Efficiency of Low Temperature Chemical Pretreatment of Fruit and Vegetable Pomace

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ABSTRACT

Subjecting lignocellulosic substrates to anaerobic digestion is a promising way of renewable energy obtaining. This method of generating energy is consistent with the sustainable development. In order to destroy the biodegradation-resistant structure of lignocellulosic materials before directing them to anaerobic decomposition, the use of pretreatment methods is required. The purpose of the present study was to assess the effect of temperature rise and a solvent type on the chemical pretreatment of fruit and vegetable pomace results. Biomass samples were placed in distilled water, 0.05 M NaOH and 0.05 M H_2SO_4 solutions and left for 20 h at 22 °C and at 50 °C (at room temperature and in a thermostated chamber). Concentrations of dissolved chemical oxygen demand ($COD_{dissolved}$), volatile fatty acids (VFA) and phenols, as well as electrolytic conductivity (EC) values, in the obtained hydrolysates were analyzed. The most significant result of temperature rise on the increase of solubility of organic compounds contained in fruit and vegetable pomace, expressed by VFA, one of the pretreatment methods efficiency indicators, was noted in the samples soaked in alkaline solution. The highest VFA level was observed in the series of the experiment conducted at 50 °C (868 mg·L^{-1}). The process carried out under these conditions resulted also in the highest concentration of another important pretreatment indicator, $COD_{dissolved}$. Hydrolysis conducted at 50 °C in a sodium hydroxide solution seems to be the most effective option for the pretreatment of fruit and vegetable pomace intended for energy production on biological way.

Keywords: fruit and vegetable waste, lignocellulosic biomass, chemical pretreatment, temperature influence.

INTRODUCTION

Burning fossil fuels in order to obtain energy necessary for the needs of developing industry and agriculture causes the environmental pollution and produces large amounts of waste [Marks-Bielska et al., 2019]. Therefore, it is becoming increasingly important to look for new energy sources that are less invasive to the environment. Nowadays, producing renewable energy is becoming more and more promising technology with biomass as one of the alternative sources. Biomass is a commonly available substrate obtained from plants and animals, consisting mainly of organic industrial, human and animal wastes, wood from forests, crops, seaweed, and wastes from agricultural and forestry processes [Saidur et al., 2011]. Using biomass for energy production can reduce or eliminate emissions of greenhouse

gases into the atmosphere in comparison to the use of fossil fuels [Demirbas, 2005]. The most popular biochemical method of biomass processing is anaerobic digestion, which is environmentally friendly and requires low financial outlays [Cong et al., 2018]. This process results in ethanol, methanol, biogas or biodiesel production [Decker et al., 2012; Das et al., 2014]. From various types of biomass, lignocellulosic materials (municipal solid waste, agricultural and forestry waste, energy crops) are considered as a material with a significant potential of biogas [Saxena et al., 2009; Liew et al., 2011]. Their main disadvantage is low biodegradability, as they consist of complex of three fractions: cellulose (40–55% of dry matter), hemicellulose (24–40% of dry matter) and lignin (18–25% dry matter [Malherbe and Cloete, 2002]). Therefore, before using lignocellulosic biomass in anaerobic processes, pretreatment

methods increasing the accessibility of hydrolytic enzymes to cellulose and hemicellulose chains are required [Frigon and Guiot, 2010]. These methods are used to shorten the first phase of the anaerobic digestion, enzymatic hydrolysis, which is regarded as a rate-limiting phase of the entire anaerobic transformation [Liew et al., 2011; Mirmohamadsadeghi et al., 2021]. The disadvantages of not using the pretreatment methods may be process disturbance and production of toxic substances (i.e. formaldehydes, phenols, formic acid and acetic acid), having negative impact on the methanogenic microorganisms [Blue et al., 2019; Mirmohamadsadeghi et al., 2021].

The most commonly used pretreatment methods are: physical, chemical and biological [Karki et al., 2011; Zheng et al., 2014]. In comparison to others, chemical methods are considered to be cheap and more efficient in solubilizing lignocellulose [Zhou et al., 2012; Song et al., 2014]. Their efficiency is connected with the kind and the concentration of the solvent, process temperature and duration [Song et al., 2014; Cabrera et al., 2014]. As part of chemical methods, acid or alkaline pretreatment can be used.

