Harvesting zero waste from co-digested fruit and vegetable peels via integrated fermentation and pyrolysis processes

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Abstract

The aim of this study is to assess an innovative economic approach for the production of both fermentative hydrogen and biochar from fruit and vegetable peels (FVPs) via fermentation/pyrolysis process. Firstly, in fermentation batches, multi-fermentation of FVPs positively affected the harvested hydrogen yield and COD reduction efficiency, which reached their maximal values of 3.9 $\pm$ 0.6 mmol/g_{COD} and 56.2 $\pm$ 4.6% at batch of 25% pea + 25% tomato + 25% banana + 25% orange (M4). Secondly, digestates produced from all batches were pyrolyzed at 500 °C for investigating the potential for biochar production. Based on the characteristics of the pyrolyzed digestate, biochar produced from S1 (spinach) exhibited the highest specific surface area, density, pore volume, biochar production yield, and pyrolysis profit of 28.43 $\pm$ 3.95 m^2/g, 1.93 $\pm$ 0.18 g/cm^3, 0.59 $\pm$ 0.08 cm^3/g, 59.04 $\pm$ 2.36%, and 3.66 \$/$kg_{feedstock}$, respectively. However, the maximum overall profit from both fermentation and pyrolysis processes was 5.21 \$/$kg_{feedstock}$ and was denoted for M4.

Keywords Fruit and vegetable peels · Hydrogen production · Biochar · Net energy gain

Introduction

Based on their growing global need, fruits and vegetables are being widely planted worldwide. Consequently, significant percentage of these fruits and vegetables converts into waste either by human consumption or processing industries. In Egypt, based on a recent report released by the Food and Agricultural Organization of the United Nation (FAO UN),

the production of oranges, bananas, tomatoes, green peas, and spinaches was estimated to be about 3.14, 1.28, 8.29, 0.18, and 0.03 million tons per year, respectively (FAOSTAT 2017). Huge amounts of wastes of fruit and vegetable peels (FVPs) are produced, as a result. Such wastes are being conventionally disposed by open burning or landfilling (Elsamadony and Tawfik 2015). However, these impractical methods of disposal have many environmental problems, e.g., the emission of greenhouse gases and toxic compounds (Mahmoud et al. 2017). On the other hand, these FVPs are perfect biomass resource for fermentation process because of their high content of carbon and nutrition (Elsamadony et al. 2015a). Fermentation process has the ability to convert biomass into hydrogen which is considered the ideal candidate to supersede traditional sources of energy. Whereas, H$_2$ yielded energy 2.75-folds higher than hydrocarbon fuels with only water as a combustion by-product (Xing et al. 2010; Farghaly et al. 2016; Mostafa et al. 2017). However, fermentation process cannot acquire a full utilization for the organic content presented in the used waste (Farghaly et al. 2017; Farhat et al. 2018). Therefore, more research efforts should be directed for valorizing the residual organic content presented after the fermentation process is over.

Currently, digestate, nutrients' rich matter generated as the main by-product for fermentation, is being used for soil

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conditioning purposes (Marone et al. 2012). Unfortunately, this function suffers from many problems, e.g., being restricted by inconstant agricultural seasonal requirements, evolving pathogens and odors as well as the presence of another cheaper compost products, which are generated from aerobic treatment plants (Ismail et al. 2019a, b). Further, a high budget is being directed to the handling, in terms of transportation and storage, of digestate that is featured of its low density. The leaching of digestate nutrients from the soil, caused by the relatively high mobility, represents an additional obstacle against the direct usage of such digestate in soil conditioning (Tenca et al. 2011). Consequently, digestate treatment seemed to be essential before its utilization in soil amendment purposes.

Recently, one of the growing concepts is the back to earth alternative (BEA), which means that the treated residues have to be returned back to their non-mobile state, similar to that before being extracted from the ground, and complete closing for the cycles of material in the environment is acquired as a result. From the view of BEA along with circular economy concept, digestate pyrolysis process is considered as an efficient strategy for maximizing energy recovery and the potential for utilization of the pyrolyzed product as soil (Changkook et al. 2007). Biochar is defined as the solid material that is gotten from the thermochemical conversion of biomass in an oxygen-limited environment. Pyrolysis process is a well-known approach for biochar production through thermal decomposition of biomass at a temperature range of 300–900 °C under oxygen-free conditions. Biochar can be used in a wide range of applications, e.g., adsorption, catalysis, and soil amendment (Vochozka et al. 2016). The reasons behind the current expansion in using biochar as an adsorbent are its high affinity and strong selectivity for different types of contaminants in an aqueous medium (Nyström 2016). Furthermore, a new study highlighted that the addition of lawn waste–based biochar to food waste composting could optimize the process through boosting the composting stability, degradation, and mineralization rate of food waste (Jouiad et al. 2015). On the other hand, biochar is rich in nutrients and stable aromatic carbon; thereby, it could be eco-friendly and used for energy generation, soil improvement, climate change mitigation, and water treatment. Soil amendment using digestate-based biochar seemed to be featured with limited leaching for nutrients, and high cation-exchange capacity and improved crop productivity are gained, as a result (Ronsse et al. 2013). However, much more research has to be focused on reducing biochar production cost in order to make it cost-effective and able to compete traditional cheap fertilizers. On the same track and based on all the aforementioned findings, our study proposes a novel approach for the valorization of VFPs via integrating both of fermentation process, targeting biohydrogen production, and pyrolysis, targeting biochar production.

Therefore, aims of this study are to assess the potential of fermentative hydrogen generation from FVPs via sole, dual, and multi-fermentation, as well as, the capability of biochar production from the formed digestate, besides performing energetic and economic analyses of the integrated system for hydrogen and biochar production from FVPs using fermentation followed by pyrolysis.

