Biogas Generation through Anaerobic Digestion of Compost Leachate in Semi-Continuous Completely Stirred Tank Reactors

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Keywords: methane, CSTR, compost leachate, biogas, anaerobic digestion

Abstract:
The composting process of organic fraction of municipal solid waste, besides to the residual compost, generates a wastewater that is characterized by a high organic load. The application of anaerobic processes represents an advantageous solution for the treatment and valorization of this type of wastewater. Nevertheless, few works have been focused on the anaerobic digestion of compost leachate. To overcome this dearth, in the present paper an extensive experimental investigation was carried out to develop and analyse the anaerobic treatment of young leachate in completely stirred tank reactors (CSTR). Initially, it was defined a suitable leachate pretreatment to correct its acidic characteristics that is potentially able to inhibit methanogenic biomass activity. The pretreated leachate was fed to the digester over the start-up phase that was completed in about 40 days. During the operational period, the organic load rate (OLR) changed between 4.25 kgCOD/m3d and 38.5 kgCOD/m3d. The chemical oxygen demand (COD) abatement was higher than 90% for OLR values up to 14.5 kgCOD/m3d and around to 80% for applied loads equal to 24.5 kgCOD/m3d. At this OLR, it was reached the maximum daily biogas production of about 9.3 Lbiogas/(Lreactord). The CH4 fraction was between 70%-78% and the methane production yield in the range 0.34-0.38 LCH4/gCODremoved. The deterioration of biogas production started for OLR values that were over the threshold of 24.5 kgCOD/m3d when a volatile fatty acids (VFA) accumulation occurred and the pH dropped below 6.5. The maximum ratio between VFA and alkalinity (ALK) tolerable in the CSTR was identified to be 0.5 gCH3COOH/gCaCO3. Through an economic analysis, it was proven that the digestion of compost leachate could ensure significant economic profits. Furthermore, the produced digestate had characteristics that were compatible for agricultural applications.

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Biogas Generation through Anaerobic Digestion of Compost Leachate in Semi-Continuous Completely Stirred Tank Reactors

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Abstract: The composting process of organic fraction of municipal solid waste, besides to the residual compost, generates a wastewater that is characterized by a high organic load. The application of anaerobic processes represents an advantageous solution for the treatment and valorization of this type of wastewater. Nevertheless, few works have been focused on the anaerobic digestion of compost leachate. To overcome this dearth, in the present paper an extensive experimental investigation was carried out to develop and analyse the anaerobic treatment of young leachate in completely stirred tank reactors (CSTR). Initially, it was defined a suitable leachate pretreatment to correct its acidic characteristics that is potentially able to inhibit methanogenic biomass activity. The pretreated leachate was fed to the digester over the start-up phase that was completed in about 40 days. During the operational period, the organic load rate (OLR) changed between 4.25 kg COD/m³d and 38.5 kg COD/m³d. The chemical oxygen demand (COD) abatement was higher than 90% for OLR values up to 14.5 kg COD/m³d and around to 80% for applied loads equal to 24.5 kg COD/m³d. At this OLR, it was reached the maximum daily biogas production of about 9.3 L biogas/(L reactor d). The CH₄ fraction was between 70%–78% and the methane production yield in the range 0.34–0.38 L CH₄/g CODremoved. The deterioration of biogas production started for OLR values that were over the threshold of 24.5 kg COD/m³d when a volatile fatty acids (VFA) accumulation occurred and the pH dropped below 6.5. The maximum ratio between VFA and alkalinity (ALK) tolerable in the CSTR was identified to be 0.5 g CH₃COOH/g CaCO₃. Through an economic analysis, it was proven that the digestion of compost leachate could ensure significant economic profits. Furthermore, the produced digestate had characteristics that were compatible for agricultural applications.

Keywords: anaerobic digestion; biogas; compost leachate; CSTR; methane

1. Introduction

The development of correct management and treatment practices of municipal solid waste represents an essential environmental and social issue. In 2016, two billion tonnes of municipal solid waste were generated, and the production is expected to grow to 3.40 billion tonnes within 2050 [1]. About of 50% of waste comprises plastic, paper, cardboard, and metal, while a percentage between 35%–40% is made up of organic waste [2,3]. Therefore, a large quantity of organic fraction of municipal solid waste (OFMSW) is generated due to the wide implementation of recycling. Among the different techniques that are available for the treatment of OFMSW, composting is one of the more profitable and widespread methods [4,5]. Indeed, through the composting process the organic matter is stabilised, in aerobic conditions, to a final product that is devoid of pathogenic microorganisms.
and with fertilizer properties [4,5]. However, in addition to the residual compost, the process gives rise to a conspicuous production of leachate [6,7]. This wastewater originates from the humidity contained in the OFMSW, from the water that is generated during the biochemical process, and from the water that is added to regulate the moisture content [8]. Averagely, composting facilities generate leachate volumes that range from 75–100 L per ton of waste [9,10]. Consequently, because of the large quantity of OFMSW treated by composting processes, remarkable volumes of wastewaters are produced daily. In general, these wastewaters contain high amounts of dissolved salts, organic matters, ammoniacal nitrogen, pathogenic microorganisms, and hazardous and toxic compounds (such as heavy metals) [11]. Specifically, the leachate composition mainly depends on the type of organic waste, the composting technology, the maturation degree and the oxygen available during the treatment [12]. In particular, the leachate with a low maturation degree is characterized by chemical oxygen demand (COD) values that are even greater than 50 g/L and relatively high ratios between the biological oxygen demand (BOD) and COD. The biodegradable organic matter mainly consists of volatile fatty acids (VFA) that formed through the hydrolysis and acidification of volatile solids [12]. As consequence of high content of VFA, these types of leachates often show acid pHs. On the contrary, mature leachates have alkaline pHs, lower COD concentrations, higher amounts of recalcitrant compounds, and small biodegradable organic fractions (BOD₅/COD: 0.05–0.2) [13]. The combination of physical, chemical and biological techniques are usually applied to treat leachates due to the high polluting loads, since a single method does not allow for efficient abatement [13–15]. Many chemical-physical methods have been investigated to treat the leachate that is produced in composting plants, such as membrane filtration technologies, coagulation-flocculation processes, advanced oxidation processes, etc. [16–20]. However, these processes are generally very expensive due to the high consumption of energy or chemicals. Moreover, they produce notable quantities of sludge that must be treated before the disposal, which further increases the operating costs. Therefore, these technologies are not economically suitable in full scale applications for the treatment of highly concentrated wastewater, such as the compost leachate.

