Effects of mixture ratio of cow manure and greenhouse wastes on anaerobic co-digestion process

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Abstract: The biogas production from the agricultural wastes is accepted as an eco-friendly solution for keeping up with increasing energy demand in the world. The cow manure which is produced in every farm is readily available source for biogas production via anaerobic digestion. The main limitation for biogas production from manure is the inhibition of anaerobic microorganisms resulted from the high ammonia/ammonium content of manure. The co-digestion of manure with agricultural wastes is frequently applied to cope with this limitation. This study aims to investigate the biogas production from the co-digestion of cow manure and greenhouse residues in different mixing ratios as input materials. Tomato and pepper wastes from greenhouses were selected as co-substrates and optimum mixing ratios for maximum biogas yield from co-digestion of cow manure with tomato and pepper wastes were determined as 55:45 and 25:75, respectively. Along with the biogas production, co-digestion kinetics was also evaluated for biogas production from cow manure and tomato with the help of well-known mathematical models. The results indicated that the co-digestion of cow manure with greenhouse wastes is a viable option for the biogas production.

Keywords: Agricultural wastes, biochemical methane production, co-digestion, cow manure

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1 Introduction

Pepper (Capsicum annuum L.) and tomato (Lycopersicon esculentum) which belong to the plant family Solanaceae, are among the important vegetables grown in Turkey. While tomatoes and peppers are grown in many countries in the world, Turkey is one of the important countries in the production of tomatoes and peppers due to favorable climatic conditions. According to Turkish Statistics Institute data, total tomato and pepper production in Turkey were about 11,820,000 t and 2,159,348 t, respectively, in 2013 (TUIK, 2013).

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Anaerobic digestion (AD) is a biological process in which microorganisms break down organic matter into energy rich biogas in the absence of oxygen. A well-managed AD system aims to maximize methane production, but not release any gases to the atmosphere (Defra, 2009). If AD can operate in well-managed way under optimum process conditions, it can make an important contribution in farming sector in terms of renewable energy production and environmental protection. Anaerobic digestion also contributes in the mitigation of greenhouse gas emissions and to improve the nutrient management with the integration of anaerobic digestion plants into manure management systems (Defra, 2009). However, extensive researches on biogas production potential from manure had revealed some limitations. Main limitation is the inhibition of anaerobic microorganisms resulted from the high ammonia/ammonium content of manure. The co-digestion of manure with crop residues is frequently applied for cope with this limitation. Co-digestion of manure with agricultural wastes can increase the biogas production via (i) maintaining an optimal pH for bacteria; (ii) decreasing free ammonia/ammonium inhibition and (iii) providing a better carbon/nitrogen ratio (C/N) during AD (Xie et al., 2011).

In summary, during the co-digestion of manure with agricultural residues, the manure fraction provides a wide range of nutrients while the high carbon content of the plant materials results in a balanced carbon/nitrogen ratio of the feedstock being loaded in the digester (Lehtomaki et al., 2007).

In this context, the aim of this study is to investigate the biogas production from the co-digestion of cow manure and green house wastes (agricultural wastes) in different mixing ratios as input materials. Tomato and pepper wastes from greenhouses, which are most abundant agricultural wastes in Antalya region of Turkey, were selected as co-substrates to investigate the effect of co-digestion on the biogas production from cow manure. In order to find optimum mixture ratios, cow manure mixed with tomato and pepper wastes in different ratios (100:0, 85:15: 70:30, 55:45, 40:60, 25:75, 10:90) and batch biochemical methane potential (BMP) tests were carried out in mesophilic (37 ℃) conditions. Along with the biogas production, co- digestion kinetic constants derived from the mathematical models (The modified Gompertz equation, Transference function and the First-Order reaction kinetic) were also evaluated.

2 Materials and methods

2.1 Raw material

Greenhouse residues were provided from greenhouses which harvested in Jan 2014. The greenhouse residues principally comprise of roots, stalks, leaves and fruits from pepper and tomato cultivation, grounded to 4–5 mm particle size. Processed greenhouse residues are stored in closed plastic bags at −20 ℃ until used for BMP tests. Before the BMP tests, characterization analysis were carried out with tomato, pepper residues and cow manure. The analyses of dry matter (TS), organic matter (VS), chemical oxygen demand (COD) were performed according to standard methods (APHA, 1995). Carbohydrate concentration was determined as glucose by Anthrone method based on quantifying the carbonyl functions (C=O) (Dreywood, 1946). Protein concentration was determined according to Lowry method (Lowry, 1951). The characterization analysis results of tomato and pepper residues and cow manure are presented in Table 1.