Materials and methods

Fruit and vegetable peels and inoculum sludge

Fruit and vegetable peels were daily harvested from FARAGALLA factory (Alexandria, Egypt). The factory produces frozen and canned vegetable besides fruits juice; therefore, about 20 tons of vegetable and fruit peels are daily generated, as a result. Peels were crushed into small particles using an electrical grinder. Afterwards, slurries were filtered using a stainless steel sieve that has openings of 2.0 mm. The obtained filtrate was then used for sole, dual, and multi-fermentation process. Complete characteristics of the FVPs are shown in Table 1.

Inoculum sludge has been collected from El-Agamy wastewater treatment plant (Alexandria, Egypt). Sludge was concentrated by settling for a day; thereafter, the supernatant was removed, while the residue is filtered through the sieve (no. 10) for removal of coarse particles. Afterwards, H_2-producing microorganism germination was conducted at an anaerobic continuous stirred-tank reactor (CSTR), of a 5-L capacity, and were initially fed with glucose as the sole carbon source under operation conditions of HRT, temperature, and pH of 2 h, 35 °C, and 5.5, respectively, for 2 consecutive months targeting removal of methanogens and enriching of the H_2-producing bacteria. Finally, the obtained HPB were pre-heated at 70 °C for half an hour in order to inhibit the bioactivity of hydrogen consumers and to harvest spore-forming anaerobic bacteria (Elsamadony et al. 2015b). The characteristics of the used HPB in terms of pH, alkalinity, total suspended solids (TSS), and volatile suspended solids (VSS) were 5.5 ± 0.2, 0.93 ± 0.1 g/L as $CaCO_3$, 30.6 ± 2.9, and 25.3 ± 2.1 g/L, respectively.

Batch fermentation experimental setup

Batch fermentation experiments were executed in 200-mL batch reactors with 150-mL working volume. Fifty milliliters of H_2-producing bacteria was added to batch reactors as seeding sludge, while the remaining volumes were filled with different volumetric ratios of fruit and vegetable peels as follows: 100% spinach (S1), 100% pea (S2), 100% tomato (S3), 100% banana (S4), 100% orange (S5), 50% S + 50% P (D1), 50% S + 50% T (D2), 50% S + 50% B (D3), 50% S + 50% O

Table 1 Characteristics of the used fruit and vegetable peels

Parameter	Vegetable peels				Fruit peels	
	Unit	Spinach (S1)	Pea (S2)	Tomato (S3)	Banana (S4)	Orange (S5)
pH		4.3 ± 0.1	5.1 ± 0.2	4.4 ± 0.32	5.1 ± 0.2	3.4 ± 0.1
Total solids (TS)	%, (w/w)	8.3 ± 0.5	18.6 ± 0.6	17.6 ± 0.3	15.2 ± 0.5	10.6 ± 0.3
Volatile solids (VS)	%, (w/w)	6.9 ± 0.4	11.8 ± 0.3	16.1 ± 0.2	13.6 ± 0.4	9.4 ± 0.2
tCOD	mg/g	233.1 ± 21.2	368.7 ± 27.4	539.0 ± 49.5	251.1 ± 22.7	657.5 ± 50.8
Total organic carbon (TOC)	mg/g	78.1 ± 6.5	145.9 ± 13.1	140.5 ± 11.8	114.1 ± 9.3	229.2 ± 15.8
Total Kjeldahl nitrogen (TKN)	mg/g	11.3 ± 1.2	7.6 ± 0.5	9.4 ± 0.7	3.0 ± 0.2	2.7 ± 0.1

(D4), 50% P + 50% T (D5), 50% P + 50% B (D6), 50% P + 50% O (D7), 50% T + 50% B (D8), 50% T + 50% O (D9), 50% B + 50% O (D10), 25% S + 25% T + 25% B + 25% O (M1), 25% S + 25% P + 25% B + 25% O (M2), 25% S + 25% P + 25% T + 25% B (M3), 25% P + 25% T + 25% B + 25% O (M4), 25% P + 25% T + 25% S + 25% O (M5), and 20% S + 20% P + 20% T + 20% B + 20% O (M6) (v/v), respectively. All batches were initially purged with pure nitrogen gas for 3 min in order to remove oxygen and provide anaerobic environment. Afterwards, batch reactors were tightly capped with rubber stoppers and aluminum caps. Prior to the fermentation start-up, the pH values of the media inside batch reactors were adjusted to 6.0 ± 0.2 using 1 N HCl and NaOH. The batches were incubated at mesophilic condition (35 ± 2 °C). All batches and experimental measurements were conducted in duplicate.

Characterization of digestate and pyrolysis process

The resultant digestates from sole, dual, and multi-fermentation process were centrifuged to separate the solids fractions. The residues were dried at 80 °C in an oven for 24 h.

The ash, carbon content (C%), nitrogen content (N%), hydrogen content (H%), surface area (m²/g), density (g/cm³), and pore volume (cm³/g) were determined for all digestates as shown in Table 2. The dried digestates were subsequently subjected to pyrolysis process as reported earlier by Bruun et al. (2017). Specifically, the dried digestates were carefully placed in a crucible and covered by a similar crucible in such a way that prevents the presence of air inside the containers that were purged by nitrogen gas for 3 min. Then, the containers were heated in an oven for 1 h at 500 °C to give biochar, whereas this temperature previously exhibited the highest stable carbon among the experimental biochar (Ronsse et al. 2013). The heating rate was adjusted to be 20 °C/min in order to augment biochar yield (wt%).

