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CHARACTERIZATION OF FRUIT AND VEGETABLE WASTES AS A SINGLE SUBSTRATE FOR THE ANAEROBIC DIGESTION

Extended abstract

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Background

Fruit and vegetable wastes (FVWs) represent a specific waste produced by all the wholesale markets and by many companies in the food industry. Due to their high perishability their handling and disposal are quite critical to community acceptance.

Since they have very high moisture contents, biochemical processes, such as anaerobic digestion, are the most suitable conversion technologies to treat FVWs. To ensure process stability and good conversion efficiencies, it is of fundamental importance to accurately characterize the feedstock properties, especially physical and chemical characteristics like the Total Solid (TS), Volatile Solid (VS), Carbon, Nitrogen, macro, micro and trace elements contents. Moreover, on the basis of such parameters, a decision on whether using FVWs as a single feedstock or as co-substrate in the anaerobic digestion process can be made.

Most of the studies on a complete residues' characterization focus on the organic fraction of the municipal solid waste (Hanc et al., 2011), on biomass produced by the forestry, agriculture, municipality and industry sectors (Chiang et al., 2012), or on food waste (Zhang et al., 2007). On the counterpart, to the authors' knowledge, most of the studies on fruit and vegetable wastes focus on their use as a co - substrate in the anaerobic digestion process (Garcia-Peña et al., 2011).

This work presents a detailed characterization study of the chemical and physical properties of representative varieties of fruits and vegetables' residues produced by the Vegetable Wholesale Market of Sardinia (Mercato Ortofrutticolo della Sardegna - Italy). In addition, this study comments the feasibility of using FVWs as a single substrate in anaerobic digestion, on the basis of the existing scholarly literature (Deublein and Steinhauser, 2008) and the results from the present analysis. More over, the study estimates the expected biogas composition from the anaerobic digestion of FVWs.

Methods

The investigated properties of FVWs were Total Solid (TS), Volatile Solid (VS), Ash, Fixed Carbon, Carbon, Hydrogen, Nitrogen, Sulphur, macro, micro, trace elements and the energy contents.

The samples of the most common varieties of fruits and vegetables produced by the Vegetable Wholesale Market of Sardinia were collected during a period of six months (from March to September). In accordance with the commercial distinction between fruits and vegetables, the samples consisted in 10 kinds of fruits (Apricot, Banana, Clementine, Lemon, Melon, Orange, Peach, Pear, Pineapple, Watermelon), 13 kinds of vegetables (Aubergine, Broccoli, Cabbage, Carrot, Cauliflower, Courgette, Cucumber, Endive, Fennel, Lettuce, Onion, Pepper, Tomato) and one of Potato. The samples were shredded and homogenised with a cutter, then were dried at 65°C in a thermostatic oven and, finally, the obtained dried samples were ground to obtain a fine powder. The Carbon, Hydrogen, Nitrogen and Sulphur contents were determined with a LECO (Leco Corporation, St. Joseph, MI) TRUSPEC CHN analyser according to the ASTM D 5373 method, and the Oxygen content was calculated as a difference. The proximate

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analysis (TS, VS, Ash and Fixed Carbon contents) was performed with a LECO (Leco Corporation, St. Joseph, MI) TGA 701 thermo gravimetric analyzer according to the ASTM D 5142 Moisture Volatile Ash method. The energy content was analysed only for the samples representative of some selected FVWs families with a LECO (Leco Corporation, St. Joseph, MI) AC500 Isoperibolic Calorimeter according to the UNI EN 14918:2009 method. The results, given in terms of Higher Heating Value, were expressed as Lower Heating Value using the formula (UNI EN 14918, 2009)(Eq 1):

$$q_{p,net,d} = q_{V,gr,d} - 212,2 \cdot w(H)_d - 0,8 \cdot \left[w(O)_d + w(N)_d \right] \tag{1}$$

where: $q_{p,net,d}$ is the net calorific value at constant pressure of the moisture - free sample [kJ/kg]; $q_{V,gr,d}$ is the gross calorific value at constant volume of the moisture - free sample; $w(H)_d$ is the Hydrogen content, in percentage by mass of the moisture - free sample; $w(O)_d$ is the Oxygen content, in percentage by mass of the moisture - free sample; $w(N)_d$ is the Nitrogen content, in percentage by mass of the moisture - free sample;