Table 1 Characterization of tomato and pepper residues and cow manure

Parameter	Tomato Residues	Pepper Residues	Cow Manure
TS (gTS/kgSample)	158.77	128.43	193.70
VS (gVS/kgSample)	132.44	104.35	149.64
tCOD (mg COD/gVS)	561.57	1154.14	2072.93
sCOD (mg COD/gVS)	301.17	258.70	300.72
tCarbohydrate (mg Glucose/gVS)	129.76	92.54	590.14
sCarbohydrate (mg Glucose/gVS)	43.80	69.39	56.20
Protein (mgPro/gVS)	280.75	416.50	320.05

Note: t: total, s: soluble

2.2 Biochemical methane potential test

Methane production via co-digestion of cow manure with tomato/ pepper residues was measured with batch BMP tests under mesophilic (37 ℃) conditions according to procedure described by Carrere et al. (2009). The mixture of cow manure and tomato or pepper residues with anaerobic seed sludge which supplied from Hurma municipal wastewater treatment plant (Antalya, Turkey) were put into 500 ml reactor. The adjusted value for food to microorganisms (F/M) ratio was 0.5 (gVS waste /gVS anaerobic seed sludge) with the solid loading of 15% TSS in BMP bottles.

The buffer solution and oligo nutrients were ensured in BMP reactors as follows (the concentrations are presented in mg/L in parenthesis): $NaHCO_3$ (2600), NH_4Cl (172), KH_2PO_4 (65), $MgCI_2$. $6H_2O$ (39), $CaCl_2.2H_2O$ (19), $FeCl_2.4H_2O$ (20), $CoCl_2.6H_2O$ (5),

$MnCl_2.4H_2O$ (1), $NiCl_2.6H_2O$ (1), $ZnCl_2$ (0.5), H_3BO_3 (0.5), Na_2SeO_3 (0.5), $CuCl_2.2H_2O$ (0.4), $Na_2(Mo)O_4.2H_2O$ (0.1). At the beginning of the BMP test, the pH was adjusted to neutral pH in all BMP reactors. BMP analyses were set in triplicate for all samples. The BMP tests were also accomplished with inoculum to take account of the biomethane produced by anaerobic seed sludge. For calculating the normalized cumulative methane potential for each sample, the quantity of methane produced by inoculum was diminished.

In order to obtain anaerobic condition in the BMP reactors the headspace of reactors was flushed with Nitrogen/Carbon dioxide (N_2/CO_2, 70/30%) gas mixture. BMP reactors were incubated at 37℃ and tests lasted until the biomethane production become unimportant. The volume of biogas was measured by water displacement device and its composition was determined using gas chromatography (GC, Varian 4900) equipped with a thermal conductivity detector (TCD) and 10 m PPQ column. The temperature of injector port, detector and column oven were 150℃, 145℃ and 150℃, respectively. Nitrogen was used as the carrier gas at a flow rate of 25 ml/min. A gas standard consisting of 60% (v/v) CH_4 and 40% of CO_2 was used for calibration.

2.3 Mathematical modelling

As the biomethane production potential is considered as a measure of the success in anaerobic treatment, evaluation of the methane potential is important for design and operation of anaerobic treatment systems. Since hydrolysis of complex organic material has been considered the rate-limiting step in anaerobic degradation, methane production data were analyzed for evaluating hydrolysis with first-order kinetics (FO) with equation introduced by Llabres-Luengo ve Mata-Alvarez (1987). Model calibration was performed by adjusting the hydrolysis rate constant (k_h), until the first order kinetic modeling results adequately matching with the cumulative methane production obtained in first three days of BMP tests. Additionally, first order kinetic was simulated to fit cumulative methane production throughout the BMP test in order to determination of the overall reaction rate constant (k_R).

Also, the most frequently used kinetic models, namely Gompertz equation and Transference were used to evaluate the co-digestion kinetic. The modified Gompertz equation (GM) is usually implemented for predicting the methane and/or hydrogen production (Buendia et al., 2009). The transference function (Reaction curve-type model) (RC) is also applied for evaluation of the anaerobic digestion (Redzwan and Banks, 2004). The parameters of biogas production potential (P), the maximum methane production rate (R_M) and duration of lag phase (λ) were estimated for each model according to best fit obtained between the experimental methane production profile and the model simulation. The optimization process ended when the change in the residual was less than the specified tolerance set on $1e^{-9}$. Model simulations were performed using the AQUASIM 2.0 (Reichert et al., 1998). For evaluating the co-digestion performance, a second term is added to each model for cumulative methane production due to different biodegradability level of components of co-digestion as proposed by Kim et al. (2003). Consequently, the models were modified as given in Table 2.