The specific surface areas of the used digestates and produced biochars were determined by nitrogen adsorption on a Micrometrics TriStar 3000 (BEl Japan Inc.). The

samples were conditioned to a dynamic vacuum system at a temperature of 150 °C for 3 h. The pore volume was calculated by converting the amount of nitrogen gas that is adsorbed at a relative pressure ca. 0.99 to the volume of liquid adsorbate. Further, a helium displacement method with a pycnometer (Micromeritics, USA) was utilized for the measurement of density of the digestate and biochar. All experiments were implemented in duplicate.

Analytical methods

Total solids (TS), volatile solids (VS), chemical oxygen demand (COD), and total Kjeldahl nitrogen (TKN) were measured according to APHA (2005). Total organic carbon (TOC) was quantified by a TOC analyzer-L CPH (Shimadzu, Japan). A pH meter (Thermo Scientific Orion 5-Star Plus) was used for pH measurement. Displacement method was utilized for measuring the volume of the evolved gas. Further, H_2 gas content was measured using gas chromatography (GC-2014, Shimadzu, Japan) that consisted of a thermal conductivity detector (TCD) and a 0.2 m × 3 mm-diameter stainless column packed with Shin carbon (50/80 mesh). The operational temperatures of GC constituents, i.e., an injection port, a column oven, and a detector, were of 100, 120, and 150 °C, respectively, with helium as the carrier gas at a flow rate of 25 mL/min.

Net energy calculations

Energy consumed during the fermentation process of sole, dual, and multi-FVPs can be classified into heat and mixing energy. Energy spent to keep batch reactors in mesophilic conditions (35 °C) is estimated according to Eq. 1, where, E_H is the energy required for heating (kJ/kg$_{feedstock}$); C_p is the specific heat constant (kJ/kg °C) (C_p of solid organic matter = 2.71 kJ/kg °C); M is the weight of the solid media inside the batch reactor (kg); X is the M of the particulate feedstock; and dT is the difference between the fermentation temperature

Table 2 Chemical and textural characteristics of sole, dual, and multi-fermented digestates

Digestate	Ash	C	N	H	Surface area	Density	Pore volume
	%	%	%	%	m²/g	g/cm³	cm³/g
Sole fermentation digestate							
S1	23.8 ± 3.1	49.4 ± 5.3	8.3 ± 1.1	6.1 ± 0.7	0.82 ± 0.09	1.38 ± 0.15	0.23 ± 0.05
S2	23.5 ± 2.8	56.7 ± 6.1	3.9 ± 0.5	4.9 ± 0.4	0.87 ± 0.07	1.32 ± 0.16	0.25 ± 0.01
S3	21.0 ± 2.5	44.5 ± 5.7	3.5 ± 0.2	5.7 ± 0.5	0.76 ± 0.06	1.23 ± 0.08	0.22 ± 0.03
S4	23.4 ± 2.7	52.9 ± 5.9	1.9 ± 0.2	6.2 ± 0.6	0.88 ± 0.07	1.31 ± 0.11	0.24 ± 0.02
S5	19.4 ± 2.1	48.2 ± 5.2	0.6 ± 0.1	6.3 ± 0.8	0.56 ± 0.08	1.13 ± 0.05	0.18 ± 0.01
Dual fermentation digestate							
D1	14.5 ± 1.6	36.5 ± 4.1	5.4 ± 0.6	5.4 ± 0.7	0.44 ± 0.05	0.65 ± 0.09	0.13 ± 0.02
D2	19.5 ± 1.9	38.2 ± 4.5	4.6 ± 0.2	5.8 ± 0.6	0.61 ± 0.08	1.16 ± 0.07	0.20 ± 0.03
D3	19.1 ± 2.3	40.9 ± 5.3	5.3 ± 0.7	6.2 ± 0.7	0.57 ± 0.03	1.01 ± 0.05	0.18 ± 0.02
D4	18.2 ± 2.1	37.6 ± 4.2	4.2 ± 0.3	6.4 ± 0.7	0.51 ± 0.07	0.93 ± 0.11	0.17 ± 0.01
D5	13.3 ± 1.5	37.2 ± 3.3	3.5 ± 0.3	5.2 ± 0.4	0.38 ± 0.03	0.52 ± 0.04	0.12 ± 0.02
D6	18.2 ± 2.9	41.1 ± 3.8	2.4 ± 0.1	5.7 ± 0.4	0.54 ± 0.04	1.07 ± 0.08	0.17 ± 0.03
D7	19.9 ± 2.3	44.7 ± 4.9	1.2 ± 0.3	5.6 ± 0.5	0.50 ± 0.07	0.95 ± 0.10	0.18 ± 0.02
D8	18.6 ± 2.0	39.1 ± 4.2	3.1 ± 0.2	5.9 ± 0.8	0.61 ± 0.08	1.13 ± 0.19	0.19 ± 0.04
D9	14.8 ± 1.9	36.2 ± 3.5	1.9 ± 0.2	6.2 ± 0.7	0.42 ± 0.05	0.64 ± 0.12	0.13 ± 0.01
D10	19.8 ± 1.4	42.3 ± 4.0	0.8 ± 0.1	6.3 ± 0.4	0.68 ± 0.04	1.17 ± 0.09	0.20 ± 0.04
Multi-fermentation digestate							
M1	14.6 ± 1.6	37.1 ± 3.9	3.5 ± 0.2	6.0 ± 0.5	0.39 ± 0.05	0.67 ± 0.11	0.13 ± 0.02
M2	18.2 ± 2.2	41.4 ± 4.3	4.3 ± 0.5	5.7 ± 0.6	0.64 ± 0.09	1.12 ± 0.09	0.19 ± 0.01
M3	20.5 ± 3.9	41.0 ± 3.8	4.4 ± 0.6	5.8 ± 0.7	0.73 ± 0.09	1.02 ± 0.08	0.22 ± 0.01
M4	18.8 ± 2.1	42.8 ± 4.4	3.3 ± 0.5	5.4 ± 0.8	0.69 ± 0.04	1.16 ± 0.15	0.19 ± 0.03
M5	15.9 ± 1.8	38.3 ± 3.6	4.3 ± 0.4	5.3 ± 0.6	0.44 ± 0.02	0.68 ± 0.09	0.14 ± 0.03
M6	17.9 ± 1.9	40.7 ± 4.2	3.7 ± 0.4	5.3 ± 0.6	0.59 ± 0.09	1.03 ± 0.08	0.18 ± 0.01

and the raw wastewater (°C) (Perera et al. 2010). While, energy consumed in mixing, E_M, is estimated based on the horse power of the mixer (0.05 HP) and operating time.

