Experimental and Numerical Analysis of the Co-Digestion Process of Municipal Sludge with Fruit and Vegetable Waste

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ABSTRACT: *Anaerobic digestion is the most commonly applied process for waste sludge treatment, which enables obtaining energy from the produced biogas. Biogas produced by anaerobic co-digestion of sludge with various additives can be used as an alternative fuel. Mathematical modeling of the Anaerobic Digestion (AD) process can greatly explain and facilitate the full-scale implementation of this process. In this work, a simulation of the process of co-digestion of waste sludge with fruit and vegetable waste was carried out numerically, with Anaerobic digestion model no. 1 model (ADM1) and experimentally. The data used to run the ADM1 model and its verification were obtained in a batch pilot reactor (25 L) and refer to Total Solids (TS), Volatile Solids (VS), Total Chemical Oxygen Demand (TCOD), Total Kjeldahl Nitrogen (TKN), total ammonia nitrogen, volatile fatty acids (VFA), pH value, conductivity, biogas volume produced and its composition. The verification of the model was performed with experimental data about the biogas production, methane production, and pH value. Also, a sensitivity analysis was performed by variation of 53 parameters, to identify the most sensitive parameters of the ADM1 model for the co-digestion process. The best agreement between experimental and simulated data was obtained for methane production, while the most sensitive parameters are the biochemical hydrogen inhibition constant and the half-saturation constant.*

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INTRODUCTION

Anaerobic digestion is a biochemical process in which biodegradable organic substrates are broken down by microbiological processes without oxygen, with the production of biogas and digestate. Anaerobic digestion is a technology that has existed for more than a century, mostly successfully applied to stabilize organic sludge obtained from the treatment of municipal wastewater and food industry wastewater. Biogas generation using food waste anaerobic co-digestion with activated sludge provides a cleaner addressable system, an excellent solution to global challenges, increasing energy demands, fuel charges, pollution, and wastewater treatment [1]. Recently, interest in this technology has grown rapidly due to the possibility of processing not only liquid and semi-liquid types of waste but also solid organic materials, all thanks to the pressure imposed by new and stricter regulations on the disposal of organic waste, as well as the need to find alternative sources of energy as a replacement for fossil fuels [2]. The type and composition of the substrate directly affect the production of biogas because the substrate contains sources of energy and nutrients: carbon, nitrogen, phosphorus, sulfur, potassium, calcium, magnesium, and iron, as well as organic components necessary for the growth of microorganisms. The composition of the substrate determines the conditions in the bioreactor, such as the pH value or the inhibitory effect of certain degradation products. Recently, the co-digestion of sludge and various types of manure has given good results and has great advantages when it comes to farms. Most current agricultural biogas facilities digest chicken, cow and pig manure with co-substrates supplemented to increase the organic material content and gas yield [3]. Also, recent research deals with the process of co-digestion with other additives, for example, fruit and vegetable waste, food industry wastes as well as municipal solid waste [4-8]. Some municipal bio-waste produced in large quantities, such as food waste, has the potential for use as feeding substrates since they arerich in easily degradable organic matter [9].

Mathematical modeling is widespread in science and engineering, with the aim of better understanding system behavior, arriving at new theoretical knowledge, predicting system performance, and, in an increasing number of cases, helping to solve practical design problems. In this context, mathematical models reduce or even replace the need for physical experimentation when exploring new materials and/or process options [10]. Mathematical modeling of anaerobic digestion processes has been motivated by the need to increase the efficiency of anaerobic digestion systems since the early seventies [11]. The International Water Association (IWA) Anaerobic Digestion Model No. 1, *Batstone et al*., [12] has mainly been used for the simulation of digestion for different substrates, and it is already a universally accepted model for anaerobic digestion. By reviewing the available literature, a large number of researchers have dealt with the adjustment of kinetic parameters in the ADM1 mathematical model. Most of this research is presented in a review *by Donoso-Bravo et al*., [11]. More recently, the adjustment of kinetic parameters was performed through the sensitivity analysis [13]. Also, similar research was carried out in the research [14-19]. The complexity of ADM1 leads to the need for many input parameters, ultimately resulting in a large number of stoichiometric and kinetic equations, for which parameter identification and manipulation could be very difficult [20]. When it comes to using the ADM1 model, the biggest problem is the characterization of the waste and the calculation of the input state variables. Default parameters for disintegration and hydrolysis kinetics can be used to obtain an estimate of biogas production adequate for the preliminary design of an industrial plant [21]. Calibration of these kinetic parameters is generally required to simulate methane production with complete accuracy [16]. Using anaerobic digestion to generate methane is considered the most promising technique for processing fruit and vegetable waste; as such, waste has a high moisture content and is easily biodegradable [22]. Large differences in the composition of the co-substrates used for the co-digestion process represent a real challenge for mathematical modelling and parameter adjustment in the ADM1 model. Therefore, it is necessary to identify the key parameters of

the ADM1 model that contribute to the adequate simulation of the process on the laboratory and industrial scales. Most research on co-digestion with fruits and vegetables was carried out by conducting experiments [23, 24] or co-digestion of fruits and vegetables with animal manure [25]. Researchers who dealt with the co-digestion process, waste sludge with fruit and vegetable waste, did not include numerical analysis with sensitivity analysis or the simulation performed using simple models for the AD process.

The goal of this research is to simulate the co-digestion of municipal sludge with fruit and vegetable waste experimentally and using the ADM1 model. The model verification will be performed according to experimental values for pH value, biogas, and methane production. Even though the ADM1 model describes the AD process in detail, for the co-digestion process, it is necessary to identify the most sensitive parameters of the model using sensitivity analysis, which is also one of the goals of this research. By reviewing the literature, it was observed that the parameters that most affect the process of co-digestion of municipal sludge with fruit and vegetable waste have not been given so far. Also, it is not known which components inhibit the methanation phase of the co-digestion process with fruit and vegetables.

