An optimal biorefinery development for pectin and biofuels production from orange wastes without enzyme consumption

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ABSTRACT

Orange wastes, including peel and pulp, were used as a biorefinery feedstock to produce pectin, ethanol, and biogas. The orange wastes were subjected to dilute acid treatment with sulfuric acid (1% w/v) at 94, 100, 140, and 180 °C for 60, 30, and 0 min. The sulfuric acid treatment was performed for pectin extraction, sugars hydrolysis, and lignocellulose pretreatment. The pectin was extracted from the hydrolysate, the liquor was used to produce ethanol, and the pretreated solid was anaerobically digested to produce biogas. The highest pectin extraction yield was 24.7 % (w/w) from orange peel and 23.7 % (w/w) from pulp, which was obtained from the supernatants of treatment at 94 °C for 60 min. Fourier transfer infrared spectrometer results confirmed the similar characteristics of the extracted pectin to a commercial product. The galacturonic acid content (an indicator of pectin purity) of pectin extracted from orange peel was 70.2 % and from orange pulp was 69.9 %, at the optimum conditions. The pectin obtained from the acid treatment at 94 °C for 60 min had a degree of esterification higher than 69 %, whereas it was less than 45 % for that obtained after treatment at 140 °C for 30 min. The maximum ethanol yields of 81.5 % (from peel) and 82.9 % (from pulp) were achieved from the hydrolysate of the acid treatment at 140 °C for 30 min. The highest methane yields were 176.8 mL/g volatile solids (from the untreated peel) and 191.8 mL/g volatile solids (from the untreated pulp). Overall, the maximum total product value was 2,472.9 USD/t orange wastes, which was achieved from dilute acid treatment at 94 °C for 60 min. At the optimal conditions for high production of pectin, without any enzyme consumption, 244 kg of pectin, 26.5 L of ethanol, and 36 m^3 of methane were produced from 1 t of orange wastes.

1. Introduction

With 78.7 Mt production in the world in 2019, orange can play an important role in the industry and economy of its major producer countries, such as Brazil, China, India, USA, Mexico, Spain, Egypt, Indonesia, and Iran. Iran is among the main orange producers worldwide with producing 2.3 Mt/y in 2019 (Faostat, 2019). The main purpose of orange growing is juice production that converts 50–60 % of the orange fruit into wastes (Jiménez-Castro et al., 2020), accounting for about 39.4–47.2 Mt in the world in 2019. The landfill disposal of orange waste is prohibited in many countries due to its serious environmental issues (Satari and Karimi, 2018). Therefore, many countries are willing to decrease the production of wastes according to the policies for waste reduction. This approach helps to develop and implement a sustainable economy. (Moreno et al., 2021).

Orange wastes contain valuable compounds such as essential oils (mainly D-limonene) and pectin (Martin et al., 2018). D-limonene is a strong inhibitor component and antimicrobial agent for microorganisms (Martin et al., 2018). Several studies have been conducted to the hamper of inhibitory of limonene, e.g., by removal of limonene and conversion of limonene into less toxic compounds (Lotito et al., 2018). According to Lotito et al. (2018), fresh citrus wastes consist of 43 % limonene. Their findings show that more than half of the limonene is removed by waste drying. They did not observe any inhibition for methanogenesis microorganisms by limonene even at the maximum applied organic load value for the dried wastes. Pectin consists of linear polysaccharides comprised of D-galacturonic acid (Xu et al., 2014). It has applications in the food industry as a thickening and gelling agent, stabilizer, and emulsifier. Pectin is beneficial to human health as it is a beneficial source of soluble fiber, where the close relationship between health and high fiber diet has been proven (Xu et al., 2014). The global demand for pectin is approximately 45,000 t/y (Quoc et al., 2015). Citrus peels (containing 20–25 % pectin) are among the richest sources for the commercial production of pectin.

In addition to limonene and pectin, various carbohydrate polymers, such as cellulose, hemicelluloses, and lignin, are other components of orange wastes (Martin et al., 2018). Cellulose and hemicellulose, the major components of orange wastes, have great potential for biofuel production, e.g., ethanol and biogas (Mirmohamadsadeghi et al., 2019). The development of biofuels, as renewable energy resources, has been considered a priority to reduce fossil fuels dependency, decrease environmental pollutions, and limit climate change (Bateni et al., 2014). Biofuel production from fruit processing wastes, e.g., orange wastes, not only reduces the disposal problems of these wastes but also provides more sustainable fuels rather than fossil fuels (Angel Siles López et al., 2010). Biogas, an important biofuel, is produced from organic wastes through microbial anaerobic digestion, which can recover energy and biofertilizer from wastes (Ofoefule et al., 2011). Anaerobic digestion is considered the most promising method for the management of orange wastes (Calabrò and Panzera, 2017). Anaerobic digestion can be categorized as either ïliquidör ädry; based on the solid concentration of less than 15 % and more than 15 % of solids, respectively. Dry feeds benefit from better utilization of available reactor working volume (Jiménez-Castro et al., 2020). Sanjaya et al. (2016) reported the mesophilic methane (CH_4) yields of 72 and 288 mL CH_4 /g volatile solids (VS) from fresh orange peel and orange pulp, respectively, which were treated by physical pretreatment. The biomethane potential of orange peel is much lower than its theoretical potential due to the recalcitrant structure of lignocelluloses and existence of limonene, an essential oil with non-reversible inhibition effect on anaerobic digestion (Ruiz and Flotats, 2014). Pretreatment of orange wastes can remove the limonene and improve digestibility by different mechanisms, including removing hemicellulose/lignin and decreasing cellulose crystallinity (Negro et al., 2016; Patel, 2017). Different chemical pretreatments can be performed on orange wastes. Among different methods, dilute acid treatment is a promising method that provides high pectin recovery. It hydrolyzes pectin to galacturonic acid and other sugars and dissolves the main part of hemicellulose (Talebnia, 2008). The hydrolysate from dilute acid treatment contains sugars that can be converted into bioethanol without enzymatic hydrolysis. The possibility of producing multi-products from citrus waste using dilute acid treatment and the abundant substrate availability are proper options to develop a biorefinery platform. Developing biorefinery platforms is a technique towards the safe and environmentally friendly production of biofuels by converting waste streams to value-added products, which has attracted researchers' attempts using different substrates (Nozari et al., 2018).

The valorization of orange waste through biorefinery is usually done by several platforms, including i) direct utilization (fertilizer and animal feed), ii) using as a feedstock for the production of biofuels and biotechnological products, and iii) extraction of pectin, enzymes, and bioactive compounds (Panić et al., 2021). Only a few attempts have been made to develop biorefineries to utilize orange wastes for the production of biofuels and value-added products (Angel Siles López et al., 2010). In subsequent years, a continuous growing trend was observed in published articles until 2019 (Jiménez-Castro et al., 2020). For instance, physicochemical pretreatment of citrus wastes was proposed to develop a biorefinery, applying enzymatic hydrolysis to release sugars (Rivas-Cantu et al., 2013). In another study, ultrasounds and microwave treatments were used for pectin and limonene extraction from citrus waste (González-Rivera et al., 2016), with no biofuel production from carbohydrates. However, innovative technologies are needed to reduce industrial costs (Jiménez-Castro et al., 2020). The high price of enzyme and its long reaction time are challenging factors in the process economy; thus, eliminating the enzymatic hydrolysis can help the process economy. Further investigations are required to develop more efficient biorefinery platforms from this substrate. To the best of our knowledge, there is no study on the biorefinery platform from orange wastes applying dilute acid pretreatment as a multi-purpose process to recover pectin, hydrolyze hemicellulose, and open up the cellulose structure.

This research aimed at developing an efficient platform for utilizing orange wastes as a biorefinery feedstock. A number of studies, including Nielfa et al. (2015), investigated biofuel production from separated fractions of wastes. Therefore, orange wastes were divided into pulp and peel and were studied to investigate their individual potentials. It should be noted that pulp and peel separation may not be practical at the industrial scale, but to find their individual potential, they should be investigated separately. For this purpose, a dilute acid treatment method was performed on orange waste to extract pectin and fermentable sugars as well as breaking down the recalcitrant structure of the remained lignocellulose. The fermentable sugars dissolved in the supernatant were used for ethanol production without enzymatic hydrolysis. The pretreated solid that remained from the acid treatment was used for biogas production. An important advantage of this biorefinery platform is the absence of enzymatic hydrolysis, a necessary step in common ethanol production processes. The flow diagram of biogas, ethanol, and pectin production in this study is depicted in Fig. 1.

