. When the equilibrium is reached, the pH will remain constant in solution [50]. A decrease in pH during atmospheric CO_2 carbonation was also observed by Prazeres et al. [25] using cheese whey wastewaters, but without sludge. The increase of redox potential is related with pH decrease due to increase in the concentration of hydrogen ions in solution [6], which is confirmed by Table 3, whose correlation is negative and significant ($r = -0.96$, $P < 0.001$). Redox potential influences the type of microbial metabolism developed and indicates the tendency of a given system to forward accepting electrons (if redox potential is positive) or donating electrons (if redox potential is negative), and predicting stability of various compounds [51,52]. Thus, at the end of 11 days it is possible to obtain a supernatant with a pH very close to the ideal (pH = 8) and a redox potential within the appropriate range (i.e between 100–350 mV) for the occurrence of denitrification process.

Conductivity and AC time are variables significantly and positively correlated ($r = 0.97$, $P < 0.001$) and conductivity increases from 9 to 10.3 mS cm^{-1} (Fig. 4B), for 11 days. This increase may be related with evaporation phenomena and/or redissolution of ions (responsible by electrical conductivity) from sludge to the supernatant. According to Table 3, conductivity presents weak correlation with calcium ($r = 0.42$, $P < 0.05$) and no correlation with magnesium is observed, as already obtained (section 3.2). The calcium and magnesium concentrations vary between 1405–1627 mg L^{-1} and 23–69 mg L^{-1}, respectively, over time. The variation of calcium and magnesium in the supernatant is due to the complex interaction between sludge and supernatant, and between supernatant and atmosphere (explained in section 3.3.1). Consequently, the dissolution rate (Eqs. (11) and (12)) is higher or lower than the precipitation velocity (Eqs. (2) and (5)) until an equilibrium is reached. It seems that this equilibrium is achieved from the 8th day, since the concentration of calcium and magnesium tends to remain constant (Fig. 4B). At the 11th day, the Langelier index value is -0.02 ± 0.04, which means that the supernatant had no tendency to precipitate, so it stabilised.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \tag{11}$$

$$MgCO_3 + CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^- \tag{12}$$

The influence of sludge on the supernatant during atmospheric carbonation has not been found in literature for simultaneous pH and ammonia decreasing. Normally in water treatment systems that uses softening, the addition of CO_2 to the water takes place soon, after the sludge is separated from the supernatant in order to convert the

