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Biofuel production from fruit and vegetable market waste and mature landfill leachate by an active filter-anaerobic digestion integrated system

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ABSTRACT

The management of municipal solid wastes represents one of the biggest challenges for the actual implementation of the circular economy. While the main "dry" fractions (such as plastics and paper) can be easily recycled, treatments for both the valorisation of the organic waste and for the disposal of leachate (produced by the landfilling of unsorted municipal waste) often turn out to be inadequate and expensive. Particularly, the leachate management is a critical issue since the mature landfill leachate (MLL) must be treated for decades even after the landfill closure. In this study, an innovative approach is proposed and it consists in an integrated system of active filters and anaerobic reactors for the simultaneous treatment of both waste streams (i.e., organic waste and MLL). Firstly, bio-refractory compounds (e.g., metals) present in MLL are removed by filtration on active materials (i.e., zero valent iron (ZVI) and granular activated carbon (GAC) or ZVI and Lapillus mixtures). The so-treated MLLs are then used as nutrient solutions for the anaerobic digestion (AD) of market wastes (MW) to optimize the C/N ratio. Moreover, during the anaerobic digestion, granular active carbon (GAC) is added in some reactors along with the feeding solution (substrate and pre-treated MLLs) to retain possible refractory or toxic compounds and to facilitate microorganisms' activities by promoting the direct interspecies electron transfer mechanism. MLLs, used as nutrient solutions, lead to a stable AD of MW with a methane yield of about 0.260 NL/gVS_{added}. GAC is proved to be also efficient in the enhancement of the methane production as higher methane yields (about 0.302 NL/gVS_{added}) are obtained in reactors where it is added as a supplement.

1. Introduction

Fossil fuels, in spite of their proved negative environmental impacts (such as emissions of climate-altering gases), still remain the main world's energy source [1–2]. In the next 20 years, CO_2 emissions are expected to double [2] and greenhouse gases (GHG) to rise to approximately over 40 billion metric tonnes [1] with consequent irreversible effects on climate change. In addition, the improper management and disposal of waste and wastewater threat also environment and human life. Water ecosystems can be severely damaged by the discharge of untreated wastewater containing hazardous contaminants or by the inefficiency of wastewater treatment plants in removing the pollutants contained in the wastewater [3–4].

Due to the above-mentioned reasons, it is necessary to search for easily-produced sustainable energy sources, possibly originating from waste or residues [5], as renewable feedstocks for the second generation biofuels production. Moreover, more research should be carried out in order to make valorization processes of biomasses into energy (i) less pollutant and thermal/electric energy requiring [6], (ii) more efficient in terms of yield of final products and reduction of low marketable by-products [7], (iii) able to recover nutrients and other value-added products from wastes (including wastewaters) [3]. In other words, renewable energy sources should be easily accessible and ready to be obtained [1,8] while process technologies should be environmentally friendly and cost effective [5].

Nowadays, the management of the municipal solid waste (MSW) ensures significative results in the recycling of its main "dry" fractions (such as plastics, glass, paper and cardboard); the unsorted MSW is commonly disposed of in landfill [9–10] while composting still represents the main approach to the recovery of the organic fraction of MSW (OFMSW). In this context, landfilling causes uncontrolled landfill gas (LFG) emissions [11] as well as production of leachate [10] the liquid polluted effluent mainly generated from the rainwater infiltration in the waste through the landfill [12–13]. LFG is mainly composed of methane, a powerful GHG, and since, even in landfills where advanced biogas collection systems are present [14–15], it is partly released in the

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atmosphere, its impact on global warming is noticeable [16]. Landfill leachate is a dark coloured polluted liquid considered one of the main causes of contamination of superficial and groundwater [12] as it is characterised by very high concentrations of organic matter, ammonia, phosphates, sulphides, heavy metals (HMs), chlorinated organic compounds, inorganic salts and other toxic compounds [12].

In addition, the OFMSW is often not properly valorised by the adoption of technologies directed to energy production such as the anaerobic digestion (AD). In fact, generally, it is addressed to energy-consuming composting plants or disposed of in landfills where it increases leachate and LFG emissions.

The composition of the landfill leachate is extremely variable [10,17–18]: the chemical oxygen demand (COD) varies from about 100 mg L^{-1} to over 150,000 mg L^{-1}, the biological oxygen demand (BOD) can reach up to 25,000 mg L^{-1}, pH varies from 5 to 11, nitrogen (especially present as ammonia) ranges from 0.2 to 13,000 mg L^{-1} and HMs from less than 0.01 mg kg^{-1} to over 10.000 mg kg^{-1}. The characteristics of the landfill leachate depend on the waste composition, seasonal rainfall variations and, in particular, the landfill age, as it changes in time along with the landfill stabilisation over the years [10,19–20]. For this reason, the landfill leachate is conventionally defined as young (less than5 years), intermediate (5–10 years) and mature (>10 years) accounting the landfill age. The biodegradability index (BOD/COD ratio) decreases with the landfill age as the organic fraction in the leachate stabilises over the time [17]. Other constituents and, in particular, HMs follow the same trend: they rapidly decrease with the landfill age. On the contrary, ammonium and chlorides production is very slow and consequently their relative importance, among the various constituents, increases with the landfill age [19]. Therefore, processing technologies for the leachate treatment must be chosen according to its characteristics.

Leachate treatments are commonly classified as biological (aerobic and anaerobic), physico-chemical processes (such as flotation, coagulation, adsorption and membrane filtration) and/or a combinations of them [10,12,17]. Biological processes generally show good performances in the treatment of the young leachate [10,21] as it is characterised by high amounts of organic matter (COD concentration over 5,000 mg L^{-1}) [10,12] and high biodegradability although the presence of ammonia (generally up to 400 mg L^{-1}, [12] could seldom limit the biological activity [17]. Among physico-chemical techniques, nanofiltration and reverse osmosis are efficiently applied for the removal of the organic matter [17] so that they also can be used for the treatment of the young leachate [10,21].

Conversely, few processes can be suitable for the treatment of mature landfill leachate (MLL), due to the diversity of its physico-chemical properties. MLL is characterised by a higher concentration of ammonia compared to the young leachate, lower concentration of COD (often less than 4,000 mg L^{-1}) and especially lower biodegradability (BOD/COD is often lower than 0.2) as the degradable organic matter is consumed during the stabilisation of the landfill [12,22–23]. The low biodegradability of the MLL is correlated to the presence of biorefractory compounds (e.g., humic and fulvic acids), produced by the anaerobic decomposition of the organic matter [12,18,24]. Consequently, biological processes are not recommended for the treatment of MLL [24] due to the scarcity of the available substrate and to the presence of NH_3 (up to 3,000 mg L^{-1} and above, [25–26], that inhibits the microorganisms' activity [18]. Conversely, physico-chemical treatments are generally suggested for the removal of refractory compounds [10,17,21]. Absorption by active filtration (such as granular activated carbon, GAC, or zero valent iron, ZVI) seems to be a potentially suitable treatment method among the physico-chemical ones as it efficiently reduces both HMs and part of non-biodegradable organic compounds [27–29]. ZVI is able to remove HMs through a mechanism of reduction, adsorption onto its corrosion products, and precipitation and coprecipitation of its precipitating oxides [30–31]. The role of GAC in the HMs removal from the leachate is well known [32–35]. For instance, its removal efficiency was tested by Wasay et al. (1999) [36] from solutions having values pH ranging from 6.0 to 7.7 removing several HMs ($Cd^{(II)}$, $Cu^{(II)}$, $Cr^{(III)}$, $Mn^{(II)}$, $Pb^{(II)}$, and $Zn^{(II)}$) in the range of 80–96 % starting from at an initial concentration of 184 mg/L. GAC can also remove HMs through sorption on its porous surface as well as through both surface and pore precipitation [37–38]. Moreover, sorption can also occur by adding organic matter because HMs in the landfill leachate are thought to form complexes with it [39].

While young and intermediate landfill leachate can be treated by using different processes, MLL is difficult to be treated, thus representing a long-term issue for the management of the municipal sanitary landfill. The need to find efficient and adequate processes for the treatment of MLL lays in the necessity of managing the landfill leachate for many years after the landfill closure according to the current norms, for example, in the EU and in the US. A moreover, the application of a single method does not allow the complete (or, at least, partial) removal of all MLL contaminants: biological processes cannot be applied to MLL for the reasons mentioned above while treatments, such as coagulation-flocculation or advanced oxidation processes (AOP), are efficient but may generate additional chemical sludge - which needs to be treated - require high oxidant doses thus making processes economically expensive, and are generally used as tertiary treatment (that means after other treatments) prior to discharge the treated leachate in the environment [18]. Therefore, it is urgent to find a treatment system for MLL that is, at the same time, efficient, environmentally sustainable and cost effective.