The macro, micro and trace elements contents were determined with a simultaneous atomic emission spectrometer ICP - OES Varian Vista - MPX (Varian Inc., Palo Alto, CA) with axial viewed plasma. To dissolve fruit and vegetables samples for elemental analysis, microwave - assisted acid decomposition was performed at high pressure and temperature. An amount of approximately 0.2 g of sample, weighed accurately, was transferred into microwave teflon vessels; 3 ml of aqua regia and 1 ml of hydrogen peroxide at 30 % were added. All samples were placed in the microwave carousel together with a blank prepared with a solvent of analytical - reagent grade. A CEM model MarsX Microwave - Assisted system was used.

Finally, the expected composition of the biogas produced by the anaerobic digestion has been calculated using the following formula of the methane formation (Deublein and Steinhauser, 2008))(Eq 2 - 4):

$$C_cH_hO_oN_nS_s + yH_2O + xCH_4 + nNH_3 + sH_2S + (c-x)CO_2 \tag{2}$$

with:

$$x = \frac{1}{8} \cdot (4c + h - 20 - 3n - 2s) \tag{3}$$

$$y = \frac{1}{4} \cdot (4c - h - 20 - 3n - 3s) \tag{4}$$

Results and discussion

The TS content and its percentage in VS indicate the fraction of organic matter that can be converted into biogas by the microorganisms, while the C/N ratio represents the availability of organic substrate in comparison to the availability of the main nutrient. Macro, micro and trace elements are the fundamental nutrients required by the microorganisms' metabolism.

Fruits residues have higher TS, VS and C/N ratio compared to the vegetable wastes. Indeed, the Total Solids of fruits are in average 14% (minimum 7.5% and maximum 23%), while in the vegetables they are 6.7% (3-11%). Volatile Solids on wet basis in the fruits are in average 10.3% (5-12%), while in the vegetables they are 4.7% (2-9%). C/N ratio is in average 40 (19-53) in the fruits residues and 13.4 (10-21) in the vegetables. Potatoes represent a separate category that reported 21.8% of TS, 17.4% of VS on wet basis, and a C/N ratio of 23.

Fig. 1 shows the qualitative descriptive profiles in terms of the C/N ratio, TS and VS contents on wet basis for fruits, vegetables and Potatoes. Fruits have generally C/N ratios in average three times and VS on wet basis two times higher than vegetables. Potatoes show TS and VS on wet basis contents higher than both fruits and vegetables, while their C/N ratio is in between.

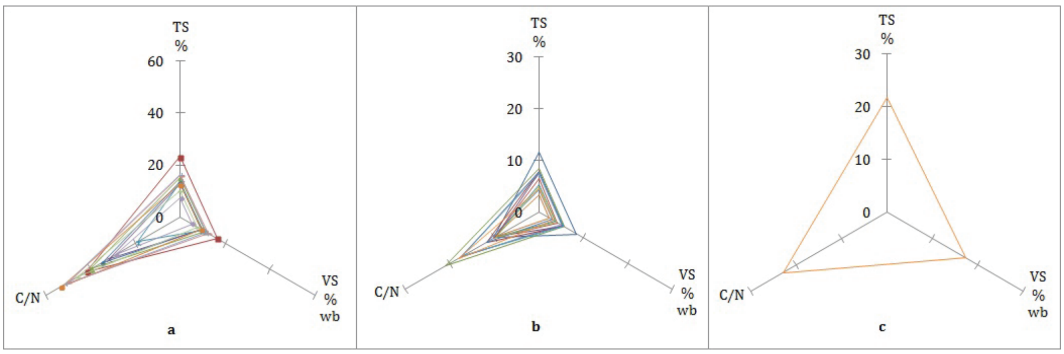

Fig. 1. Qualitative descriptive profiles of the Total Solid (TS) content, Volatile Solid (VS) content and C/N ratio: 1a – Fruits, 1b – Vegetables, 1c – Potatoes

The distribution of C/N ratio, Volatile Solids and Sulphur contents are also reported in the bar graphs in Fig. 2, that shows fruits and vegetables grouped together in terms of VS and C/N. In addition, Sulphur content is also pictured, as it is a relevant characteristic of the feedstock. Sulphur concentration in fruits is generally lower than in vegetables.