$$E_H = (C_p \times M \times dT)/X \qquad (1)$$

H_2 energy E_{H_2} (kJ/kg$_{feedstock}$) is determined from Eq. 2, where, G is the volume of evolved hydrogen (L); ρ_{H_2} is the density of hydrogen gas (8.9×10^{-5} kg/L); and LHV is the lower heating value of hydrogen (120,000 kJ/kg) (Perera et al. 2010);

$$E_{H_2} = (G \times \rho_{H_2} \times (\text{LHV}_{H_2}))/X \qquad (2)$$

$$\text{Net–Energy (kJ/kg}_{feedstock}) = E_{H_2} - E_H - E_M \qquad (3)$$

Therefore, Eq. (3) represents the objective function for the net energy obtained from the fermentation process, in terms of hydrogen, subtracted by the consumed energy in heating and mixing (Elsheikh et al. 2013).

On the other hand, the thermochemical conversion of digestate to biochar follows the auger-based pyrolysis system with biochar-only operation. This process, basically, contains two main heating steps, i.e., the moister-reducing stage and the stage of dried digestate pyrolysis at an oxygen-free environment at 500 °C. In real field, vapors released from the pyrolysis step are recycled in order to support the drying step as well as run the pyrolyzer (Campbell et al. 2018). At a small-scale auger-based pyrolysis system, which includes drying and pyrolysis, a previous investigation conducted by Huang et al. (2015) estimated the electrical cost utilized for biochar production, as 43 $/kg$_{feedstock}$.

Results and discussion

Fruit and vegetable peel fermentation process

Fruit and vegetable peel fermentation exhibited large variation in terms of H_2 production. Sole fermentation of vegetable wastes such as spinach (S1), pea (S2), and tomato (S3) revealed H_2 production (HP) of 1.61 ± 0.36, 6.93 ± 0.78, and

5.34 ± 0.30 mmol, respectively. On the other hand, fruit peels like banana (S4) and orange (S5) peels released H_2 amount of 7.48 ± 0.53 and 1.03 ± 0.16 mmol, respectively, as depicted from Fig. 1a. Low H_2 production may relate to high nitrogen content that originated in some types of waste. However, balanced carbon to nitrogen ratio at the range of 20 to 30 exhibited microbial growth augmentation and substrate utilization valorization, in turn improving the hydrogen fermentative process (Elsamadony et al. 2015a; Wazeri et al. 2018a). Previously, Danial and Abdel-Basset (2015) stated that small amounts of orange peels have the ability to enhance H_2 production as a result of uptake hydrogenase (Hup) activity inhibition. On the other hand, large amount is attributed to low H_2 production due to pharmaceutical compounds in orange peels. HP ranged from 4.1 to 3.2 mmol corresponding to 1 and 3 g of orange peels, respectively. In addition, a relatively higher value of HP of 15.8 mmol was obtained from banana peels by

Nathoa et al. (2014). This refers that banana peels have higher H_2 potential compared to orange peels. A similar conclusion was found in our study. Pea peels, related to 5% (w/v) total solids content, revealed HP of 2.1 mmol (Kalia and Joshi 1995). Vegetable peels earlier demonstrated higher hydrogen potential compared to fruit peels. In particular, Soltan et al. (2017) acquired limited HP of 810 mL/L from the mixed fruit peels. Contrarily, HP of 1620 mL/L was observed by Marone et al. (2012) for vegetable waste.

Dual fermentation presented in Fig. 1b showed that the batch reactor that contained 50% spinach + 50% pea (D1) generated the minimum H_2 amount of 2.10 ± 0.21 mmol, which is lower than sole fermentation. While, high HP of 14.0 ± 0.79 mmol was recorded at 50% pea + 50% banana (D6). Moreover, the maximum harvested HP of 17.09 ± 0.48 mmol was observed when using the mixture of 25% pea + 25% tomato + 25% banana + 25% orange (M4) as depicted in Fig. 1c. Mixing fruit and vegetable peels, in some cases, witnessed HP of 600 mL/L, which was lower than that those achieved in separately fermented fruit and vegetable peels (Jia et al. 2014). Nevertheless, Tenca et al. (2011) referred to higher HP 2820 ± 670 mL/L/day corresponding to mixture of fruit and vegetables waste fermented in continuous mode. All the aforementioned results confirm that the performance among the fermentation process is deeply affected by the composition of the used mixture between fruits and vegetables. Interestingly, Akinbomi and Taherzadeh (2015) stated that uplifting orange peel concentration in the fruit peels mixture from 20 to 70% attributed to a decline in HP by 55.2% due to increasing anti-microbial effect of limonene in the fruit mixture, while small amount of their concentration upgrades HP as a result of H_2 oxidation enhancement due to catalyzing the uptake hydrogenase (Hup) activity inhibition, besides being a source of nutrients (Danial and Abdel-Basset 2015). This may be the reason behind the low HP from 100% (v/v) orange peels compared with maximum HP recorded at M4 with only 25% (v/v) orange peels.