The treatment of the OFMSW also represents a challenge since energy-consuming aerobic composting plants are the predominant technique for its treatment in more advanced management systems, while in many countries the organic waste is still mainly landfilled with the consequent adverse impacts in terms of biogas diffused emissions and leachate production. The switch from an aerobic to an anaerobic biological process, considering the daily high production of organic wastes, would allow the recovery of the organic matter in the form of biogas. The obtained biofuel could be directly used for energy production and/or upgraded to obtain high quality methane to be sold in transport or energy production sectors. OFMSW is basically composed of three different organic waste streams: the green waste (residues of pruning derived from the maintenance of private or public gardens), the food waste (that includes the organic fraction derived from household and other commercial activities, e.g. restaurants) and the market waste (MW). The last mainly consists of fruits and vegetables residues, such as fruit skins, potatoes, onions and other rotten vegetables [40] and is produced, in huge amount [41–43], and constitutes an easy source that can be separated even in countries where a simplified MSW management is adopted. MW is thought to be a suitable source for biogas production as it is characterised by a high level of carbohydrates and moisture [44]. However, highly degradable sugars are readily converted to volatile fatty acids (VFAs) and their accumulation causes inhibition of the process [45] leading to low biogas production [44]. The use of a source of nitrogen compounds to balance the high Carbon to Nitrogen (C/N) ratio of the MW, could be an effective solution to enhance the methane yield and to stabilise the biological process.

Due to aforementioned reasons, a novel approach to the valorisation of these two waste streams, MW and MLL, is proposed in this research (Fig. 1. The purpose of the work is to exploit the metal and nitrogen content of the MLL as a supplement of macro- (nitrogen) and micro- (e.g. trace metals as Cu, Ni, Zn) nutrients for bacteria involved in the AD [46]. In particular, the supplementation of nitrogen is necessary to balance the high carbon content of the MW (that is a carbonaceous substrate). Following this way, it would be possible to turn the problems related to the management of MLL into an advantage for the biological methanisation of the MW. Furthermore, in order to avoid an excessive presence of HMs, the raw MLL is subjected to a physico-chemical pre-treatment by means of active granular filters obtained by mixtures of either ZVI and lapillus and ZVI and GAC [47]. Then, semi-continuous anaerobic digestion tests are to be carried out at a laboratory scale using pre-treated MLL and MW. GAC needs also to be added to the reactors

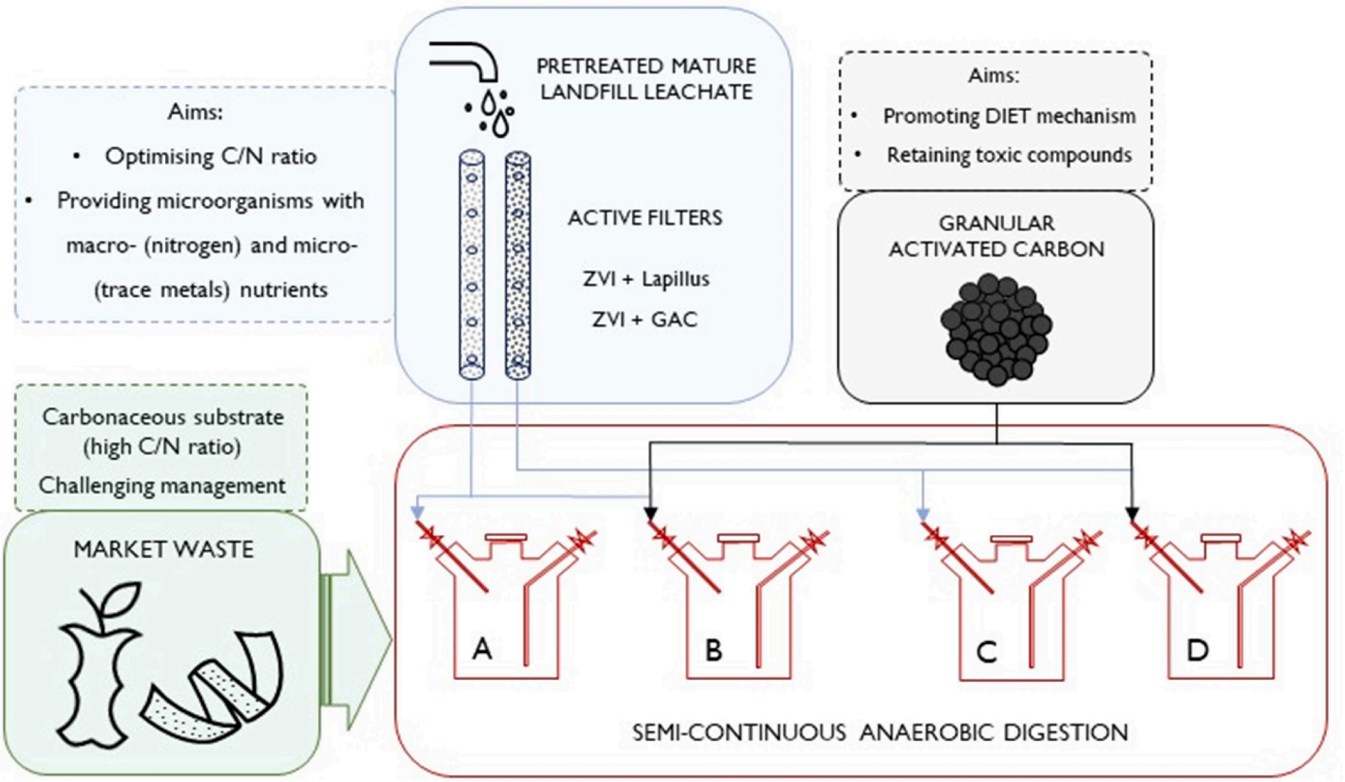

Fig. 1. Experimental design of semi-continuous anaerobic digestion of fruit and vegetable market waste and mature landfill leachate.

during semi-continuous AD tests with multiple purposes. In fact, it can stimulate the direct interspecies electron transfer (DIET) mechanism [48] (which facilitates the syntrophic metabolism between bacteria and methanogens to degrade organic matter by exchanging free electrons and protons or using molecular hydrogen or formate [49]. Moreover, GAC is also useful to isolate possible residual refractory compounds in order to enhance the process performance. This paper focuses mostly on the semi-continuous AD test since the pre-treatment has been presented in detail elsewhere [46].

Results would contribute to define possible new strategies for the treatment and valorisation of municipal waste streams in the perspective of a circular economy.

2. Materials and methods

The first phase of the study concerns the treatment of the MLL with two mixtures of active filtration materials [29,50], ZVI/Lapillus and ZVI/GAC, with the aim of reducing bio-refractory compounds (especially HMs). The second phase includes the semi-continuous anaerobic digestion of the MW, using pre-treated MLL as nutrient solution, and supplementing GAC in some of the reactors (see experimental design in Fig. 1.

The treatment of the MLL was carried out by simulating a full scale active filtration by columns filled with mixtures of ZVI/Lapillus and ZVI/GAC and according to the detailed procedure described in the paper of Fazzino et al. (2021) [46] (Fig. 2, a). Due to the daily and seasonal variability of leachate characteristics and in order to ensure the reproducibility of the experiment, a MLL was reconstructed in our laboratory according to the typical composition found in literature [46]. The column tests were carried out for 38 days in columns made of polymethyl methacrylate (PMMA – Plexiglas). At the end of the tests, treated MLLs were collected and stored before use for performing the AD of MW. The detailed characteristics of the MLLs obtained are reported in Section 2.4.

The used ZVI was FERBLAST RI 850/3.5, distributed by Pometon S.p.

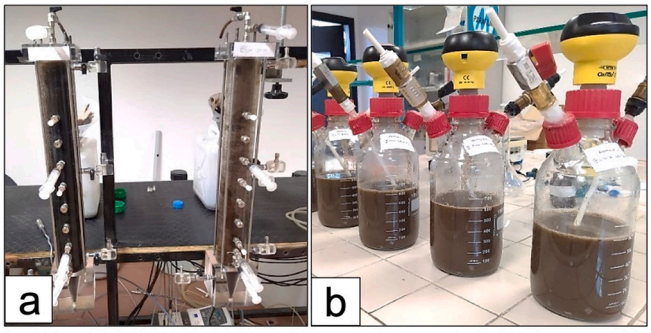

Fig. 2. Experimental setup: a) MLL pre-treatment; b) semi-continuous anaerobic reactors.

A. (Mestre, Italy) and mainly composed of iron (>99.74 %). The granular lapillus was distributed by the SEM s.r.l. (Viterbo, Italy) and the GAC (type CARBOSORB 2040) was provided by the Comelt s.r.l. (Milan, Italy). The three active materials (ZVI, lapillus and GAC) were chosen because of their wide availability and cheapness.

2.1. Experimental setup

The experiment includes four reactors designed as A, B, C and D (Fig. 2, b): the leachate pre-treated by the ZVI/Lapillus mixture was fed to reactors A and B while the leachate pre-treated with a ZVI/GAC mix was added to reactors C and D. Reactors B and D were also supplied with GAC in a concentration of 5 g/L. This concentration was kept constant during the tests by adding a quantity of GAC in feeding mixtures equal to that of GAC lost with digestate withdrawals (0.25 g/d).

Each reactor had a total operational volume of 600 mL and an initial Total Solids (TS) content (1,8%) of the mixture, the 2.3 % in GAC-amended reactors (i.e., B and D). The Organic Loading Rate (OLR) and

the Hydraulic Residence Time (HRT) were set at 1.0 gVS/L•d and 20 days, respectively, for the whole duration of tests. The C/N ratio in the fed material was set at its optimal value of 25 [51] in each reactor by mixing specific quantities of MW and pre-treated MLL. All tests were stopped after 80 days of operation (about eleven weeks). In Table 1, reactor types and pre-treated MLL, water and GAC daily dosages are reported.