Biological technologies are much more advantageous and sustainable when compared to chemical-physical processes. Among these, aerobic processes are easy to manage and evolve more quickly than anaerobic treatments [21–23]. Nevertheless, aerobic biological plants are more energivorous and they give rise to a high sludge production. On the contrary, anaerobic digestion (AD) processes are environmentally friendly and profitable for the treatment of wastewater with high content of carbonaceous substrates [24]. In anaerobic treatments, the organic matter is stabilized through a series of sequential phases conducted by many microorganisms types that operate in the absence of dissolved oxygen at two typical temperature ranges, mesophilic (35–40 °C) or thermophilic (55–60 °C) [25]. As a consequence of these reactions, a valuable biogas, mainly composed of CH₄ (65%–80%) and CO₂ (20%–35%), and a wet residue (digestate) are produced. The performances of anaerobic treatments, besides the reactors type and the operating conditions, are largely affected by the feedstock properties [26]. The applicability of digestion processes for the treatment of many types of organic residues has been investigated in the last years [27–31]. However, few studies have been focused on the treatment of compost leachate by means of anaerobic reactors. Moreover, the researches conducted so far mainly refer to the use of complex reactors, such as anaerobic migrating blanket reactor (AMBR), anaerobic baffled reactor (ABR), expanded granular sludge bed bioreactor (EGSB), and hybrid anaerobic reactor (HAR) [10,12,32–35]. In particular, the anaerobic migrating blanket reactors were also used in the removal of hazardous compounds [35]. The above systems showed different behaviors and performances. Indeed, COD removals between 71 and 99.4% were detected while using anaerobic systems, with the AMBR reactors having the highest removal rates reported [36]. Mokhtarani et al. [12] found that the COD removal efficiency was independent of organic load rate (OLR) below a value of 6 kgCOD/m³d, while the COD removal efficiency was significantly reduced above that threshold. However, these findings disagree with those of Liu et al. [10], who found that an OLR around of 22.5 kgCOD/m³d was optimal.
Lim et al. [37] observed a decrease of biogas yield for organic loads that were over 4 kgCOD/m³·d. On the contrary, other works identified much higher OLR values as the most profitable for biogas production [10]. The literature reports are quite different also in regards to the methane content of biogas originating from the anaerobic digestion of composting leachate [36]. These differences, probably, depend on the reactor type and on the characteristics of treated leachate and highlight how the digestion of compost leachate is not well clarified yet. Furthermore, there is a lack of research concerning the effects of some relevant parameters, such as the VFA/ALK, COD/N ratios, etc., on the performance of biogas production processes from compost leachate.

In addition, limited studies have been conducted regarding the use of completely stirred tank reactors (CSTR) for the anaerobic digestion of compost leachate [11,38,39], despite these reactors having many advantages, such as the management simplicity, the high flexibility, the possibility to operate in sequential mode, etc. What is more, the CSTR systems were applied in sequencing batch mode exclusively to treat compost leachate pretreated in AMBR reactors [11,38,39]. In effect, to the best of our knowledge, the anaerobic digestion process of raw compost leachate in semi-continuous completely stirred tank reactors was not analysed yet.

All of these aspects underline the necessity of investigating the anaerobic treatments of compost leachate in CSTR to identify the suitable operating conditions to maximize the biogas production.

In this regard, the goals of the present work were to evaluate the effectiveness of CSTR for the digestion of raw compost leachates under mesophilic conditions, verify the influence of wastewater characteristics, investigate the effects of operation parameters (OLR, pH, VFA/Alkalinity, COD/N, etc.) on the process performance, and optimize the management conditions. Furthermore, it was defined a suitable method for the pretreatment of leachate to be fed during the start-up phase of the reactor. In addition, the characteristics of produced digestate were analysed to verify its possible use in agronomic practice. Finally, an estimate of economic benefits detectable through the treatment of leachate in anaerobic CSTR systems was conducted.

2. Materials and Methods

2.1. Materials

During the experiments a leachate that was withdrawn from a tunnel compost facility located near Cosenza (Calabria Region, Italy) was used as feedstock. The installation treats about 2000 ton per month of organic residues composed, approximately in equal parts, of source-sorted organic household residues and solid wastes from gardens and parks. The facility processes the organic wastes, which are previously shredded, while using both mechanical mixing as well as forced ventilation.

Activated sludge collected from the recirculation line of the wastewater treatment plant of Lamezia Terme (Calabria Region, Italy) was used as inoculum to start the anaerobic reactor. The samples were stored in 30 L tanks at 4 °C.

Sodium hydroxide (NaOH), magnesium oxide (MgO), and potassium hydrogen carbonate (KHCO₃) of analytical grade were used to perform leachate pretreatment tests.

2.2. Pilot Plant

The anaerobic digestion process was conducted while using a laboratory pilot-plant designed and constructed in the laboratory of Environmental Sanitary Engineering of University of Calabria (Figure 1a). The digester consists of a completely stirred tank reactor (CSTR) made of stainless steel (AISI 316) with a vertical cylindrical shape and a semi-spherical bottom (Figure 1b). The inner diameter and height are equal to 13.6 cm and 21.5 cm, respectively, with a maximum working volume of 3 L (Figure 1b). An insulated heating jacket wraps the reactor and the external dimensions are: diameter of 26.2 cm and height of 39.2 cm (Figure 1b). The unit is hermetically closed by a top flange equipped with a nozzle pipe that is suitable for digestate withdrawal and leachate feeding (Figure 1a,b). A manometer and a quick coupling for gas outlet are placed on the top cover (Figure 1a,b). The reactor is equipped
with a steel vertical mixer with two impellers that are spaced about 10 cm from each other (Figure 1b). The mixer rod is powered by a 0.33 KW gear motor (Figure 1a).

The heating system consists of a stainless steel thermostatic bath that is connected to the heating jacket of the reactor by multilayer pipes and equipped with a volumetric pump for the recirculation of heat transfer fluid (Figure 1a).

The biogas measurement device is made up of two plexiglass cylinders with an inner diameter of 19 cm and a height of 32 cm (Figure 1a). The two cylinders are connected each other and the first one is also linked to the reactor through the quick coupling that is placed on the top cover. The device works in cyclical mode and allows for the biogas measurement through the displacement of a given volume of water put inside it. In a typical cycle, the first cylinder is initially filled with water, which is progressively displaced in the second one by the biogas flow. Therefore, the first unit is being gradually filled by biogas and the second one by water. The level of water is measured through an ultrasonic sensor that is placed on the top of the second cylinder (Microsonic mic +25/DIU/TC), which sends an analogical signal (0–5 V) to a programmable logic controller (PLC) (Arduino® Mega 250, Turin, Italy) for data acquisition (Figure 1a). This measure is then converted as volume of produced biogas. When the maximum water level is reached in the cylinder, the PLC activates both a two-way solenoid valve, for the discharge of biogas accumulated in the first cylinder, and a peristaltic pump to recirculate the water from the second cylinder to the first one. This operational mode can be sequentially repeated and, therefore, it allows for continuous biogas measurement.