EXPERIMENTAL SECTION

Experimental setup

The experiment was carried out under laboratory conditions to research the use of waste sludge from municipal wastewater treatment plants in biogas production. The process of anaerobic digestion was conducted under mesophilic conditions (35 °C) with the addition of waste from the food industry (fruit and vegetable waste). The waste sludge from the municipal wastewater treatment plant and the organic waste used in the experiment were characterized and the following parameters were measured: pH-value, electrical conductivity, dry matter content, volatile organic matter content, ammonia nitrogen, total nitrogen, volatile fatty acids, phosphorus content, and chemical oxygen consumption. Waste sludge from the municipal wastewater treatment plant owned by the Srebrenik utility company was used as the basic substrate. Waste from the food industry, i.e. the rest after processing fruits and vegetables from the company "Fana" d.o.o., Srebrenik, Bosnia and Herzegovina, was used as an addition.

After the characterization of the raw materials, it was necessary to mix the basic substrate, i.e. waste sludge from municipal wastewater treatment plants with organic waste from the food industry. Taking into account the fact that the content of dry matter in the digestion mixture ranges from 3 to 10%, waste from the food industry was added in the amount of 25% by mass. Control of the process was carried out by determining the pH-value, electrical conductivity, and dry matter content, content of volatile organic matter, ammonia nitrogen, free ammonia, Kjeldahl nitrogen, total volatile fatty acids, phosphorus, chemical oxygen demand, production and composition of biogas. Analyses were performed on the first, fifth, ninth, fifteenth, twenty-first and last day of the experiment, with the measurement of biogas production, pH-value and electrical conductivity realized every day between the first and ninth day, due to the possibility of inhibiting the process with volatile fatty acids. When determining, measuring, or calculating parameters, except the composition of biogas and the concentration of volatile fatty acids, all analyses were performed three times. For research purposes, a pilot reactor system of the batch type, volume 25 L, was designed. The total mass of waste in the reactor was 15 kg. The volume of the gas phase in the reactor was approximately 15%. The reactor was made of plastic mass with a double jacket, which was used to heat it with hot water coming from the boiler, which ensures the constant required temperature in the reactor (35°C). Heating water was recirculated using a circulation pump. Thermometers and barometers were placed on the reactor to control the necessary process parameters, as well as manual mixers with paddles. An opening at the bottom of the reactor was used for sampling. Anaerobic conditions were ensured by blowing nitrogen from a pressure bottle. A valve for the exit of produced biogas was installed at the top of the reactor. The volume of biogas produced was measured according to the principle of Marriott bottles, with 25 L plastic containers filled with a 22% NaCl solution for gas reception. Due to the pressure of the produced biogas, the solution was transported through a rubber hose into graduated secondary tanks, where the equivalent volume of biogas from the reactor can be read based on the volume of the displaced liquid (Fig. 1).

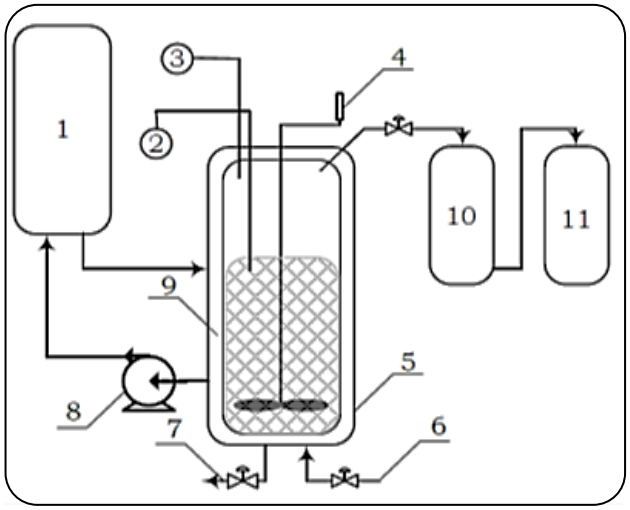

Fig. 1: Pilot reactor system for anaerobic digestion: 1-boiler, 2-thermometer, 3-manometer, 4-mixer, 5-reactor body, 6-reactor blow-down inlet, 7-sampling point, 8-recirculation pump, 9-reactor double jacket, 10-container filled with NaCl solution, 11-container for collecting the squeezed liquid.

The process was carried out at a constant temperature of 35±2 ºC, lasting 34 days.

Analytical methods

The dry matter and volatile organic substances were determined according to Method 2540-SolidB, (APHA, 2005) [26]. Electrometric measurements of pH-value and electrical conductivity were carried out by direct measurement of values on a pH-meter/conductometer METTLER TOLEDO FE 20/EL 20- FE 30/EL 30. The nitrogen content was determined by a Kjeldahl apparatus Gerhardt according to Method 4500-Norg B (APHA, 1998) [27].

Ammonia nitrogen concentration was determined according to the Method 4500-NH3 C (APHA, 2005) [26].

With the known values of ammonia nitrogen, pH-value, and temperature prevailing in the reactor, the concentration of free ammonia was calculated according to the equation obtained from the chemical balance [28]:

$$[NH_3] = \frac{[NH_3 + NH_4]}{1 + \frac{[H^+]}{Ka}} \quad (1)$$

Were in:

$[H^+] = 10^{-pH}$

$Ka = 10^{-pKa}$.

The relation obtained by regression was used to calculate the *pKa* value depending on the temperature:

$$pKa = 4 \cdot 10^{-8} \cdot T^3 + 9 \cdot 10^5 \cdot T^2 - 0.0356 \cdot T + 10.072 \quad (2)$$

The analysis of the concentration of volatile fatty acids was carried out by Method 5560-Organic and volatile acids C. (APHA, 2005) [26].