2.2. Semi-continuous AD tests equipment

Semi-continuous anaerobic digestion tests were carried out in 1.1 l three necks sealed glass reactors (WTW-Germany): the central one was used to load reactors at the beginning of the tests and then closed by a stopper; both lateral necks were equipped with valves and flexible tubes so that periodically allowing, in order, biogas collection, digestate withdrawal (discharging) and feeding by using a syringe (Fig. 2, b). Reactors were placed in a thermostatic cabinet at $35 \pm 0.5\,^{\circ}C$ (mesophilic conditions) under continuous mixing, during the tests period, by a magnetic stirrer. Two or three times per week, biogas generated by the digestion was withdrawn by a 100 mL graduated syringe [52–54] and its methane content was evaluated by slowly transferring biogas into an alkaline trap (NaOH, 3 M). In this way, carbon dioxide, present in the biogas, was absorbed by the alkaline solution while the remaining methane volume, collected in the trap, induces, finally, the displacement of an equivalent volume of solution so that it can be measured in a graduated volumetric cylinder [48].

2.3. Inoculum, substrate and conductive materials

Inoculum, used in our experiment, was a residual digestate coming from previous anaerobic digestion tests, carried out in authors' laboratory. Before the beginning of tests, inoculum was sieved and stored at 35 °C.

In general, MW consists of rotten fruit and vegetables and originates from wholesale markets (pre-consumers waste). In order to obtain a representative sample for a laboratory experiment, it was decided to prepare a synthetic MW by shredding and homogenising common commercial fruits and vegetables such as apples, potatoes and carrots (45%, 49% and 6%, w/w, respectively).

Both inoculum and substrate were characterised by measuring pH, Total Solids (TS) and Volatile Solids (VS) according to standard methods [55,56] whereas the C/N ratio of MW was determined through an elemental analyser TOC-LCSH (Shimadzu, Kyoto - Japan). Results are summarised in Table 2. Synthetic MW, in particular, fulfills specific characteristics reported in literature [57,58].

GAC used as conductive material in the AD process, as for the treatment phase in the column test, was of type CARBOSORB 2040 and was provided by Comelt s.r.l. (Milan, Italy).

Table 1
Semi-continuous anaerobic digestion tests programme.

Reactor	Leachate pre-treatment	GAC addition	Pre-treated leachate [mL/d]	Dilution water [mL/d]	GAC [g/d]
A	ZVI/Lapillus	×	20.3	9.7	–
B	ZVI/Lapillus	✓	20.3	9.7	0.25
C	ZVI/GAC	×	21.3	8.7	–
D	ZVI/GAC	✓	21.3	8.7	0.25

Table 2
Inoculum and substrate characterisation

Parameter	Inoculum	Market waste
pH	7.9	5.3
Total Solids, TS [%]	2.8%	19.4%
Volatile Solids, VS [%TS]	64.9%	93.3%
C/N	–	36.3

2.4. Pre-treated MLLs used as nutrient solutions in semi-continuous AD tests

After 38 days of continuous operations, relative to each column, a composite sample of pre-treated leachate was prepared by mixing weekly samples coming from the respective column outputs. Their chemical compositions are summarised in Table 3 [46].

2.5. Digestate analyses

The digestate was then withdrawn from each reactor before the feeding procedure. With the exception for the pH value, that was measured directly on digestate samples, other analyses were carried out on average weekly digestates. pH, TS and VS were measured on raw digestates whereas total Nitrogen (N_{tot}), total Volatile Fatty Acids (VFAs) and Volatile Organic Acids/Buffering Capacity ratio (FOS/TAC) were determined on the liquid fractions resulting from digestates centrifugation (10,000 rpm for 10 min). In particular, the VFAs and FOS/TAC determination include a four-point titration method [59] in which 20 mL of the centrifuged digestate was titrated up to pH values of 5.0, 4.4, 4.3 and 4.0, using a 0.1 N sulphuric acid solution. The parameters were calculated by using equations (1) and (2) [59–60]:

$$\text{TotalVFAs}[\text{mg/L}] = \left[131140 \bullet \left(V_{pH_{4.0}} - V_{pH_{5.0}}\right) \bullet \frac{N_{H_2SO_4}}{V_{sample}}\right] - \left[3.08 \bullet V_{pH_{4.3}} \bullet \frac{N_{H_2SO_4}}{V_{sample}} \bullet 1000\right] - 10.9 \quad (1)$$

$$\text{FOS/TAC} = \frac{\left[\left(V_{pH_{4.4}} \bullet 1.66\right) - 0.15\right] \bullet 500}{V_{pH_{5.0}} \bullet 250} \quad (2)$$

where: $V_{pH_{4.0}}$, $V_{pH_{4.4}}$, $V_{pH_{4.3}}$, $V_{pH_{5.0}}$ stand for volumes (in mL) of added solution until a pH of 4.0, 4.4, 4.3 and 5.0, respectively, was reached; V_{sample} stands for the volume (in mL) of the sample (20 mL); $N_{H_2SO_4}$ is the normality of the acid solution (0.1). VFAs and FOS are calculated as acetic acid equivalent (mg_{HAC}/L) and TAC as lime equivalent (mg_{CaCO3}/L).

Table 3
Chemical compositions of pre-treated leachates [46]

Parameter	Leachate pre-treatment ZVI/Lapillus	ZVI/GAC
pH	7.5	7.1
COD [mg/L]	2,363	1,533
N_{tot} [mg/L]	860	820
NH_4-N [mg/L]	838.7	827.3
Cl^- [mg/L]	3,067	3,013
Cu [mg/L]	0.30	0.41
Ni [mg/L]	0.52	0.55
Zn [mg/L]	1.64	0.97

3. Results and discussion

3.1. Semi-continuous anaerobic digestion tests

The performance of each semi-continuous anaerobic reactor is mainly evaluated on the basis of the methane production, expressed in terms of both methane yield and cumulative methane production. The former represents the volume of methane produced in the digestion process per mass of VS added in the reactor. When the process runs stably, it exhibits a constant trend demostrating that biodegradable matter is thoroughly consumed by bacteria, leading to methane formation. The latter represents the total volume of methane generated in the reactor over all the test duration. Alongside these two parameters, the digestate analyses are also presented in order to complete processes assessment and to allow a better understanding of their evolution over time.

Methane yields and cumulated methane productions of all reactors are depicted in Figs. 3 and 4, respectively.

After the first HRT (20 days), required for the acclimatation of the microbial consortium, methane yield trends of all reactors remain practically levelled until the end of tests. In particular, reactors B and D (supplied with GAC) reach the highest methane yield values. From the day 20 onwards, methane yields were, on average, 0.297 and 0.302 NL/gVS_{added}, respectively, with negligible standard deviations (0.005 and 0.010 NL/gVS_{added}, respectively). In the same range of time, 0.256 and 0.264 NL/gVS_{added} (on average) were calculated for reactors A and C, respectively. Looking at the trends, it can be stated that all processes were running stably over the tests time and that reactors B and D performed about 14% and 13%, respectively, better than the corresponding reactors A and C.

The expected MW conversion to methane, through a semi-continuous anaerobic digestion process, was calculated on the basis of the MW Biochemical Methane Potential (BMP) assessed by a previous batch test, carried out on the same substrate used in semi-continuous tests (data not shown). The BMP of MW was determined as average of three batch replicates and was found to be 422 ± 14.7 NmL/gVS_{added}. The expected cumulative methane production from the conversion of MW through a semi-continuous anaerobic digestion process (dashed line in Fig. 4 was calculated by reducing of 30% the batch tests production (295 NmL/gVS_{added}) according to the literature, in order to evaluate the reduction of production in continuous processes with respect to the batch tests [61–64]. Fig. 4 highlights how methanogenesis proceeds steadily in all the reactors and cumulative methane production of reactors B and D clearly follows the expected methane production from the MW semi-continuous AD. At the end of all tests, reactors A, B, C and D produced 13.0, 14.5, 13.2 and 14.3 NL of methane, respectively, versus the expected cumulative methane production of 14.5 NL. Also from these data, it is evident how the supplementation of GAC enhances the process performance.

In Fig. 5, pH trends of the four reactors measured over the tests time are reported. At the beginning of the tests, a pH of 7.9 was measured in all reactors. In the first days of digestion, a decrease was observed. Shortly before completing the first twenty days of acclimatation (day 17), the addition of 2 g of $NaHCO_3$ was necessary to stop the pH decrease. As a result, a peak in pH trends was recorded in all reactors on day 21. For about two HRT (from day 21 to 59), pH fluctuated around the acceptable value of 6.8. Within this range of time, four times (days 26, 31, 42 and 46) 2 g of $NaHCO_3$ were still added to the reactors. At the beginning of the last HRT, all reactors appeared to severely suffer from the acidification increase (pH of 6.6 on day 66). This could have affected methanogenic bacteria since methane generation, in all reactors, correspondingly slowed down, as it can be observed in Fig. 3. For this reason, 4 g of $NaHCO_3$ were added to the systems favouring a pH increase up to about 7.0. After that, experiments did not require further pH adjustments until the end of the tests on day 80 (i.e., three HRT excluding the start-up). According to Steinhauser and Deublein (2011) [51] the metabolism of most of methane-forming microorganisms is considerably suppressed at pH less than 6.7, therefore it can be deduced that bacteria, involved in the processes, did not suffer acidic environmental conditions during our experiments.