Figure 1. Schematic diagram of pilot plant (a), vertical section of completely stirred tank reactor (CSTR) (b).

2.3. Leachate Pretreatment Tests

Pretreatment tests were conducted to balance the high content of acids in the leachate by increasing the quantity of alkaline compounds. In particular, reducing the volatile fatty acids/alkalinity ratio (VFA/ALK) to around 0.3 gCH₃COOH/gCaCO₃ by keeping, in the same time, the pH between 6.5 and 8 was established. In this regard, NaOH, MgO, and KHCO₃ were investigated as alkaline compounds. In particular, NaOH was applied as a concentrated solution (10 N), testing dosages of 4, 20, and 40 g/L. Magnesium oxide and KHCO₃ were used as powders by testing dosages of 5, 25, and 50 g/L in the tests with MgO, and 45, 85, and 140 g/L in those with KHCO₃.

The experiments were performed at room temperature and pressure on 50 mL of leachate. In a typical experiment, the leachate was fed in a beaker of 100 mL and then added the fixed amount of the selected alkaline reactant. Afterwards, the mixture was magnetically stirred for 3 h. The pH was continuously monitored over the reaction period. At the end of the tests, the amounts the VFA and alkalinity (ALK) were determined on the pretreated leachate.
2.4. Operational Pattern of Semi-Continuous Anaerobic Digestion Process

Prior to perform the digestion process, the reactor was inoculated with 1.5 L of activated sludge that was maintained in anaerobic condition for 15 days at 37 ± 2 °C. During this period, no organic substrate was fed in the digester. After the preliminary step, the CSTR was started in semi-continuous mode. Initially, the organic loading rate (OLR) was kept between 1–2 kg$_{\text{COD}}$/m$^3$d until biomass acclimatization and the process parameters stabilization. After the start-up phase, the organic loading rate was increased stepwise from 4.25 kg$_{\text{COD}}$/m$^3$d to 38.5 kg$_{\text{COD}}$/m$^3$d. The reactor, in general, was fed daily. Table 1 reports the applied OLR, the corresponding hydraulic retention time (HRT), and the volumes of fed leachate. The operational period lasted about 115 days. The reactor operated in mesophilic conditions at a temperature of 37 ± 2 °C and the stirring was conducted twelve times per day at 33 rpm for 15 min. The working volume in the digester was kept constant at 1.5 L over the entire investigation. The reactor feeding and the digestate withdrawal were manually carried out. The taken digestate samples were left to settle for about 1 h and they were then characterized with respect to the main chemical parameters. The produced biogas was continuously monitored through the measurement system of the pilot plant. The CH$_4$ percentage was detected daily after the neutralization of CO$_2$ and other acid gases by means of NaOH beads. In particular, 50 mL of biogas, withdrawn by means of a graduated syringe from the cylinders of biogas measurement system, were made to flow slowly through a small plexiglass box containing 8 g of NaOH beads and, subsequently, in a next one graduated syringe. The volume measured in the last syringe, after that the biogas passed through the NaOH beads, mainly consisted in the methane amount.

### Table 1. Operational pattern of semi-continuous anaerobic digestion process.

| Stat-Up Phase | Operational Phase |
|---------------|-------------------|
| OLR (kg$_{\text{COD}}$/m$^3$d) | 1–2  | 4.25  | 5.25  | 6.0  | 9.25  | 11.0  | 14.5  | 18.25 | 24.5  | 32.0  | 38.5  |
| HRT (d)       | 66–33 | 15.5  | 12.5  | 11.0  | 7.25  | 6.0   | 4.5   | 3.6   | 2.7   | 2.0   | 1.8   |
| Volume of fed leachate (L/d) | 0.022–0.044 | 0.097  | 0.12  | 0.14  | 0.21  | 0.25  | 0.33  | 0.415 | 0.555 | 0.75  | 0.833 |

2.5. Analytical Methods

The pH and conductivity were measured by means of bench analyzers. Total solids (TS) and volatile solids (VS) were determined by weighing analysis after drying the samples at 105 °C and 550°C, respectively [40]. Total COD were measured through digestion with potassium dichromate and volumetric titration with ammonium iron sulfate [40]. The soluble COD was determined after a coagulation treatment with zinc sulfate. Volatile fatty acids (VFA) and total Kjeldahl nitrogen (TKN) were determined by sample distillation and titration with sodium hydroxide and hydrochloridric acid, respectively [40]. Alkalinity (ALK) was detected by the potentiometric procedure [40]. Ammoniacal nitrogen (N-NH$_4^+$), reactive phosphorus (P-P$_{\text{PO}_4^{3-}$), and sulfate (SO$_4^{2-}$) were determined by spectrophotometric analyses [40]. In particular, ammoniacal nitrogen was estimated by the phenate method at a wavelength of 640 nm, phosphate were detected by means of ascorbic acid method at wavelength of 880 nm, and sulfate were measured by turbidimetric method at 420 nm [40]. Metal ions were determined through atomic absorption spectrophotometry [40]. Each analysis was carried out in triplicate and the mean value was assumed. The relative standard deviation was less than 10% in all of the measurements.
3. Results and Discussion