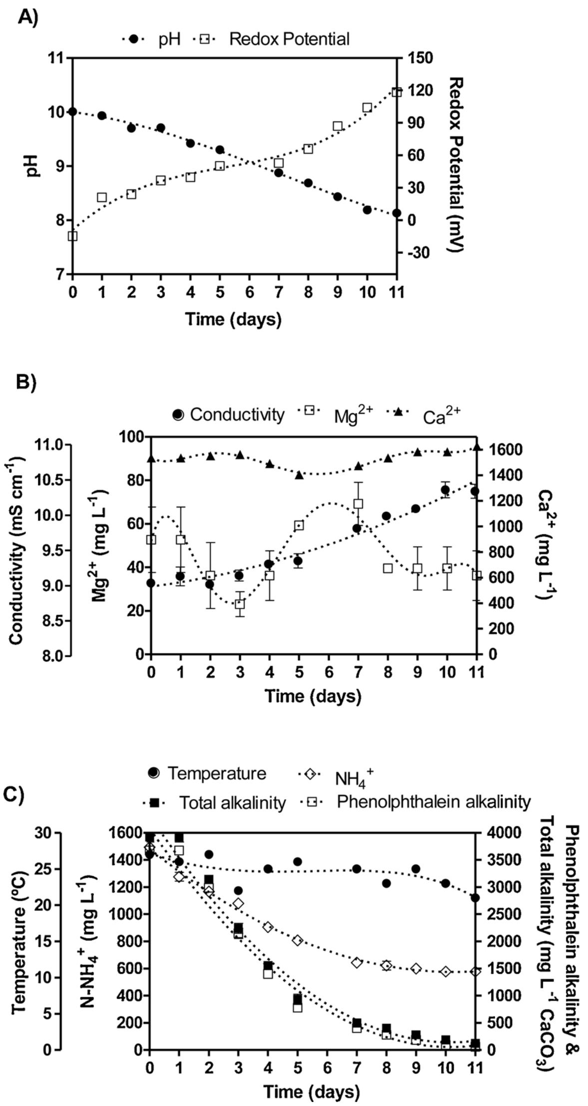


Fig. 4. Evolution of supernatant characteristics (EW treated with 7.76 g L^{-1} of hydrated lime) in terms of: **A)** pH and redox potential; **B)** electrical conductivity, magnesium and calcium concentration; and **C)** temperature, phenolphthalein alkalinity and total alkalinity and ammonium concentration, during 11 days of atmospheric CO_2 carbonation, in contact with the sludge.

residual calcium carbonate into calcium bicarbonate [19].

Fig. 4C shows that the total and phenolphthalein alkalinities decrease from 3923 to 125 mg $CaCO_3$ L^{-1} and 3674 to 62 mg $CaCO_3$ L^{-1}, respectively, for 11 days, with the same significant negative correlation (r = -0.94, $P < 0.001$, Table 3). This decrease is mainly due to the hydroxides consumption during the reaction with atmospheric CO_2 and in the conversion of the ammonium ion to ammonia to maintain the chemical equilibrium NH_3/NH_4^+ (Eq.1) which has been changing due to the loss of ammonia in the system [36]. Ammonium concentration shows significant negative correlation with AC time (r = -0.95, $P < 0.001$, Table 3), and decreases from 1505 to 556 mg N-NH_4^+ L^{-1} over time, reaching a maximum removal of 61 % and stabilising at the 7th day of experiment (Fig. 4C). According to Berge et al. [42], temperature and pH are two parameters that may influence the form of ammoniacal nitrogen (NH_3 or NH_4^+) in solution, and consequently its volatilization capacity. Temperature remained constant over time, around 24.5 ± 2.0 °C (Fig. 4C), so temperature has weak and significant correlation with ammoniacal nitrogen (r = 0.59, $P < 0.001$, Table 3). Thus, pH is responsible for the observed decrease in the ammoniacal nitrogen concentration. In fact, when pH is above 9.25 the chemical balance (Eq. 1) is displaced in the direction of converting ammoniacal nitrogen into ammonia which favours the removal of ammoniacal nitrogen by volatilization of the ammonia. This equilibrium displacement decreases when the pH of the solution decreases to 9.25, reaching the same percentage of species NH_4^+ and NH_3 in the solution [36]. Below pH 9.25, this equilibrium is displaced to the formation of ammonium ion, which being non-volatile remains in the solution [36]. On the 11th day, at pH = 8.1 and 21 °C, the percentage of ammonia is low (5.5 %) compared with the ammonium ion (94.5 %). So, the integrated treatment solution (IOSLM + AC) for the chosen hydrated lime dose can remove 62.8 % of ammoniacal nitrogen. The collection and subsequently reuse of ammonia in the industry is an advantage, since it will contribute to eliminate nitrification in biological treatment (i.e. to produce nitrate) and consequently in denitrification process organic matter may be added in less concentrations.

Table 4
Characteristics of the treated effluent for the optimised conditions.

Parameters	Unit	
COD	mg O_2 L^{-1}	468 ± 24
BOD_5	mg O_2 L^{-1}	3 ± 1
BOD_5 / COD	–	0.006
Ammonium nitrogen	mg N-NH_4^+ L^{-1}	577.9 ± 18.9
pH	Sorensen	8.13 ± 0.02
Redox Potential	mV	118.5 ± 0.78
Conductivity	mS cm^{-1}	10.3 ± 0.1
Nitrates	mg L^{-1}	7230 ± 50
Nitrites	mg N L^{-1}	11.0 ± 0.1 3
Calcium hardness	mg L^{-1} $CaCO_3$	4068 ± 40.7
Calcium	mg L^{-1}	1627
Total hardness	mg L^{-1} $CaCO_3$	4217 ± 23.5
Magnesium hardness	mg L^{-1} $CaCO_3$	149.2
Magnesium	mg L^{-1}	36.2
Phenolphthalein alkalinity	mg L^{-1} $CaCO_3$	62.0 ± 27.0
Total alkalinity	mg L^{-1} $CaCO_3$	125 ± 53.9
Bicarbonate	mg L^{-1} $CaCO_3$	123.0 ± 53.3
Carbonate	mg L^{-1} $CaCO_3$	1.40 ± 0.66
Organic-N	mg N L^{-1}	Not detected
Oils and fats	mg L^{-1}	5.13
Total hydrocarbons	mg L^{-1}	5.34 ± 0.12