Analyses carried out on weekly digestates withdrawn from respective reactors are reported in Figs. 6, 7, 8 and 9 (TS and VS, VFAs, FOS/TAC and N_{tot} contents, respectively).

In general, TS content trends of all reactors were slowly decrease over tests time indicating that the degradation of the organic solid matter was higher than the amount of solids added by feeding: the TS content was found to be reduced of about 1% (absolute value) after eighty days of digestion in all reactors. Starting from an initial TS fixed

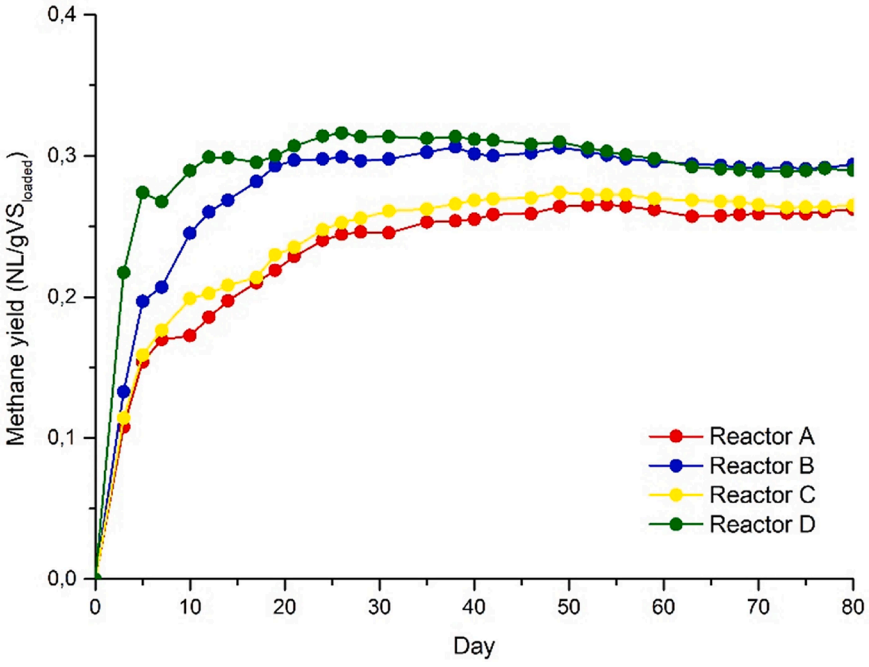

Fig. 3. Semi-continuous anaerobic reactors methane yield.

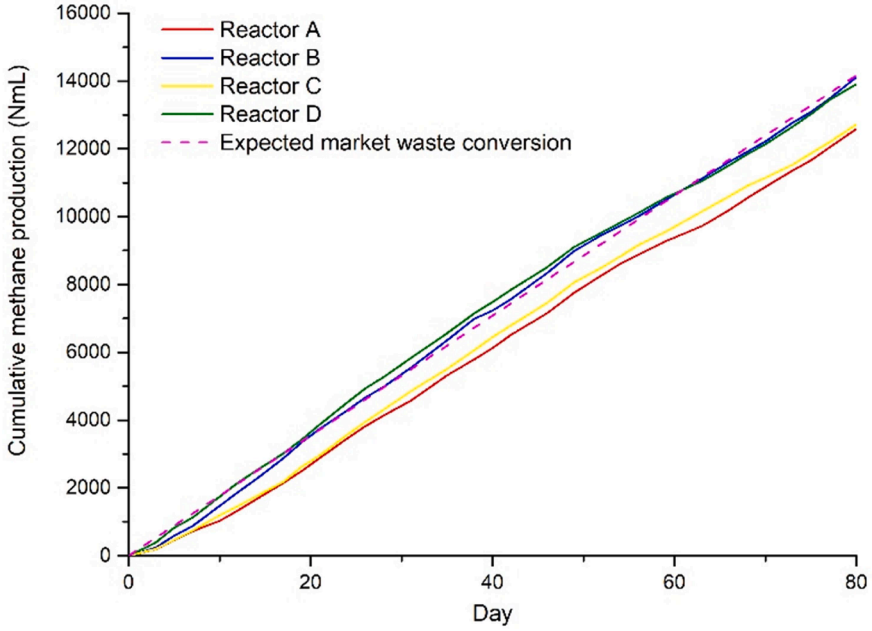

Fig. 4. Semi-continuous anaerobic reactors cumulative methane production.

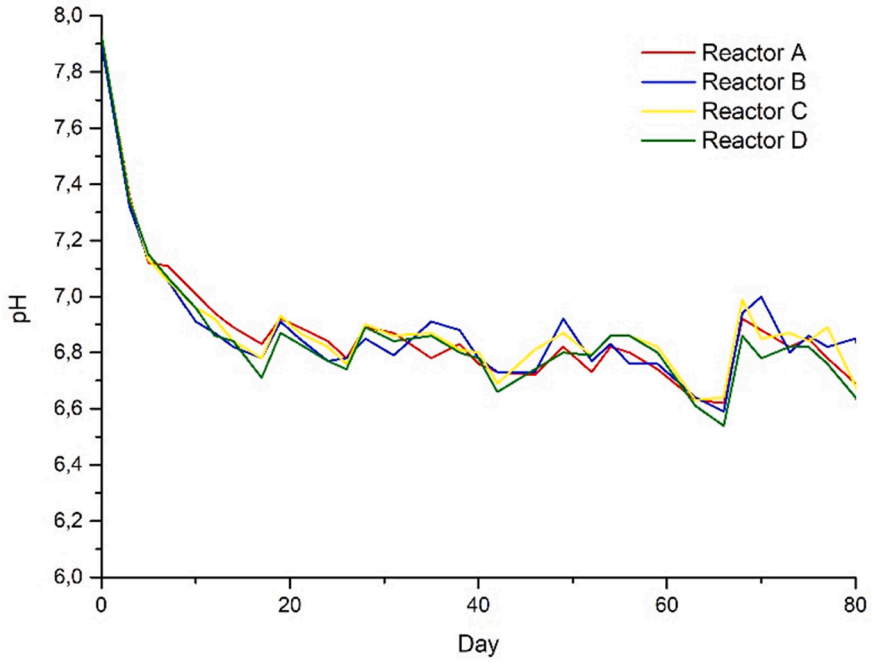

Fig. 5. Semi-continuous anaerobic reactors pH trends.

value of 1.8% in reactors A and C and 2.3% in reactors B and D (larger due to the GAC presence), after the first week of operation, basically only in reactor B the solid matter was consumed. Instead, in other reactors, TS consumption started to be observed from the second week of tests. In particular, whilst TS contents of reactors A, B and C appear to remain almost levelled until the end of the tests, the solid matter of reactor D shows large variations over the test time probably due to some sampling problems.

Furthermore, the VS content of all reactors was decreasing during the experiments. Whereas the same value in reactors supplemented with GAC was higher due to its contribution. Likewise the TS behaviour, by analysing VS trends, it can be stated that the rate of conversion of the biodegradable matter in all reactors was efficient and regular so that no accumulation of organic matter was detected.

Besides the first two weeks when reactors B and, especially, C had relatively high concentrations of total VFAs (about 1100 mg/L in the first week), for the remaining tests time the amount of VFAs was kept under control in all reactors. Indeed, VFAs values of all reactors ranged from 241 mg/L (reactor D on week VIII) to 528 mg/L (reactor C on week III). Since no accumulation of acids did occur, it can be stated that all the processes proceeded in a stable way.

The FOS/TAC parameter allows the evaluation of the anaerobic digestion process stability. In general, a FOS/TAC ratio ranging from 0.15 to 0.45 is assumed to be a general reference value for a stable process. A FOS/TAC ratio lower than 0.15 increases pH values and decrease organic acids contents (alkalosis) whereas values higher than

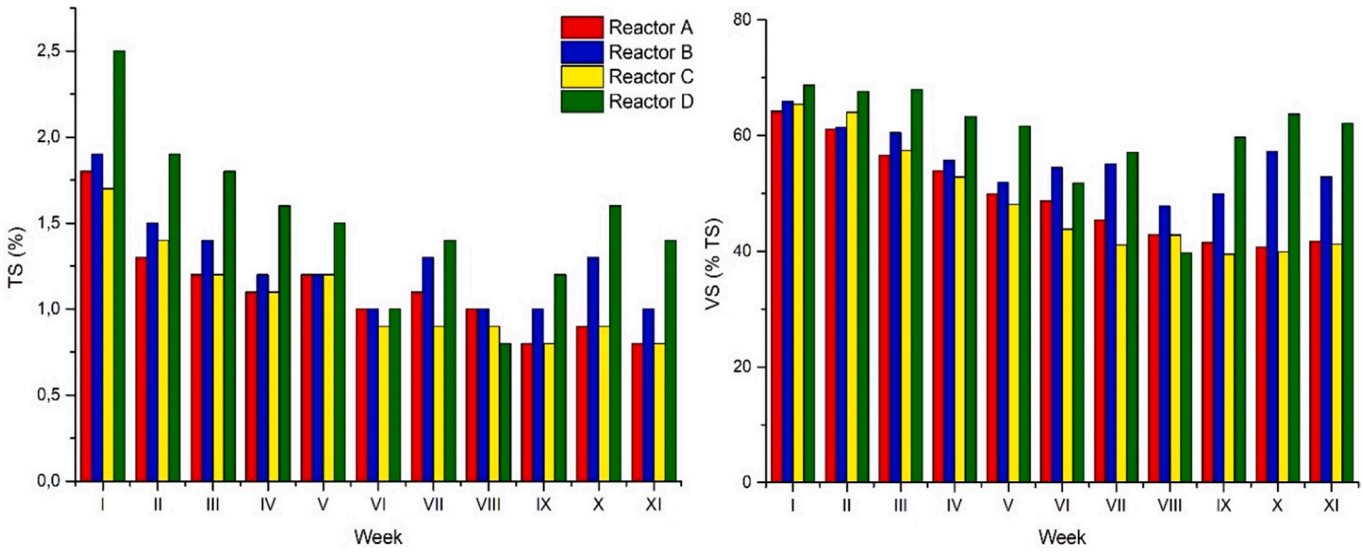

Fig. 6. TS and VS contents in weekly digestates.