3.1. Compost Leachate and Activated Sludge Characteristics

Table 2 shows the chemical characteristics of compost leachate and activated sludge used during the experiments. The leachate had a high value of COD about 66.5 g/L and a soluble component close to 54.3 g/L, which was around to 81% of the total organic matter content. The total solids (TS) amounted to almost 62 g/L, whose organic fraction (VS) was around to 62%. The sample showed an acid pH of 5.3 and a remarkable conductivity of about 5.6 mS/cm. Congruent with the pH value, a notable amount of volatile fatty acids, close to 15.2 g CH₃COOH/L, was detected, while the alkalinity value was found to be 12.5 g CaCO₃/L. Because of the acid characteristic, quite high amounts of some metallic ions, such as Fe, Pb, and Zn, were detected. The total Kjeldahl nitrogen was approximately of 1.5 g/L, while the free N-NH₄⁺ concentration was around 0.66 g/L. The levels of reactive phosphorus (P-PO₄³⁻) and sulfate (SO₄²⁻) were of about 0.55 g/L and 0.45 g/L, respectively. The detected values suggest that the leachate was withdrawn from a composting process with a low maturation degree that evolved in micro-aerobic conditions. Indeed, its characteristics were similar to those of young leachates that were produced in municipal landfills. Actually, the high levels both of total and dissolved COD indicate that the hydrolysis of solid waste must have already taken place during the sample collection. This was also confirmed by the conductivity that underlines a great content of dissolved elements in the leachate. Moreover, the notably level of volatile fatty acids and the acid pH suggest that the organic matter transformation evolved with a low presence of oxygen, similarly to the typical acid-acetogenic phases. The characteristics of the sample used in this study were analogous to those reported by other authors [10]. On the contrary, some other works found concentrations of compost leachate that were substantially different when compared to our results [41]. Clearly, the leachate can vary notably with the nature of the feedstock, with the maturity of the compost giving rise to the leachate, the employed composting technology, and the operating conditions applied. All of these aspects explain the differences in terms of properties of compost leachate reported in the technical literature. The characteristics that were obtained during the investigations clearly show that the exploited leachate had a remarkable organic content, which could give a great biogas production through an anaerobic biological process. Nevertheless, some of the found characteristics are able to hinder the evolution of digestion. In particular, the acid pH and the high content of volatile fatty acids with respect to the alkalinity level (VFA/ALK = 1.2 g CH₃COOH/g CaCO₃) represent adverse factors. In fact, the activity of methanogenic bacteria is repressed by low pH values and high VFA/ALK ratios [24]. Furthermore, the remarkable presence of some metals can produce inhibitory effects on biomass activity. Therefore, it was necessary to carefully analyse the operating conditions to efficiently exploit the young compost leachate in anaerobic CSTR systems.

As regarding the sludge used as inoculum to start the digester, it showed typical characteristics of an activated sludge that was withdrawn from the recirculation line of a conventional wastewater treatment plant (Table 2). In particular, the solids content (TS) was about of 11 g/L, with a volatile fraction average of 82%. The COD was almost exclusively imputable to the suspended biomass and a very low concentration of free ammonium was detected. The pH was close to neutral value and the conductivity result was around 1.2 mS/cm.
Table 2. Characteristics of compost leachate and activated sludge.

| Parameters   | U.M.     | Leachate  | Activated Sludge |
|--------------|----------|-----------|------------------|
| pH           | -        | 5.3 ± 0.2 | 6.9 ± 0.1        |
| Conductivity | mS/cm    | 5.6 ± 0.1 | 1.2 ± 0.1        |
| TS           | g/L      | 61.9 ± 2.01 | 10.8 ± 0.08     |
| VS           | g/L      | 38.2 ± 2.11 | 8.9 ± 0.09      |
| COD          | g/L      | 66.5 ± 3.5 | 12.8 ± 0.33     |
| COD\textsubscript{sol} | g/L | 54.3 ± 0.24 | 1.7 ± 0.11     |
| Alkalinity   | g\textsubscript{CaCO\textsubscript{3}}/L | 12.6 ± 0.77 | 0.5 ± 0.04     |
| VFA          | g\textsubscript{CH\textsubscript{3}COOH}/L | 15.2 ± 0.78 | 0.08 ± 0.003   |
| TKN          | g/L      | 1.52 ± 0.14 | 0.78 ± 0.008   |
| N-NH\textsubscript{4} | g/L | 0.66 ± 0.05 | 1.4 ± 0.11     |
| P-PO\textsubscript{4} | g/L | 0.55 ± 0.03 | 39.3 ± 3.6    |
| SO\textsubscript{4} | g/L | 0.45 ± 0.028 | 88.7 ± 2.3   |
| Ca           | g/L      | 3.55 ± 0.021 | 0.098 ± 0.002  |
| Mg           | g/L      | 0.82 ± 0.036 | 0.039 ± 0.001  |
| K            | g/L      | 0.61 ± 0.017 | -              |
| Fe           | mg/L     | 113.8 ± 4.1 | 0.3 ± 0.01     |
| Pb           | mg/L     | 34.4 ± 1.1  | -               |
| Mn           | mg/L     | 10.6 ± 0.21 | 0.1 ± 0.005    |
| Cr           | mg/L     | -          | -               |
| Cu           | mg/L     | -          | -               |
| Cd           | mg/L     | -          | -               |
| Hg           | mg/L     | -          | -               |
| Zn           | mg/L     | 20.0 ± 0.40 | -              |
| Ni           | mg/L     | 0.2 ± 0.01  | -               |

3.2. Pretreatment Tests

As previously discussed, the compost leachate used in this study had some characteristics that are able to hinder the evolution of digestion process. Therefore, preliminary pretreatment tests were carried out in order to identify proper modalities to make the leachate suitable for anaerobic biological treatments. In particular, the tests aimed to balance the high content of acids by increasing the amount of alkaline compounds. In this regard, reducing the VFA/ALK ratio to a value of about 0.3 g\textsubscript{CH\textsubscript{3}COOH}/g\textsubscript{CaCO\textsubscript{3}}, considered to be adequate to properly perform the anaerobic digestion process [24], by maintaining, in the same time, the pH value comprised between 6.5 and 8, was established. Often, lime was used to compensate the acidity of wastes fed in the digesters or it was added directly in the reactors to counteract a possible excess of VFA production [31]. However, Ca(OH)\textsubscript{2} can cause the incorporation and the precipitation of suspended organic matter reducing the availability of substrate for biogas production [31]. Moreover, the addition of lime increases the fraction of inert solids in the reactors. We have tested three different alkaline compounds to correct the characteristics of compost leachate to avoid the above mentioned drawbacks. Specifically, MgO grains, NaOH and KHCO\textsubscript{3} powder were used. The experimental results proved that the mixing of magnesium oxide with the compost leachate led to a remarkable increase of pH that reached values between 9.1 and 10.8 (Table 3). In fact, the initial acid characteristics of leachate promoted the solubilisation of MgO powder and the consequent rapid pH increase. Despite this, being the magnesium oxide insoluble in neutral and alkaline solutions, the initial pH rise arrested the further dissolution of reactant. As a consequence of this behaviour, nevertheless the high pH values, the VFA/ALK ratios remained far above the target value of 0.3 g\textsubscript{CH\textsubscript{3}COOH}/g\textsubscript{CaCO\textsubscript{3}} (Table 3). Therefore, the magnesium oxide was not considered to be suitable to correct the acidity of leachate.
Table 3. pH and volatile fatty acids/alkalinity (VFA/ALK) ratio after leachate pretreatment.