Table 2 Modified models used for the evaluation of the co-digestion performance

Model	Modified equations for co-digestion
Gompertz Model	$M_P = P_{M1}\exp\left(-\exp\left[\frac{R_{M1}\times e}{P_{M1}}(\lambda_1 - t)+1\right]\right) + P_{M2}\exp\left(-\exp\left[\frac{R_{M2}\times e}{P_{M2}}(\lambda_2 - t)+1\right]\right)$
Transference Model	$M_P = P_{M1}\left(1-\exp\left[-\frac{R_{M1}(t-\lambda_1)}{P_{M1}}\right]\right) + P_{M2}\left(1-\exp\left[-\frac{R_{M2}(t-\lambda_2)}{P_{M2}}\right]\right)$
First Order Model	$M_P = P_{M1}(1-\exp[-k_{h1}\times t]) + P_{M2}(1-\exp[-k_{h2}\times t])$

3 Result and discussion

3.1 Anaerobic co-digestion of cow manure with tomato residues

For the determination of the optimum mixing ratio for co-digestion of cow manure with tomato residues, the tomato residues were added as a 15%, 30%, 45%, 60%, 75%, 90% of total volatile suspended solid as a co-substrate to cow manure. The cumulative methane production profiles of co-digested cow manure (CM) and tomato residues (TR) were presented in Figure 1a and the normalized BMP of samples calculated with substracting the biogas production from the seed sludge were given in Figure 1b.

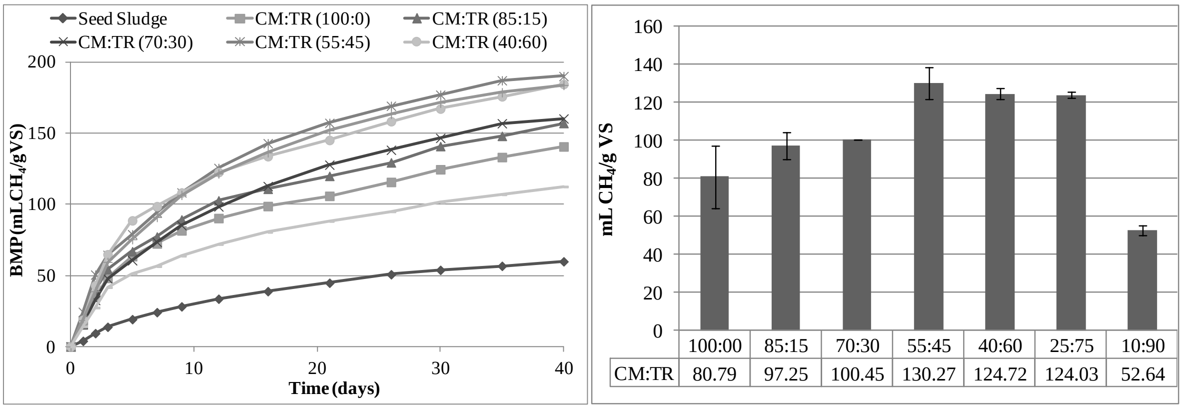

Figure 1 (a) Cumulative biomethane production from the co-digestion of cow manure (CM) and tomato residues (TR) (b) Normalized cumulative biomethane production from mixed samples

As can be seen from Figure 1, the highest cumulative methane production was obtained as 130.27 mlCH_4/gVS from co-digestion of cow manure with tomato resiues at a ratio of 55:45. In this ratio, the produced biomethane is almost 62% higher than the methane production obtained from the digestion of cow manure alone. Any more increase in the contribution of tomato residues as co-substrate leads a decrease in the biomethane production. Therefore, the mixing ratio of 55:45 was determined as an optimum mixing ratio for co-digestion of cow manure with tomato residues at a solid loading of 15%.