The chemical compound most frequently used in acid pretreatment is sulfuric acid; hydrochloric or acetic acid are used less often [González et al., 2005; Us and Perendeci, 2012]. This method disrupts van der Waals forces, hydrogen and covalent bonds binding lignocellulosic substrate components, resulting in hemicellulose solubilization and cellulose reduction [Li et al., 2010]. The main drawback of this method is the possibility of undesirable inhibitory products, such as 5-hydroxymethylfurfural (HMF), formation [Zheng et al., 2014; Blue et al., 2019]. Its main advantage is high solubility of hemicellulose and lignin in acid [Kumar et al., 2009].

Alkaline methods of lignocellulosic biomass pretreatment are carried out using mainly sodium hydroxide, potassium hydroxide, lime and ammonia [González et al. 2005; Us and Perendeci, 2012]. Lignocellulosic biomass swelling, lignin structure disruption and the degree of cellulose crystallinity decrease are their effect. This in turn results in the increase of porosity of the matter and its accessible surface area [Zheng et al., 2014]. The efficiency of alkaline treatment depends on the lignin amount in the biomass: as the lignin content in the substrate increases, the efficiency of the method decreases [Chen et al., 2013]. The advantage of this method is the use of easily

available and environmentally friendly chemicals in low doses [Cabrera et al., 2014]. The process duration, temperature and pressure required to obtain the desired efficiency are usually lower than in the case of other processing methods [Kim and Han, 2012; Menon and Rao, 2012]. However, there is a risk of phenolic inhibitors creating, which is considered as a main drawback of the process [Chen et al., 2013; Zheng et al., 2014].

Methods of pretreatment are required to make the availability of lignocellulosic biomass for microorganisms higher in the process of anaerobic digestion. Various types of lignocellulosic substrates are used to produce biogas on biological way. One of them includes fruit and vegetable waste. It is estimated that more than 1700 million tons of fruit and vegetable waste are generated annually in the world [Edwiges et al., 2018]. It constitutes a large part of the mass of food waste, especially in industrialized countries [McCarthy et al., 2020; Li et al., 2021]. Markets, supermarkets and agricultural activities are the main sources of these waste [Chatterjee and Mazumder, 2020]. Fruit and vegetable waste contain a lot of water and biodegradable organic substances (organic acids, carbohydrates and lipids [Li et al., 2020]). Reusing or recycling them is more beneficial for the environment than storing or burning [Plazzotta et al., 2017].

Fruit and vegetable waste can be used for the production of chemicals, ethanol, essential oil, fertilizers, cattle feed, pectin and absorbent materials [Boukroufa et al., 2015; Oliveira et al., 2023]. Many studies have focused on determining methane and biogas production efficiency of this biomass during anaerobic digestion [Jiang et al., 2012; Ji et al., 2017; Olatunji et al., 2023; Agrawal et al., 2023; Kalogiannis et al., 2024]. The impact of thermal and chemical methods of pretreatment on the lignocellulosic materials properties was also analyzed [Chen et al., 2013; Song et al., 2014; Barlianti et al., 2015; Li et al., 2016; Pagliaccia et al., 2019; Blue et al., 2019; Günerhan et al., 2020; Mozhiarasi, 2022; Schirmer et al., 2023; Chaurasia et al., 2023]. Authors of most of these works analyzed the concentration of individual monosaccharides which were released in pretreatment processes as the result of changes in the chemical composition of lignocellulosic biomass [Barlianti et al., 2015; Blue et al., 2019; Günerhan et al., 2020; Schirmer et al., 2023]. There are very few studies in which parameters such as electrolytic conductivity (EC), concentration of volatile fatty acids (VFA) and dissolved chemical oxygen demand ($COD_{dissolved}$) of

the substrate were examined [Günerhan et al., 2020; Schirmer et al., 2023], although these parameters are regarded as significant indicators of the biomass solubilization and pretreatment efficiency.

The purpose of the present study was to assess the influence of chemical pretreatment conducted at low temperature conditions on the efficiency of the solubilization of organic matter contained in fruit and vegetable pomace. In order to evaluate the efficiency of the process, the substrate was soaked in solutions of diluted NaOH and H_2SO_4 at temperatures of 22 °C and 50 °C. The following parameters: VFA and $COD_{dissolved}$, demonstrating the biomass solubilization efficiency, were examined.

MATERIALS AND METHODS

Materials used in the experiment

Fruit and vegetable pomace was taken from the storehouse of the biopower plant situated in Siedliszczki (Lublin Province, Poland). The pomace samples after transport to the research laboratory were collected in a freezer at -17 °C. Then, after thawing at room temperature, were prepared for pretreatment processes. The main substrate parameters are presented in Table 1. The chemical compounds used in the experiment were sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) pellets (Avantor, Poland).