The phosphorus content was determined by the standard method BAS EN ISO 6878 [29]. A modified standard method according to BAS ISO 6060 was used to determine COD [30]. The volume of biogas produced from the reactor was measured by the standard DIN 38 414, part 8 [31]. Gas composition analysis was performed

on a Clarus 500 gas chromatograph (Perkin-Elmer, India), equipped with a Thermal Conductivity Detector (TCD-R) and a gas analyzer model 4016 Arnel Total Chrom Work-station software.

Mathematical model

The ADM1 model developed by the IWA AD Modeling Task Group is arguably the most widely applied model in the research area [32]. The ADM1 model is a structured model that describes the processes involved in the conversion of complex organic substrates into methane, carbon dioxide, and inert by-products. The breakdown products are hydrolyzed into sugars, amino acids, and Long Chain Fatty Acids (LCFA). Carbohydrates and proteins are fermented to produce volatile organic acids and molecular hydrogen while LCFAs are oxidized anaerobically to produce acetate and molecular hydrogen. Propionate, butyrate and valerate are converted into acetate (acidogenesis) and molecular hydrogen, and further methane is produced by the decomposition of acetate into methane (acetic methanogenesis) and the reduction of carbon dioxide with molecular hydrogen (hydrogen trophic methanogenesis). ADM1 includes:

- 19 biochemical processes, of which 4 equations capture particulate matter degradation, 8 equations describe soluble matter degradation and 7 equations represent biomass concentrations;
- 6 acid/base equilibria in association with pH calculation;
- 3 gas-liquid transfer processes (CH_4, CO_2, H_2);
- inhibitions, and
- several variables, of which 12 variables represent particulates (Xi), 24 variables represent soluble (Si) and 3 variables represent gases.

The mathematical model used in this research can be found in the original research by *Batstone et. al*., [12].

Table 1: Results of physico-chemical analysis of waste

Parameter	Unit	Sludge	Fruit and vegetable waste (FVW)	Sludge + 25% FVW
TS	%	4.27	6.80	6.10
VS	%	2.77	6.00	4.68
pH	-	7.89	4.90	7.29
EC	mS/cm	3.70	14.01	13.56
COD	g/kg	48.56	91.23	74.86
TKN	g/kg	1.49	3.80	1.75
$N\text{-}NH_4$	mg/kg	58.31	115.50	92.98
NH_3	mg/kg	15.58	19.64	18.80
total P	g/kg	11.06	12.68	12.20
VFA	g/kg	6.90	11.46	10.78

Numerical simulation and sensitivity analysis of the ADM1 model

The ADM1 model is implemented in the MATLAB software package (MathWorks, R2016a, USA). The model consists of 39 differential equations and a large number of algebraic equations, both linear and non-linear. The implemented model can be used as an independent model for testing a specific composition or can be used as a base for further applications. The input data used were recalculated as kg COD/m^3 and kmole/m^3 (kmole/$m^3 \equiv$ M). The unit of g COD/m^3 is used for the concentrations of substrates and biomass, where the g N/m^3 and mole/m^3 are for Nitrogen and inorganic carbon (IC) respectively. The other physical units of bar (pressure), m (distance), m^3 (volume) and day (time) are used. The MATLAB solver ODE23s was used for the simulation, which is suitable for solving rigid systems, i.e. systems with rigid tolerance. To apply the simulation results in real plants, it is important to define how the model parameters affect the reliability of the results.

The sensitivity of the model was calculated using the finite difference method, which, like other methods, gives indications about which parameters must be examined in a given mathematical model. The sensitivity of the model in this paper was tested for methane production and pH value, for parameter variations of ±1%.

A file was created in MATLAB to perform the sensitivity analysis and graphical representation of the results. To apply the simulation results in real plants, it is important to define how the model parameters affect the reliability of the results. The equation used to calculate methane production and pH values are:

$$sensitivity = [f(x \cdot 1 \pm 0.01) - f(x)] \quad (5)$$

werein:

x-observed parameter,

sensitivity-change in objective function, i.e. change in pH and methane production,

f(x)-observed objective function.

The created MATLAB file loads the initial parameters and calculates the methane production or pH values for the unchanged system then, for the changed parameter value, calculates the new value of the objective function followed by calculating the sensitivity according to Eq. (5).

Characterization of substrate input

Table 1 shows the experimental data that were used to start the main program for the optimization of kinetic parameters and the simulation of the anaerobic digestion process with the ADM1 model. The above data were converted to the appropriate units and values that are necessary for the application of the ADM1 mathematical model.

Table 2 presents the physicochemical and stoichiometric constants used in the model, while the biochemical constants are taken from the literature [33].

RESULTS AND DISCUSSION

Simulation of the process of co-digestion of sewage sludge and fruit and vegetable waste

Considering that to run the numerical simulation of the ADM1 mathematical model, it is necessary to recalculate the input data obtained from the physicochemical analysis of the substrate (Table 1). In Table 3 the input data values for the ADM1 model are given. The flow of the material in the model can be seen

Table 2: Physico-chemical and stoichiometric constants used in the model for simulation