There are lots of studies investigating the BMP of cow manure in literature (Pretti Rao and Seenayya, 1994; Ahring et al., 2001; Lehtomäki et al., 2007; Ashekuzzaman et al., 2011). The ranges of cow manure BMP values are 128-310 ml CH_4/g VS. BMP results of cow manure from this study are lower than the findings reported in literature. Furthermore, there are very limited studies (Sozer, 2008; Saev et al., 2009) searching the co-digestion of cow manure with tomato residues in literature. Saev et al. (2009) co-digested the cow manure and tomato residues with the mixing ratio of 100:0, 60:40, 40:60 and 20:80 and the BMP values were found as 0.08, 0.18, 0.18 and 0.22 m^3 CH_4/kg VS, respectively. Result from this study for the co-digestion of cow manure with tomato residues is consistent with the results of Saev et al. (2009).

3.2 Anaerobic co-digestion of cow manure with pepper residues

Similar to co-digestion of cow manure with tomato residues, the pepper residues was also added as co-substrate for digestion of cow manure at a ratio of 15%, 30%, 45%, 60%, 75%, 90% of total volatile suspended solid. The cumulative methane production profiles of co-digested cow manure (CM) and pepper residues (PR) were presented in Figure 2a and the normalized BMP of samples calculated with substracting the biogas production from the seed sludge were given in Figure 2b.

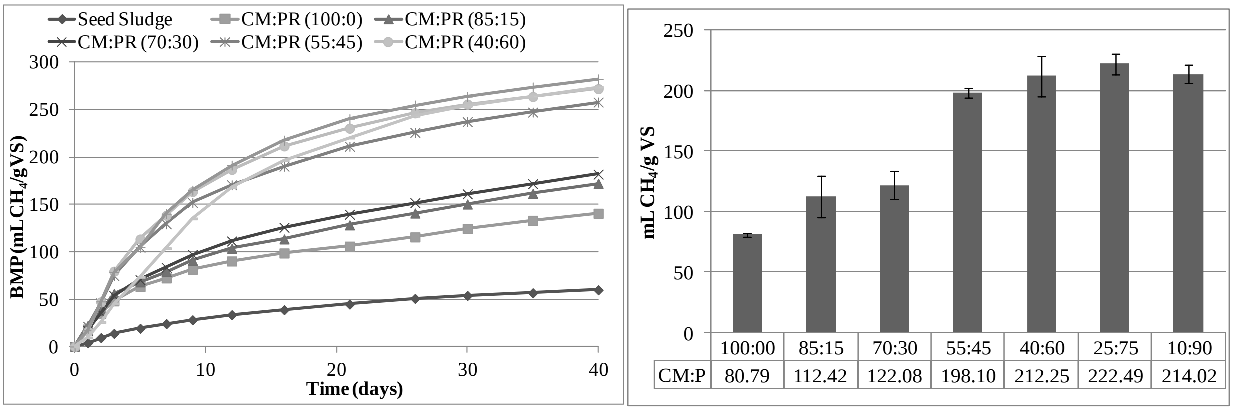

Figure 2 (a) Cumulative biomethane production from the co-digestion of cow manure (CM) and pepper residues (PR) (b) Normalized cumulative biomethane production from mixed samples

As illustrated in Figure 2, the relatively more biogas production was possible with the co-digestion of cow manure with pepper residues compared to co-digestion of cow manure with tomato residues. The highest cumulative methane production was achieved as 222.49 $mlCH_4/gVS$ which was 175% higher than the biomethane production from the digestion of cow manure alone. According to BMP test results, the optimum mixing ratio was determined as 25:75 for co-digestion of cow manure with pepper residues.There is only one work related to co-digestion of cow manure with pepper residues (Sozer, 2008) Sozer (2008) co-digested the cow manure and pepper residues with the mixing ratio of 70:30 and 90:10 at 7% VS and the BMP values were found as 146 and 9 ml CH_4/kg VS, respectively. Result from this study for the co-digestion of cow manure with pepper residues is parallel with the results of Sozer (2008).

3.3 Anaerobic co-digestion kinetic

Since the methane production from co-digestion of cow manure with tomato residues lower than the co-digestion of cow manure with pepper residues, this study focused to understand kinetics of co-digestion of cow manure with tomato residues by the help of well known mathematical modeling. As a first step, the kinetic parameters were determined for cow manure by the modified Gompertz equation (GM), reaction curve type model (RC) and the First-Order reaction kinetic (FO). The simulations were performed until the desired best fits were obtained between the experimental profile of cumulative individual methane production of cow manure and the model simulation. After the determination of the kinetic constants for digestion of cow manure, the differences in these constants were evaluated in case of co-digestion of cow manure with tomato residues. For determination of the kinetic constants of co-digestion, the modified models given in Table 2 were used. The kinetic constants of P, R_M and λ, k_R and regression coefficient for each model were determined as given in Table 3.