Following the same attitude, H_2 yield (HY) obtained from 25% pea + 25% tomato + 25% banana + 25% orange (M4) of 3.9 ± 0.6 mmol/g_{COD} was the maximum among all other batches. Such a high value exceed that denoted from sole peel fermentation of orange (S5), spinach (S1), tomato (S3), pea (S2), and banana (S4) peels, which showed HY values of 1.3 ± 0.2, 1.5 ± 0.2, 2.7 ± 0.4, 2.9 ± 0.4, and 2.9 ± 0.5 mmol/g_{COD}, respectively. Likely, H_2 content, presented at Fig. 1, was enriched from the maximum H_2 content (51.8%) for sole fermentation recorded at S4 to a peak H_2 content (64.7%) registered for the multi-fermentation batch reactor (M4). Balanced nutrients found at M4 might lead to stimulating the activities of H_2-producing bacteria (Wazeri et al. 2018b), whereas the increases of HY and H_2 contents refer to the bacterial metabolites shifting to the H_2-producing pathway rather than the H_2-consuming one (Elreedy et al. 2018).
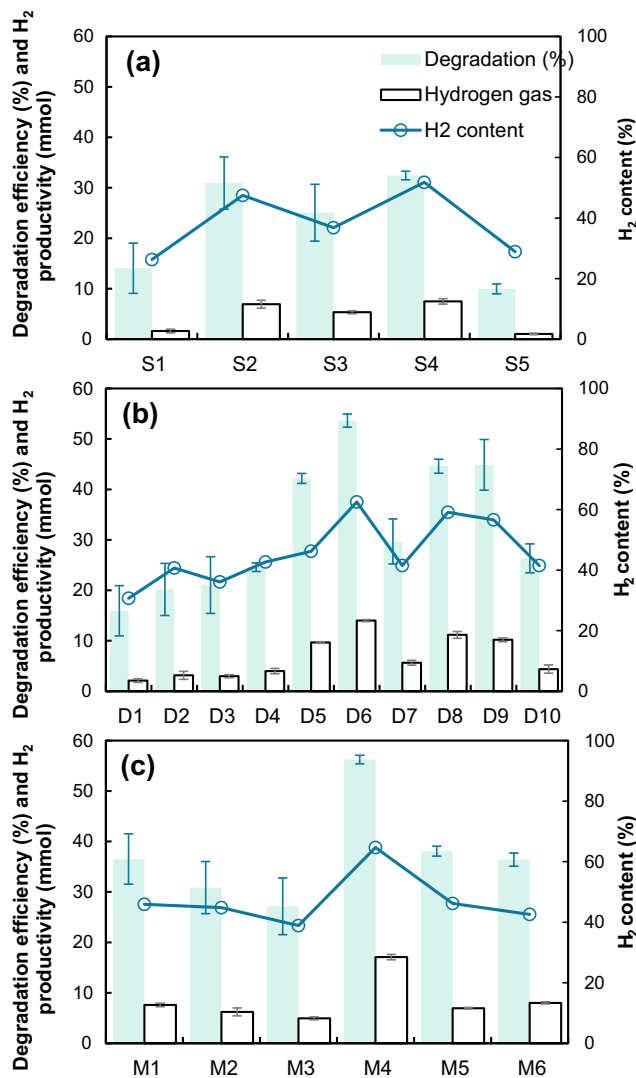

Fig. 1 Degradation efficiency (%), H_2 productivity, and content via sole (a), dual (b), and multi (c) peel fermentation

Comparable results are found by Kalia and Joshi (1995), who harvested a HY of 2.1 mmol/$g_{organic\ solids}$ from pea-shell slurries at 5% TS. Moreover, banana peels acquired HY of 1.7 mmol/g_{VS} at food to biomass ratio of 10, whereas, orange peel revealed a lower HY of 1.1 mmol/g_{OP} (Nathoa et al. 2014). In addition, mixed fruit peels produced HY of 2 mmol/g_{COD} (Soltan et al. 2017). On the other hand, the HY range in the case of vegetable waste was found to be 1–3.8 mmol/g_{VS} when a supplementation with different anaerobic species was implemented (Marone et al. 2012).

Figure 1a revealed COD degradation efficiency (%) at sole fermentation of FVPs, and in this case, sole fermentation of orange (S5) and banana (S4) peels achieved the minimum and maximum COD removal of 10.0 ± 1.0 and $32.4 \pm 0.9\%$, respectively. Such a performance was upgraded through dual fermentation, which witnessed COD removal range of $16.0 \pm 1.3\%$ at 50% spinach + 50% pea (D1) to $53.6 \pm 5.9\%$ at 50% pea + 50% banana (D6), respectively (Fig. 1b). However, higher removal efficiency values were recorded during the multi-fermentation batches as depicted from Fig. 1c, at which maximal COD removal efficiency of $56.2 \pm 4.6\%$ was acquired by batch of 25% P + 25% T + 25% B + 25% O (M4), at which maximal HY was acquired, as well. These findings, therefore, strongly confirm the positive effect of peels mixing upon COD removal efficiency. Comparable results were previously registered by Soltan et al. (2017) and Tenca et al. (2011). Whereas, Soltan et al. (2017) achieved 21.6% of COD conversion from fruit peel fermentation; however, this value augmented to 54.9% when fruit peels co-fermented with paper mill sludge with ratio of 30/70. Furthermore, Tenca et al. (2011) obtained maximum COD conversion of 32% from dual fermentation of fruit and vegetable mixtures and swine manure with ratio of 35/65. This value was reduced to 23% at ratio of 55/45.