Parameter	Value	Unit	Reference
k_{La}	200	d^{-1}	*Roséni Jeppssons* (2006) [33]
$K_{H_{CO_2}}$	$0.035 \exp\left(\frac{-19410}{R \cdot 100}\left(\frac{1}{T}-\frac{1}{T_{op}}\right)\right)$	$M_{liq}\ bar^{-1}$	
$K_{H_{CH_4}}$	$0.0014 \exp\left(\frac{-14240}{R \cdot 100}\left(\frac{1}{T}-\frac{1}{T_{op}}\right)\right)$	$M_{liq}\ bar^{-1}$	
$K_{H_{H_2}}$	$7.8\ e\ {-4} \exp\left(\frac{-19410}{R \cdot 100}\left(\frac{1}{T}-\frac{1}{T_{op}}\right)\right)$	$M_{liq}\ bar^{-1}$	
$f_{ac.aa}$	0.40	-	
$f_{bu.aa}$	0.26	-	
$f_{bu.su}$	0.13	-	
$f_{fa.li}$	0.95	-	
$f_{H_2.aa}$	0.06	-	
$f_{H_2.su}$	0.19	-	
$f_{pro.aa}$	0.05	-	
$f_{pro.su}$	0.27	-	
$f_{va.aa}$	0.23	-	
$f_{sI.xc}$	0.10	-	
$f_{xI.xc}$	0.20	-	
Y_{aa}	0.08	-	
Y_{c_4}	0.04	-	
Y_{H_2}	0.06	-	
$Y_{lac.f}$	0.055	-	
$Y_{lac.o}$	0.055	-	
Y_{pro}	0.04	-	
N_{aa}	0.007	$kmolN \cdot (kgCOD)^{-1}$	
N_{ac}	0.08/14		
N_I	0.06/14		
N_{xc}	0.0376/14		
$f_{ac.su}$	0.41	-	Kleerebezem & Loosdrecht (2006) [34]
$f_{ch.xc}$	0.20	-	
$f_{li.xc}$	0.30	-	
$f_{pr.xc}$	0.20	-	
Y_{su}	0.11	-	
Y_{ac}	0.04	-	
Y_{fa}	0.06	-	

as the flow of COD in the model. Fractionation of organic substrates is required as an input state variable for ADM1. The methodology described in paper [35] was used to obtain the above data. The calculation of the COD proportion of proteins, lipids and carbohydrates was obtained by the methodology described by Girault [36] and the calculated values were: 19.65%, 8.35% and 71.90% for proteins, lipids and carbohydrates respectively.

Fig. 2 shows a comparison of the simulation results with the experimental results from the pilot reactor.

The biggest problem of applying the ADM1 model is the conversion of experimentally measured quantities into the units used in the ADM1 model.

Table 3: Model input

Variable	Value	Unit
Ssu,in	0.0250	$kgCODm^{-3}$
Saa,in	0.0420	$kgCODm^{-3}$
Sfa,in	0.0260	$kgCODm^{-3}$
Sva,in	0.0001	$kgCODm^{-3}$
Sbu,in	0.0001	$kgCODm^{-3}$
Spro,in	0.57600	$kgCODm^{-3}$
Sac,in	0.5700	$kgCODm^{-3}$
Sh2,in	2.22E-09	$kgCODm^{-3}$
Sch4,in	2.22E-06	$kgCODm^{-3}$
SIC,in	0.0480	$kmoleCm^{-3}$
SIN,in	0.0909	$kmoleNm^{-3}$
SI,in	0.0100	$kgCODm^{-3}$
Xxc,in	0.1543	$kgCODm^{-3}$
Xch,in	0.2413	$kgCODm^{-3}$
Xpr,in	0.0656	$kgCODm^{-3}$
Xli,in	0.1203	$kgCODm^{-3}$
Xsu,in	0.0220	$kgCODm^{-3}$
Xaa,in	0.0118	$kgCODm^{-3}$
Xfa,in	0.0024	$kgCODm^{-3}$
Xc4,in	0.0043	$kgCODm^{-3}$
Xpro,in	0.0137	$kgCODm^{-3}$
Xac,in	0.0760	$kgCODm^{-3}$
Xh2,in	0.0317	$kgCODm^{-3}$
XI,in	29.85	$kgCODm^{-3}$
Scat,in	0.0706	$kmolem^{-3}$
San,in	0.0200	$kmolem^{-3}$
S,vam	2.13E-4	$kgCODm^{-3}$
S,bum	3.417E-4	$kgCODm^{-3}$
S,prom	0.5740	$kgCODm^{-3}$
S,acm	0.5657	$kgCODm^{-3}$
S,hco3m	0.0463	$kmoleCm^{-3}$
S,nh3	2.83E-4	$kmoleNm^{-3}$
Sgas,h2	7.4E-06	$kgCODm^{-3}$
Sgas,ch4	0.0514	$kgCODm^{-3}$
Sgas,co2	0.0053	$kmoleCm^{-3}$

The majority of the study shows, that the system pH is the most important parameter, which greatly affects the co-digestion process [37]. However, as can be seen from Fig. 2 (a), the initial pH value obtained by the model is 8.13, while the experimentally measured value is 7.29 so there is a negligible deviation in the case of the initial pH value. Given that the pH value depends on other variables that are converted to COD and some of them are SIN, Snh_3, SIC and which cannot be corrected, it is necessary to check the values of the constants that affect the pH value during the digestion process. The works of *Batstone et. al.*, [12] and *Rossen and Jeppsson* [33] describe in detail the calculation of the pH value, in which, among other things, constants such as pKa values of valeric, butyric, propionic acid, Ka,