4. Conclusions

A novel integrated pre-treatment that combines immediate one-step lime precipitation (IOSLM) with atmospheric CO_2 carbonation (AC) in the presence of the sludge is proposed in this work. The integrated treatment, IOSLM and AC, was evaluated for low biodegradable organic matter and ammonia removal using ANFO and emulsion explosives wastewaters as case study.

For the optimal hydrated lime dose (7.76 g L^{-1}), IOSLM removed 92.1 % of organic matter, 98.2 % of oils and fats, and 100 % of organic nitrogen, as well as reached the maximum conductivity reduction. However, as expected, it was not effective in ammonium nitrogen and nitrates removals, resulting in high concentrations of these compounds in the wastewater. These compounds are expected to be removed in next sequence treatment processes. AC process removed 61 % of ammoniacal nitrogen in 7 days and pH decreased to approximately 8. Table 4 present the treated wastewater quality.

The proposed sequence is a low-cost and easy-to-apply wastewater treatment solution, since lime is a cheap product widely used in industry and wastewater treatment, and AC does not need chemicals or specialized maintenance and is a low energy consumption process. The idea of this integrated solution is to pre-treat wastewaters that can be used in subsequent conventional biological treatments, in green solutions like phytoremediation processes or in the industry. Future studies should be developed in order to reduce the hydraulic retention time of system.

CRediT authorship contribution statement

Luís Madeira: Investigation, Writing - original draft. **Adelaide Almeida:** Methodology. **Margarida Ribau Teixeira:** Writing - review & editing, Supervision. **Ana Prazeres:** Conceptualization. **Humberto Chaves:** Resources. **Fátima Carvalho:** Conceptualization, Resources, Writing - review & editing.

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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References

[1] S.M. Ghoreishi, R. Haghighi, Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent, Chem. Eng. J. 95 (2003) 163–169, https://doi.org/10.1016/S1385-8947(03)00100-1.

[2] A. Vijaya Chitra, P. Lakshmanaperumalsamy, Biodegradation of nitrate in wastestreams from explosives manufacturing plants, Res. J. Microbiol. 1 (2006) 142–151, https://doi.org/10.3923/jm.2006.142.151.

[3] S. Zodi, J.-N. Louvet, C. Michon, O. Potier, M.-N. Pons, F. Lapicque, J.-P. Leclerc, Electrocoagulation as a tertiary treatment for paper mill wastewater: removal of non-biodegradable organic pollution and arsenic, Sep. Purif. Technol. 81 (2011) 62–68, https://doi.org/10.1016/j.seppur.2011.07.002.

[4] G. Mariliz, J. Benvenuti, J. Fontoura, S. Ortiz-Monsalve, Characterization of raw wastewater from tanneries, J. Soc. Leather Technol. Chem. 99 (2015) 280–287.

[5] S. Chatterjee, U. Deb, S. Datta, C. Walther, D.K. Gupta, Common explosives (TNT, RDX, HMX) and their fate in the environment: emphasizing bioremediation, Chemosphere 184 (2017) 438–451, https://doi.org/10.1016/j.chemosphere.2017.06.008.

[6] R.D. DeLaune, K.R. Reddy, Redox potenial, encycl, Soils Environ (2005) 366–371, https://doi.org/10.1016/B0-12-348530-4/00212-5.

[7] J. Van Leeuwen, A. Sridhar, A.K. Harrata, M. Esplugas, S. Onuki, L. Cai, J.A. Koziel, Improving the biodegradation of organic pollutants with ozonation during biological wastewater treatment, Ozone Sci. Eng. 31 (2009) 63–70, https://doi.org/10.1080/01919510802668380.