Biochar yield and its characteristics

Among all batches, maximum biochar yields harvested from digestates of sole, dual, and multi-fermentations were found at S1, D7, and M3, respectively (Fig. 2). As depicted from Table 3, ash contents were increased up to 35.7 ± 4.1, 28.4 ± 3.8, and $28.9 \pm 3.2\%$ for S1, D7, and M3, respectively, after pyrolysis process. Such increases in ash contents are principally ascribed to the high metals' contents (calcium, iron, manganese, zinc, and sodium metals) that originated in the digestates, beside the ability of biochar to retain minerals in the form of ash (Fuertes et al. 2010). Based on losing oxygen (O) and hydrogen (H), carbon was concentrated in the produced biochar reaching values of 58.8 ± 6.7, 46.3 ± 5.0, and $46.4 \pm 4.6\%$ for S1, D7, and M3, respectively. It is worthy to highlight that the increases in the carbon content were so limited although the recalcitrant nature of the carbon content existed in the digestate. This may be attributed to the high
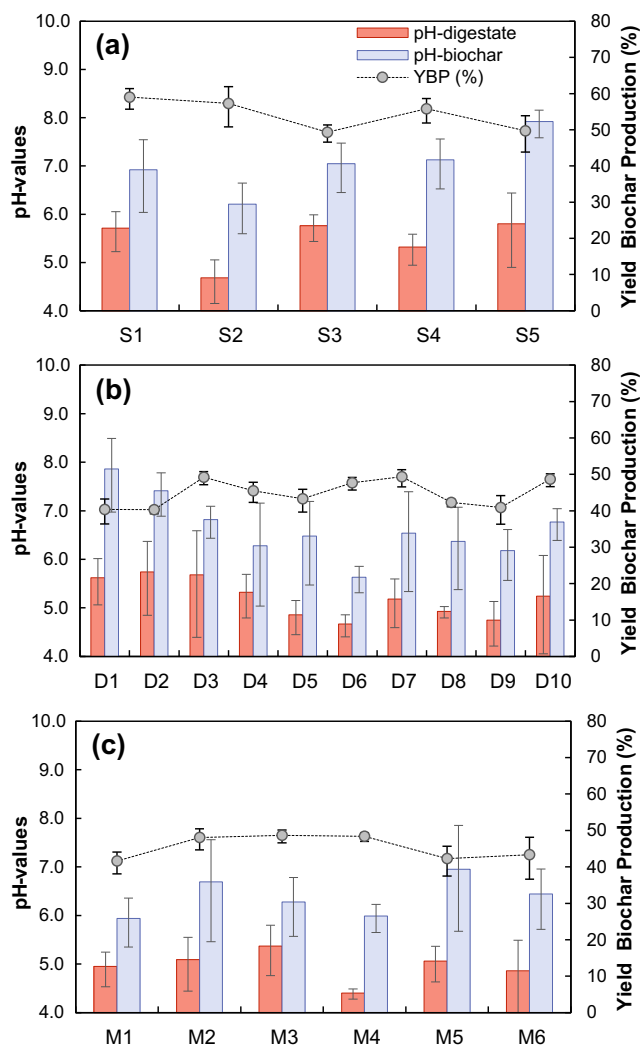

Fig. 2 pH values of digestate and biochar versus biochar yields after pyrolysis step for sole (a), dual (b), and multi (c)-fermented digestates

ash content presented in the digestate (Bruun et al. 2017). This was not the case for nitrogen content, which depleted after pyrolysis process to 4.6 ± 0.1, 0.7 ± 0.1, and $2.6 \pm 0.3\%$ for S1, D7, and M3, respectively, since N_2 started to volatilize once digestates were subjected to high temperature. Furthermore, the pH value has augmented to higher levels after pyrolysis process as a result of the decline in the carboxyl groups and/or the deprotonation of acidic groups leading to more alkaline pH in the harvested biochar (Ronsse et al. 2013). On the other hand, peak values of yield of biochar production (YBP) amounted to 59.04 ± 2.36, 49.32 ± 1.97, and $48.67 \pm 1.46\%$ that were harvested from sole, dual, and multi-fermented digestates of S1, D7, and M3, respectively, since YBP is directly proportional to ash content in the digestate (Ronsse et al. 2013). Therefore, overall maximum YBR was also recorded at S1. Similar trends were obtained by Bruun et al. (2017) who harvest YBP of 55.0% from digestate of biogas unit.

Textural characteristics of the maximal biochar yields are presented at Table 3. Data revealed that the high increase in ash content (%) at the harvested biochar is offset by the increase in the pore volume and specific surface area. As when digestates were subjected to pyrolysis temperature, organics volatilize during the process; thereby, voids in the matter appear, causing a rise in both surface area and porosity (Jouiad et al. 2015). In addition, because of applied temperature, pore-blocking substances were thermally cracked, leading to increases in the externally accessible surface area (Ronsse et al. 2013). Therefore, maximum values of specific surface area, density, and pore volume of 28.43 ± 3.95 m^2/g, 1.93 ± 0.18 g/cm^3, and 0.59 ± 0.08 cm^3/g, respectively, were registered for biochar from S1 digestate. This is corresponding to the high conversion ratio of ash noticed in S1. Specifically, by pyrolyzing S1 digestate to biochar, ash content incremented from 23.8 ± 3.1 to $35.7 \pm 4.1\%$, respectively. Likewise, Liu et al. (2010) obtained biochar with specific surface area of 29 m^2/g after pyrolysis process for pinewood. In addition, the density increase could be assigned to the enhanced graphitization conditions founded at high temperatures of pyrolysis process. Our maximal density value could be comparable to the 1.81 cm^3/g provided for biochar derived from raw food waste (Opatokun et al. 2016).