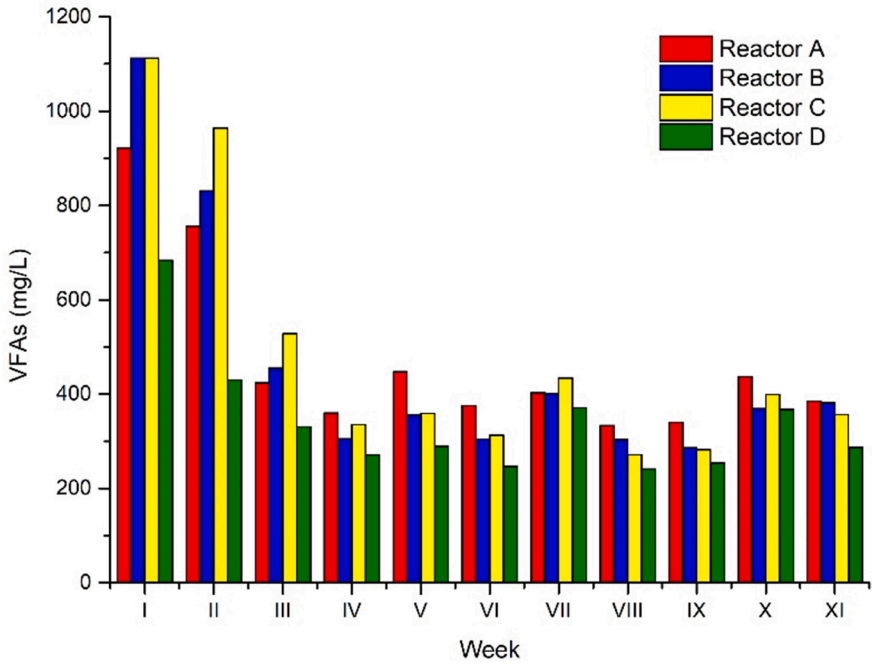

Fig. 7. VFAs contents in weekly digestates.

0.45 entail an excessive accumulation of organic acids (acidosis) [65]. At the beginning of the cycle tests, the FOS/TAC of reactors A, B and C were relatively high in the first two weeks compared to the remaining observed values. In particular, in reactor C, the FOS/TAC was higher than 0.3 in the week II. Nevertheless, FOS/TAC values of all reactors levelled off from the third week onwards around the value of 0.15 until the end of the tests. According to Mézes et al. (2011) [60], when the FOS/TAC is around 0.2, the biomass input is considered low and, therefore, it would be advisable to increase the organic loading. For this reason, it is possible to assume that the systems OLR could have been increased.

The total nitrogen content in reactor A was close to 1,000 mg/L in the first week of operation and then it reduced down to 570 mg/L on week III. On the fourth week, the concentration of nitrogen rose up to 750 mg/L before decreasing at the end of the test (480 mg/L on week XI). The N_{tot} content, in reactor B, ranged from the initial value of 820 mg/L to 530 mg/L on the fourth week before increasing up to 770 mg/L. Besides the peak at the seventh week, probably an outlier, from the fifth week onwards, the N_{tot} content followed a downward trend reaching the lowest value on the last week (280 mg/L). In reactor C, the total nitrogen content, after an early increase (860 mg/L on week II), declined down to 430 mg/L on week IV. Later, it climbed up to 770 mg/L on week VI with its trend continuously decreasing until the end of the test (400 mg/L). Finally, reactor D exhibited the same behaviour, in terms of N_{tot} concentration as reactor B.

Concentrations of HMs and chloride ion coming from pre-treated MLLs in the feed of the anaerobic tests have been preliminary calculated on the basis of volumes of pre-treated MLLs and dilution water supplied (Table 4. Under the reasonable hypothesis that both HMs and chloride ion are unaffected by the biological process in AD reactors and considering that before the feeding procedure an equal volume of digestate was discharged, these concentrations were considered as the

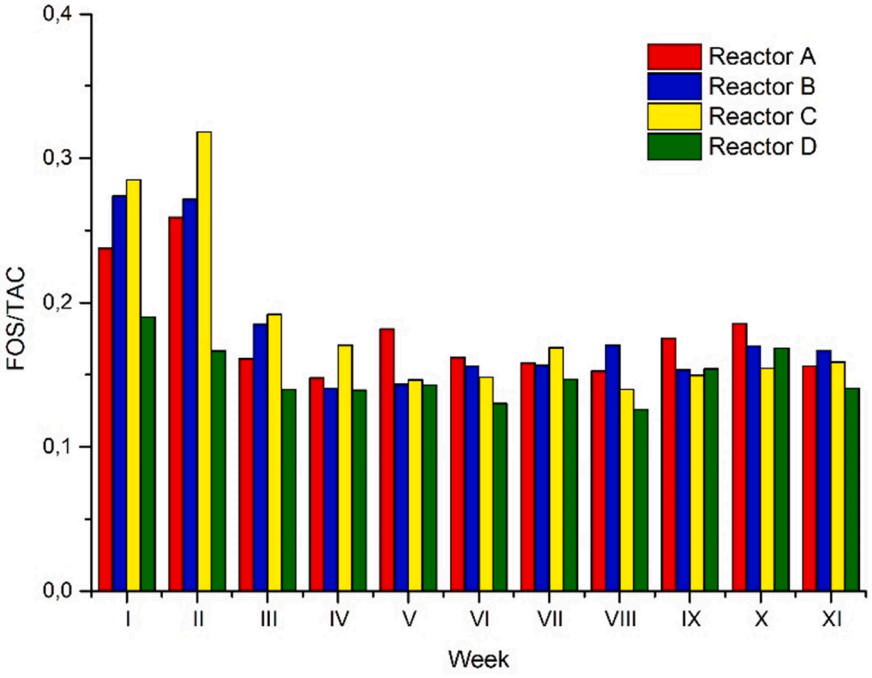

Fig. 8. FOS/TAC in weekly digestates.

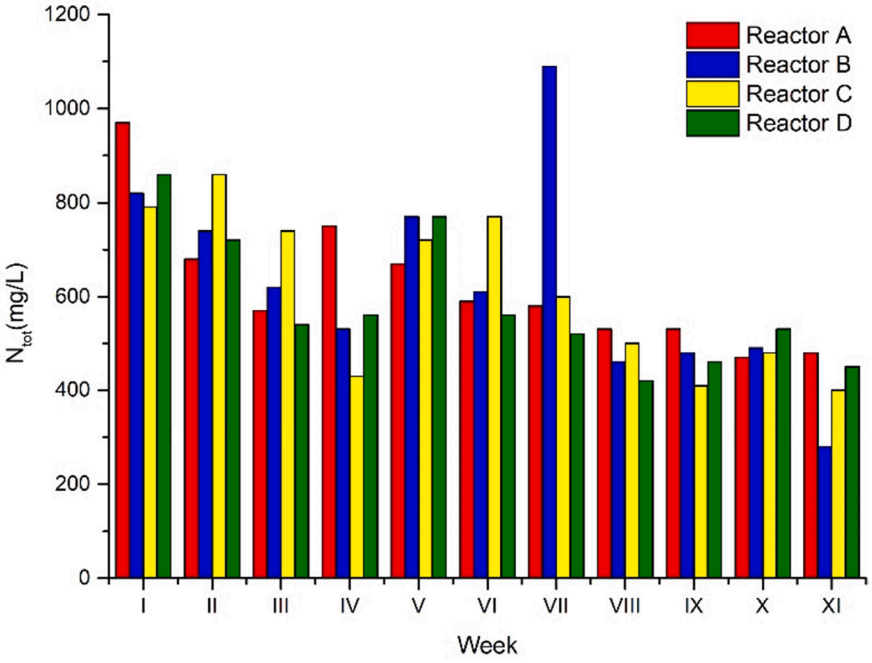

Fig. 9. N_{tot} contents in weekly digestates.

Table 4
Maximum concentrations of HMs and chloride in anaerobic reactors

Reactors	Cu [mg/L]	Ni [mg/L]	Zn [mg/L]	Cl [mg/L]
A, B	0.20	0.35	1.11	2,077
C, D	0.29	0.39	0.69	2,140

maximum values present in the anaerobic systems over the tests duration.