[8] H.F. Schröder, Non-biodegradable wastewater compounds treated by ozone or ozone/UV - Conversion monitoring by substance-specific analysis and biotoxicity testing, Water Sci. Technol. 33 (1996) 331–338, https://doi.org/10.1016/0273-1223(96)00283-1.

[9] M.B. Carboneras, P. Cañizares, M.A. Rodrigo, J. Villaseñor, F.J. Fernandez-Morales, Improving biodegradability of soil washing effluents using anodic oxidation, Bioresour. Technol. 252 (2018) 1–6, https://doi.org/10.1016/j.biortech.2017.12.060.

[10] G. Ren, M. Zhou, Q. Zhang, X. Xu, Y. Li, P. Su, M. Paidar, K. Bouzek, Cost-efficient improvement of coking wastewater biodegradability by multi-stages flow through peroxi-coagulation under low current load, Water Res. 154 (2019) 336–348, https://doi.org/10.1016/j.watres.2019.02.013.

[11] G.Y.S. Chan, J. Chang, T.A. Kurniawan, C.X. Fu, H. Jiang, Y. Je, Removal of non-biodegradable compounds from stabilized leachate using VSEPRO membrane filtration, Desalination 202 (2007) 310–317, https://doi.org/10.1016/j.desal.2005.12.069.

[12] J. Rodríguez, L. Castrillón, E. Marañón, H. Sastre, E. Fernández, Removal of non-biodegradable organic matter from landfill leachates by adsorption, Water Res. 38 (2004) 3297–3303, https://doi.org/10.1016/j.watres.2004.04.032.

[13] D. Georgiou, V. Liliopoulos, A. Aivasidis, Investigation of an integrated treatment technique for anaerobically digested animal manure: lime reaction and settling, ammonia stripping and neutralization by biogas scrubbing, Biorecur. Technol. Reports 5 (2019) 127–133, https://doi.org/10.1016/j.biteb.2019.01.001.

[14] Aideen Dowling, Jean O.' Dwyer, Catherine C. Adley, Lime in the limelight, J Cleaner Prod. 92 (2015) 13–22, https://doi.org/10.1016/j.jclepor.2014.12.047.

[15] Quanyuan Chen, Zhou Luo, Colin Hills, Gang Xue, Mark Tyrer, Precipitation of heavy metals from wastewater usingsimulated flue gas: sequent additions of fly ash, lime and carbon dioxide, Water Res. 3 (2009) 2605–2614, https://doi.org/10.1016/j.watres.2009.03.007.

[16] Hong-Jie Wang, Wen-Xin Gong, Rui-Ping Liu, Hui-Juan Liu, Jiu-Hui Qu, Treatment of high arsenic content wastewater by a combined physical–chemical process, Colloids Surf. A Physicochem. Eng. Asp. 379 (2011) 116–120, https://doi.org/10.1016/j.colsurfa.2010.11.047.

[17] M.H. Yuan, Y.H. Chen, J.Y. Tsai, C.Y. Chang, Ammonia removal from ammonia-rich wastewater by air stripping using a rotating packed bed, Process Saf. Environ. Prot. 102 (2016) 777–785, https://doi.org/10.1016/j.psep.2016.06.021.

[18] H. Gulyas, Processes for the removal of recalcitrant organics from industrial wastewaters, Water Sci. Technol. 36 (1997) 9–16, https://doi.org/10.1016/S0273-1223(97)00364-8.

[19] M.L. Davis, Water and Wastewater Engineering : Design Principles and Practice, Profession, McGraw-Hill, New York, 2010.

[20] A. Dowling, J. O'Dwyer, C.C. Adley, Lime in the limelight, J. Clean. Prod. 92 (2015) 13–22, https://doi.org/10.1016/j.jclepro.2014.12.047.

[21] A. Zayen, G. Schories, S. Sayadi, Incorporation of an anaerobic digestion step in a multistage treatment system for sanitary landfill leachate, Waste Manag. 53 (2016) 32–39, https://doi.org/10.1016/j.wasman.2016.04.030.