2. Material and methods

2.1. Materials

Fresh orange, i.e., Thomson navel orange (*Citrus sinensis*), cultivated in northern Iran (Mazandaran Province), was used as a feedstock. The fruits were washed, and their juices were taken. The pulp and peel were manually separated, dried for two weeks at ambient temperature, and milled by a grinder (EG500, Feller Company, China). The particles sized between 0.85 mm (20 mesh) and 0.180 mm (80 mesh) were collected for further analysis. The prepared substrate was kept in sealed plastic bags at room temperature. The prepared orange peel contained 92.6 total solids (TS) and 87.3 % VS. The corresponding values for orange pulp were 93.6 % and 89.9 %.

Saccharomyces cerevisiae yeast, CCUG 53310, was obtained from the Culture Collection, University of Gothenburg, Sweden, and was applied for ethanol production. The yeast maintenance and cultivation were based on the procedure provided by Karimi et al. (2006).
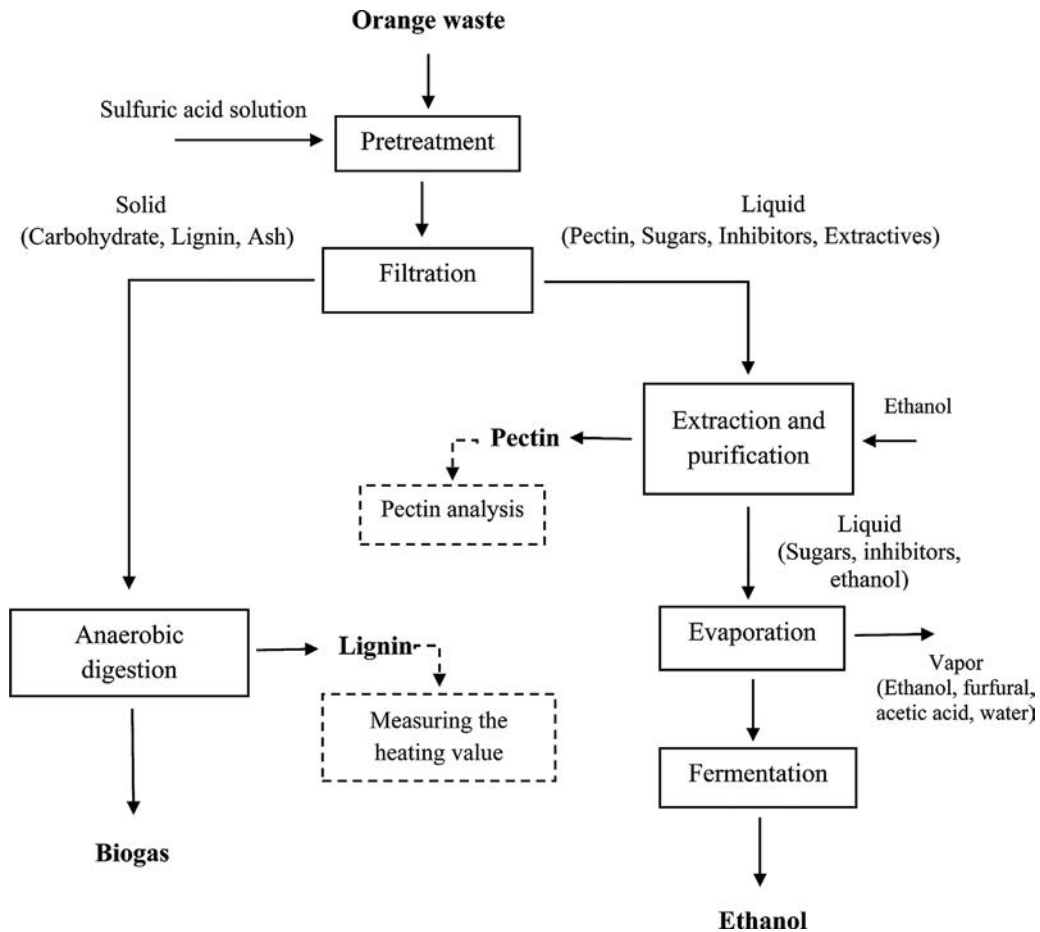
Fig. 1. Block flow diagram of biogas, ethanol, and pectin production from orange wastes.

2.2. Dilute acid treatment

The treatment was carried out with sulfuric acid solution (1% w/v) at different temperatures (100, 140, and 180 °C) for different residence times (0, 30, and 60 min) using 101SSHPR reactor (Steel Sanat, Isfahan, Iran) in an oil bath. Besides, treatment at 94 °C (boiling water temperature in our laboratory, about 1,590 m above sea level) for 60 min with 1% sulfuric acid was conducted, which was the optimum conditions for pectin extraction from orange peel, according to preliminary experiment not shown in this paper. The orange peel or pulp (10 g) was loaded in the reactor and mixed with 140 mL sulfuric acid (1% w/v). The suspension was warmed up to the desired temperature in a bath (Oilbath ONE, Memmert, Germany). At the end of the desired time, the temperature was quickly decreased using an ice bath. To treat orange wastes for 0 min, the reactor was cooled rapidly right after heating up to the desired temperature. The hydrolyzed slurry was filtered through linen bags for solid and liquid separation. The remained solids were neutralized by rinsing with distilled water to make sure that there is no chemical or inhibitor on the solid residue. The samples were freeze dried (Christ, Alpha 1–2 LD, Germany) and kept in sealed plastic bags at room temperature. The liquid fraction was kept in plastic bottles at −20 °C for further applications.

2.3. Pectin extraction and purification

Pectin was extracted from the liquid fraction of the acid-treated citrus waste. To obtain the maximum pectin yield, pH was adjusted to 3.5 by gradual addition of sodium hydroxide (1 M) solution (Kalapathy and Proctor, 2001). The solution was dispersed in ethanol (the same volume) and left settling overnight at 4 °C. The precipitates were separated by centrifugation at 4,000 rpm for 20 min. The separated solids were rinsed with 70 % (v/v) ethanol solution and then with a 96 % (v/v) ethanol solution. Afterward, the mixture was centrifuged (at 4,000 rpm for 30 min) to separate the pectin. The separated pectin was dissolved in deionized water, freeze dried (Christ, Alpha 1–2 LD, Germany), and maintained at room temperature. The yield of pectin extraction (Y_{pec}) was calculated using Eq. (1):

$$Y_{pec}(\%) = \frac{p}{Bi} \times 100 \tag{1}$$

where Bi is the initial quantity of substrate and p is the quantity of obtained pectin, both in g.

Ethanol was separated from the supernatants by distillation, and the remaining solution was used for ethanol production.

2.4. Ethanol production

The remaining liquor after pectin separation from the dilute acid-treated citrus waste was used for ethanol production. To accomplish this, 18 mL of the liquor was added to each 118 mL fermentation bottle. The bottle was supplemented with a nutrient-rich medium containing 7.5 g/L ammonium sulfate, 5 g/L yeast extract, 3.5 g/L dipotassium hydrogen phosphate, 1 g/L calcium chloride, and 0.75 g/L magnesium sulfate, and the solution pH was adjusted to 4.8. (Karimi et al., 2006). The bottles were autoclaved for 20 min at 121 °C and left under a sterile microbial hood to cool. The concentrated solution of *S. cerevisiae* (20 g/L) was added to the

bottles. The bottles were closed with aluminum and rubber caps. The anaerobic conditions were provided in the bottles by purging nitrogen (N_2) gas for 2 min. All analyses were carried out with two replicates, and the calculation of ethanol yield was performed using Eq. (2):

$$Ethanol\,yield = (Produced\,ethanol(g))/(Consumed\,glucose(g) \times 0.51) \qquad (2)$$

2.5. Biogas production

The solid remained from the dilute acid pretreatment and the untreated orange wastes were exposed to mesophilic anaerobic digestion at 37 °C in 118 mL dark glass bottles to evaluate their potential CH_4 yield (Hansen et al., 2004). The sludge from a mesophilic anaerobic digestion unit (Isfahan Sewage Treatment Unit, Isfahan, Iran) was used as the inoculum. The inoculum was passed through a sieve to eliminate the large particles (> 0.2 cm). The amounts of TS (3.8 %) and VS (2.9 %) of the inoculum were determined using the National Renewable Energy Laboratory (NREL) protocol (Sluiter et al., 2008a).