It is worth considering that estimated concentrations were far lower than the inhibitory thresholds found to be 500, 100, and 50 mg/L respectively for Cu, Ni, and Zn, [66] and 4–9 g/L for the chloride ion [67]. As consequence, it can be also stated that the low amount of pre-treated added MLLs as well as the water dilution and inoculum would

significantly reduce the concentration, in A-D reactors, of other persistent contaminants possibly present in leachates (e.g., pharmaceuticals and microplastics).

Inhibition of hydrolysis and methanogenesis, due to humic substances as described by Li et al. (2019) and Fazzino et al. (2021) [46,68] did not occur in our experiment, albeit the humic acids presence in the leachate, is probably due, at first, to three factors: i) the synergic/antagonistic interactions occurring among chemicals (trace metals, anions, organic compounds) in the anaerobic systems; ii) the choice of a relatively large HRT (i.e., 20 days) allowing methanogens to take the right time to grow; iii) the role played by the GAC described below.

Previously, Liao et al. (2014) [69] have performed a stable single-batch anaerobic digestion of the food waste (methane yield of 369 – 466 mL/gVS) at high OLR (41.8 gVS/L) by adding the raw leachate, found to be able to prevent the acidic inhibition of the process. In fact, according to the authors, the introduction in the system of all the ammonia present in the leachate, buffered the VFAs accumulation as well as providing bacteria, feeded by the ammonia presence. This mechanism could have been trigged in this experiment since both VFAs and ammonia remained almost levelled over the tests time (Figs. 7 and 9 and well below the inhibitory thresholds found in the literature [51,70]. Guven et al. (2018) [71] performed a co-digestion of OFMSW and landfill leachate with and without sewage sludge, testing different ratios. Particularly, the co-digestion of OFMSW and leachate led to a methane yield of 0.232 NL/gVS$_{added}$, consistent with the results of reactors A and C of this experiment (i.e., 0.256 and 0.264 NL/gVS$_{added}$ on average, respectively, Fig. 3 even if leachate in Guven et al.'s study could be classified as young because of its high biodegradability. For this reason, the enhancement of the methane production due to GAC addition (i.e., methane yields of 0.297 and 0.302 NL/gVS$_{added}$ on average, respectively for reactors B and D, Fig. 3 is remarkable.

On the other hand, from the analyses of some digestates parameters, it can be inferred is that reactors appear to be underloaded. Particularly, downward trends of TS and VS (Fig. 6 suggest that processes consume more organic solid matter than that added on feeding the systems. This observation is confirmed by the relatively low FOS/TAC values during the regime phase (Fig. 8 and this contributes to explain the low biomass input in the systems. Also, VFAs concentrations (Fig. 7 turn out to be well below the inhibitory thresholds found in literature [72]. Being the AD of food and market wastes potentially problematic because of low methane yields and fast acidification, due to its high simple sugars content [73], the maximum OLR for the process, was found to be below 3 gVS $L^{-1}d^{-1}$ [74] and several authors report satisfactory methane productions (0.5 NL/gVS$_{added}$ on average) for a HRT of 20 days or more [40,74–75]. For these reasons, in a further research, OLR could be increased in order to optimize the process.

It was demonstrated that GAC supplied to reactors B and D makes the digestion process more efficient in terms of methane generation compared to reactors A and C (controls) where no GAC was added. The GAC beneficial action in anaerobic digestion processes is known to be related to its capacity to stimulate the DIET mechanism, namely promoting electron transfer among bacterial species involved in the biological process [76]. In this experiment, the GAC presence enhances the methane yield by 13 – 14% (Fig. 3 as also observed, for instance, by Peng et al.'s (2018) [77]. In this case the GAC addition to the anaerobic digestion of sludge increases the methane yield by 13.1%. Furthermore, the establishment of the DIET mechanism can shorten the lag time for the start-up of the anaerobic digestion by 6 – 65% [78]. In this study, when GAC-amended reactors reach their regime phase after 19 days, methane yields of control reactors (i.e., A and C) continue to smoothly rise until the value was stabilized on day 40, (Fig. 3. On the other hand, the improvement of the methane content in the produced biogas was not observed (on average, roughly 64% of methane in biogas was generally recorded in all reactors at regime phase) although carbon materials are known to raise the CH_4 content [79]. Furthermore, carbon-based materials can adsorb toxic organic compounds from an anaerobic system so reducing the wastewater toxicity [80–81]. For this reason, it can be reasonably supposed that the GAC presence better protects reactors B and D from the inhibitory effect of humic substances added with leachates.

Table 5
Maximum expected HMs concentrations in digestate.

Reactor	Cu [mg/kg$_{TS}$]	Ni [mg/kg$_{TS}$]	Zn [mg/kg$_{TS}$]
A	24.1	41.7	131.7
B	20.2	35.1	110.6
C	35.9	48.2	85.0
D	35.1	47.1	83.1

Finally, concentrations of HMs in weekly collected digestates were calculated, under the hypothesis that the biological process does not affect their amount, by separating expected regime concentrations of HMs, in anaerobic reactors (Table 4, by total solid contents of weekly digestates (Fig. 6. Results are reported in Table 5 only for the worst case possible (lowest amount of TS in digestates) that corresponds to the maximum expected HMs concentrations.

Values reported in Table 5 widely fulfil the limits set by the Italian Standard for waste admission to compost production (i.e., 1,000 mg/kg$_{TS}$, 300 mg/kg$_{TS}$, 2,500 mg/kg$_{TS}$ for Cu, Ni and Zn, respectively). This implies that HMs addition during anaerobic digestion processes does not affect the quality of effluents eventually employed as material for compost production and this definitely closes the loop of leachate and market waste treatment.

4. Conclusions

This study presents a novel system for the treatment of both the mature landfill leachate and market wastes. Active materials, consisting of mixtures of ZVI/Lapillus and ZVI/GAC, were used as adsorbent filters for the treatment of MLL and, subsequently, as a nutrient solution in the AD of market wastes to balance the C/N ratio and to provide an adequate concentration of micro- and macro-nutrients to microorganisms. The obtained pre-treated MLLs were added to two semi-continuous AD reactors fed with MW (A and C, used as controls) and then to reactors (B, D) in which GAC was supplemented along with the main substrate to test its ability to retain bio-refractory compounds and to facilitate the DIET mechanism.

Taking into account all results obtained, it can be stated that all processes stably run and no sign of inhibition occurs. Besides, pre-treated MLLs seem to not negatively affect the MW/AD regardless of the type of the active filter material used. Rather, it was demonstrated that, under specific operational conditions, MLLs can be successfully employed in AD of MW with the double aim of balancing the C/N ratio of carbonaceous substrates and providing microorganisms with micro-nutrients. Methane yield and cumulative methane production were stable and constant in all tests. Better performances in terms of methane yield (about 0.302 NL/gVS$_{added}$) were detected in the reactors where GAC was added compared with those fed without its supplement (about 0.260 NL/gVS$_{added}$). The degradation of the organic matter during the tests was confirmed by the analyses of TS, VS, VFAs and total ammonia compared with their respective initial values so that even a higher OLR could be adopted in further studies. Finally, HMs concentrations, in the effluent, do not affect the quality of the digestate that can be used for further compost production.

CRediT authorship contribution statement

F. Fazzino: Methodology, Investigation, Writing – original draft, Writing – review & editing. **A. Folino:** Writing – original draft. **F. Mauriello:** Methodology, Writing – original draft, Writing – review & editing. **A. Pedullà:** Investigation, Writing – original draft, Writing – review & editing. **P.S. Calabrò:** Conceptualization, Investigation, Resources, Writing – original draft, 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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This work is dedicated to Prof. R. Pietropaolo in honour of his 80th birthday.