Net energy gain and profit volume analysis

The net energy gains (NEGs) and profits harvested from sole, dual, and multi-peels fermentation processes are described in Fig. 3. Sole fermentation of spinach (S1), pea (S2), tomato (S3), banana (S4), and orange (S5) peels achieved NEG of -0.43, 0.01, -0.17, 0.28, and -0.66 kJ/g$_{feedstock}$, respectively, as depicted from Fig. 3a. However, Fig. 3b shows that specific mixtures of dual fermentation augmented the NEGs up to 0.74, 0.84, and 1.09 kJ/g$_{feedstock}$ as recorded at 50% tomato + 50% banana (D8), 50% tomato + 50% orange (D9), and 50% pea + 50% banana (D6), respectively. While, other dual peel mixtures revealed limited NEG with minimum value of -0.52 kJ/g$_{feedstock}$ at 50% spinach + 50% pea (D1). Multi-peel fermentation of 25% pea + 25% tomato + 25% banana + 25% orange (M4) revealed the maximum NEG of 1.74 kJ/g$_{feedstock}$ (Fig. 3c). This strongly showed the superiority of balancing nutrients in the anaerobic media and its remarkable effect on the harvested amount of energy. Negative NEGs that ranged from 0.0 to -9.4 kJ/g$_{feedstock}$ had been recorded earlier from various particulate organic wastes at a mesophilic condition (35 to 37 °C) (Perera et al. 2010). In addition, NEG acquired in this study surpassed NEG of 0.032 kJ/g$_{feedstock}$

Table 3 Chemical and textural characteristics for the harvested biochars

| Biochar	Ash %	C %	N %	H %	Surface area m^2/g	Density g/cm^3	Pore volume cm^3/g
Sole fermentation digestate							
S1	35.7 ± 4.1	58.8 ± 6.7	4.6 ± 0.1	2.2 ± 0.2	28.43 ± 3.95	1.93 ± 0.18	0.59 ± 0.08
S2	27.6 ± 3.2	58.1 ± 5.8	2.4 ± 0.2	1.6 ± 0.2	27.49 ± 2.81	1.87 ± 0.21	0.56 ± 0.07
S3	30.1 ± 2.7	45.8 ± 5.3	2.3 ± 0.1	1.1 ± 0.1	17.44 ± 1.94	1.64 ± 0.19	0.57 ± 0.04
S4	33.7 ± 3.6	54.3 ± 4.9	1.3 ± 0.1	2.1 ± 0.1	22.89 ± 2.75	1.75 ± 0.18	0.54 ± 0.06
S5	27.5 ± 3.0	49.5 ± 5.1	0.5 ± 0.1	1.8 ± 0.1	14.94 ± 1.69	1.49 ± 0.17	0.52 ± 0.05
Dual fermentation digestate							
D1	20.3 ± 2.4	38.0 ± 4.1	2.6 ± 0.3	1.8 ± 0.2	13.59 ± 1.63	1.18 ± 0.17	0.47 ± 0.06
D2	27.6 ± 2.6	39.6 ± 4.5	2.8 ± 0.3	1.4 ± 0.2	19.42 ± 2.09	1.58 ± 0.19	0.50 ± 0.07
D3	27.1 ± 2.1	42.3 ± 4.6	3.6 ± 0.4	2.1 ± 0.2	15.93 ± 1.75	1.62 ± 0.15	0.53 ± 0.06
D4	25.4 ± 2.9	39.1 ± 3.2	2.8 ± 0.2	2.0 ± 0.3	17.32 ± 1.94	1.24 ± 0.16	0.51 ± 0.05
D5	18.5 ± 2.2	38.6 ± 4.3	2.1 ± 0.2	1.4 ± 0.1	12.93 ± 1.42	1.07 ± 0.12	0.45 ± 0.06
D6	25.5 ± 2.8	42.5 ± 4.7	1.6 ± 0.1	1.9 ± 0.2	18.45 ± 2.06	1.32 ± 0.17	0.53 ± 0.08
D7	28.4 ± 3.8	46.3 ± 5.0	0.7 ± 0.1	1.7 ± 0.2	19.99 ± 2.53	1.72 ± 0.19	0.54 ± 0.06
D8	26.1 ± 2.4	40.8 ± 4.2	1.6 ± 0.2	1.7 ± 0.2	14.97 ± 1.74	1.70 ± 0.21	0.52 ± 0.04
D9	20.6 ± 2.1	37.5 ± 4.4	1.2 ± 0.1	1.6 ± 0.2	16.34 ± 1.95	1.36 ± 0.18	0.46 ± 0.03
D10	27.9 ± 2.9	43.7 ± 4.8	0.6 ± 0.1	2.0 ± 0.2	18.35 ± 1.53	1.63 ± 0.22	0.52 ± 0.06
Multi-fermentation digestate							
M1	20.4 ± 2.3	38.5 ± 4.1	1.8 ± 0.1	1.8 ± 0.2	12.75 ± 2.41	1.13 ± 0.14	0.41 ± 0.03
M2	25.5 ± 2.7	42.8 ± 4.5	2.7 ± 0.2	2.0 ± 0.2	17.30 ± 2.87	1.59 ± 0.19	0.45 ± 0.06
M3	28.9 ± 3.2	46.4 ± 4.6	2.6 ± 0.3	1.8 ± 0.1	18.32 ± 3.11	1.62 ± 0.16	0.57 ± 0.05
M4	26.3 ± 2.9	44.3 ± 4.9	1.8 ± 0.1	1.6 ± 0.1	15.73 ± 2.95	1.42 ± 0.17	0.51 ± 0.04
M5	22.1 ± 2.5	39.5 ± 4.3	2.4 ± 0.2	1.7 ± 0.2	14.58 ± 1.84	1.26 ± 0.15	0.47 ± 0.06
M6	25.1 ± 2.1	42.9 ± 5.1	2.2 ± 0.2	1.8 ± 0.2	16.46 ± 1.73	1.48 ± 0.19	0.52 ± 0.06
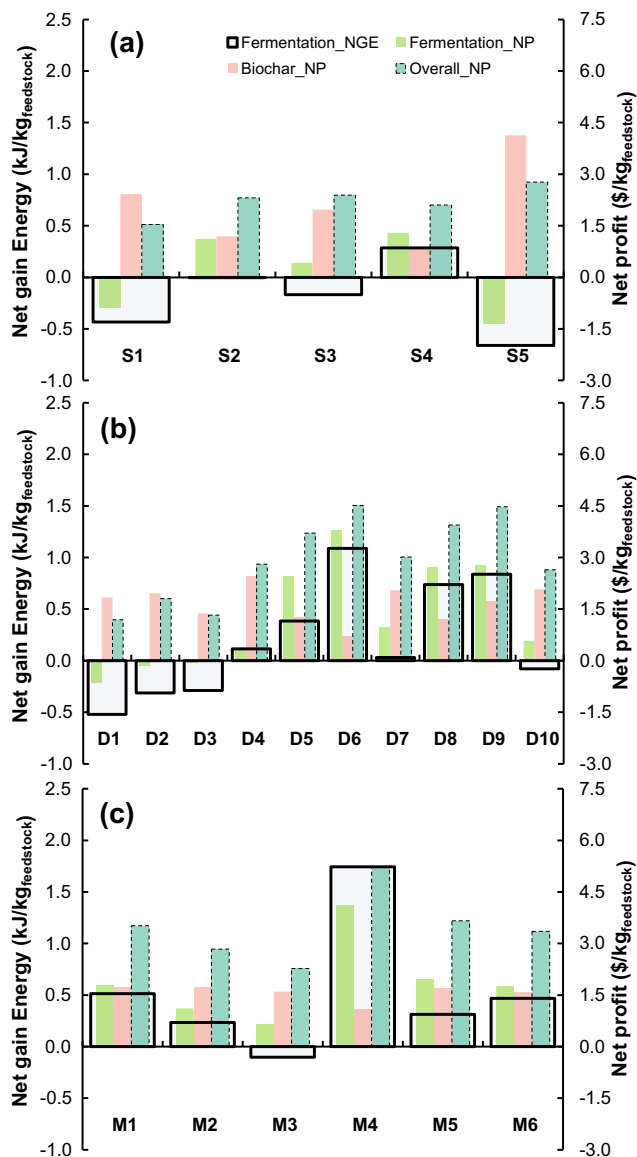
Fig. 3 Net energy gain (NEG) and net profit from fermentation process (a), net profit gain from pyrolysis process (b), and overall net profit of integrated process of fermentation and pyrolysis (c)