Fruit and vegetable pomace pretreatment

Twelve samples of air-dried fruit and vegetable pomace, each of 5 g of weight, were put into glass flasks with 250 ml of volume. Then, 0.05 M H_2SO_4

Table 1. The main parameters of fruit and vegetable pomace determined in the samples after air drying

Parameter	Unit	Value
Total solids (TS)	%	80.35 ± 0.07
Volatile solids (VS)	% TS	95.88 ± 0.83

solution was poured into four of them, the next four were filled with 0.05 M solution of NaOH and the remaining ones were distilled water-filled in a weight/volume proportion of 1:20. The latter samples were used as a control. In order to ensure wetting the whole samples with the solutions, the glass flasks contents were then mixed. After that, two samples with each solution were inserted into a thermostated chamber (50 °C) for a time of 20 hours and the remaining 6 flasks (two with each solution) were placed at 22 °C (room temperature) for the same time. Next, the heated samples were chilled down to 22 °C. After that, all samples were subjected to centrifugation for 20 min by 4000 rpm and filtered through paper filters (84 g·m⁻²). The obtained filtrates were collected in the glass vials of volume of 40 ml and tested for VFA, $COD_{dissolved}$ and phenols concentration. Electrolytic conductivity was analyzed as well.

Analytical methods

All parameters were measured in duplicate. Analytical methods used in the experiment are presented in the Table 2.

RESULTS

Electrolytic conductivity in hydrolysates

It was observed that in the case of pretreatment carried out at 22 °C, the highest value of electrolytic conductivity was noted during acid hydrolysis (23.75 mS·cm⁻¹). In the alkaline hydrolyzed samples, its value was 4.45 mS·cm⁻¹, and in the samples hydrolyzed in distilled water, 0.16 mS·cm⁻¹ (Fig. 1). It was found that the increase in process temperature in the case of acid hydrolysis did not significantly affect the conductivity value. Only 3% increase, reaching an average of 24.55 mS·cm⁻¹, was observed. Similarly, in the case of distilled water, the difference in electrolytic conductivity values in both temperatures was

Table 2. Analytical methods used during the experiment

| Parameter	Method/procedure/standard	Device
Total solids	PN-EN ISO 18134-2:2017-03	SUP-4 Wamed drying chamber
Volatile solids	PN-EN ISO 18122:2016-01	Czylok FCF 2.5 S muffle furnace
Electrolytic conductivity	PN-EN 27888:1999	Elmetron CPC-501 detector
Volatile fatty acids	HACH Method 8196	VIS DR 3900 spectrophotometer and HACH HT 200S thermostat with HACH cuvette tests (LCK365, LCK514 and LCK345)
Dissolved chemical oxygen demand	HACH Method 8000	
Phenols	DOC312.53.94050	
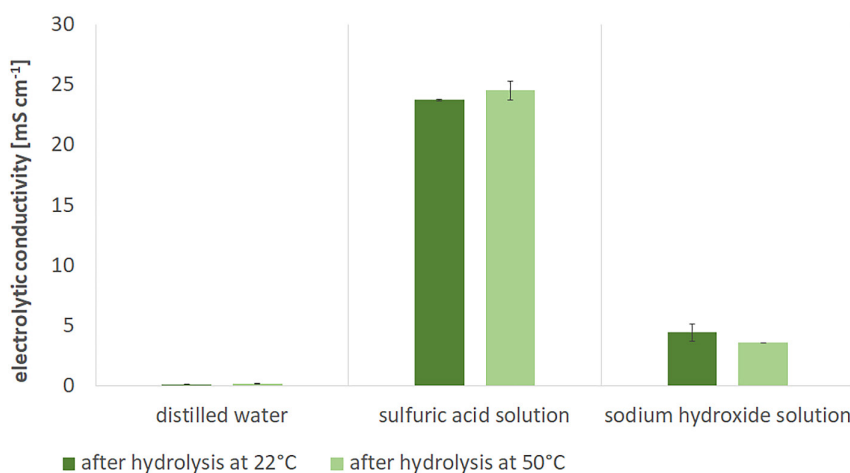
Figure 1. Electrolytic conductivity values measured in the samples obtained after hydrolysis conducted in distilled water and solutions of NaOH and H_2SO_4 at various temperatures

negligible. However, during the alkaline hydrolysis, after temperature increase, the conductivity level was 19% lower compared to the value obtained during the process carried out at 22 °C and was equal to 3.6 mS·cm^{-1}.