References

[1] Malode SJ, Prabhu KK, Mascarenhas RJ, Shetti NP, Aminabhavi TM. Recent advances and viability in biofuel production. Energy Convers Manag X 2021;10:100070. https://doi.org/10.1016/j.ecmx.2020.100070.
[2] Subramaniam Y, Masron TA. The impact of economic globalization on biofuel in developing countries. Energy Convers Manag X 2021;10:100064. https://doi.org/10.1016/j.ecmx.2020.100064.
[3] Wang X-W, Huang Lu, Ji P-Y, Chen C-P, Li X-S, Gao Y-H, et al. Using a mixture of wastewater and seawater as the growth medium for wastewater treatment and lipid production by the marine diatom Phaeodactylum tricornutum. Bioresour Technol 2019;289:121681. https://doi.org/10.1016/j.biortech.2019.121681.
[4] Kumar Singh P, Bhattacharjya R, Saxena A, Mishra B, Tiwari A. Utilization of wastewater as nutrient media and biomass valorization in marine Chrysophytes-Chaetoceros and Isochrysis. Energy Convers Manag X 2021;10:100062. https://doi.org/10.1016/j.ecmx.2020.100062.
[5] Kumari D, Jain Y, Singh R. A study on green pretreatment of rice straw using Petha wastewater and Mausami waste assisted with microwave for production of ethanol and methane. Energy Convers Manag X 2021;10:100067. https://doi.org/10.1016/j.ecmx.2020.100067.
[6] Andersson J, Krüger A, Grönkvist S. Methanol as a carrier of hydrogen and carbon in fossil-free production of direct reduced iron. Energy Convers Manag X 2020;7:100051. https://doi.org/10.1016/j.ecmx.2020.100051.
[7] Akkarawatkhoosith N, Tongtummachat T, Kaewchada A, Jaree A. Non-catalytic and glycerol-free biodiesel production from rice bran oil fatty acid distillate in a microreactor. Energy Convers Manag X 2021;11:100096. https://doi.org/10.1016/j.ecmx.2021.100096.
[8] Li M, Luo N, Lu Y. Biomass Energy Technological Paradigm (BETP): Trends in This Sector. Sustain 2017;9:567. https://doi.org/10.3390/SU9040567.
[9] Argun ME, Akkuş M, Ateş H. Investigation of micropollutants removal from landfill leachate in a full-scale advanced treatment plant in Istanbul city. Turkey. Sci Total Environ 2020;748:141423. https://doi.org/10.1016/j.scitotenv.2020.141423.
[10] Luo H, Zeng Y, Cheng Y, He D, Pan X. Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment. Sci Total Environ 2020;703:135468. https://doi.org/10.1016/j.scitotenv.2019.135468.
[11] Kale C, Gökçek M. A techno-economic assessment of landfill gas emissions and energy recovery potential of different landfill areas in Turkey. J Clean Prod 2020;275:122946. https://doi.org/10.1016/j.jclepro.2020.122946.
[12] Ahmad I, Chelliapan S, Othman N, Mohammad R. A Review (MSW) Landfill Management and Treatment of Leachate. Int J Civ Eng Technol 2018;9:336–48.
[13] Wiszniowski J, Robert D, Surmacz-Gorska J, Miksch K, Weber JV. Landfill leachate treatment methods: A review. Environ Chem Lett 2006;4(1):51–61. https://doi.org/10.1007/s10311-005-0016-z.
[14] Calabrò PS, Orsi S, Gentili E, Carlo M. Modelling of biogas extraction at an Italian landfill accepting mechanically and biologically treated municipal solid waste. Waste Manag Res 2011;29(12):1277–85. https://doi.org/10.1177/0734242X11417487.
[15] Calabrò PS, Sbaffoni S, Orsi S, Gentili E, Meoni C. The landfill reinjection of concentrated leachate: Findings from a monitoring study at an Italian site. J Hazard Mater 2010;181(1-3):962–8. https://doi.org/10.1016/j.jhazmat.2010.05.107.
[16] Calabrò PS, Gori M, Lubello C. European trends in greenhouse gases emissions from integrated solid waste management. Environ Technol 2015;36(16):2125–37. https://doi.org/10.1080/09593330.2015.1022230.
[17] Torretta V, Ferronato N, Katsoyiannis IA, Tolkou AK, Airoldi M. Novel and conventional technologies for landfill leachates treatment: A review. Sustain 2017;9:1–39. https://doi.org/10.3390/su9010009.
[18] Renou S, Givaudan JG, Poulain S, Dirassouyan F, Moulin P. Landfill leachate treatment: Review and opportunity. J Hazard Mater 2008;150(3):468–93. https://doi.org/10.1016/j.jhazmat.2007.09.077.
[19] Kjeldsen P, Barlaz MA, Rooker AP, Baun A, Ledin A, Christensen TH. Present and long-term composition of MSW landfill leachate: A review. Crit Rev Environ Sci Technol 2002;32(4):297–336. https://doi.org/10.1080/10643380290813462.
[20] Kulikowska D, Klimiuk E. The effect of landfill age on municipal leachate composition. Bioresour Technol 2008;99(13):5981–5. https://doi.org/10.1016/j.biortech.2007.10.015.
[21] Costa AM, Alfaia RG de SM, Campos JC. Landfill leachate treatment in Brazil – An overview. J Environ Manage 2019;232:110–6. 10.1016/J.JENVMAN.2018.11.006.
[22] Li W, Hua T, Zhou Q, Zhang S, Li F. Treatment of stabilized landfill leachate by the combined process of coagulation/flocculation and powder activated carbon adsorption. Desalination 2010;264(1-2):56–62. https://doi.org/10.1016/j.desal.2010.07.004.
[23] Chapter LPRO. 14 Landfilling * 2004:1–94.
[24] Bashir MJK, Aziz HA, Amr SSA, Sethupathi Sa/p, Ng CA, Lim JW. The competency of various applied strategies in treating tropical municipal landfill leachate. Desalin Water Treat 2015;54(9):2382–95. https://doi.org/10.1080/19443994.2014.901189.
[25] Burton SAQ, Watson-Craik IA. Ammonia and nitrogen fluxes in landfill sites: Applicability to sustainable landfilling. Waste Manag Res 1998;16(1):41–53. https://doi.org/10.1177/0734242X9801600106.
[26] Youcai Z. Leachate Generation and Characteristics. Pollut Control Technol Leachate from Munic Solid Waste 2018:1–30. https://doi.org/10.1016/b978-0-12-815813-5.00001-2.
[27] Rodríguez J, Castrillón L, Marañón E, Sastre H, Fernández E. Removal of non-biodegradable organic matter from landfill leachates by adsorption. Water Res 2004;38(14-15):3297–303. https://doi.org/10.1016/j.watres.2004.04.032.
[28] Singh SK, Townsend TG, Mazyck D, Boyer TH. Equilibrium and intra-particle diffusion of stabilized landfill leachate onto micro- and meso-porous activated carbon. Water Res 2012;46(2):491–9. https://doi.org/10.1016/j.watres.2011.11.007.
[29] Calabrò PS, Bilardi S, Moraci N. Advancements in the use of filtration materials for the removal of heavy metals from multicontaminated solutions. Curr Opin Environ Sci Heal 2021;20:100241. https://doi.org/10.1016/j.coesh.2021.100241.
[30] Wu Y, Guan C-Y, Griswold N, Hou L-yuan, Fang X, Hu A, et al. Zero-valent iron-based technologies for removal of heavy metal(loid)s and organic pollutants from the aquatic environment: Recent advances and perspectives. J Clean Prod 2020;277:123478. https://doi.org/10.1016/j.jclepro.2020.123478.
[31] Madaffari MG, Bilardi S, Calabrò PS, Moraci N. Nickel removal by zero valent iron/lapillus mixtures in column systems. Soils Found 2017;57(5):745–59. https://doi.org/10.1016/j.sandf.2017.08.006.
[32] Foo KY, Hameed BH. An overview of landfill leachate treatment via activated carbon adsorption process. J Hazard Mater 2009;171(1-3):54–60. https://doi.org/10.1016/j.jhazmat.2009.06.038.
[33] Erabee IK, Ahsan A, Jose B, Aziz MMA, Ng AWM, Idrus S, et al. Adsorptive Treatment of Landfill Leachate using Activated Carbon Modified with Three Different Methods. KSCE. J Civ Eng 2018;22(4):1083–95. https://doi.org/10.1007/s12205-017-1430-z.
[34] Mohammad-pajooh E, Turcios AE, Cuff G, Weichgrebe D, Rosenwinkel K-H, Vedenyapina MD, et al. Removal of inert COD and trace metals from stabilized landfill leachate by granular activated carbon (GAC) adsorption. J Environ Manage 2018;228:189–96.
[35] Bandala ER, Liu A, Wijesiri B, Zeidman AB, Goonetilleke A. Emerging materials and technologies for landfill leachate treatment: A critical review. Environ Pollut 2021;291:118133. https://doi.org/10.1016/j.envpol.2021.118133.
[36] Wasay SA, Barrington S, Tokunaga S. Efficiency of GAC for treatment of leachate from soil washing process. Water Air Soil Pollut 1999;116:449–60. https://doi.org/10.1023/A:1005115820429.
[37] Reed BE. Identification of Removal Mechanisms for Lead in Granular Activated Carbon (GAC) Columns. Sep Sci Technol 1995;30(1):101–16. https://doi.org/10.1080/01496399508012216.
[38] Chen JP, Wang X. Removing copper, zinc, and lead ion by granular activated carbon in pretreated fixed-bed columns. Sep Purif Technol 2000;19(3):157–67. https://doi.org/10.1016/S1383-5866(99)00069-6.
[39] Modin H, Persson KM, Andersson A, van Praagh M. Removal of metals from landfill leachate by sorption to activated carbon, bone meal and iron fines. J Hazard Mater 2011;189(3):749–54. https://doi.org/10.1016/j.jhazmat.2011.03.001.
[40] Ranade DR, Yeole TY, Godbole SH. Production of biogas from market waste. Biomass 1987;13(3):147–53. https://doi.org/10.1016/0144-4565(87)90024-2.
[41] Masebinu SO, Akinlabi ET, Muzenda E, Aboyade AO, Mbohwa C. Experimental and feasibility assessment of biogas production by anaerobic digestion of fruit and vegetable waste from Joburg Market. Waste Manag 2018;75:236–50. https://doi.org/10.1016/J.WASMAN.2018.02.011.
[42] Mattsson L, Williams H, Berghel J. Waste of fresh fruit and vegetables at retailers in Sweden – Measuring and calculation of mass, economic cost and climate impact. Resour Conserv Recycl 2018;130:118–26. https://doi.org/10.1016/J.RESCONREC.2017.10.037.
[43] Sitorus B, Panjaitan SD. International Conference on Sustainable Energy Engineering and Application Biogas recovery from anaerobic digestion process of mixed fruit-vegetable wastes. Berlian Sitorus Al / Energy Procedia 2013;32:176–82. 10.1016/j.egypro.2013.05.023.
[44] G NS, T NR, G S V, Sameer S. Effects of Process Variables on Biomethane Productivity in Anaerobic Digestion of Market waste co-fermented with Food Waste. Int J Eng Trends Technol 2021;69(5):109–18.
[45] Wang L, Shen F, Yuan H, Zou D, Liu Y, Zhu B, et al. Anaerobic co-digestion of kitchen waste and fruit/vegetable waste: Lab-scale and pilot-scale studies. Waste Manag 2014;34(12):2627–33. https://doi.org/10.1016/j.wasman.2014.08.005.
[46] Fazzino F, Bilardi S, Moraci N, Calabrò PS. Integrated Treatment at Laboratory Scale of a Mature Landfill Leachate via Active Filtration and Anaerobic Digestion: Preliminary Results. Water (Switzerland) 2021:2845.
[47] Bilardi S, Calabrò PS, Greco R, Moraci N. Removal of heavy metals from landfill leachate using zero valent iron and granular activated carbon. Environ Technol (United Kingdom) 2020;41(4):498–510. https://doi.org/10.1080/09593330.2018.1503725.
[48] Calabrò PS, Fazzino F, Folino A, Scibetta S, Sidari R. Improvement of semi-continuous anaerobic digestion of pre-treated orange peel waste by the combined