In particular, Broccoli, Cauliflower, Cabbage and Onion have the highest Sulphur contents on dry basis (0.7 - 1.1 %). As for the Carbon and Nitrogen ratio, Sulphur in Potatoes is approximately in between fruits and vegetables.

The analytical determinations showed no substantial differences in the fixed Carbon, Hydrogen and Oxygen contents on dry basis in fruits (22 %, 6.5 % and 44 % respectively), vegetables (20 %, 6.5 %, 40 %) and Potatoes (15 %, 6.5 %, 43 %), while the ash content on dry basis is different depending on fruits (minimum 2 % and maximum 9 %), vegetables (0.7 – 16 %) and Potatoes (5 %).

The energy content analysis reported a LHV on wet basis ranging between 0.7 and 1.9 MJ/kg for the vegetables and between 1.2 and 3.9 MJ/kg for the fruits. The LHV on wet basis of Potatoes is 3.5 MJ/kg. The energetic analysis allows to quantify the total energy introduced in the anaerobic digestion reactor and, thus, the energy that can be obtained in the form of biogas and that remains in the digestate.

Macro, micro and trace elements determination is shown in Table 1. No particular differences between the content of nutrients and metals in fruits and vegetables have been found. Calcium, Potassium, Magnesium and Sodium are the most abundant.

Arsenic, Cadmium, Mercury, Lithium, Selenium, Tin, Vanadium are present at trace concentration or absent, while heavy metals like Copper, Nickel, Lead and Zinc are higher in all the samples and occasionally overcome the minimum concentration required as trace elements.

Few high values are found (for instance, Nickel, Lead and Zinc in the Peach), that could be related to isolated cases of pollution. Finally, depending on the examined fruit or vegetable, the expected methane concentration in biogas ranges between 43 % and 70 %, the carbon dioxide between 30 % and 57 %. In particular, the highest methane contents (> 60 %) are expected from the anaerobic digestion of fruits rather than of potatoes and vegetables.

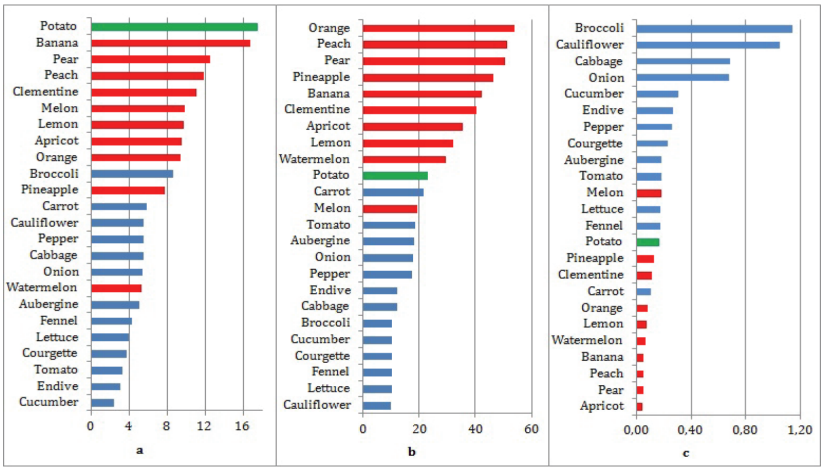

Fig. 2. Distribution of the main substrate properties among fruits, vegetables and Potatoes.
2a - Volatile Solids content on wet basis. 2b - C/N ratio. 2c - Sulphur content on dry basis

The analytical results of this study allow to make some considerations on the FVWs main properties. Fruits and vegetables show different characteristics in terms of C/N ratio, TS, VS and Sulphur contents.

In particular, all samples have high moisture and Volatile Solids contents, with Potatoes having in average the highest VS% on wet basis. Not all samples show optimal Nitrogen and Sulphur contents as feedstock for anaerobic digestion.

According to literature (Deublein and Steinhauser, 2008), the optimal Carbon and Nitrogen ratio should be lower than 25 and the N/S ratio should be 15-20:3. C/N ratio in fruits is generally higher than 30, while most of the FVWs have a Nitrogen/Sulphur ratio higher than 6.