$COD_{dissolved}$ in hydrolysates

The use of an alkali solution improved the solubilization effect of organic compounds contained in fruit and vegetable pomace in terms of dissolved COD concentration in comparison to the control sample, while the use of an acid solution worsened the release of organic matter. It was observed both at 22 °C and 50 °C (Fig. 2). The highest value of $COD_{dissolved}$ obtained at room temperature was noted in the alkaline hydrolyzed samples (3210 mg·L^{-1}). It

was the value 45% higher than measured in the samples soaked in distilled water (with the average concentration of dissolved chemical oxygen demand of 2210 mg·L^{-1}) and 73% higher than the corresponding value measured in the acid hydrolyzed sample (with the average value of 1852 mg·L^{-1}). A significant impact of temperature on hydrolysis efficiency was noted. In the case of alkaline hydrolysis, a temperature rise to 50 °C increased the intensity of organic compounds solubilization by 25% compared to the process carried out under the same conditions at room temperature. A similar pattern occurred during acid hydrolysis, where 20% higher $COD_{dissolved}$ concentration was noted at 50 °C. There was no significant effect of temperature increase on the concentration of this parameter during the process carried out in distilled water.
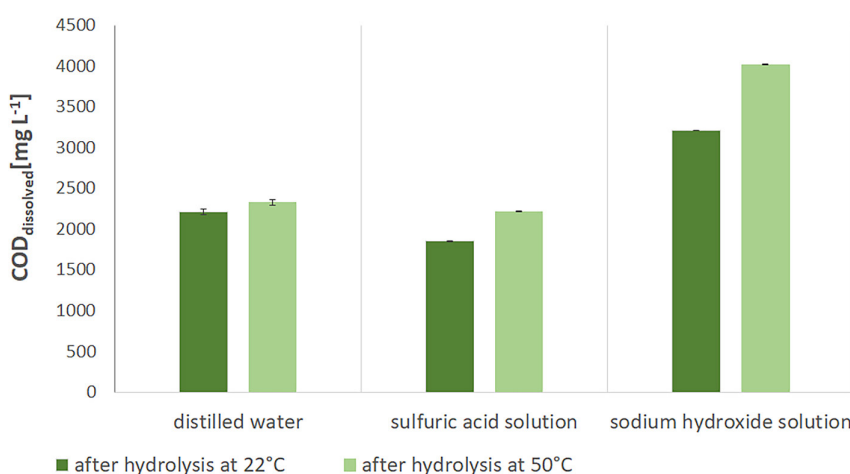

Figure 2. $COD_{dissolved}$ values measured in the samples obtained after hydrolysis conducted in distilled water and solutions of NaOH and H_2SO_4 at various temperatures

VFA in hydrolysates

It was noted that during the process conducted at 22 °C, the VFA release into the solution was most effective in alkaline environment. Under these conditions, the VFA concentration value was 749 mg·L^{-1}. In the sample hydrolyzed under acidic conditions at the same temperature, the concentration of VFA was 698 mg·L^{-1} (Fig. 3). The lowest parameter value was observed when distilled water was used (299 mg·L^{-1}). The impact of temperature rise on the efficiency of solubilization of organic compounds (VFA release) was the most visible in the samples subjected to alkaline pretreatment, where a 16% increase in VFA concentration was achieved in comparison to the value obtained at room temperature. A less significant effect of temperature increase on the release of VFA was observed in the samples soaked in distilled water (VFA concentration was higher by only 8% compared to the value achieved at 22 °C). Inhibition of volatile fatty acids release at higher temperature was noted in the acidic environment, in which the concentration of the parameter decreased from 698 mg·L^{-1} observed at room temperature to 477 mg·L^{-1} at 50 °C.

Phenols in hydrolysates

The concentrations of phenols were analyzed only in the filtrates obtained after hydrolysis conducted at 50 °C. A higher level of this parameter was noted during alkaline hydrolysis: it was 18.73 mg·L^{-1} which was more than 3.5 times higher than in the samples hydrolyzed in acidic environment (5.27 mg·L^{-1}).