The digesters were filled with 0.25 g (dry weight) untreated and treated orange wastes, 5 mL tap water, and 20 mL inoculum (Hansen et al., 2004). The ratio of inoculum to feedstock was about 3:1 (based on VS content). The fermenters were sealed with aluminum and butyl rubber caps, and the anaerobic environment was provided by 2-min purging with pure N_2 gas. A reference digester, which only contained tap water and the inoculum, was set to analyze the volume of biogas production from the sludge. Another reference digester, which contained pure cellulose (avicell, Merck), tap water, and the inoculum, was also set to check if anaerobic digestion worked well. The digesters were placed in an incubator (JSH20LURS, Jal Tajhiz Labtech Co., Tehran, Iran) at 37 °C for 50 d and shaken manually once a day. All fermentation analyses were performed in duplicates.

2.6. Heating value of anaerobic digestion residues

The heating value of the residues from anaerobic digestion was measured using a bomb calorimeter (Adak Tajhiz Iranian, Iran) after drying the residue at 105 °C for 24 h. The equipment was filled with 1.3 L distilled water, and the initial temperature (T_C) was recorded. The hot distilled water (1.3 L) was loaded into the equipment, and T_H was detected. After reaching the equilibrium temperature, the balance temperature (T_T) was measured. The heat capacity of the bomb calorimeter (A) was calculated using Eq. (3) (Smith et al., 2005), in which m_H, m_C, and C are the mass of hot water, the mass of cold water, and the specific heat capacity of water.

$$A = \frac{m_H C(T_H - T_T) - m_C C(T_T - T_C)}{(T_T - T_C)} \qquad (3)$$

To measure the heating value of the remained solids, the combustion tank was filled with a certain amount of dried digestion residue (around 0.2 g), and the sample was burned by the injection of oxygen gas and spark. The ignition of the residue warmed the water around the chamber. The heating value of the residue (Q) was calculated using Eq. (4), in which m, T_2, and T_1 are the mass of water and the secondary and the primary temperature of the water around the reservoir.

$$Q = mC(T_2 - T_1) + A(T_2 - T_1) \qquad (4)$$

2.7. Energy content and gasoline equivalent calculations

the heating values of the produced ethanol and biogas as well as that of the digestion residue were expressed as gasoline-equivalent as well as energy content. For this aim, the lower heating values of gasoline, ethanol, and methane were considered 32 MJ/L, 21.2 MJ/L, and 36.1 MJ/m^3, respectively. The calculations were performed on the basis of 1 t of the substrate. The measured heating values of digestion residues were also used to calculate the energy content on the basis of 1 t of orange wastes.

2.8. Products value

The price of biogas and lignin was estimated by considering their conversion to electricity with the generator conversion efficiencies of 0.4545 kW h/m^3 biogas (Ciotola et al., 2011) and 188.9 kW h/GJ of the lignin higher heating value (Liu and Bao, 2017). The prices of pectin, bioethanol, and electricity, produced from the proposed biorefinery platform were estimated based on their USA market prices as USD 10/kg (Citrus pectin, Guangzhou ZIO Chemical Co., 2019), USD 0.7/L (Ethanol price, Global Petrol Price web page, 2019), and USD 0.15/kWh (Electricity price, Global Petrol Price web page, 2019). For economic potential calculations, orange wastes consisted of 70 % peel and 30 % pulp was considered.

2.9. Analytical methods

2.9.1. Substrate characterization

The TS and VS contents (Sluiter et al., 2008b) as well as lignin, structural carbohydrate, and ash content of the orange wastes were measured based on the standard methods provided by the NREL (Sluiter et al., 2012). Furthermore, the extractive amounts in the substrates were determined based on the NREL protocol (Sluiter et al., 2008c). Scanning electron microscopy (SEM) was employed to observe the acid treatment effect on the morphology of the substrate. The freeze-dried substrates were gold-coated (Emitech SC7640 sputter coater, UK), and images were captured with SEM (Zeiss, EVO LS, Jena, Germany) at 15 kV.

2.9.2. Pectin characterization

Pectin characteristics, including chemical structure, galacturonic acid content, and the degree of esterification (DE), were determined.

The chemical structure of the pectin was assessed by a Fourier transfer infrared spectrometer (FTIR) (WQF-510A, Beijing, China) equipped with a deuterated-triglycine sulfate detector, and it was compared with the chemical structure of commercial pectin. The analysis was performed at the resolution of 1 cm^{-1}, with average 32 scans in the range of 4,400 cm^{-1} to 400 cm^{-1}.

The content of galacturonic acid in pectin was quantified using the method presented by Ramos-Aguilar et al. (2015). Pectin (5 mg) was added to 2 mL of concentrated sulfuric acid (98 %) and 1 mL of deionized water in glass tubes. The volume of reaction was adjusted with water to 10 mL. After 10 min in an ice bath, the contents of the glass tube were centrifuged at room temperature at 2,000 × g for 10 min. The separated liquid (400 μL) was mixed with 2.4 mL of sodium tetraborate (75 mM in concentrated sulfuric acid) and 40 μL of 4 M potassium sulfamate solution (pH = 1.6). The glass tubes were inserted in boiling water (20 min), and their temperature decreased using indirect contact in an ice bath. The M-hydroxydiphenyl solution (80 μL, 3-phenylphenol (0.15 %) in sodium hydroxide (NaOH) (0.5 %)) in NaOH (0.5 %, control reaction) was added to the tubes. A UV–vis spectrophotometry (Jenway Co., Staffordshire, England) was used to determine the absorbance of the samples at 525 nm.

The DE of the pectin was evaluated using a protocol developed by Santos et al. (2013). The pectin (0.1 g dry mass) was mixed with

ethanol 96 % (3 mL) in 100 mL Erlenmeyer flasks. A volume of 20 mL distilled water was added to the flasks and stirred at 40 °C until the complete dissolution of pectin. The titration of the solution was performed with sodium hydroxide solution (V_1 mL, 0.1 M) until the appearance of pale pink in the presence of phenolphthalein (5 drops) as the indicator. The sodium hydroxide solution (10 mL, 0.1 M) was added and stirred. The hydrochloric acid solution (0.1 M, 10 mL) was added and stirred until the complete disappearance of the pink color. The titration was performed with sodium hydroxide (V_2 mL, 0.1 M) until the solution color changed to pink (V_2). The DE of the pectin was determined using Eq. (5).

$$DE(\%) = \frac{V_2}{(V_1 + V_2)} \times 100 \qquad (5)$$

2.9.3. Sugars and ethanol analysis

A high performance liquid chromatograph (HPLC) (1260 Infinity, Agilent Co., Santa Clara, CA, USA) equipped with refractive index (RI) and UV–vis detectors was used to determined sugars and ethanol contents. The sugars concentrations (glucose, xylose, galactose, arabinose, mannose, and fructose) were measured by Aminex HPX-87 P ion-exchange column (Bio-Rad, Richmond, CA, USA) at the temperature of 85 °C with a mobile phase of deionized water at 0.6 mL/min. To analyze the ethanol concentration, the Aminex HPX-87H column (Bio-Rad, Richmond, USA) at the temperature of 65 °C with the mobile phase of sulfuric acid (5 mM) at 0.6 mL/min was employed.

2.9.4. Biogas analysis

A gas chromatograph (GC, GC-2552, Tief Gostar Faraz Co., Iran) was used for the analysis of methane and carbon dioxide (CO_2) contents of the produced biogas. The instrument was equipped with a packed column (3 m ×3 mm ID, Porapak Q, Chrompack, Germany). The analytical grade of N_2 gas at 50 mL/min was the mobile phase. The temperature of injector, column, and detector was 100, 40, and 150 °C. A sealable syringe (250 μL, 250R-V-GT, SGE Analytical Science, Trajan Co., Melbourne, Australia) was used for the sampling and the injection of the gas samples into the injector. Gas sampling was performed once every 3 d during the first 15 d and once every 5 d during the rest period of time. The analytical grades of CH_4 and CO_2 gases ($\geq$ 99.0 % pure) were applied to obtain the calibration curves of CH_4 and CO_2.

2.10. Statistical analysis

Analysis of variance of results was applied by the least significant difference (LSD) and Tukey methods, using SAS 9.1.3 software (SAS Institute, Inc., 1999, Cary, NC, USA). The LSD technique was applied for the determination of the significant difference with p < 0.05 (Montgomery and Runger, 2011).