Vegetables show a lower C/N ratio (13 in average) instead, while only Broccoli, Cauliflower, Cabbage and Onion have a N/S ratio lower than 6. Nutrients such as Sodium, Potassium, Calcium, Magnesium and the main micro and trace elements are present at sufficient concentration to limit or avoid the adding of external sources.

As a conclusion, all the FVWs varieties examined in this study contain a high percentage of organic matter that can be converted into biogas.

Due to the presence of the main macro, micro, and trace elements, the use of FVWs in anaerobic digestion without adding additives or other organic materials as co-substrate is possible, while heavy metals are generally lacking. The calculated biogas composition shows that fruits are expected to produce the highest methane content. Nevertheless, it is important that fruits and vegetables are mixed together in order to balance the possible excess or deficiency of nutrients, like Sulphur, and dilute occasional inhibitive elements' peaks.

Table 1. The macro, micro and trace elements in the fruit and vegetable wastes

	Al	*As*	*B*	*Ba*	*Ca*	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Hg*	*K*	*Li*	*Mg*	*Mn*	*Mo*	*Na*	*Ni*	*Pb*	*Se*	*Sn*	*Sr*	*V*	*Zn*
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Apricot	0.95	<0.05	0.10	0.014	3.67	0.002	0.029	0.648	0.04	2.37	<0.05	29.81	<0.005	1.31	0.31	0.022	0.08	2.88	0.04	<0.1	<0.25	0.01	0.007	0.08
Aubergin	3.40	<0.05	0.03	0.006	2.68	<0.001	<0.004	0.001	0.42	0.07	<0.05	20.75	<0.005	1.80	0.02	0.001	0.30	0.22	0.13	<0.1	<0.25	0.02	<0.001	0.49
Banana	0.68	<0.05	0.06	0.005	1.79	<0.001	0.015	0.033	0.44	0.26	<0.05	51.70	<0.005	4.35	0.08	0.012	0.08	2.58	0.08	<0.1	<0.25	0.03	<0.002	0.46
Broccoli	0.07	<0.05	0.06	0.015	14.03	<0.001	<0.006	0.002	0.31	0.11	<0.05	27.46	<0.005	4.36	0.02	0.008	3.28	0.27	0.06	<0.1	<0.25	0.08	<0.001	0.30
Cabbage	0.09	<0.05	0.04	0.006	7.96	<0.001	0.004	0.001	0.18	0.08	<0.05	21.15	<0.005	3.02	0.02	0.002	3.43	0.51	0.04	<0.1	<0.25	0.04	<0.001	0.22
Carrot	1.01	<0.05	0.03	0.021	6.27	<0.001	<0.004	0.004	0.15	0.12	<0.05	14.27	<0.005	2.24	0.03	0.003	8.75	0.16	0.02	<0.1	<0.25	0.03	<0.001	0.10
Cauliflow	0.12	<0.05	0.03	0.006	4.22	<0.001	0.005	0.000	0.37	0.08	<0.05	23.04	<0.005	2.87	0.02	0.003	2.89	0.72	0.03	<0.1	<0.25	0.02	<0.001	0.29
Clementin	1.07	<0.05	0.13	0.014	16.53	<0.001	<0.008	0.005	0.98	0.14	<0.05	16.78	<0.005	2.17	0.02	0.003	0.22	1.24	0.19	<0.1	<0.25	0.15	<0.002	0.98
Courgette	0.14	<0.05	0.02	0.002	2.38	<0.001	0.003	0.002	1.68	0.08	<0.05	18.51	<0.005	1.96	0.01	0.002	0.18	0.66	0.07	<0.1	<0.25	0.01	<0.001	1.16
Cucumbe	2.28	<0.05	0.02	0.004	3.78	<0.001	<0.002	0.001	0.05	0.05	<0.05	12.41	<0.005	1.85	0.01	0.002	1.19	0.07	0.01	<0.1	<0.25	0.02	<0.001	0.06