use of zero valent iron and granular activated carbon. Biomass Bioenergy 2019; 129:105337. https://doi.org/10.1016/j.biombioe.2019.105337.
[49] Martins G, Salvador AF, Pereira L, Alves MM. Methane Production and Conductive Materials: A Critical Review. Environ Sci Technol 2018;52(18):10241–53. https://doi.org/10.1021/acs.est.8b0191310.1021/acs.est.8b01913.s001.
[50] Bilardi S, Calabrò PS, Greco R, Moraci N. Selective removal of heavy metals from landfill leachate by reactive granular filters 2018;644:335–41. 10.1016/j.scitotenv.2018.06.353.
[51] Steinhauser A, Deublein D. Biogas from Waste and Renewables Energy. 2011.
[52] Schievano A, Scaglia B, D'Imporzano G, Malagutti L, Gozzi A, Adani F. Prediction of biogas potentials using quick laboratory analyses: upgrading previous models for application to heterogeneous organic matrices. Bioresour Technol 2009;100(23): 5777–82. https://doi.org/10.1016/j.biortech.2009.05.075.
[53] Calabrò P, Panzera M. Biomethane production tests on ensiled orange peel waste. Int J Heat Technol 2017;35(Special Issue1):S130–6.
[54] Calabro' PS, Folino A, Fazzino F, Komilis D. Preliminary evaluation of the anaerobic biodegradability of three biobased materials used for the production of disposable plastics. J Hazard Mater 2020;390:121653. https://doi.org/10.1016/j.jhazmat.2019.121653.
[55] APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater, 22nd Edition. American Public Health Association, American Water Works Association, Water Environment Federation; 2012.
[56] APAT, IRSA-CNR. Metodi analitici per le acque. Manuali e linee guida 29/2003 - Sezione 2000 Parametri fisici, chimici e chimico-fisici 2003.
[57] Bouallagui H, Touhami Y, Ben Cheikh R, Hamdi M. Bioreactor performance in anaerobic digestion of fruit and vegetable wastes. Process Biochem 2005;40(3-4): 989–95. https://doi.org/10.1016/j.procbio.2004.03.007.
[58] ZHANG R, ELMASHAD H, HARTMAN K, WANG F, LIU G, CHOATE C, et al. Characterization of food waste as feedstock for anaerobic digestion. Bioresour Technol 2007;98(4):929–35. https://doi.org/10.1016/j.biortech.2006.02.039.
[59] Liebetrau J, Pfeiffer D, Thrän D. Collection of Methods for Biogas; 2016.
[60] Mézes L, Tamas J, Borbely J. Novel approach of the basis of FOS / TAC method. Int Symp "Risk Factors Environ Food Safety" "Natural Resour Sustain Dev "50 Years Agric Res Oradea". Fac Environ Prot 2011:803–7.
[61] Zhang C, Su H, Tan T. Batch and semi-continuous anaerobic digestion of food waste in a dual solid-liquid system. Bioresour Technol 2013;145:10–6. https://doi.org/10.1016/j.biortech.2013.03.030.
[62] Ruffino B, Fiore S, Roati C, Campo G, Novarino D, Zanetti M. Scale effect of anaerobic digestion tests in fed-batch and semi-continuous mode for the technical and economic feasibility of a full scale digester. Bioresour Technol 2015;182: 302–13. https://doi.org/10.1016/j.biortech.2015.02.021.
[63] Browne JD, Allen E, Murphy JD. Assessing the variability in biomethane production from the organic fraction of municipal solid waste in batch and continuous operation. Appl Energy 2014;128:307–14. https://doi.org/10.1016/j.apenergy.2014.04.097.
[64] Moeller L, Zehnsdorf A, Müller RA. Effect of Triticale Milling Coarseness on Biogas Production. Chem-Ing-Tech 2018;90:249–55. https://doi.org/10.1002/cite.201600111.
[65] Weichgrebe D. FOS / TAC – Deduction, Methods. Application and Significance 2009:1–7.
[66] Guo Q, Majeed S, Xu R, Zhang K, Kakade A, Khan A. Heavy metals interact with the microbial community and a ff ect biogas production in anaerobic digestion : A review. J Environ Manage 2019;240:266–72. https://doi.org/10.1016/j.jenvman.2019.03.104.
[67] Viana MB, Freitas AV, Leitão RC, Pinto GAS, Santaella ST. Anaerobic digestion of crude glycerol: a review. Environ Technol Rev 2012;1(1):81–92. https://doi.org/10.1080/09593330.2012.692723.
[68] Li J, Hao X, van Loosdrecht MCM, Luo Y, Cao D. Effect of humic acids on batch anaerobic digestion of excess sludge. Water Res 2019;155:431–43. https://doi.org/10.1016/j.watres.2018.12.009.
[69] Liao X, Zhu S, Zhong D, Zhu J, Liao L. Anaerobic co-digestion of food waste and landfill leachate in single-phase batch reactors. Waste Manag 2014;34(11): 2278–84. https://doi.org/10.1016/j.wasman.2014.06.014.
[70] Yenigün O, Demirel B. Ammonia inhibition in anaerobic digestion: A review. Process Biochem 2013;48(5-6):901–11. https://doi.org/10.1016/j.procbio.2013.04.012.
[71] Guven H, Akca MS, Iren E, Keles F, Ozturk I, Altinbas M. Co-digestion performance of organic fraction of municipal solid waste with leachate: Preliminary studies. Waste Manag 2018;71:775–84. https://doi.org/10.1016/J.WASMAN.2017.04.039.
[72] Wang Y, Zhang Y, Wang J, Meng L. Effects of volatile fatty acid concentrations on methane yield and methanogenic bacteria. Biomass Bioenergy 2009;33(5):848–53. https://doi.org/10.1016/j.biombioe.2009.01.007.
[73] Xu F, Li YY, Ge X, Yang L, Li YY. Anaerobic digestion of food waste – Challenges and opportunities. Bioresour Technol 2018;247:1047–58. https://doi.org/10.1016/j.biortech.2017.09.020.
[74] Mata-Alvarez J, Llabrés P, Cecchi F, Pavan P. Anaerobic digestion of the Barcelona central food market organic wastes: Experimental study. Bioresour Technol 1992; 39(1):39–48. https://doi.org/10.1016/0960-8524(92)90054-2.
[75] Scano EA, Asquer C, Pistis A, Ortu L, Demontis V, Cocco D. Biogas from anaerobic digestion of fruit and vegetable wastes: Experimental results on pilot-scale and preliminary performance evaluation of a full-scale power plant. Energy Convers Manag 2014;77:22–30. https://doi.org/10.1016/j.enconman.2013.09.004.
[76] Liu F, Rotaru A-E, Shrestha PM, Malvankar NS, Nevin KP, Lovley DR. Promoting direct interspecies electron transfer with activated carbon. Energy Environ Sci 2012;5:8982–9. https://doi.org/10.1039/C2EE22459C.
[77] Peng H, Zhang Y, Tan D, Zhao Z, Zhao H, Quan X. Roles of magnetite and granular activated carbon in improvement of anaerobic sludge digestion. Bioresour Technol 2018;249:666–72.
[78] Wang Z, Wang T, Si B, Watson J, Zhang Y. Accelerating anaerobic digestion for methane production: Potential role of direct interspecies electron transfer. Renew Sustain Energy Rev 2021;145:111069. https://doi.org/10.1016/j.rser.2021.111069.
[79] Zhang J, Zhao W, Zhang H, Wang Z, Fan C, Zang L. Recent achievements in enhancing anaerobic digestion with carbon- based functional materials. Bioresour Technol 2018;266:555–67. https://doi.org/10.1016/j.biortech.2018.07.076.
[80] Calabrò PS, Fazzino F, Folino A, Komilis D. Semi-continuous Anaerobic Digestion of Orange Peel Waste: Preliminary Results; 2020:309–11. 10.1007/978-3-030-13068-8_77.
[81] Zhu H, Han Y, Ma W, Han H, Ma W, Xu C. New insights into enhanced anaerobic degradation of coal gasification wastewater (CGW) with the assistance of graphene. Bioresour Technol 2018;262:302–9. https://doi.org/10.1016/J.BIORTECH.2018.04.080.