3. Results and discussion

3.1. Acid treatment effects on substrate morphology

The orange peel and pulp were pretreated with dilute sulfuric acid (1% w/v) at temperatures of 94, 100, 140, and 180 °C for 0, 30, and 60 min. The SEM images of the orange peel and orange pulp were captured to investigate the morphological changes during the pretreatment. As shown in Fig. 2, the untreated samples have a compact, flat, and integrated structure. The purpose of pretreatment is to eliminate the crystalline structure, increase porosity, and weaken the linkages between lignin, hemicellulose, and cellulose, to provide better access and greater penetration of microorganisms to the substrate. The dilute acid pretreatment can significantly remove hemicellulose. It can disrupt lignin and increase the suscep-

tibility of cellulose. The dilute acid pretreatment can dissolve the pectin and consequently increase the porosity of cell wall. Since pectin functions in wall hydration and cell adhesion, its removal can yield an opened-up structure. The SEM images of the pretreated samples confirmed an increase in the structural porosity of the substrates. This suggests that the pretreatment was able to disrupt the lignin and dissolve the pectin (Xiao and Anderson, 2013).

3.2. Acid treatment effects on chemical composition of substrate

The solid recovery and composition of substrates were determined to investigate the effect of the pretreatment on the orange wastes, as shown in Table 1. A slight decrease in solid recovery values was observed with increasing the temperature. The maximum solid recovery was gained using the treatment at 94 °C for 60 min for both peel and pulp. The dilute acid treatment partially removed xylan and other sugars (components of hemicellulose), while it increased glucan and lignin content. Raising the temperature and time of acid treatment increased the glucan and lignin contents, whereas it reduced the contents of hemicellulose. The acid treatment at 180 °C for 60 min reduced the hemicellulose contents of orange peel from 17.2 % to 1.2 % and that of pulp from 20.6 % to 3.0 %. The increase of glucan content can be due to the partial dissolution of hemicellulose and its release into the liquid phase (Hashemi et al., 2016). However, the observed increase in lignin content could be due to the Maillard reactions. The Maillard reactions occur between amino acids and reducing sugars and can produce melanoidins, which leads to a determined lignin content higher than the real value (Li et al., 2017). For untreated substrates, the maximum amount of carbohydrate belonged to glucan. The untreated orange peel contained 36.5 % glucan, 17.2 % hemicellulose, and 7.7 % lignin, while the corresponding values were 34.9, 20.6, and 8.2 % for the untreated orange pulp, based on dry weight. These observations are similar to the values reported for orange peel (i.e., 37.1 % cellulose, 11 % hemicellulose, and 7.5 % lignin) by Marín et al. (2007).

3.3. Acid treatment effects on pectin extraction

3.3.1. Pectin extraction yield

Various parameters can affect the pectin extraction yield. The pectin extraction yield was highly dependent on the temperature, presented in Table 2. The increase in extraction (pretreatment) temperature led to a considerable reduction in pectin extraction. This can be due to the pectin degradation at higher temperatures. Previous studies and the present research are in satisfying agreement. For instance, Masmoudi et al. (2008) stated that high temperatures in pectin extraction from lemon lesions would degrade the dissolved pectin. El-Nawawi and Shehata (1987) obtained the maximum pectin yield at 90 °C and reported a decrease in the extraction yield upon increasing the temperature due to pectin degradation.

Ortiz-Sanchez et al. (2020) studied pectin extraction from orange peel wastes using citric acid for 60 min. They reported that the maximum amount of extracted pectin was 11.2 % (w/w dry). Comparing with the results of the present study, it seems that sulfuric acid has a better performance than citric acid for pectin extraction.

3.3.2. Pectin chemical structure

FTIR analysis was performed to compare the chemical structure of the extracted pectin with that of the commercial pectin (Fig. 3). The comparison showed similar functional groups in both pectin samples. The FTIR signals between 800 and 1,800 cm^{-1} show the main functional groups in the pectin, which can be used to compare the structure of the extracted pectin. The band at 1,740
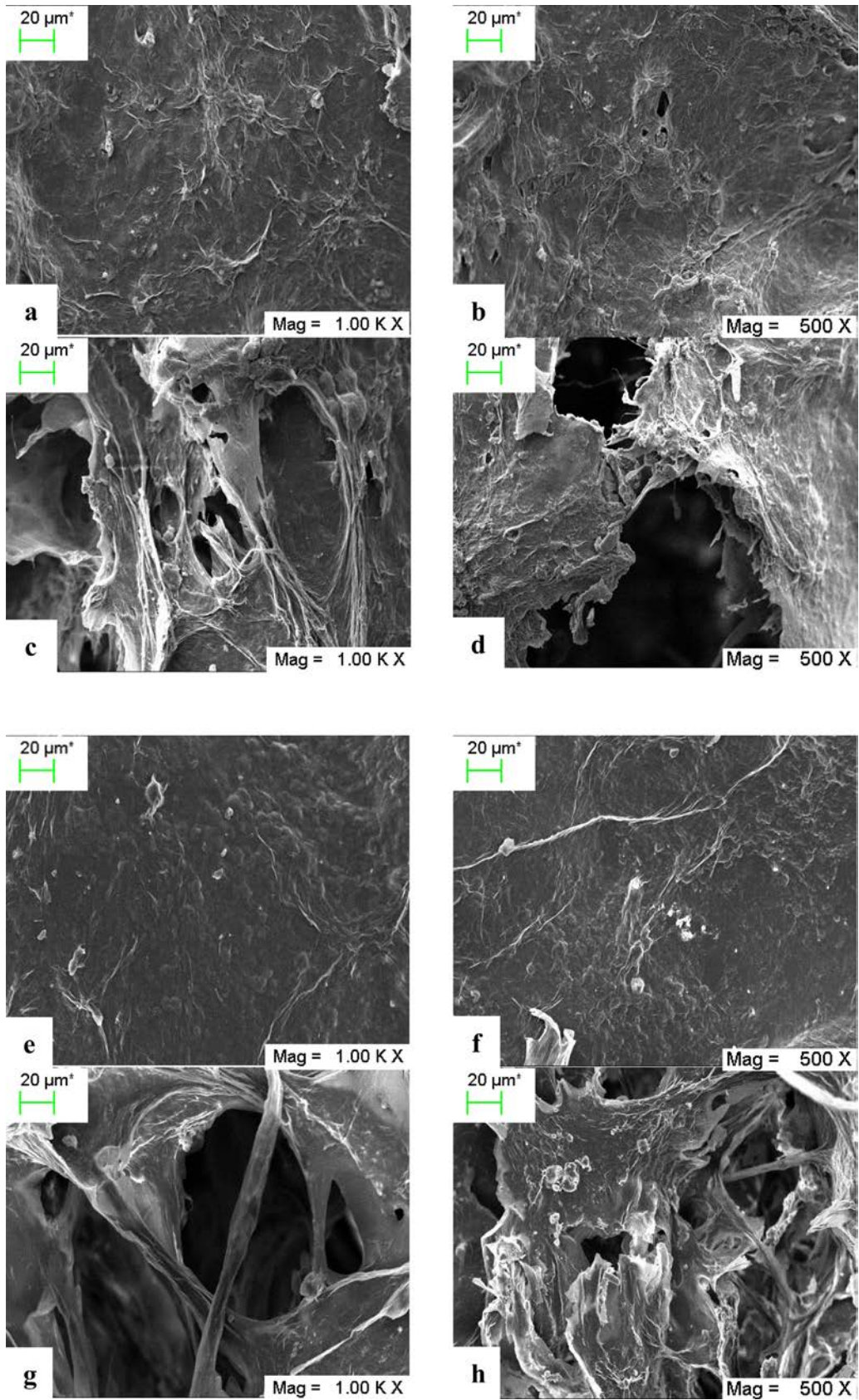
Fig. 2. SEM images of orange peel (a, b, c, d) and pulp (e, f, g, h) for untreated samples (a, b, e, f) and treated samples (c, d, g, h) at 140 °C and 30 min.

Table 1

Chemical composition and solid recovery of pretreated and untreated orange wastes (The average standard deviation were less than 0.1).

Substrate	Pretreatment conditions		Solid recovery(%)	Glucan(%*)	Xylan(%*)	Other sugars (%*)	Lignin(%*)	Ash(%*)
	T(°C)	Time(min)						
	94	60	27.6	56.6	2.5	12.1	8.6	2.3
		0	24.6	55.4	2.4	12.9	8.5	2.5
	100	30	25.1	57.6	1.8	11.4	8.5	2.7
		60	24.2	59.1	1.8	9.8	9.6	2.5
		0	24.5	62.9	1.06	5.8	11.2	2.7
Orange peel	140	30	24.2	65.2	1.1	4.5	21.1	3.0
		60	25.3	64.4	0.9	3.2	23.8	2.7
		0	23.5	66.2	0.4	1.9	25.1	3.0
	180	30	23.4	67.1	0.3	0.9	24.3	3.1
		60	23.1	66.2	0.4	0.8	25.4	2.9
	Untreated		–	36.5	2.8	14.4	7.7	2.5
	94	60	20.7	50.7	3.1	15.5	9.3	2.3
		0	19.6	49.4	3.2	15.6	8.7	2.3
	100	30	18.6	51.5	2.8	14.5	10.0	1.7
		60	18.5	53.7	2.5	13.5	10.1	2.9
		0	17.9	54.1	2.7	12.3	11.2	3.3
Orange pulp	140	30	18.1	57.1	1.5	10.4	18.8	2.9
		60	18.3	56.8	1.7	7.0	22.9	3.4
		0	17.8	58.9	0.6	4.2	21.6	3.7
	180	30	17.9	60.9	0.5	3.1	25.3	3.9
		60	18.5	59.6	0.3	2.7	26.3	4.0
	Untreated		–	34.9	3.2	17.4	8.2	1.1

* Percentage of dry solid content.