| Dosage (g/L) | pH (-) | VFA/ALK (gCH₃COOH/gCaCO₃) |
|-------------|--------|----------------------------|
| MgO         |        |                            |
| 5           | 9.1 ± 0.1 | 1.06 ± 0.050 |
| 25          | 10.1 ± 0.1 | 0.86 ± 0.022 |
| 50          | 10.8 ± 0.1 | 0.84 ± 0.031 |
| NaOH        |        |                            |
| 4           | 10.4 ± 0.2 | 0.84 ± 0.011 |
| 20          | 13.2 ± 0.1 | 0.42 ± 0.025 |
| 40          | 13.7 ± 0.1 | 0.26 ± 0.018 |
| KHCO₃       |        |                            |
| 45          | 6.5 ± 0.1  | 0.51 ± 0.024 |
| 85          | 7.6 ± 0.2  | 0.27 ± 0.011 |
| 140         | 7.9 ± 0.1  | 0.18 ± 0.008 |

In the tests with NaOH, with the dosage increase, a progressive decline of VFA/ALK ratio reaching values even lower than 0.3 gCH₃COOH/gCaCO₃ (Table 3) was observed. However, being the sodium hydroxide a strong base, its addition always caused very marked pH increases (Table 3). The final pHs were clearly not appropriate to feed the leachate to the subsequent anaerobic digestion process.

The results of experiments that were conducted with KHCO₃ showed a linear decrease of VFA/ALK in response to the KHCO₃ dose (Table 3). Despite this, the pH remained in the range 6.5–8 (Table 3). This is attributable to the high solubility of potassium bicarbonate and to the occurrence of carbonate equilibrium that allowed for the alkalinity to increase without causing excessive pH growth. From the analysis of Table 3, it can be easily noticed that, with a dosage of 85 g/L of KHCO₃, it is possible to reach a VFA/ALK ratio of about 0.27 gCH₃COOH/gCaCO₃ and a pH value around of 7.6. Both of these values are adequate for treating the compost leachate in anaerobic digesters. Moreover, such a pH level allows for the precipitation of most of metallic ions, so as to prevent inhibition phenomena. Therefore, the above dosage was applied to correct the characteristics of leachate fed in the digester during the start-up phase. As discussed below, after the launch phase, the pre-treatment was not more necessary and the raw leachate was directly fed in the reactor. In this way, it was possible to avoid the excessive consumption of reagents.

3.3. Semi-Continuous Digestion Process

3.3.1. Start-Up Phase

The semi-continuous digester was started by using a settled activated sludge as inoculum. Specifically, 1.5 L of sludge were put into the reactor and then maintained in anaerobic condition for 15 days without substrate addition. Afterwards, the feeding of compost leachate began. During the start-up phase, the pretreated leachate was supplied. The organic loading rate (OLR) was maintained between 1–2 kgCOD/m³d until the process parameters stabilization and an effective biogas production took place. During the entire period, pH and VFA values compatible with the digestion process were monitored in the reactor. Indeed, the pH resulted comprised between 7.2–8.1 and the VFA/ALK ratio between 0.19–0.36 gCH₃COOH/gCaCO₃. The maintenance of these values is attributable to the pretreatment of leachate that avoided the onset of excessive acidity conditions. After a period of 40 days, the volatile solids content in the reactor was stably around 10 g/L and it was reached a methane production yield (MPY) of about 0.24 LCH₄/gCODremoved, sign of the completion of biomass acclimatation and the occurrence of an efficient anaerobic digestion. The extension of the period required for the digester start-up is similar to those that were performed in anaerobic migrating blanket reactors [32] and lower than that observed in hybrid anaerobic reactors [12].
3.3.2. Operational Phase

- COD removal and biogas production

Once accomplishing the launch phase, it was possible to feed the reactor with the raw leachate. In fact, the system reached an adequate buffering capacity that made unnecessary the pretreatment aimed to correct the leachate characteristics [32]. The supply of raw leachate, without the addition of potassium bicarbonate, avoided excessive accumulation of dissolved salts in the reactor, which could have hindered bacteria activity.

During the operational phase, the OLR was increased from 4.25 kg$_{\text{COD}}$/m$^3$/d to a maximum value of 38.5 kg$_{\text{COD}}$/m$^3$/d. With the increase in volumetric organic loads, the hydraulic retention time decreased (HRT) from 15.5 days to a rather low value of about 1.8 days (Table 1). During the entire operational period, the reactor performance, in terms of organic matter conversion and biogas production, was monitored. Figure 2 presents the COD removal efficiency versus time and OLR values. As can easily be noticed, the abatements were always greater than 90% for organic loads up to 14.5 kg$_{\text{COD}}$/m$^3$/d, to which a hydraulic retention time of about 4.5 days corresponds. This high yields underline the remarkable performance of CSTR in the treatment of compost leachate greater than those that were detected in previous research conducted with different type of reactors. Indeed, Mokhtarani et al. [12] found that the increase of volumetric organic load to above 6 kg$_{\text{COD}}$/m$^3$/d significantly reduced the COD removal efficiency in hybrid biological anaerobic reactors that were fed with a compost leachate comparable to the one used in the present study. During our experiments, instead, the decrease in COD abatement occurred when the organic load rate was increased beyond 14.5 kg$_{\text{COD}}$/m$^3$/d. Nevertheless, satisfactory yields were observed until OLR values of about 24.5 kg$_{\text{COD}}$/m$^3$/d. Indeed, the average abatement was around 88% and 80% at OLR of 18.25 kg$_{\text{COD}}$/m$^3$/d and 24.5 kg$_{\text{COD}}$/m$^3$/d, respectively. Afterwards, the efficiency dropped to 60% and 35% when the volumetric organic load was brought to 32 kg$_{\text{COD}}$/m$^3$/d and 38.5 kg$_{\text{COD}}$/m$^3$/d. The distinct efficiency decline occurred despite a high biomass concentration in the reactor that grew from a value of about 32 gVS/L to about 58 gVS/L, by increasing the OLR values over 24.5 kg$_{\text{COD}}$/m$^3$/d. This is attributable to the severe overloading conditions also underlined by the HRT values. Indeed, to the highest OLR corresponded very restricted values of hydraulic retention time, lower than 2 days, which prevented the satisfactory degradation of fed organic matter.