DISCUSSION

Fruit and vegetable waste (FVW) is a waste group produced in large amounts around the world [Li et al., 2021]. It is considered that around 25% of vegetables and 15% of fruit are becoming waste at the bottom of the production chain [FAO, 2014]. Food and vegetable waste contains a large amount of organic matter (about 85%) and is characterized by low solid content (under 10%) and high moisture [Scano et al., 2014; Wang et al., 2014]. FVW due to its properties can be used as a substrate to biogas production in anaerobic process. Many studies concerned this issue [Jiang et al., 2012; Wang et al., 2014]. However, because of the fact that the lignocellulosic biomass contains strongly chemically bonded by covalent crosslinkages or non-covalent forces cellulose, hemicelluloses and lignin, the process of obtaining biogas by its fermentation is complicated [Jin et al., 2006]. That is why the methods of substrates pretreatment causing fragmentation of the solid phase and damaging the compact structure of lignocellulose are used. They result in transforming more complex organic compounds into simpler ones and in releasing them into the solution. Chemical pretreatment is one way for making biodegradation-resistant structure of lignocellulosic materials more available for microorganisms in the process of anaerobic digestion. Using dilute sodium base and sulfuric acid solutions as pretreatment agents has many advantages: it is believed that is more efficient, requires lower financial outlays and is more environmentally friendly in comparison to concentrated ones
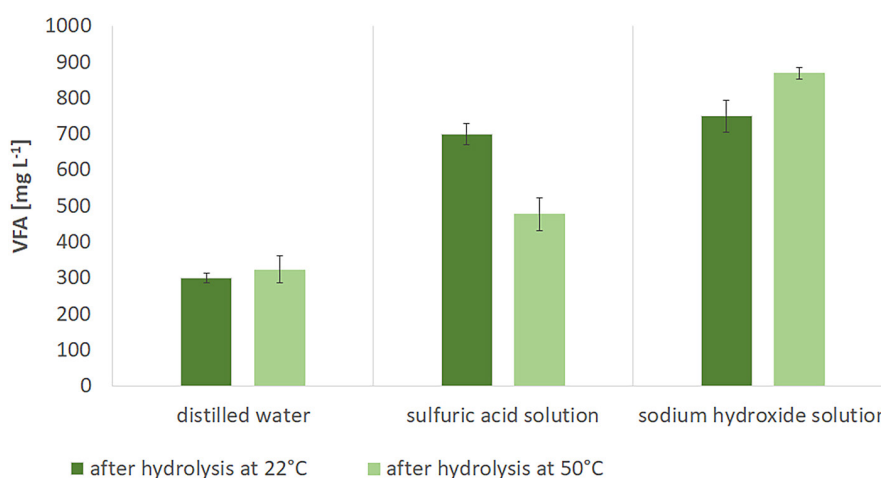

Figure 3. VFA values measured in the samples obtained after hydrolysis conducted in distilled water and solutions of NaOH and H$_2$SO$_4$ at various temperatures

[Kassim et al., 2022]. In the conducted study, the chemicals to biomass ratios were 4% and 10% w/w for NaOH and H_2SO_4, respectively.

Electrolytic conductivity values indicate the presence and quantity of ions in the solution. The factors influencing the EC values are type and concentration of ions, the motion of ionic charge and the solution temperature [Wagner, 2012]. Each ion is characterized by specific mobility, so it is difficult to generalize when determining the influence of temperature on their behavior. In general, EC increases with temperature. In the conducted study, the highest electrolytic conductivity value at temperature of 50 °C was reached after soaking the samples in H_2SO_4 solution. In the samples soaked in alkaline solution, the EC level decreased after temperature rise, while in the control samples, it was very similar to the value obtained at room temperature. This is probably because of the fact that temperature rise improved ion mobility during acid hydrolysis, simultaneously making it worse in the case of alkaline conditions. In the samples soaked in distilled water, the temperature increase had no significant effect on electrolytic conductivity value. EC values obtained in the samples soaked in NaOH and H_2SO_4 solutions at the same temperature were significantly different - the difference was 19.30 mS·cm^{-1} and 20.95 mS·cm^{-1} for 22 °C and for 50 °C, respectively. Higher values in each of these cases were achieved in the samples hydrolyzed in acid solutions. However, such dissimilarities do not indicate a significant difference in the efficiency of hydrolysis, but result from the different abilities of particular ions from the solution to conduct electricity. It is well known that Na$^+$ and OH$^-$ ions conduct electricity worse than H$^+$ ions, hence the difference [Lee and Rasaiah, 2011].