Table 2

Pectin and ethanol yield obtained from the liquor of sulfuric acid treatment of orange wastes as well as the characteristics of the pectin.

Pretreatment conditions		Orange part	Pectin extraction yield%	Galacturonic acid content (%)	Degree of esterification (%)	Ethanol yield (%)
Temp(°C)	Time(min)					
94	60	Peel	24.7±0.2	70.1±2.5	76.8±2.7	49.2±1.7
		Pulp	23.7±0.3	69.9±2.7	69.4±2.2	52.4±0.4
	0	Peel	22.5±0.3	ND	ND	ND
		Pulp	21.6±0.2	ND	ND	ND
100	30	Peel	22.2±0.5	ND	ND	ND
		Pulp	21.2±0.3	ND	ND	ND
	60	Peel	19.4±0.5	ND	ND	ND
		Pulp	18.9±0.5	ND	ND	ND
	0	Peel	4.3±0.3	ND	ND	78.6±4.3
		Pulp	4.0±0.5	ND	ND	79.6±3.5
140	30	Peel	3.7±0.5	52.4±1.3	44.3±2.0	81.5±2.6
		Pulp	3.2±0.3	47.2±2.6	39.6±2.1	82.9±1.8
	60	Peel	2.3±0.3	ND	ND	74.5±1.5
		Pulp	2.5±0.3	ND	ND	81.2±2.2
	0	Peel	<1	ND	ND	ND
		Pulp	<1	ND	ND	ND
180	30	Peel	<1	ND	ND	ND
		Pulp	<1	ND	ND	ND
	60	Peel	<1	ND	ND	ND
		Pulp	<1	ND	ND	ND

ND: Not determined.

cm^{-1} belongs to OC—H$_3$ groups. Carboxylate groups in pectin structure have two peaks: 1) asymmetric tensile vibrations at around 1,627 cm^{-1}, and 2) symmetrically tensile vibrations at around 1,436 cm^{-1}. The observed signals between 1,623 and 1,428 cm^{-1} are related to polygalacturonic acid. The peaks at 1,103 cm^{-1} and 1,018 cm^{-1} are related to the glycosidic bonds between sugar units, and this is a characteristic of the backbone structure of pectin. The signal at 2,950 cm^{-1} is related to CH— vibrations of carbohydrate components. The broad peak between 3,500 cm^{-1} and 3,300 cm^{-1} is related to the O—H groups in different parts of the galacturonic acid polymer structure (Santos et al., 2013; Kosalova et al., 2013). Comparing the spectra of the extracted pectin with the commercial pectin indicated that the pectin extracted using the acid treatment at 94 °C for 60 min had the structure most similar to the commercial pectin. The differences between the spectra of the pectin extracted at 140 °C for 30 min and the commercial pectin also confirm the degradation of pectin at the higher temperature. The peaks show that the content of galacturonic acid in the pectin extracted at the low temperature was greater than that in the pectin extracted at the high temperature.

3.3.3. Galacturonic acid content

The content of galacturonic acid in the extracted pectin was determined, indicating the pectin purity (Table 2). The highest content of galacturonic acid in the pectin extracted from orange peel was 70.2 % and that of pulp was 69.9 %, obtained from the treatment at 94 °C for 60 min. However, the corresponding values were 52.4 % and 47.2 % at the conditions that the maximum biofuel production was obtained (at 140 °C for 30 min). The pectin purity was decreased with increasing temperature. This can be due to the further release of impurities, such as hemicelluloses, at higher temperatures and their precipitation simultaneously with the pectin.
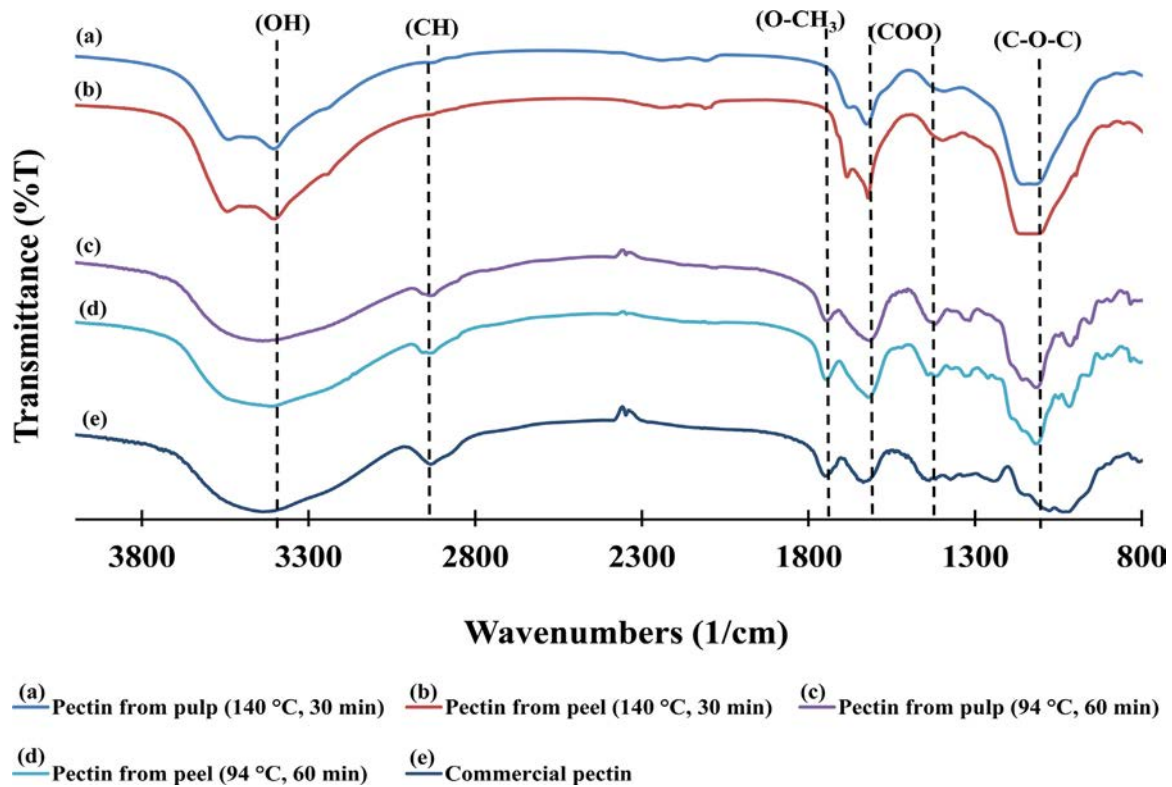
Fig. 3. FTIR spectra of commercial pectin and the extracted pectin samples from orange wastes.

These observations are comparable with the results published by El-Nawawi and Shehata (1988) on acid extraction of pectin at different temperatures (in the range of 50−110 °C). They reported that with the increase of temperature from 50 to 90 °C, the galacturonic acid content of the obtained pectin rose from 62.2 % to 71.0 %, whereas additional increase in temperature up to 110 °C reduced the galacturonic acid content to 66.0 %.

Tsouko et al. (2020) used dilute HCl and citric acid treatment at 90 °C for 160 min to extract pectin from orange wastes. They reported that the purity of the extracted pectin was in the range of 28.0–30.1 % for citric acid treatment and 48.0–54.0 % for HCl treatment, which are lower than those of the present study.

3.3.4. Degree of esterification (DE)

The DE, an index of the ability to form pectin gels, was analyzed and is tabulated in Table 2. The DE value of pectin obtained at 94 °C for 60 min (the conditions yielding the maximum pectin amount) was higher than that at 140 °C for 30 min (the conditions yielding the maximum biofuel production). The DE of the pectin obtained at 94 °C for 60 min from orange pulp was 69.4 % and that of peel was 76.8 %, whereas the corresponding DE values of the pectin extracted at 140 °C for 30 min were 44.3 % for orange peel and 39.6 % for orange pulp. The lower DE in the pectin extracted at 140 °C for 30 min could be because of the partial degradation of pectin at the risen temperature since the deesterification of the pectin chain occurs more intensely at severe conditions of extraction (Happi Emaga et al., 2008). Similar observations have been published by Garna et al. (2007), that an increase in the extraction temperature from 80 to 90 °C decreased the DE of pectin.