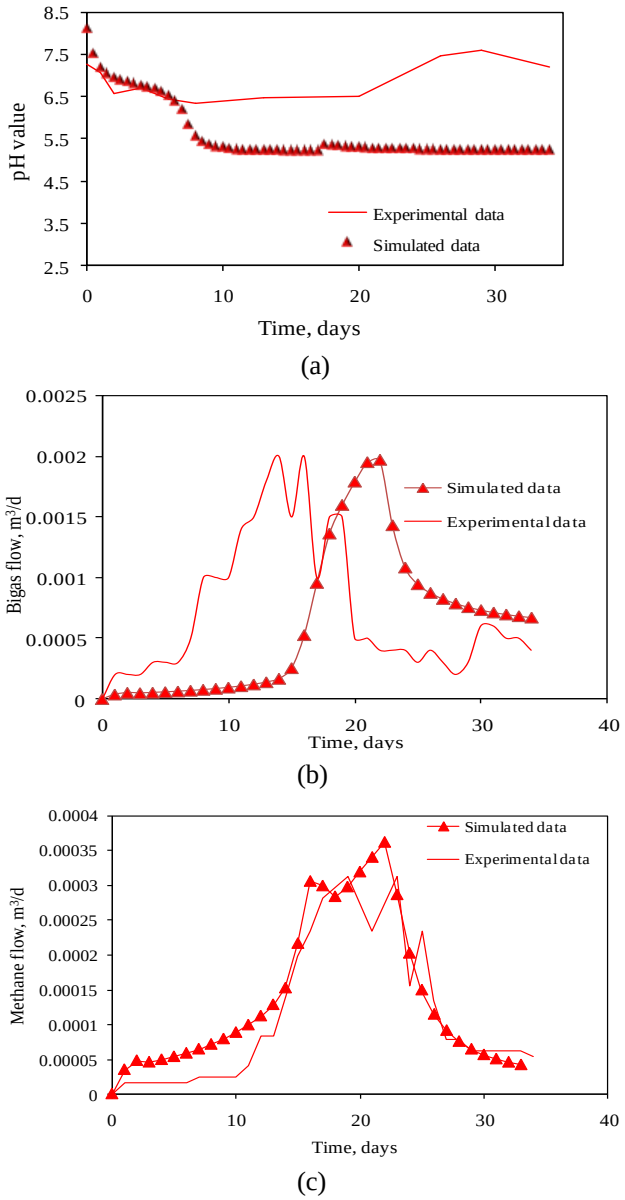

Fig. 2 Simulation results versus experimental values: (a) pH value; (b) biogas production; (c) methane production.

and Kw constants are shown, it is necessary to check the influence of these values constants to the change in pH value. Also, after the seventh day (Fig. 2 (a)), the pH value obtained by simulation drops sharply compared to the pH value obtained experimentally, which is much closer to the neutral pH value. A sudden drop in pH value indicates the processes of acidogenesis and acetogenesis, which in the ADM1 model are described by thermodynamic reactions only for a narrow interval of hydrogen concentration. Hydrogen inhibition for acetogenesis is the simple non-competitive inhibition used

in the model and liquid-phase hydrogen concentration is used for hydrogen inhibition [38]. Also, a drop in pH value can lead to a change in biogas production, due to the processes that occur during the key stages of the anaerobic digestion process, such as acidogenesis and acetogenesis. The optimal pH values for mesophilic digestion are in the range of 6.5 to 8, and inhibition of the process occurs if the pH value falls below 6 or rises above 8.3 [39]. The accumulation of volatile fatty acids leads to a lowering of the pH value. The reasons for this deviation should be sought in the ADM1 model and the inhibition predicted by the model.

When it comes to biogas production, the comparison results are significantly better (Fig. 2 (b)). The profile of biogas production obtained by simulation fully follows the profile of experimental data, with the model data being slightly shifted to the right. The model predicts a significant production of biogas only after 15 days, while the experiment shows significantly faster production. The maximum difference of 0.19% is found on the fifteenth day, during the maximum biogas production obtained by the experiment. The maximum production of biogas by the model occurs only after 20 days, so the stated deviations between experimental and simulation data are due to differences in the time of biogas production. Most researchers have shown that the co-digestion process with food waste (fruits and vegetables) significantly accelerates the co-digestion process [40]. Similarly, as in the case of the verification of the pH value, the gas production predicted by the model is significantly slower, i.e. the hydrolysis process is significantly slower compared to the actual co-digestion process and the possible cause is inhibition, which needs to be investigated. Most of the researchers who modeled the process of co-digestion with experimental data obtained somewhat different deviations, which are mainly related to the beginning of the digestion process, where the deviations are the largest.

When it comes to methane production Fig.2 (c), the deviations are significantly smaller, the model perfectly describes the data obtained by the experiment and methanation starts at the same time. Given that the percentage of methane ranges from 50-60% in the total amount of biogas produced at the end of the process [15, 41], it is necessary to check the model and parameters that affect the amount of biogas produced and its composition. As a percentage, the amount of methane obtained experimentally is 64.64% (0.000314 m^3/day) and this value reached on the 19th day, while in the case of the data obtained by simulation, this value was 69.86% of the produced biogas (0.0003612 m^3/day) and that was on 22nd day. According to the data obtained by simulation, biogas production starts significantly later compared to experimental data and methane production. The maximum deviations of the simulated and experimental data for the amount of methane produced are 26.5% which happened on the 21st day. As can be seen in Fig. 2 (c), the experimental data show a decrease in the amount of methane produced on the 21st and 24th days, which can be explained by the fact that samples were taken for analysis at that moment.

Parameter sensitivity analysis

Although the ADM1 model represents a standard model for simulating the digestion process, in most cases it is necessary to calibrate the parameters in the model, to better match the data. It is especially important to calibrate parameters in co-digestion processes due to the heterogeneity of the composition of the substrate undergoing the digestion process. Danielsson (2014) states [38], in the case of dynamic change of input variables, there is a change in the sensitivity of the parameters. The reason why the sensitivity analysis was performed in the manner described earlier lies in the fact that the ADM1 model is described by a large number of parameters and constants that individually or simultaneously greatly affect the final result of the simulation. Ultimately, the efficiency of the anaerobic digestion process and the numerical simulation of this process are reflected in the amount of methane produced. Due to the mentioned fact, the selected objective function for the sensitivity analysis is methane production. To adequately select the parameters that would undergo the calibration-optimization process, it is necessary to perform a sensitivity analysis in the manner described earlier in the paper. Below are the results of the sensitivity analysis of the ADM1 model, in which the influence of 53 parameters was examined. Parameters subjected to sensitivity analysis are biochemical constants and stoichiometric coefficients that Fig. in the ADM1 mathematical model [12]. Table 4 lists the parameters and constants that were subjected to sensitivity analysis, i.e. testing their impact on methane production.