![Figure 2. Chemical oxygen demand (COD) removal over the pilot plant operational phase.](image-url)
The daily biogas production that was detected during the entire operational period was generally consistent with the amounts of COD removed (Figure 3). Indeed, the high COD conversion detected with the increase of organic load up to 14.5 kg_{COD}/m^3d promoted a growing biogas generation, which was more marked for OLR values that were higher than 9 kg_{COD}/m^3d (Figure 3). Moreover, it can be observed a distinct increase of daily biogas production, up to values of about 14 L/d (9.3 L/L_{reactor}d), in response to the OLR increase to 18.25 and 24.5 kg_{COD}/m^3d (Figure 3), despite the decrease in COD removal yield monitored at these applied loads (Figure 2). Such behaviour is explainable by considering that, as discussed above, the reactor ensured organic matter abatements around to 88% at 18.25 kg_{COD}/m^3d, and around to 80% during the phase at 24.5 kg_{COD}/m^3d. These notable efficiencies, which were obtained with elevated values of fed organic loads, obviously, fostered the biogas generation. The daily biogas production rapidly decreased when the organic load grew over the threshold of 24.5 kg_{COD}/m^3d (Figure 3). In previous works that were conducted using CSTR fed with compost leachate pretreated in AMBR reactors, the reduction of daily biogas production started for OLR values (10–12 kg_{COD}/m^3d) smaller than half of that observed in our experiments [11,38,39]. Therefore, when compared to those tested by other authors, the system used in the present study showed very satisfactory yields. In particular, it was found that the CSTR can efficiently treat raw compost leachate reaching performances that were comparable to those detected with more complex reactors [10]. This was also confirmed by the methane content in the biogas. Indeed, the CH\textsubscript{4} fraction resulted comprised between 70%–78% for OLR values up to 24.5 kg_{COD}/m^3d (Figure 3). This statement suggests that the biomass consortium in the digester was quite stable, varying the organic load within the above-mentioned values. In effect, the methane fraction exclusively dropped below to 70% when the highest organic loads were applied. The CH\textsubscript{4} percentages detected in this research are in lines with those reached by Liu et al. [10] by treating raw compost leachate. Some other studies, instead, reported lower content of methane in the produced biogas [11,42]. The differences in the literature reports are attributable to many factors, such as the systems used, the applied operating conditions, and the characteristics of treated wastewater.

![Figure 3. Biogas and methane productions over the pilot plant operational phase.](image-url)

The good performance that was detected during our experiments is also underlined by the values of methane production yield (MPY: litres of methane produced per gram of COD removed). In particular, the MPY increased for OLR values that were lower than 9.25 kg_{COD}/m^3d (Figure 4). Afterwards, the methane yield ranged between 0.34–0.38 L_{CH\textsubscript{4}}/g_{CODremoved} up to the threshold load of 24.5 kg_{COD}/m^3d and then declined to around 0.22 L_{CH\textsubscript{4}}/g_{CODremoved} (Figure 4). The highest MPY values reached in
the present research are quite close to the stoichiometric value which, at the temperature of 37 °C, amounts to 0.4 L CH₄/g CODremoved [4]. From the estimates of MPY it can be deduced that, at the best conditions, about of 85% ÷ 95% (0.34 ÷ 0.38/0.4 ÷ 100%) of consumed COD in the reactor was converted to methane. The lower methane yield detected at OLR values that were greater than 24.5 kg COD/m³ d indicates a reduction of organic matter fraction transformed to CH₄. In these conditions, the conversion of COD leads to higher aliquots of carbon dioxide and greater biomass formation. Indeed, in addition to a notably lower daily biogas production, the CH₄ fraction declined below 70% when the greatest volumetric organic loads were applied (OLR > 24.5 kg COD/m³ d). Moreover, due to the major organic substrate availability, a remarkable growth of VS in the reactor occurred up to values of about 58 g/L. Nevertheless, the increase in biomass amount was not sufficient to guarantee satisfactory reactor performance. In effect, as discussed in the next paragraph, the high applied load and the correspondent short retention time did not allow for an effective degradation of organic compounds produced by acetogenic phase, which, consequently, led to the inhibition of methanogenic microorganisms. In addition, it is interesting to note that methane yields lower than 0.3 L CH₄/g CODremoved were also monitored with OLR values below to 6 kg COD/m³ d (Figure 4). This smaller efficiency, as compared to the highest MPY values found in this study, is attributable to the low substrate availability that may not fairly support the bacterial activity and, therefore, may cause a reduction in methane yield. These statements agree with Hartman and Ahring [43], who found that a high-solids anaerobic process was more efficient when the reactor operated at OLR higher than 6 kg VS/m³ d.

Figure 4. Methane production yield over the pilot plant operational phase.

All things considered, based on the experimental results, the optimal conditions for anaerobic degradation of raw compost leachate in a completely mixed reactor can be identified with the OLR threshold value of about 24.5 kg COD/m³ d and the hydraulic retention time of around 2.7 days. Indeed, with these operational modalities, the system guarantees a COD removal average of 80% and a methane yield close to 0.37 L CH₄/g CODremoved. The identified optimal values for the volumetric organic load and the HRT are in line with those that were found by Liu et al. [10] for an expanded granular sludge bed bioreactor. On the contrary, other research reported lower values of OLR or higher hydraulic retention times to reach the best digestion performances [11,38,42].