3.4. Fermentation

The supernatant that remained after pectin extraction contained fermentable sugars, Fig. 4. The content of fermentable sugars in the supernatant obtained from orange waste increased by increas-

ing the temperature to 140 °C, at which point the concentration reached its maximum level. Increasing temperature and time firstly destroyed fructose, followed by glucose and galactose degradation, which resulted in the reduction of the fermentable sugars concentration. According to the statistical analysis, the highest concentration of fermentable sugar was observed in the supernatant obtained from the treatment of orange peel and pulp at 140 °C. However, the time duration of treatment did not have significant effects on the sugars' concentration.

After ethanol separation from the supernatant, the liquor was subjected to anaerobic fermentation by *S. cerevisiae* to produce ethanol. In fact, the dilute acid treatment in the proposed biorefinery platform acts as acid hydrolysis, which is a substitute for the enzymatic hydrolysis process. Enzymatic hydrolysis, a high-cost process due to applying enzymes, is a required step in ethanol production from lignocelluloses. The supernatant that contained the highest concentration of fermentable sugar (treated at 140 °C) was subjected to fermentation to produce ethanol. The supernatant obtained at the optimum conditions for pectin extraction (94 °C, 60 min) was used for ethanol production to facilitate a fair decision about the conditions that gave the highest yield of value-added products.

The anaerobic fermentation was carried at 32 °C for 24 h, and the results are shown in Table 2. An increase in the hydrolysis temperature from 94 to 140 °C led to an increase in the ethanol concentration from 2.0 g/L to 6.2 g/L for orange peel and from 2.7 g/L to 7.5 g/L for orange pulp. The observed trend in ethanol concentration is similar to the observed increasing trend of the sugars' concentration (Fig. 4) obtained by increasing the treatment temperature from 94 to 140 °C. The corresponding ethanol yields were between 49.2 % and 81.5 % for orange peel and between 52.4 % and 82.8 % for orange pulp. The highest concentration and yield of ethanol were achieved from the hydrolysate treated at 140 °C for 30 min. In general, the ethanol concentration and yield from orange pulp were higher than those from orange peel. This is because of the higher
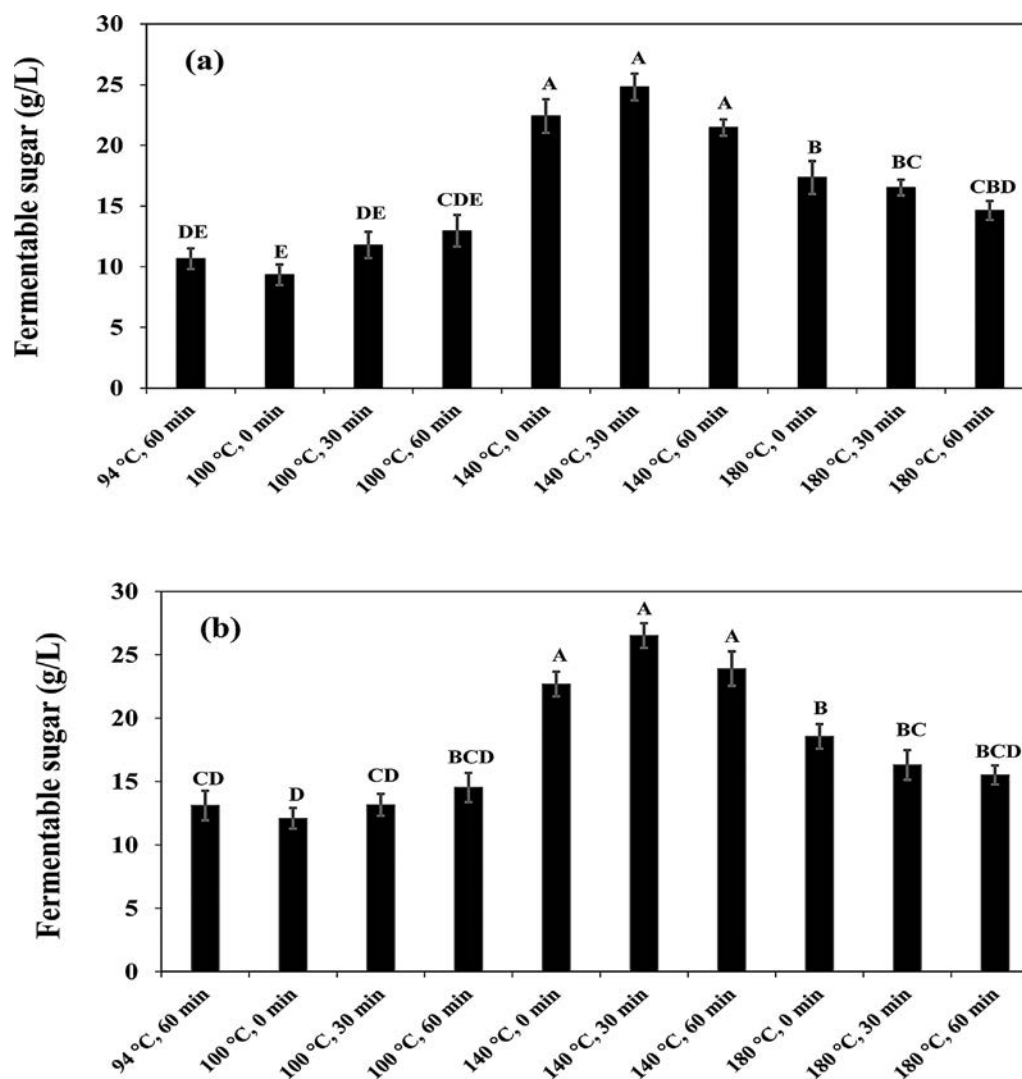
Fig. 4. Concentration of fermentable sugars in liquid fraction of the (a) pretreated orange peel and (b) pulp; Error bars show standard deviation. Means with the same letters are not significantly different (Tukey-adjusted comparisons).

concentration of fermentable sugar released from orange pulp compared with that from orange peel with the same treatments. In addition, the orange peels contain essential oils that have antibacterial properties. Limonene, as the main component of the essential oils of oranges, has inhibitory effects on microorganisms, starting at concentrations between 0.01–2 % (v/v) (Satari and Karimi, 2018). A very low concentration of limonene was detected in the dried orange waste.

Santi et al. (2014) used orange peel to produce ethanol using acid-catalyzed steam explosion pretreatment. They obtained the maximum ethanol concentration (15 g/L) at the pretreatment conditions of 180 °C and 150 s. Steam explosion pretreatment was also applied by Wilkins et al. (2007) to produce ethanol from citrus waste by *S. cerevisiae*. They reported that the treatment could remove most D-limonene (> 90 %) and yielded the highest ethanol concentration of 39.6 g/L. The higher ethanol concentration reported by the mentioned papers compared to those of the present study can be related to applying enzymatic hydrolysis, as in most other researches. However, applying enzymes can greatly increase the cost of the process. In another study, Satari et al. (2016) used water extraction to extract free sugars from citrus waste prior to fungal fermentation by *M. indicus* and *Rhizopus oryzae* in an airlift bioreactor and shake flask. Similar to the present study, they

did not apply enzymatic hydrolysis, and they obtained the maximum ethanol concentration of 5 g/L in airlift bioreactor and 6.5 g/L in shake flask using *M. indicus* supplemented with all nutrients. Applying dilute acid treatment in this study yielded higher ethanol concentrations compared to applying water extraction by Satari et al. (2016).

Patsalou et al. (2019) used citrus peel wastes for ethanol production at an optimum condition of 116 °C and 10 min with dilute acid and enzymatic hydrolysis. Their study was conducted using three yeasts. Based on their results, when *Saccharomyces cerevisiae* was used for ethanol production, the concentration of 4.2 g/L was achieved.