Each of the parameters was increased or decreased by 1% and a sensitivity value was given for each variation.

Tabel 4 Parameters for sensitivity analysis

Name of Parameter	Abbrev.	Position	Name of Parameter	Abbrev.	Position	Name of Parameter	Abbrev.	Position
Solubile inerts, particulate inerts, carbohydrates, proteins and lipids from composites Yield of: H_2, Butyrate, Propionate, acetate on sugar	f_sI_{xc}	1	Monod maximum specific uptake rate for amino acid	k_m_{aa}	33	No inhibition on acetate degradation when pH is above this level	pH_UL_{ac}	47
	f_xI_{xc}	2						
	f_ch_{xc}	3						
	f_pr_{xc}	4	Monod half saturation value for amino acids	K_S_{aa}	34			
	f_li_{xc}	5						
	f_h2_{su}	6						
	f_bu_{su}	7	Monod maximum specific uptake rate for LCFA	k_m_{fa}	35			
	f_pro_{su}	8						
	f_ac_{su}	9						
Yield of: H_2, Valerate, Butyrate, Propionate, Acetate on amino acids	f_h2_{aa}	10	Monod half saturation value for LCFA	K_S_{fa}	36	Full inhibition on acetate degradation when pH is below this level	pH_LL_{ac}	48
	f_va_{aa}	11						
	f_bu_{aa}	12						
	f_pro_{aa}	13						
	f_ac_{aa}	14						
Yield of biomass on: sugar, amino acid, fatti acid, Butyrate and Valerate particulate	Y_{su}	15	Hydrogen inhibitory concentration for LCFA	$K\_I\_h2_{fa}$	37	Monod maximum specific uptake rate for H_2	k_m_{h2}	49
	Y_{aa}	16						
	Y_{fa}	17	Monod maximum specific uptake rate for valerate & butyrate	k_m_{c4}	38	Monod half saturation value for H_2	K_S_{h2}	50
	Y_{c4}	18						
Yield of biomass on: Propionate, Acetate, H_2, Particulate lactate (fermentation and oxidation) Disintegration factor	Y_{pro}	19	Monod half saturation value for valerate & butyrate Hydrogen inhibitory concentration for valerate & butyrate	K_S_{c4}	39	No inhibition on H_2 degradation when pH is above this level	pH_UL_{h2}	51
	Y_{ac}	20						
	Y_{h2}	21						
	Y_lac_f	22				Full inhibition on H_2 degradation when pH is below this level	pH_LL_{h2}	52
	Y_lac_o	23		$K\_I\_h2_{c4}$	40			
	k_{dis}	24						
Hydrolysis rate constant for carbohydrates, protein and lipids Monod half saturation constant of Inorganic nitrogen	k_hyd_{ch}	25	Monod maximum specific uptake rate for propionate	k_m_{pro}	41	Inhibition constan for VFA	K_I_{vfa}	53
	k_hyd_{pr}	26						
	k_hyd_{li}	27	Monod half saturation value for propionate	K_S_{pro}	42			
	K_S_{IN}	28						
Monod maximum specific uptake rate for monosaccharide	k_m_{su}	29	Hydrogen inhibitory concentration for propionate	$K\_I\_h2_{pro}$	43			
Monod half saturation value for monosaccharide	K_S_{su}	30	Monod maximum specific uptake rate for acetate	k_m_{ac}	44			
No inhibition on amino acid when pH is above this level	pH_UL_{aa}	31	Monod half saturation value for acetate	K_S_{ac}	45			
Full inhibition on amino acid when pH is below this level	pH_LL_{aa}	3	Inhibition constan for NH_3	K_I_{nh3}	46			

Even though the sensitivity of the parameters can only be investigated based on a +1% change in the parameter value, the paper also performed a sensitivity analysis for a -1% change in the parameters. The reason for this is

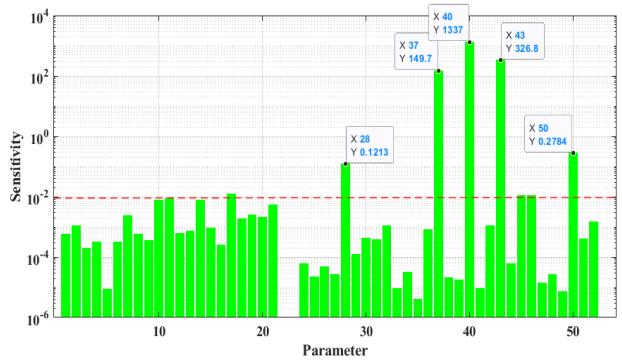

Fig. 3: Change in methane production for parameter variation +1%

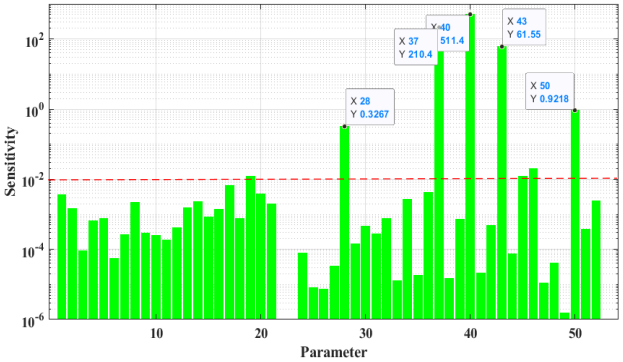

Fig. 4: Change in methane production for parameter variation -1%

the ability to observe how parameters affect changes in target production. Table 4 shows the parameters whose value was changed. Figs. 3 and 4 show the results of the sensitivity analysis.