[22] S. Renou, S. Poulain, J.G. Givaudan, P. Moulin, Amelioration of ultrafiltration process by lime treatment: case of landfill leachate, Desalination 249 (2009) 72–82, https://doi.org/10.1016/j.desal.2008.09.007.

[23] W.A. Martin, S.L. Larson, C.C. Nestler, G. Fabian, G. O'Connor, D.R. Felt, Hydrated lime for metals immobilization and explosives transformation: treatability study, J. Hazard. Mater. 215–216 (2012) 280–286, https://doi.org/10.1016/j.jhazmat.2012.02.066.

[24] A.R. Prazeres, J. Lelis, J. Alves-Ferreira, F. Carvalho, Treatment of vinasse from sugarcane ethanol industry: H2SO4, NaOH and Ca(OH)2 precipitations, FeCl3 coagulation-flocculation and atmospheric CO2 carbonation, J. Environ. Chem. Eng. 7 (2019) 103203, , https://doi.org/10.1016/j.jece.2019.103203.

[25] A.R. Prazeres, J. Rivas, Ú. Paulo, F. Ruas, F. Carvalho, Sustainable treatment of different high-strength cheese whey wastewaters: an innovative approach for atmospheric CO2 mitigation and fertilizer production, Environ. Sci. Pollut. Res. Int. 23 (2016) 13062–13075, https://doi.org/10.1007/s11356-016-6429-3.

[26] S. Satsangi, Industrial Explosives Market by Type, End-use Industry - Global Opportunity Analyses and Industry Forecast 2014-2022, Portland, United States, 2016.

[27] S. Schoch, N. Nikiforakis, B.J. Lee, R. Saurel, Multi-phase simulation of ammonium nitrate emulsion detonations, Combust. Flame 160 (2013) 1883–1899, https://doi.org/10.1016/j.combustflame.2013.03.033.

[28] V.V. Hernandes, M.F. Franco, J.M. Santos, J.J. Melendez-Perez, D.R. de Morais, W.F. de, C. Rocha, R. Borges, W. de Souza, J.J. Zacca, L.P.L. Logrado, M.N. Eberlin, D.N. Correa, Characterization of ANFO explosive by high accuracy ESI(±)-FTMS with forensic identification on real samples by EASI(-)-MS, Forensic Sci. Int. 249 (2015) 156–164, https://doi.org/10.1016/j.forsciint.2015.01.006.

[29] A.M. Al-Sabagh, M.A. Hussien, M.R. Mishrif, A.E. El-Tabey, A.A.A. Elawady, Preparation and investigation of emulsion explosive matrix based on gas oil for mining process, J. Mol. Liq. 238 (2017) 198–207, https://doi.org/10.1016/j.molliq.2017.04.085.

[30] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 22nd ed., American Public Health Association, Washington, 2012.

[31] C.N. Sawyer, P.L. McCarty, G.F. Parkin, Chemistry for Environmental Engineering, 5th ed., McGraw-Hill, Inc., New York, United States, 2003.

[32] M.I.C. Monteiro, F.N. Ferreira, N.M.M. De Oliveira, A.K. Ávila, Simplified version of the sodium salicylate method for analysis of nitrate in drinking waters, Anal. Chim. Acta. 477 (2003) 125–129, https://doi.org/10.1016/S0003-2670(02)01395-8.

[33] R.S. Ramalho, Tratamiento De Aguas Residuals, Revisada, Editorial Reverté, S. A., Barcelona, España, 1996.

[34] S. Ghafari, M. Hasan, M.K. Aroua, Bio-electrochemical removal of nitrate from water and wastewater-A review, Bioresour. Technol. 99 (2008) 3965–3974, https://doi.org/10.1016/j.biortech.2007.05.026.

[35] M.F.N. Carvalho, M.A.A. Almeida, M.M.C.G.R. Teixeira, A.R. Prazeres, H.M.I.T. Chaves, L.M.S. Madeira, Process for Treatment and Recovery of Waste Water From Explosive Industries, EP 3339251B1 (2019).

[36] L. Lin, S. Yuan, L. Lin, S. Yuan, J. Chen, Z. Xu, X. Lu, Removal of ammonia nitrogen in wastewater by microwave radiation, J. Hazard. Mater. 161 (2009) 1063–1068, https://doi.org/10.1016/j.jhazmat.2008.04.053.