- Effects of pH and VFA/ALK ratio

With the aim of extensively analysing the dynamic of anaerobic degradation of compost leachate in CSTR systems, in addition to COD removal and biogas production, many other parameters that
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may affect the digestion process were monitored over the entire experimental period. Among these, pH represents a key factor for the stability of biological anaerobic reactors. Indeed, each group of microorganisms is characterized by different optimal pH ranges. Methanogenic bacteria can operate within a quite restricted pH range, with the optimal values being 6.5–8.0 [27]. Fermentative bacteria can work within a wider pH range of 4–8.5 [27]. In a mixed culture anaerobic digester, since methanogenesis is considered to be the limiting step, it is fundamental to maintain the pH in the range 6.8–8.0 to avoid inhibition phenomena [27]. During our investigations, the pH remained around 8, until reaching OLR values of 24.5 kgCOD/m³d (Figure 5). The pH stability is also probably imputable to the buffer capacity reached in the reactor as a consequence of the feeding of pretreated leachate during the start-up phase. By working at 24.5 kgCOD/m³d, a moderate pH decrease occurred, while the further increase in OLR caused a pH decline down to a value lower than 6.5 and, consequently, the deterioration of biogas production (Figure 5). This trend clearly indicates that the anaerobic digestion can stably evolve by operating with organic loads up to 24.5 kgCOD/m³d. Indeed, the decline of pH only took place with the highest OLR values tested in this study, when there was a notable VFA accumulation that led to the inhibition of anaerobic digestion process. This increase of volatile fatty acids content is evidenced by the trend of VFA/ALK ratio (Figure 5). In particular, in can be noticed how the ratio ranged between 0.15 and 0.30 gCH₃COOH/gCaCO₃ when the volumetric organic load was lower than 14.5 kgCOD/m³d (Figure 5). Beyond this load, the VFA/ALK ratio increased, reaching values of about 0.5 gCH₃COOH/gCaCO₃ at 24.5 kgCOD/m³d and greater than 1 gCH₃COOH/gCaCO₃ when the maximum OLR values were applied and the process performance deteriorated (Figure 5). On the basis of these results it can be argued that the CSTR systems in the treatment of raw compost leachate tolerate VFA/ALK values up to 0.5 gCH₃COOH/gCaCO₃. In effect, this ratio was reached during the higher biogas production phase. Instead, the increase of VFA/ALK beyond the above value caused the pH drop and significant inhibition effects. The threshold value of 0.5 gCH₃COOH/gCaCO₃ that was identified in this study is greater than those generally assumed in the technical literature. Indeed, Khanal [24] reported that VFA/ALK ratios of 0.1–0.25 gCH₃COOH/gCaCO₃ are considered to be favourable without the risk of acidification, while ratios beyond 0.3–0.4 gCH₃COOH/gCaCO₃ require corrective measures.

![Figure 5. pH and VFA/ALK over the pilot plant operational phase.](image-url)
• COD/N ratio

Another important factor that affects the anaerobic biological processes is the availability of adequate amount of nitrogen, which represents the main macronutrient to support the biomass metabolism. According to Khanal [24], the theoretical minimum COD/N ratio amounts to 50/1 for highly loaded anaerobic digestion processes. The leachate that was treated in this study had a proper level of TKN, as underlined by the COD/N ratio of about 44/1 (Table 2), which made it unnecessary to feed external nitrogen sources. During the digestion process, the COD/N was always quite low in the CSTR. In particular, the ratio remained between 3 and 7 gCOD/gN for OLR values that were lower than 14.5 kgCOD/m^3d (Figure 6). These extremely low ratios are a consequence of the notable abatements of organic load and underline again the stability of digestion process. Beyond the OLR value of 14.5 kgCOD/m^3d, the COD/N grew because of the progressive deterioration of COD abatements (Figure 6). Nevertheless, the COD/N reached maximum values of around to 35 gCOD/gN and, therefore, lower than the threshold ratio of 50 gCOD/gN. These results prove that the availability of nitrogen was never a limiting factor for digestion process. In particular, the TKN in the reactor was mainly composed of dissolved ammonium due to the conversion of most of organic nitrogen into inorganic forms. Indeed, the concentration of N-NH_4^+, as was to be expected, increased during the experimental investigation up to a maximum concentration close to 1.5 g/L. This concentration, anyhow, was much lower than the threshold value, of about 3 g/L, which is considered to be tolerable for anaerobic processes [24]. Therefore, the occurrence of potential toxic phenomena due to excessive amounts of ammoniacal compounds was prevented.

![Figure 6. COD/N ratio over the pilot plant operational phase.](image)

• COD/SO_4 ratio

The level of sulfate may produce both inhibitory and competing conditions for methanogenic activity [13]. When SO_4 is present at high concentrations in the digester, sulfate-reducing bacteria (SRB) oxidize the organic matter through the sulfate-reducing mechanism [13]. Under such conditions, methanogenic bacteria and SRB compete with each other, as they have many physiological and ecological similarities. Moreover the sulfate reduction generates sulfide, which can induce toxic effects on anaerobic bacteria. The degree of competitiveness between methanogenic and sulfate-reducing activity is related to COD/SO_4 ratio [24].
According to Yilmaz et al. [13], the total or partial inhibition of methanogenesis might occur for COD/SO₄ ratios lower than 4 or between 4–10 gCOD/gSO₄, respectively. The leachate that was treated in this study was characterized by an extremely high COD/SO₄ value that underlines the great surplus of organic matter available for methane production (Table 2). In the reactor, the ratio generally remained above 10 gCOD/gSO₄ over the entire experimental period, and only in some cases it has fallen just below the threshold value (Figure 7). It must be observed that the exponential increase of the COD/SO₄ ratio detected during the last phase of investigation is, obviously, a consequence of COD removal deterioration caused by the reactor overloading. This trend clearly indicates that the COD was mainly consumed through methanogenic metabolism and no inhibition phenomena attributable to sulfate degradation occurred.

![Figure 7. COD/SO₄ ratio over the operational phase of pilot plant.](image)

### 3.4. Characteristics of Digestate

The previously discussed results clearly demonstrated that the compost leachate could be effectively exploited to produce biomethane through the anaerobic treatment in CSTR systems. Furthermore, besides the high methane production, the digestion of raw leachate generates a waste potentially exploitable in agronomic practices. In Table 4, the characteristics of digestate produced when the reactor worked at the identified optimal conditions (OLR = 24.5 5 kgCOD/m³d, HRT = 2.7 days) are reported. It can be easily noticed that the presence of dissolved heavy metals is not problematic in the digestate. In fact, the concentrations were significantly reduced during anaerobic treatment due to the moderate alkaline pH, which induced the precipitation of metals as insoluble compounds. In effect, the residual concentrations were below the permissible limits for fertilizers [44].

As regards the nutrients requirement, the digestate showed a high level of ammoniacal nitrogen that, obviously, represents a valuable aspect (Table 4). Moreover, as recommended for agricultural applications, the waste was characterized by a low ratio between organic matter content and nitrogen compounds [41]. This parameter has a notable significance, because it affects the availability of nitrogen in soils. In fact, when the ratio is high soil microorganisms need additional nitrogen to breakdown organic matter and nitrogen immobilization will organically occur [41].
Table 4. Characteristics of digestate produced when the reactor worked at OLR = 24.5 kg\textsubscript{COD}/m\textsuperscript{3}d and HRT = 2.7 days.