The sensitivity of the model, i.e. the production of methane for changing the parameters, ranged from 10^{-6} to 10^{3}. Considering that there are a large number of parameters that were subjected to sensitivity analysis and a wide sensitivity interval, only parameters whose sensitivity amounted to above 10^{-2} were selected for the most sensitive parameters. By the above, as seen in Figs. 3 and 4, the most sensitive parameters are: Monod half-saturation constant of Inorganic nitrogen (*K_SIN*), hydrogen inhibitory concentration constant for LCFA (*K_I_h2fa*), hydrogen inhibitory concentration constant for valerate & butyrate (*K_I_h2c4*), hydrogen inhibitory concentration constant for propionate *(K_I_h2pro)* and Monod half-saturation constant for H_2 *(K_Sh2)*. Of the mentioned parameters, the hydrogen inhibitory concentration constant for valerate & and butyrate degraders showed the highest sensitivity for both cases of variation, with the model's sensitivity being slightly lower for negative variation.

The sensitivity analysis showed slightly unexpected results considering that the most sensitive parameters are related to biochemical constants, namely constants related to process inhibition and half-saturation constants. It is interesting that for the case of the parameters: *K_SIN*, *K_I_h2fa* and *K_Sh2*, negative variations increase the sensitivity value of the model. The constants *K_I_h2* affect the inhibition function of hydrogen to the uptake of propionate, fatty acids, valerate and butyrate.

In most of the earlier studies in which sensitivity analysis was performed, and which were performed in different ways, model sensitivity analyses showed the sensitivity of the model to dissociation and hydrolysis constants, then Monod's constants (maximum specific consumption of sugar, protein, etc.)[42-44]. Given that the ADM1 model was primarily developed for the simulation of the process of anaerobic digestion of sludge, and in this research, the co-digestion of sludge and fruit and vegetable waste was performed, the performed sensitivity analysis shows that the model has considerable limitations with the change of substrate, i.e. the addition of co-substrate. Considering the results of the simulation and the sensitivity analysis, the first three phases of the process (hydrolysis, acidogenesis and acetogenesis) are strongly inhibited by the presence of co-substrates, i.e. fruits and vegetables. Since the sensitivity analysis of the ADM1 model was performed, the given explanation refers only to the model. The most sensitive parameters, the inhibition constants related to hydrogen, come to the fore only in the acetogenesis phase. In this phase, among other things, acetic acid and H_2 are formed, which explains the lower pH value (Fig. 2 (a)) and the weak methanogenesis that takes place in parallel with acetogenesis, due to the inhibition of H_2. In the paper (*Koch et al*., 2013) [45], only changes in hydrogen inhibition constants and acetate absorption maxima compared to the suggested values according to ADM1 were needed to match the measurement.

Figs. 5 and 6 show the sensitivity of pH values to variations in the parameters of±1%.

Compared to the sensitivity of methane production, the sensitivity of the change in pH value is significantly higher, that is, the number of parameters that affect pH is greater. As can be seen in Figs. 5 and 6, the sensitivity value greater than 10^{-2} is marked with a blue line and a large number of parameters in that interval affect the pH

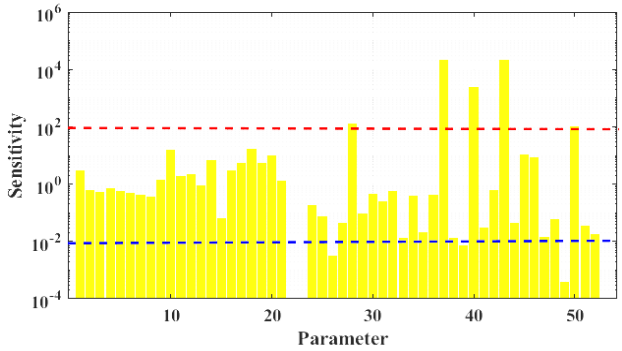

Fig. 5: Change in pH for parameter variation +1%

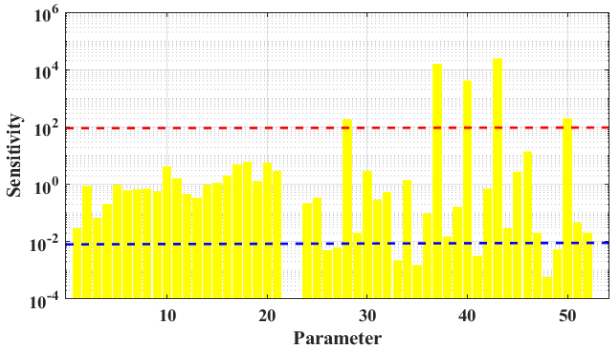

Fig. 6: Change in pH for parameter variation -1%

value, and some of them are stoichiometric coefficients (Table 4 stoichiometric coefficients from 1-20). However, adjusting a large number of parameters in the ADM1 model requires high-end computer equipment, appropriate software and methods. Accordingly, the sensitivity value above 10^2 is marked with a red line. In that case, only three parameters show the sensitivity of the model, namely: hydrogen inhibitory concentration constant for LCFA (K_I_h2fa), hydrogen inhibitory concentration constant for valerate and butyrate (K_I_h2c4), hydrogen inhibitory concentration constant for propionate *(K_I_h2pro)*. In all three cases, it is about the same constants that affect methane production, that is, the hydrogen inhibition constants. As significant deviations were observed in the previous part of the research, which pointed to the problem of inhibition, in this case, inhibition by hydrogen, special attention should be paid to the phase of the process that describes the generation of hydrogen and its participation in the reactions of methane generation. The model inhibits the process of converting acetate into products, which slows down and reduces biogas production and mechanization. For the case of a parameter variation of -1%, sensitivity greater than 10^2 is shown by the Monod half saturation constant of Inorganic nitrogen (K_SIN) and Monod half saturation constant for H_2 (*K_Sh2)*, that is, they are the same constants as in the case of a change in methane production. It can be said that the ADM1 model is sensitive to the same parameters regardless of the selection of the objective function when performing the sensitivity analysis. *Koch et al*., [45] and *Bulkowska et al*. [15] reached similar results in their research.