obtained by Soltan et al. (2017) via fermentation of 30% mixed fruit peels with 70% paperboard mill sludge.

Economic analyses for fermentation and pyrolysis processes of sole, dual, and multi-fermented peels were evaluated for 1 kg of feedstocks. Periodic costs that consist of required expenses for operation, maintenance, and chemicals, as well as, energy consumption for heating and mixing of the batches were assumed to be 0.42$, 2.1$, and $0.106/KWh, respectively (Elsamadony and Tawfik 2018). On the other side, revenues were assessed based on three terms: (1) environment protection, in which, the estimated value for organics removal was 0.1312 €/kg-COD$_{removed}$ as reported earlier by Molinos-Senante et al. (2010), (2) energy profits in the form of produced hydrogen and ethanol, and (3) an average biochar

profits of 4.47 $/kg, since Nyström (2016) reported that biochar price varies from 0.09 $/kg up to 8.85 $/kg. At fermentation process, the estimated maximum net profit amounted to 4.11 $/kg$_{feedstock}$ for multi-fermentation of 25% pea + 25% tomato + 25% banana + 25% orange (M4) compared to − 0.88, 1.11, 0.42, 1.29, and − 1.36 $/kg$_{feedstock}$ at the sole fermentations of spinach (S1), pea (S2), tomato (S3), banana (S4), and orange (S5) peels, respectively, as described in Fig. 3a and c. However, pyrolysis process exhibited a maximum profit of 4.13 $/kg$_{feedstock}$ for the digestate of orange (S5) calculated based on profits of + 0.05, + 4.97, and − 0.89 $/kg$_{feedstock}$ for prices of produced biochar, environmental protection, and consumed energy, respectively. This surpassed biochar profit that has been harvested from the digestate of M4 (1.10 $/kg$_{feedstock}$). However, overall profit from the combination of fermentation and pyrolysis processes revealed positive values for all sole, dual, and multi-fermented peels in the range of 1.18 to 5.21 $/kg$_{feedstock}$. M4 exhibited the maximum overall profit of 5.21 $/kg$_{feedstock}$ (Fig. 3c) as a sum of 4.11 and 1.10 $/kg$_{feedstock}$ harvested from fermentation and pyrolysis processes, respectively.

Conclusions

Hydrogen generation and subsequent biochar production from fruit and vegetable peels using integrated process, i.e., fermentation/pyrolysis, represented a promising approach from an economic and environmental point of view. Biochar net profit obtained from orange (S5) batch was about three times higher than that acquired by 25% pea + 25% tomato + 25% banana + 25% orange (M4) batch. On the other hand, the latter batch achieved an overall profit volume (PV) of 5.21 $/kg$_{feedstock}$ that is 88.3% higher than that denoted for S5. This is ascribed to the relatively high positive PV values found for multi-fermentation process.

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