3.5. Biogas production

The residual solid fraction of dilute acid treatment was anaerobically digested to produce biogas and the results are shown in Fig. 5. The CH_4 content in the produced biogas was between 41–52 % for all samples. The orange peel treated at 94 °C for 60 min yielded the maximum CH_4 yield (151.3 mL CH_4/g VS), compared to other treatment conditions. An increase in the treatment temperature from 94 °C to 180 °C negatively affected the CH_4 yield. The negative effect of higher temperatures on CH_4 production can be due
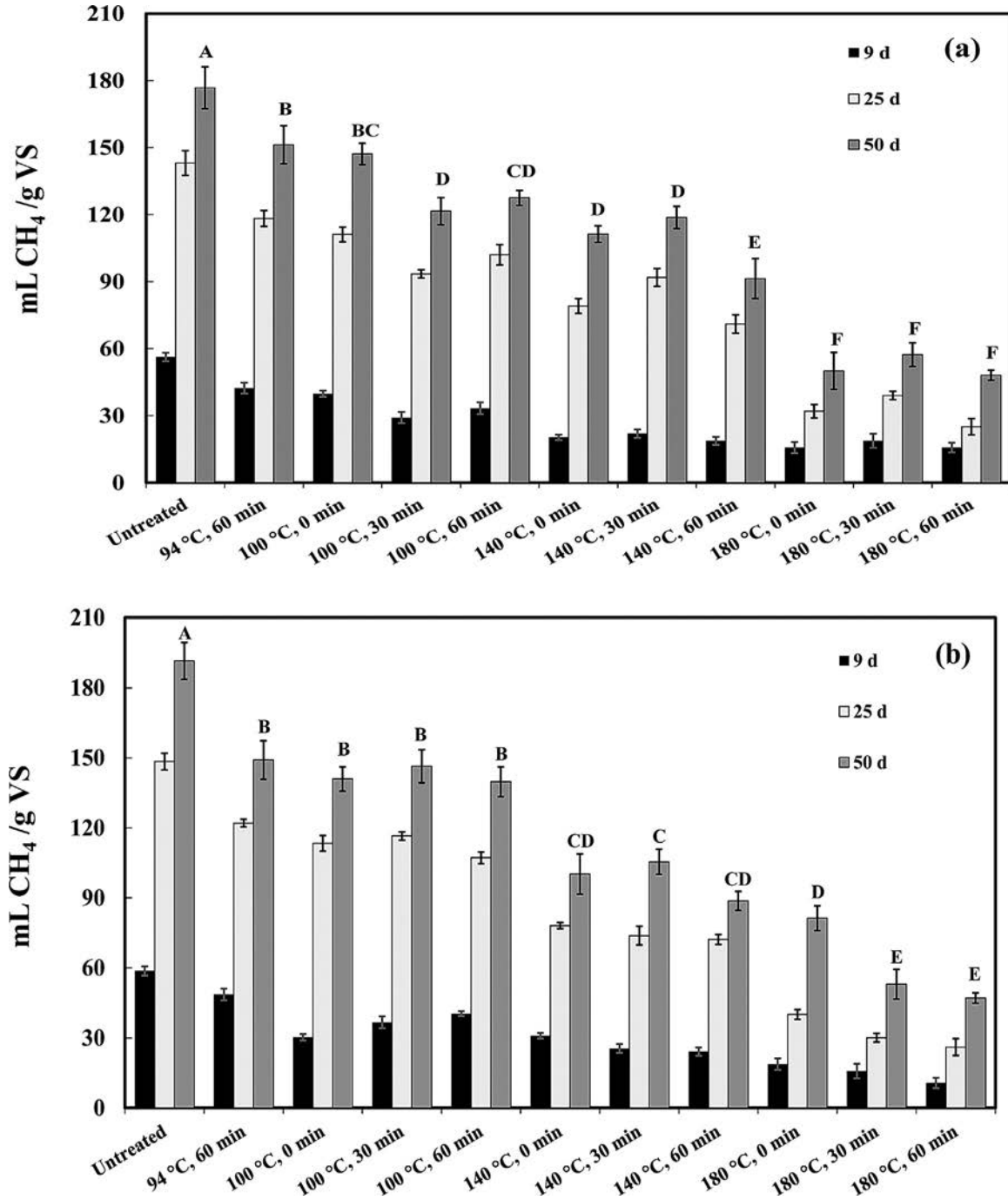
Fig. 5. Methane production yield from pretreated and untreated (a) orange peel and (b) orange pulp after 9 d (black), 25 d (bright gray), and 50 d (dark gray); Error bars show standard deviation. Means with the same letters are not significantly different (Tukey-adjusted comparisons).

Table 3
The energy content, gasoline equivalent, and products values obtained from the developed biorefinery platforms.

| Feedstock	Pretreatment conditions		Energy content (MJ/t OW)				Pectin (kg/t OW)	Products value (USD/t OW)
			(Gasoline equivalent (L/t OW))					
	Temp (°C)	Time (min)	Ethanol	Biogas	Residue	Total		
Untreated OW*	–	–	–	5,369.6(167.8 ± 8)	969.6(30.3 ± 2.8)	6,339.2(198.1 ± 10.8)	–	32.5 ± 1.7
	94	60	560.0 (17.5 ± 1.5)	1,299.2(40.6 ± 2.2)	288.0 (9.0 ± 0.5)	2,147.2 (67.1 ± 4.2)	244.0 ± 2.1	2,472.9 ± 23.3
Pretreated OW		0	2,307.2(72.1 ± 4.4)	828.8 (25.9 ± 1.1)	342.4(10.7 ± 0.6)	3,478.4 (108.7 ± 6.1)	42.3 ± 3.5	521.3 ± 40.7
	140	30	2,704.0(84.5 ± 3.9)	864.0 (27.0 ± 1.2)	662.4(20.7 ± 0.9)	4,230.4 (132.2 ± 6)	35.8 ± 4.4	474.1 ± 48.9
		60	2,214.4(69.2 ± 4.2)	713.6 (22.3 ± 1.9)	835.2(26.1 ± 0.9)	3,763.2 (117.6 ± 7)	23.4 ± 3.2	337.4 ± 39.1

* Orange waste.
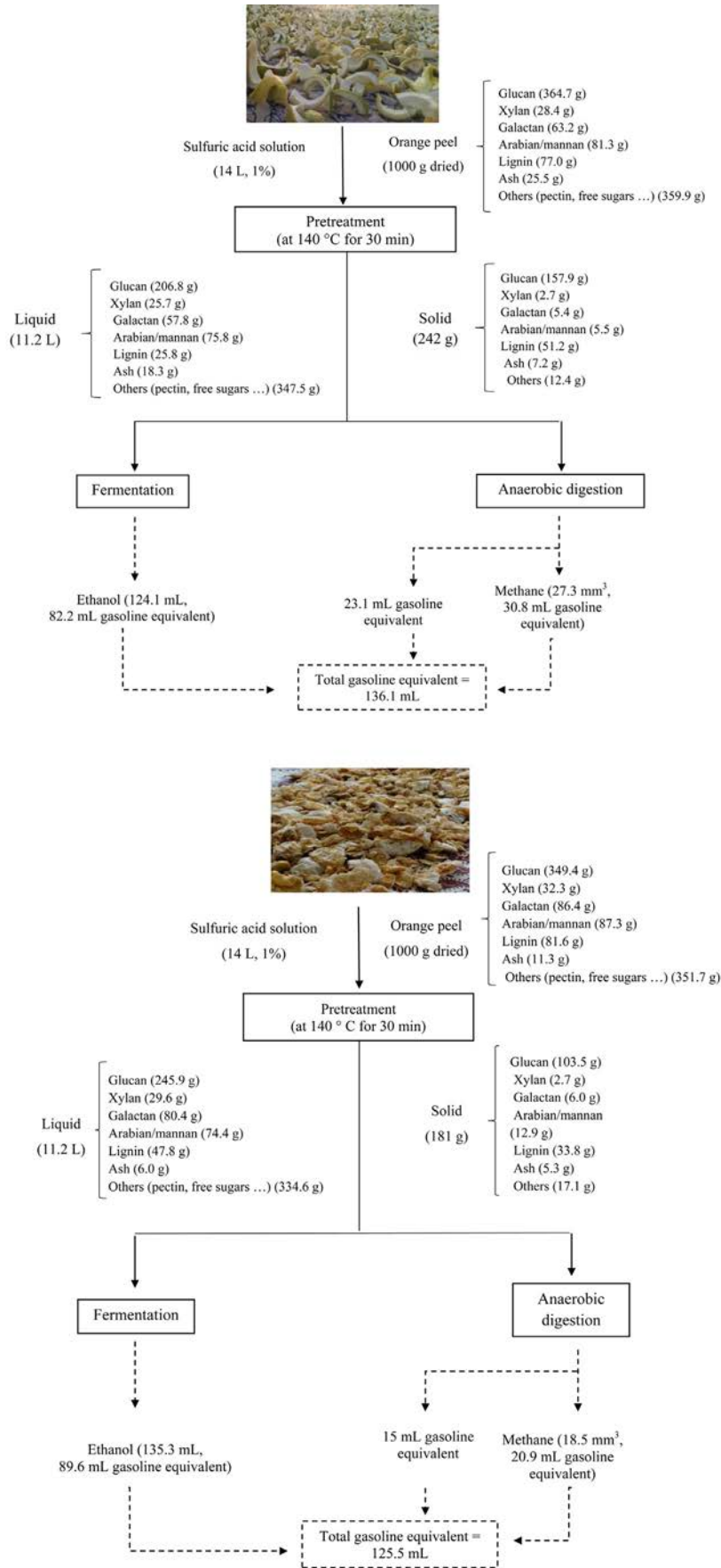
Fig. 6. The gasoline equivalent from 1 kg dry orange peel (the first subfigure) and pulp (the second subfigure) after treatment with 1% (w/v) sulfuric acid at 140 °C for 30 min.