Also, comparing the values of sensitivity for the objective functions, the pH value shows a significantly higher sensitivity. In accordance with the above, it is necessary to calibrate the most sensitive parameters in future research. Also, in this research, direct validation was performed, so it is necessary to perform cross-validation of the model with the specified set of the most sensitive parameters for the co-digestion of waste sludge and fruit and vegetable waste.

CONCLUSIONS

In the research, an experimental and numerical simulation of the co-digestion process of waste sludge with fruit and vegetable waste was conducted. Experimental data for pH value, biogas production and methane production indicate the usual trend for batch systems although there is a possibility of inhibition. For the numerical simulation, the ADM1 mathematical model of the anaerobic digestion process was applied, which was primarily developed for the simulation of the waste sludge digestion process, so as expected, certain deviations were observed between the experimentally and numerically obtained data. The best agreement was obtained for the case of methane production, but with the slightly slower biogas production obtained numerically. The sensitivity analysis, which was performed for the case by variation of 53 parameters (±1%), for two objective functions (change in pH value and change in methane production), showed that the most sensitive parameters are: Monod half saturation constant of Inorganic nitrogen (K_SIN), hydrogen inhibitory concentration constant for LCFA (K_I_h2fa), hydrogen inhibitory concentration constant for valerate & butyrate (K_I_h2c4), hydrogen inhibitory concentration constant for propionate (K_I_h2pro) and Monod half saturation constant for H_2 (K_Sh2). The mentioned ADM1 model parameters indicate that the addition of co-substrate significantly affects the numerical simulation of biogas production.

In future research, adjustment of the most sensitive parameters of the ADM1 model for the co-digestion process is necessary, especially regarding hydrogen inhibition constants and fruit and vegetable waste as a cosubstrate. The results of this research represent a significant source of information for the modelling of anaerobic co-digestion process of waste sludge with fruit and vegetable waste.

Nomenclatures

ADM1	Anaerobe Digestion Model no. 1
COD	Chemical Oxygen Demand
NH4-N	Ammonium Nitrogen (g/L)
pH	Power of Hydrogen
R	Universal gas constant
V	Volume(m^3/day)
V_{gas}	Volume of gas phase (m^3)
Vliq	Volume of liquid phase (m^3)
VFA	Volatile Fatty Acids
kLa	Gas-liquid transfer coefficient d^{-1}
Ka	Acid-base equilibrium constant M ($kmole/m^3$)
K_I	inhibition constant kgCOD/m^3
K_S	Monod half saturation constant kgCOD/m^3
Ni	nitrogen content of component I kmoleN/kg COD[1]
pgas	The pressure of gas Bar
pKa	–log10[Ka]
q	flow m^3
Si	soluble component i kgCOD/m^3
SI	inhibitory component kgCOD/m^3
t	time day
f_(product,substrate)	product yield in substrate (-)
I_(inhibitor, process)	inhibition function (-)
K_(a,acid)	acid-base balance coefficient ($kmol/m^3$)
K_(A/Bi)	acid-base kinetic parameter ($kmol/m^3d$)
k_dis	coefficient of the first order for the hydrolysis process (d^{-1})
k_La	gas-liquid transfer coefficient (d^{-1})
k_(m,process)	Monod maximum rate constant (d^{-1})
k_process	First-order parameter (d^{-1})
K_(I, inhibitor, process)	inhibition constant (kg/COD^3)
K_(S, process)	semi-saturation constant (kg/COD^3)
N_(i)	Nitrogen content of component i (kmol N /kg COD)
S_(gas,i)	Gas phase concentration, i (kg COD/m^3)
S_(in,i)	The initial concentration of component i (kg COD/m^3)
S_su	substrate concentration (kg COD/m^3)
S_(su,in)	substrate concentration at the entrance (kg COD/m^3)
Ssu	Soluble component sugar
Saa	Soluble component amino acid
Sfa	Soluble component fatty acid
Sva	Soluble component valerate
Sbu	Soluble component butyrate
Spro	Soluble component propionate
Sac	Soluble component acetate
Sh2	Soluble component hydrogen
Sch4	Soluble component methane
SIC	Soluble component inorganic carbon
SIN	Soluble component inorganic nitrogen
SI	Soluble component inerts
Xc	Particulate component composites
Xch	Particulate component carbohydrates
Xpr	Particulate component proteins
Xli	Particulate component lipids
Xsu	Particulate component sugar
Xaa	Particulate component amino acids
Xfa	Particulate component fatty acids
Xc4	Particulate component
Xpro	Particulate component propionate
Xac	Particulate component acetate
Xh2	Particulate component hydrogen
XI	Particulate component inerts
Scat	Soluble component cations
San	Soluble component anions
Sva-	Soluble component valerate ions
Sbu-	Soluble component butyrate ions
Spro-	Soluble component propionate ions
Sac-	Soluble component acetate ions
Shco3-	Soluble component hydrogen carbonate
Snh3	Soluble component ammonia ions
Sgas,h2	Soluble component hydrogen gas
Sgas,ch4	Soluble component methane gas
Sgas,co2	Soluble component carbon dioxide gas

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