COD is a parameter showing the solubilization of organic matter, but it is very rarely described in the literature as an indicator of its efficiency, although it is much easier to determine than estimating changes in biomass fiber composition. One of the few works that analyzed the changes in COD concentration resulting from the use of biomass pretreatment is the paper by Ozkan et al. [2011]. These authors analyzed the efficiency of various pretreatment methods of sugar beet-pulp (alkaline, microwave, thermal, microwave-alkaline and thermal-alkaline) on dissolved COD concentration. They noted several times higher solubilization of organic matter expressed in COD than in the conducted work:

6739 ± 587 mg·dm^{-3} and 20884 ± 818 mg·dm^{-3}, after alkaline and thermal-alkaline pretreatment, respectively. Such high COD levels in the cited work result probably from the use of higher pressure and temperature than in the conducted study. The positive influence of temperature on the solubilization rise of organic compounds was noted in several works on chemical pretreatment methods of lignocellulosic biomass, i.e. in the work of Zheng et al. [2013], who studied the dilute acid sugar beet pulp pretreatment. The influence of chemical pretreatment conducted at various temperatures on the efficiency of organic matter solubilization expressed as dissolved COD in fruit and vegetable harvesting waste was also studied by Günerhan et al. [2020], who analyzed the influence of chemicals (NaOH and HCl) concentration, treatment time and temperature, and samples mixing speed. The most effective solubilization was achieved at the highest of analyzed temperatures: 100 °C, by NaOH concentration of 6.5%, after reaction time of 1 hour and with mixing speed of 500 rpm. The solubilization efficiency growing with temperature rise, expressed by dissolved COD concentration, was observed by Ding et al. [2017] who studied the influence of hydrothermal pretreatment of food waste on hydrogen and methane co-production in anaerobic process. The pretreatment was conducted in the temperature range from 100 to 200 °C. It was stated that the concentration of $COD_{dissolved}$ was higher in the biomass subjected to hydrothermal pretreatment in comparison to its level in untreated samples. Additionally, its concentration increased with pretreatment temperature rise from 100 to 180 °C and then started to decrease.

Releasing volatile fatty acids being a main substrate for acetotrophic methanogenesis can be another indicator of biomass pretreatment efficiency. It was noted that in the control samples and these soaked in NaOH solution, the temperature rise resulted in the increase of VFA releasing (in the alkaline environment it was more significant than in distilled water). In the studies concerning the hydrothermal pretreatment of food waste conducted by Ding et al. [2017], the positive effect of temperature rise on VFA concentration was observed in the range from 100 to 160 °C. Ziemiński et al. [2014], who studied liquid hot water treatment of beet pulp (in temperature from 120 to 200 °C, high pressure), also noted the positive temperature influence on the organic substrate solubilization.

Additionally, the concentration of phenols, being toxicants to microorganisms, was measured. It was observed that their level was more than 3.5 times higher in the samples hydrolyzed under alkaline conditions comparing to acid hydrolysis (at 50 °C). It can be explained as follows: phenols are the product of decomposition of lignin, occurring very intensively during alkaline pretreatment of lignocellulosic substrate [Nenkova et al., 2008; Ares-Peón et al., 2016]. Teghammar et al. [2010] noted that increasing NaOH concentration resulted in higher phenolic compounds solubilization. Kayembe et al. [2013] and Wang et al. [1988] stated that concentrations of phenols exceeding 1000 mg·dm^{-3} had toxic effects on the methanogens. The concentrations of these compounds obtained in the conducted study probably will not be toxic to methanogenic microorganisms, as they were several dozen times lower than those achieved by mentioned authors.

CONCLUSIONS

On the basis of the results of the conducted experiment, the visible effect of temperature and type of the solvent on the solubilization intensity of organic matter contained in fruit and vegetable pomace was observed. The highest efficiency of applied pretreatment method, expressed by concentration of two main indicators: $COD_{dissolved}$ and VFA, was noted during the hydrolysis carried out in alkaline environment at 50 °C. The most significant impact of temperature on the increasing the biodegradability of studied lignocellulosic biomass was also observed during the chemical pretreatment process carried out under alkaline conditions. A higher level of phenols in dissolved form was noted after the alkaline hydrolysis process compared to acid hydrolysis, as phenols are the effect of lignin decomposition taking place more intensely during alkaline pretreatment of lignocellulosic substrate.

Summing up, the most effective method of pretreatment of the fruit and vegetable pomace intended for energy production using biological methods seems to be the chemical treatment with use of NaOH solution as the hydrolyzing agent, carried out at 50 °C. This can be stated based on the fact that the concentration of substances easily absorbed by microorganisms ($COD_{dissolved}$, VFA) obtained after applying this method was the highest, which suggests that potential biogas yield will also be high.

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