Table 3 Predicted kinetic parameters of co-digestion of cow manure with tomato residues

Mixing Ratio (CM:TR)	Model	Experimental BMP (ml/ g VS)	PM (ml/ g VS)	R_M (ml/g VS.d)	k_R (L/d)	λ (d)	R^2
	GM		80.00	7.445		0	0.920
100:0	RC	80.79	80.00	10.720		0	0.967
	FO		80.00		0.138		0.967
	GM		95.38	7.584		0	0.953
85:15	RC	97.25	91.10	10.720		0	0.971
	FO		104.26		0.138		0.979
	GM		96.46	7.584		0	0.986
70:30	RC	100.45	96.71	10.968		0	0.972
	FO		110.05		0.141		0.993
	GM		126.22	7.584			0.978
55:45	RC	130.27	129.87	10.968			0.991
	FO		124.87		0.141		0.983
	GM		118.24	7.358		0.058	0.960
40:60	RC	124.72	119.12	9.866		0	0.982
	FO		118.16		0.138		0.973
	GM		122.58	7.358		0.058	0.987
25:75	RC	124.03	122.89	9.866		0	0.997
	FO		116.09		0.138		0.985
	GM		51.39	7.163		0.182	0.934
10:90	RC	52.64	52.03	9.919		0	0.971
	FO		50.64		0.129		0.950

As seen from Table 3, the co-digestion of cow manure with tomato residues results with an increase in the maximum methane production rates (R_M) and overall reaction rate constant (k_R) until the contribution of tomato residues to be increased 45%. When the tomato residues were added more than the 45% of total volatile solid, the methane production rate and reaction rate of cow digestion was decreased. This is indicated that the optimum mixing ratio is 55:45 for co-digestion of cow manure with tomato residues similar to observed in BMP results.

Mähnert and Linke (2009) found overall reaction rate constant (k_R) of cow manure as 0.049 d^{-1}. This result indicating the slow reaction rate is lower than our findings. Gunaseelan (2004) investigated the anaerobic digestion of different kind of vegetable wastes, overall reaction rate constant of vegetable wastes are calculated in the range of 0,053-0,125 d^{-1}. Results from this study matched with the results of Gunaseelan (2004). To our knowledge, this study reports for the first time the kinetic evaluation of cow manure with tomato residues.

The simulation results for digestion of cow manure alone were illustrated in Figure 3a. The representative simulation results for co-digestion of cow manure with tomato residues were illustrated in Figure 3b-d. Also, the additional model simulations which were carried out for determination of hydrolysis rate constants were given in Figure 3e.