to the higher dissolution of hemicellulose, which is an easily fermentable component for biogas production (Hashemi et al., 2016). The treatment at 180 °C resulted in releasing the most hemicellulose from solid to the supernatant (Table 1). About 67 % of the initial xylan in orange peel was dissolved and transferred to the liquid fraction after treatment at 180 °C for 60 min. Sugars at high temperatures react with amino acids via the Maillard reaction (Li et al., 2017), which creates difficulties in anaerobic digestion. Decreasing the bioavailability of sugars and proteins during the Maillard reaction can lead to the reduction of CH_4 yield (Li et al., 2017). The highest amount of CH_4 yield, 176.8 mL CH_4/g VS, was obtained from untreated orange wastes. The untreated wastes contain a significant amount of pectin and hemicellulose. Pectin is a kind of carbohydrate that can be easily consumed by microorganisms to produce CH_4.

The CH_4 production yield from orange pulp had a trend similar to that of orange peel, as a general decrease was observed with increasing temperature. The highest CH_4 production was related to the untreated pulp with 192 mL CH_4/g VS, which was more than the CH_4 yield from the untreated orange peel. According to compositional analysis, the amount of carbohydrates in orange pulp (55.5 %) is higher than that of orange peel (53.7 %). This can be a reason for the higher CH_4 production obtained from untreated orange pulp compared to the untreated peel. Despite having the highest CH_4 production from the untreated orange peel, producing other value-added products such as ethanol and pectin makes the biorefinery approach important. The observed CH_4 yield from untreated orange waste is within the range reported by Satari and Karimi (2018) (176–330 mL CH_4/g VS). Nielfa et al. (2015) anaerobically digested different fractions of municipal solid wastes (MSW). Among different fractions of MSW (including fruit/vegetable, meat/fish, cereal, garden, paper), the garden and fruit wastes had the lowest CH_4 yield of 77 and 163 mL CH_4/g VS, respectively. The low CH_4 yield of citrus waste is always predictable. This can be due to the existence of D-limonene and the production of other inhibitors such as alcohol, aldehydes, and terpenes (Ruiz and Flotats, 2014).

The heating values of the residual biomass (which is mainly lignin) from anaerobic digestion of orange peel were between 13.0 and 15.1 kJ/g and those of orange pulp were between 12.4 and 15.1 kJ/g. Overall, the heating value of the treated samples was higher than that of the untreated samples. The most likely reason is the higher lignin content in the residual biomass from anaerobic digestion of pretreated orange waste rather than that of the untreated one. The heating value of lignin (22.2–28.5 MJ/kg) was more than that of cellulose and hemicellulose (17.5 MJ/kg) because of lignin's higher carbon content (Demirbas, 2017). The dilute acid treatment removed most hemicelluloses from the lignocelluloses' structure. The pretreated orange waste that remained from the digestion contained higher amounts of lignin than the untreated sample. The heating value of the treated sample was more than those of the untreated samples. The note is that heat recovery from the digestate might be difficult due to its high moisture contents. Although, heating values were measured and reported in this research to present the energy content of all the products and by-products obtained in this biorefinery platform.

3.6. Gasoline equivalent and products value

In this study, dilute acid treatment was performed on orange peel and pulp as a multi-functional process. It extracted pectin as a value-added product, hydrolyzed sugars for ethanol production, and pretreated the lignocellulose to increase its biodegradability. The gasoline equivalent of the biofuels produced from the whole citrus wastes was calculated to compare the overall biofuel yields from different conditions (Table 3). Three cases were considered to compare their gasoline equivalent: (I) the untreated citrus wastes,

(II) the citrus waste pretreated at 94 °C for 60 min (yielded the maximum pectin extraction), and (III) the citrus waste pretreated at 140 °C (yielded the maximum fermentable sugars (Fig. 6). In case I, orange waste was anaerobically digested to produce biogas, and the remained lignin was considered a solid fuel. In cases II and III, the pretreatment liquor was fermented to produce ethanol, the solid portion of the pretreatment was anaerobically digested to produce biogas, and the remained lignin was considered a solid fuel.

The untreated orange wastes have the highest potential of biogas production and yielded the maximum amount of total produced energy, equivalent to 198.1 L gasoline per ton of untreated dry orange wastes. The reason that untreated orange wastes have such high potential is the presence of a wide variety of components, such as free sugars, pectin, and proteins in the untreated samples, all of which can be converted to biogas. If citrus wastes were used for biofuel production, the anaerobic digestion of the raw substrate would yield the maximum biofuel production, among the other cases studied in this research. However, the highest biofuel production is not the primary purpose of this study since citrus wastes contain pectin, which can be separated as a high value-added product prior to biofuel production. Considering the multiple products produced within this biorefinery platform, the total market value of the products was calculated and compared (Table 3). The results indicated that the acid treatment at 94 °C for 60 min led to the maximum products value (USD 2472.9 /t orange wastes), remarkably higher than that obtained by treatment at other conditions. The value-added of case II is over 75 times higher than that of case I and 4.7–7.3 times higher than that of case III. The energy consumption, in this case, is less than the other treatment conditions because of the lower treatment temperature. This research provided a detailed assessment of developing biorefinery from citrus wastes, which can help decision-makers considering different priorities. However, further studies on the life cycle sustainability assessment of the biorefinery platform are required to generate a comprehensive view of its full potential.

Overall, dilute acid hydrolysis of cellulose is incomplete and not as efficient as that by enzymatic hydrolysis. However, the efficiency depends on the nature of cellulose in the structure. For high crystalline cellulose with a high degree of polymerization, e.g., cotton, dilute acid efficiency is low; however, for the short chains cellulose and amorphous cellulose, e.g., the pretreated cellulose, it was found to have better yields (Amiri and Karimi, 2013). For example, dilute acid hydrolysis of untreated cotton at 150 °C for 60 min with 1% acid was only 13.8 % (Amiri and Karimi, 2013). After pretreatment, the yield was increased to over 30 % at the same conditions. This was also the reason for reaching higher hydrolysis yield by two stages dilute acid hydrolysis (first stage at high temperature and the second at the less severe conditions). The present study indicated that the cellulose in the orange waste is more like a pretreated low crystalline and amorphous cellulose. Moreover, the formation of inhibitors, which is also a chelleng in dilute acid processes, was less than 0.2 g/L for furfural and HMF. On the other hand, the price of hydrolytic enzymes is one of the current challenges in the second generation of ethanol production, while the acid consumption price is ignorable. Thus, considering biorefinery purposes, i.e., economical production of biochemicals and bioenergy from renewable resources, dilute acid hydrolysis is an advantageous process.

4. Conclusions

Orange wastes, with high availability and multiple valuable components, showed excellent potential as a biorefinery feedstock to produce pectin and biofuels. Dilute acid treatment was successfully used as a multi-purpose process to extract pectin as a value-added product, to hydrolyze sugars instead of enzymatic

hydrolysis for ethanol production, and to increase the digestibility of lignocelluloses as a chemical pretreatment before anaerobic digestion. The treatment conditions to optimize pectin extraction and biofuel production were different. Most likely, for the case that pectin is the desired product (because of its high price), the treatment at 94 °C for 60 min is the optimum condition. For the case that ethanol production has priority, since the treatment of citrus waste at 140 °C for 30 min yields the highest ethanol production. If biogas is the only product, no citrus waste treatment is needed. This biorefinery platform can increase the total products value up to 75 times, compared to the anaerobic digestion of citrus waste that is the typical waste management method.

Further investigations, such as techno-economic analysis and life cycle assessment, are needed to develop a more circular design for citrus waste biorefineries.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgment

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