| Parameters | U.M. | Digestate  |
|------------|------|------------|
| pH         | -    | 7.8 ± 0.2  |
| Conductivity | mS/cm | 23.6 ± 0.2 |
| TS         | g/L  | 21.6 ± 1.1 |
| VS         | g/L  | 10.2 ± 0.65 |
| COD        | g/L  | 12.5 ± 0.96 |
| Alkalinity | g CaCO\textsubscript{3}/L | 13.6 ± 0.78 |
| VFA        | g CH\textsubscript{3}COOH/L | 6.7 ± 0.31 |
| TKN        | g/L  | 1.52 ± 0.04 |
| N-NH\textsubscript{4} | g/L | 1.36 ± 0.06 |
| P-PO\textsubscript{4} | mg/L | 6.9 ± 0.02 |
| SO\textsubscript{4} | g/L | 0.54 ± 0.03 |
| Ca         | g/L  | 0.65 ± 0.02 |
| Mg         | g/L  | 0.14 ± 0.01 |
| K          | g/L  | 0.61 ± 0.02 |
| Fe         | mg/L | 21.0 ± 1.6  |
| Pb         | mg/L | 0.51 ± 0.01 |
| Mn         | mg/L | 0.60 ± 0.02 |
| Cr         | mg/L | -           |
| Cu         | mg/L | -           |
| Cd         | mg/L | -           |
| Hg         | mg/L | -           |
| Zn         | mg/L | 0.3 ± 0.01  |
| Ni         | mg/L | -           |

The digestate also had an appreciable amount of potassium, while the content of phosphorus was quite low due to the utilization by microorganisms during the anaerobic degradation process and to the precipitation as phosphate salts [41]. Anyhow, according to Romero et al. [41], low phosphorus content is not always negative, because the positive effect of application of phosphate fertilizer decreases as the concentration of P in the soil increases. Therefore, the digestate of compost leachate would be more desirable in soils with sufficient content in phosphorus [41]. Finally, the use of digestate as fertilizer requires the absence of pathogenic microorganisms. A hygienization process is advisable because mesophilic digestion does not guarantee obtaining a sanitary safe product. This step could be carried out by heating the residual digestate up to thermophilic temperatures (55–60 °C) for a proper time.

3.5. Economic Evaluation

By referring to the defined operating conditions (OLR = 24.5 5 kg\textsubscript{COD}/m\textsuperscript{3}d, HRT = 2.7 days), the treatment in a CSTR system of a compost leachate, with characteristics that are comparable to that used in this study, ensures COD removal of about 80% and methane yields close to 0.37 m\textsuperscript{3}CH\textsubscript{4}/kg\textsubscript{COD}removed. The daily methane production per m\textsuperscript{3} of treated leachate accounts to 19.7 m\textsuperscript{3}CH\textsubscript{4}/m\textsuperscript{3} leachate. This production ensures a significant profit, because, in many countries, the production of biomethane through the digestion of organic wastes and wastewaters is promoted and economically incentivized. For example, the Italian regulation, in agreement with the European directives, incentives the production of biomethane for injection in the distribution grid infrastructures of natural gas. In particular, the methane for the transport sector is paid a price of about 0.134 €/m\textsuperscript{3}CH\textsubscript{4} (quotation in June 2019) plus an incentive quote that is estimable to around to 0.608 equal €/m\textsuperscript{3}CH\textsubscript{4}. Therefore, the overall benefit amounts to about 0.742 €/m\textsuperscript{3}CH\textsubscript{4}. By considering this value and the specific methane production (19.7 m\textsuperscript{3}CH\textsubscript{4}/m\textsuperscript{3} leachate), a profit up to 14.61 €/m\textsuperscript{3} leachate could be obtained from the anaerobic treatment of compost leachate. Obviously, the digestion process is even more attractive taking into account that it avoids the necessity of expensive alternative treatments of the raw leachate and that the residual digestate could be exploited in agronomic practices.
4. Conclusions

In this work, a wide experimental investigation was carried out to assess the effectiveness and define the operational conditions of anaerobic digestion process of raw young compost leachate in CSTR systems. The characterization of wastewater underlined that the leachates of immature compost have acidic properties that are potentially able to hinder the methanogenic biomass activity. Therefore, a suitable pretreatment to correct the pH value and the VFA/ALK ratio of raw wastewater was defined. Different reactants were investigated and potassium bicarbonate allowed for increasing the alkalinity without causing excessive growth of pH, so as to obtain values that are adequate for feeding the leachate during the digester start-up. The launch phase lasted about 40 days, after which a stable biogas production was reached.

During the operational phase, raw compost leachate was fed in the reactor and COD removals greater than 90% were detected for OLR up to 14.5 kg\text{COD}/m^3d. Over this value, a decline in organic matter abatement was detected. Nevertheless, satisfactory yields, of about 80%, were observed for OLR equal to 24.5 kg\text{COD}/m^3d. Until reaching this OLR value, congruent with the high COD removals, an increase of daily biogas production up to 9.3 L/(L\text{reactor}d) was observed and the CH\text{4} fraction ranged between 70%–78%. The good reactor performance was also underlined by the high methane production yield that reached values between 0.34–0.38 L_{CH\text{4}}/g\text{COD}_{removed}. The deterioration of biogas production only occurred when OLR greater than 24.5 kg\text{COD}/m^3d were applied. This threshold value is notably higher than those that were identified by other authors by using CSTR to treat compost leachate pretreated in AMBR reactors. Furthermore, the performances that were detected in the present work are higher than those of hybrid reactors and comparable to those of expanded granular sludge bed bioreactors. Over the above OLR, the marked overloading condition prevented the effective degradation of organic compounds that are produced by acetogenic phase causing the inhibition of methanogenic bacteria. Indeed, with the highest OLR values, a VFA accumulation occurred that led the pH below 6.5. The trend of VFA/ALK ratio that was monitored over the entire experimental period demonstrated that a maximum value of 0.5 \text{gCH}_3\text{COOH}/\text{gCaCO}_3 could be tolerated in CSTR systems. Furthermore, the reactor monitoring proved that no limiting or inhibition effects that were attributable to the amounts of sulfate and nitrogen compounds occurred.

Taking into account all of these aspects, the present work proves that CSTR reactors are valid and attractive systems for the treatment of raw compost leachate and the detected results give a significant contribution for the development of this technology. Indeed, new information are provided to identify the values of parameters (OLR, HRT) for the design and the management of CSTR to achieve optimal organic matter conversion and biogas production. Moreover, the findings fill the lack of information regarding the effects of some relevant parameters, such as the VFA/ALK ratio, on the digestion of compost leachate. This aspect is particularly meaning in order to avoid inhibition phenomena of anaerobic biomass. Furthermore, the work proved that the digestion of raw leachate, with the identified optimal operating conditions, generates a digestate that is potentially exploitable in agronomic practices and that could ensure a significant economic profit.

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