[37] L. Wang, Y.T. Hung, N.K. Shammas, Physicochemical Treatment Processes, Humana Press, New Jersey, 2005, https://doi.org/10.5772/63666.

[38] S.A. Rounds, Chapter A6. Section 6.6. Alkalinity and Acid Neutralizing Capacity, (2012), https://doi.org/10.3133/twri09A6.6.

[39] S. Renou, S. Poulain, J.G. Givaudan, P. Moulin, Treatment process adapted to stabilized leachates: lime precipitation-prefiltration-reverse osmosis, J. Memb. Sci. 313 (2008) 9–22, https://doi.org/10.1016/j.memsci.2007.11.023.

[40] U.S. EPA, Wastewater Technology Fact Sheet: Chemical Precipitation, Washington, D.C., 2000, https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey = P1001QTR.txt.

[41] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, J. Hazard. Mater. 150 (2008) 468–493, https://doi.org/10.1016/j.jhazmat.2007.09.077.

[42] N.D. Berge, D.R. Reinhart, T.G. Townsend, The fate of nitrogen in bioreactor landfills, Crit. Rev. Environ. Sci. Technol. 35 (2005) 365–399, https://doi.org/10.1080/10643380590945003.

[43] Z. Wang, Y. Jiang, M.K. Awasthi, J. Wang, X. Yang, A. Amjad, Q. Wang, A.H. Lahori, Z. Zhang, Nitrate removal by combined heterotrophic and autotrophic denitrification processes: Impact of coexistent ions, Bioresour. Technol. 250 (2018) 838–845, https://doi.org/10.1016/j.biortech.2017.12.009.

[44] C. Lee, J. Robinson, M. Chong, A review on application of flocculants inwastewater treatment, Process Saf. Environ. 9 (2014) 489–508, https://doi.org/10.1016/j.psep.2014.04.010.

[45] H. Wei, B. Gao, J. Ren, A. Li, H. Yan, Coagulation/flocculation in dewatering of sludge: a review, Water Res. 143 (2018) 608–631, https://doi.org/10.1016/j.watres.2018.07.029.

[46] P. Vashistha, V. Kumar, S. Singh, D. Dutt, G. Tomar, P. Yadav, Valorization of paper mill lime sludge via application in building construction materials: a review, Const. Build Mater. 211 (2019) 371–382, https://doi.org/10.1016/j.conbuildmat.2019.03.085.

[47] H. Rughoonundun, M. Holtzapple, Converting wastewater sludge and lime-treated sugarcane bagasse to mixed carboxylic acids – a potential pathway to ethanol biofuel production, Biomass and Bioenerg 105 (2017) 73–82, https://doi.org/10.1016/j.biombioe.2017.06.007.

[48] C.áia V.T. Mendes, Jorge M.S. Rocha, M. Gracą, V.S. Carvalho, Valorization of Residual Streams from Pulp and Paper Mills: Pretreatment and Bioconversion of Primary Sludge to Bioethanol, Ind. Eng. Chem. Res. 53 (2014) 19398–19404, https://doi.org/10.1021/ie503021y.

[49] J. Vymazal, Removal of nutrients in various types of constructed wetlands, Sci. Total Environ. 380 (2007) 48–65, https://doi.org/10.1016/j.scitotenv.2006.09.014.

[50] J.R. Mihelcic, J.B. Zimmerman, M.T. Auer, Environmental Engineering : Fundamentals, Sustainability, Design, 2nd ed., Wiley Global Education, 2014.

[51] K.R. Reddy, R.D. DeLaune, Biogeochemistry of Wetlands: Science and Applications, CRC Press, Taylor & Francis Group, Boca Raton, New York, 2008, https://doi.org/10.1201/9780203491454.

[52] J.L. Faulwetter, V. Gagnon, C. Sundberg, F. Chazarenc, M.D. Burr, J. Brisson, A.K. Camper, O.R. Stein, Microbial processes influencing performance of treatment wetlands: a review, Ecol. Eng. 35 (2009) 987–1004, https://doi.org/10.1016/j.ecoleng.2008.12.030.