Endive	1.02	<0.05	0.01	0.000	3.68	<0.001	0.002	0.025	0.08	0.14	<0.05	12.49	<0.005	1.30	0.03	0.001	0.19	0.31	0.02	<0.1	<0.25	0.00	<0.001	0.08
Fennel	1.74	<0.05	0.02	0.007	5.47	<0.001	0.018	0.080	0.35	0.52	<0.05	21.62	<0.005	1.38	0.09	0.005	5.59	0.37	0.12	<0.1	<0.25	0.03	0.001	0.54
Lemon	3.16	<0.05	0.04	0.021	13.56	<0.001	<0.006	0.005	0.69	0.10	<0.05	19.71	<0.005	1.64	0.03	<0.001	0.42	0.41	0.31	<0.1	<0.25	0.07	<0.001	1.14
Lettuce	3.05	<0.05	0.01	0.005	6.93	<0.001	0.026	0.038	0.31	0.42	<0.05	30.11	<0.005	1.67	0.08	0.001	1.26	0.28	0.17	<0.1	<0.25	0.02	<0.001	1.13
Melon	3.43	<0.05	0.03	0.001	3.70	<0.001	0.010	0.001	0.80	0.19	<0.05	37.60	<0.005	3.60	0.02	<0.001	1.15	0.59	0.11	<0.1	<0.25	0.02	<0.001	0.93
Onion	0.78	<0.05	0.07	0.021	9.26	<0.001	0.004	0.001	0.51	0.11	<0.05	12.21	<0.005	1.73	0.02	0.002	0.97	0.54	0.13	<0.1	<0.25	0.05	<0.001	0.80
Orange	0.39	<0.05	0.05	0.016	17.61	<0.001	0.012	0.029	0.05	0.25	<0.05	11.85	<0.005	1.63	0.03	0.007	0.11	2.43	0.02	<0.1	<0.25	0.23	<0.001	0.05
Peach	0.68	<0.05	0.04	<0.002	1.28	0.001	0.020	0.001	1.31	0.24	<0.05	19.06	<0.005	1.28	0.01	<0.002	0.11	3.25	1.50	<0.1	<0.25	0.02	<0.002	8.40
Pear	0.12	<0.05	0.06	0.001	0.94	<0.001	0.007	0.006	0.49	0.08	<0.05	7.86	<0.005	0.68	0.01	<0.002	0.29	0.98	0.31	<0.1	<0.25	0.01	<0.002	1.25
Pepper	0.34	<0.05	0.01	0.001	0.61	<0.001	<0.004	<0.001	0.83	0.09	<0.05	15.84	<0.005	1.10	0.01	<0.001	0.18	0.77	0.09	<0.1	<0.25	0.00	<0.001	0.76
Pineapple	4.86	<0.05	0.02	0.009	3.08	<0.001	0.005	0.001	1.99	0.07	<0.05	12.90	<0.005	1.33	0.16	<0.001	0.08	0.51	0.05	<0.1	<0.25	0.02	<0.001	1.53
Potato	5.48	<0.05	0.07	0.017	4.86	<0.001	0.012	<0.001	0.41	0.19	<0.05	45.30	<0.005	3.33	0.03	<0.002	0.35	0.24	0.13	<0.1	<0.25	0.01	<0.002	0.70
Tomato	0.48	<0.05	0.01	0.000	1.23	<0.001	0.003	0.001	0.35	0.07	<0.05	9.97	<0.005	0.64	0.01	0.001	0.21	0.68	0.04	<0.1	<0.25	0.00	<0.001	0.39
Watermelo	2.08	<0.05	0.03	0.006	1.57	0.001	0.013	0.203	0.004	0.81	<0.05	17.13	<0.005	1.65	0.16	0.007	0.08	2.29	0.01	<0.1	<0.25	0.01	0.002	0.02

Concluding remarks

The results of the characterization presented in this study demonstrate that FVWs are an eligible single feedstock for anaerobic digestion. Indeed, they have optimal moisture and Volatile Solid contents and, in accordance with their chemical composition, the maximum expected methane concentration in the biogas produced is 70 %.

Proper mixtures of fruits and vegetables allow having a feedstock with balanced properties in terms of macro, micro and trace elements that prevent the instability of the anaerobic digestion process. The practice of adding external sources of nutrients can be avoided, generating cost savings for the anaerobic digestion plants.

Keywords: Anaerobic digestion, chemical and physical properties, fruits and vegetables waste, nutrients.

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