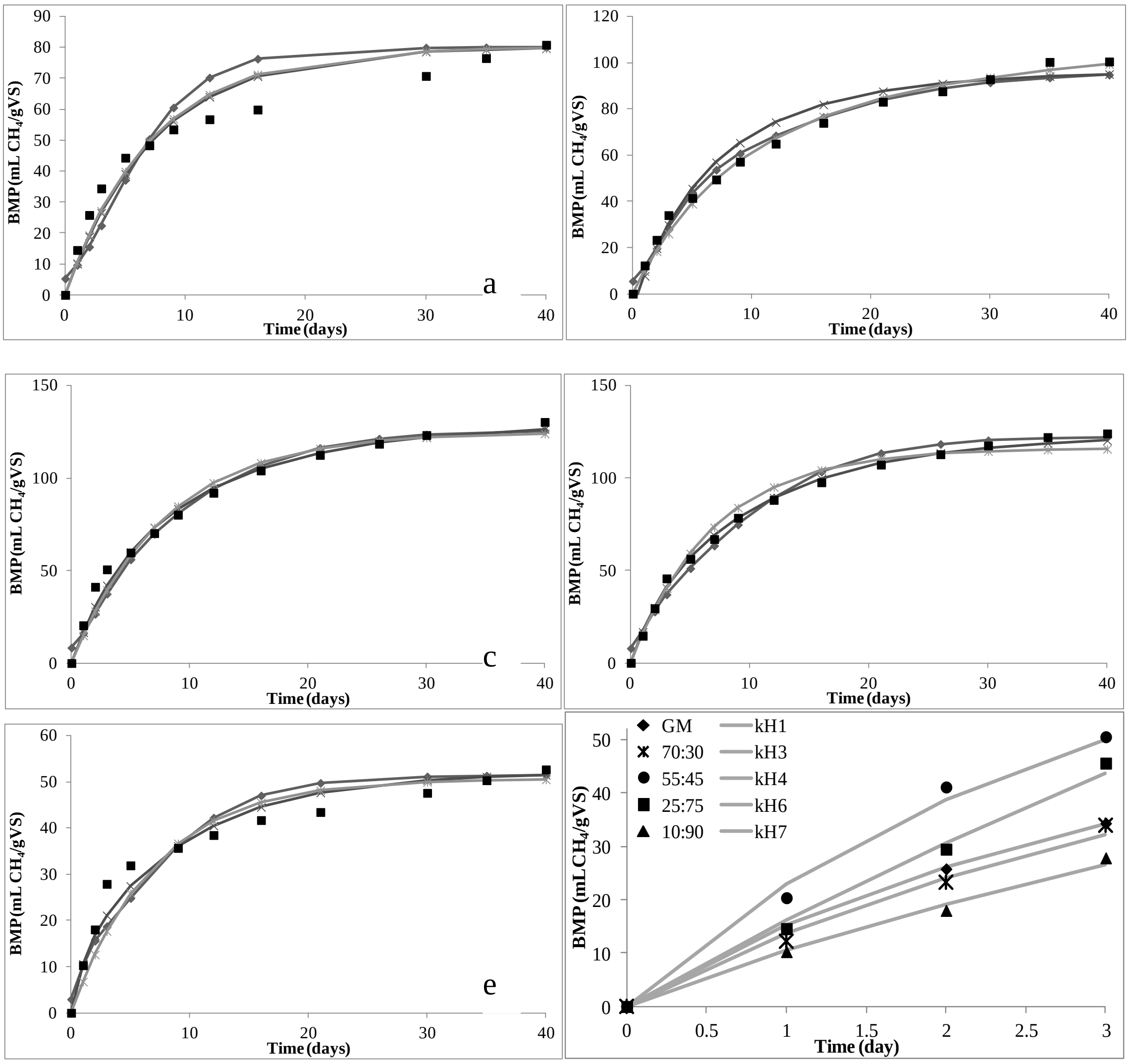

Figure 3 The simulation results for (a) digestion of cow manure alone and, for co-digestion of cow manure with tomato residues (b) 70:30, (c) 55:45, (d) 25:75, (e) 10:90, (f) simulation results for k_H

The hydrolysis rate constants (k_H) illustrated in Figure 3f were determined by simulation of the first three days of BMP tests. The determined k_H values and their regression coefficients were given in Table 4. The k_H values were determined with high regression coefficients (R2>0.98) for digestion of cow manure alone and for co-digestion of cow manure with tomato residues. The kH values indicated the positive effect of tomato residues addition on the hydrolysis of cow manure until the 45% again similar to observed in BMP results. Differently, the maximum mixing ratio was appear as 70:30 for efficiently hydrolysis of tomato residues if the kinetic was

Table 4 Calculated k_H values for co-digestion of cow manure with tomato residues

Mixing Ratio (CM:TR)	Cow Manure k_H (L/d)	Tomato Residues k_H (L/d)	R^2
100:0	0.347	-	0.999
85:15	0.368	0.197	0.982
70:30	0.368	0.197	0.992
55:45	0.368	0.100	0.993
40:60	0.288	0.100	0.993
25:75	0.288	0.100	0.995
10:90	0.208	0.100	0.993

■ Experimental BMP —◆—BMP-GE —✕—BMP-RC —✳—BMP-FO evaluated in terms of tomato residues removal.

4 Conclusions

The evaluation of co-digestion for efficiently biogas production from cow manure is showed that:

- The optimum mixing ratio for co-digestion of the cow manure with tomato residues was obtained 55:45 with a biomethane production 130.27 mlCH_4/gVS which is almost 62% higher than the methane production obtained from the digestion of cow manure alone.
- The optimum mixing ratio for co-digestion of the cow manure with pepper residues was obtained 25:75 with a biomethane production 222.49 mlCH_4/gVS which is almost 175% higher than the methane production obtained from the digestion of cow manure alone.
- The kinetic evaluation of the co-digestion of cow manure with tomato residues indicated the correlation between the decrease in the biogas production with a decrease in methane production rates, overall reaction rate constants and hydrolysis rates.

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