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Research paper

Biogas Production from Combined Irish Potato and Poultry Wastes: Optimization and Kinetic Studies

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Abstract

The combination of Irish potato waste (IPW) and poultry waste (PW) can form a synergy resulting into an effective substrate for a better biogas production due to some materials they contain. In this work, optimization and kinetic study of biogas production from anaerobic digestion of IPW and PW was investigated. Response surface methodology (RSM) was applied to optimize conditions such as initial pH, solids concentrations and waste ratios. The anaerobic digestion of the two wastes was carried out in the mesophilic condition and Box-Behnken design (BBD) was used to develop and analyze a predictive model which describes the biogas yield. The results revealed that there is a good fit between the experimental and the predicted biogas yield as revealed by the coefficient of determination (R2) value of 97.93%. Optimization using quadratic RSM predicts biogas yield of 19.75% at the optimal conditions of initial pH value 7.28, solids concentration (w/v) 9.85% and waste ratio (IPW:PW) 45:55%. The reaction was observed to have followed a first order kinetics having R2 and relative squared error (RSE) values of 90.61 and 9.63% respectively. Kinetic parameters, such as rate constant and half-life of the biogas yield were evaluated at optimum conditions to be 0.0392 day-1 and 17.68 days respectively. The optimum conditions and kinetic parameters generated from this research can be used to design real bio-digesters, monitor substrate concentrations, simulate biochemical processes and predict performance of bio-digesters using IPW and PW as substrate.

Keywords: *Anaerobic digestion; Irish potato waste; Kinetic; Optimization, Poultry waste.*

1. Introduction

Nigeria generates waste at the rate of 0.43 kg per person per day and the waste contains 60 to 80 percent of biodegradable wastes [1] & [2]. It has been estimated that Nigeria produces about 1 502 kg of food wastes and 227 500 tons of fresh animal waste daily, much of which are not effectively utilized [3] & [4]. Wastes pose serious environmental and health problems, promote insect vectors like mosquitoes and flies, rats and mice, cause fire hazards, flooding of streams, development of aquatic weeds, odour problems, nuisance, and so on. Some activities at potato industries generate wastes which includes rotten potatoes, potato skins and tubers, those with defects due to mechanical damages and are therefore rejected. These residues have a high perishability and their quick removal and disposal is therefore mandatory, with consequent high costs [5]. Since these materials have high moisture content, they are an eligible feedstock for anaerobic digestion (AD) [6].
The most promising alternative to incinerating, composting and landfilling of these wastes is to digest its organic matter using AD [7] & [8]. AD is a biological process that takes place naturally when microorganisms break down organic matter in the absence of oxygen. The main advantage of this process is the production of biogas, which can be used to produce electricity [9]. A valuable effluent called digestate is also obtained, which eventually can be used as an excellent soil condi-tioner (biofertilizer) after minor treatments [9]. Biogas is seen as an important source of energy to meet the electricity de-mands for small towns and rural areas [10]. Biogas is produced by AD of organic feedstock, the most common being ani-mal wastes and crop residues, dedicated energy crops, domestic food waste and municipal solid waste (MSW) [9] & [11].
Anaerobic digestion of wastes is suitable for greenhouse gases (GHGs) mitigation and waste management practices and the benefits are the production of biogas for cooking, heating, lighting and electricity generation and the production of bio-fertilizer for agricultural land application. The use of Irish potato waste (IPW) and poultry waste (PW) as raw materials for biogas and bio-fertilizer production will reduce the volume of wastes dumped in solid waste disposal sites (SWDs) and the odour emanating from the poultry farms respectively. There have been many previous studies on the optimization and kinetics of biogas production from anaerobic digestion of agricultural slurries and energy crops or organic wastes [12], [13], [14], [15] & [16]. However, there are publications on the optimization and kinetics of biogas production from anaerobic digestion of IPW and PW is scarce. There is therefore the need to fill this research gap as the literature on the subject matter is scarce.
Process optimization and kinetic study of biogas production from biodegradable wastes will assist to improve the anaerobic digestion process for industrial application.
Therefore, the aim of this research work is to carry out process optimization and kinetics study of biogas production from anaerobic digestion of Irish potato and poultry wastes. The kinetics parameter generated from this research can be used to size bio-digesters, monitor substrate concentration, simulate biochemical processes and predict bio-digesters performance.

2. Methodology

2.1. Experimental design and fabrication of bio-digesters

This section explains the factors, levels, range of values and number of runs needed for the optimization using RSM. RSM is a package containing Box-Behnken Design.
The number of experimental runs (N) for the Box-Behnken design (BBD) which is in three levels was calculated using (1) [12].

$$N = 2k(k-1) + cp \tag{1}$$

Where; k is the number of factors and cp is the number of centre points.
The factors that affect biogas production process such as initial pH, solids concentration, waste ratio and the range of values were obtained from [6], [13] & [17]. Table 1 presents factors, levels and range of values for the experimental plan.

Table 1: Levels of Factors and Codes used for Optimization

Factor	Level and code		
	-1	0	1
Initial pH value, A	6	7	8
Solids concentration (w/v), B (%)	5	10	15
Waste ratio (IPW:PW), C (%)	0:100	50:50	100:0

Fifteen (15) anaerobic bio-digesters was determined by (1) and therefore fabricated for the anaerobic digestion of IPW and PW. The bio-digesters were equipped with a digestion chamber, slurry inlet from the top cover, thermometer fixed at the top cover of the bio-digesters, biogas outlet from the top cover and tap head for sampling. The total volume of each bio-digester was 4.63 L with a working volume of 3.70 L and gas storage bag of 2.00 L [13], [18], [19] & [20]. Furthermore, the temperature of the bio-digester content was monitored using thermometer with temperature ranges between 0-100^{o}C.

2.2. Preparation of solutions and biogas production

The preparation of slurry of IPW and PW, HCl and NaOH used for this study were in accordance with the standard methods for the preparation of solutions. The solids concentration of the slurry was evaluated using (2) [13] & [17].

$$\text{Solids concentration} = \frac{\text{Mass of dried solids}}{\text{Volume of distilled water}} \times 100\% \tag{2}$$

The slurry was prepared to have solid concentrations (w/v) of 5%, 10% and 15%. The initial pH values of the slurry were adjusted to 6, 7 and 8 using 5 mol.dm-3 HCl and NaOH solutions in accordance with the experimental design.
The biogas production from anaerobic digestion of IPW and PW were carried out under ambient temperature in batch bio-digesters. Stirring of the slurry was done in the afternoon for 1 minute and the temperature of the bio-digesters were monitored daily. Retention time for the anaerobic digestion was 35 days [6] & [18]. The biogas yield (Y) was evaluated using (3).

$$\text{Biogas yield, } Y = \frac{\text{Mass of biogas produced}}{\text{Mass of slurry}} \times 100\% \tag{3}$$

2.3. Regression, optimization and verification experiment

A second order polynomial model was fitted to the experimental results and the regression model was calculated by analyzing the analysis of variance (ANOVA), p-value and F-value. The adequacy of the model was expressed by the coefficient of determination (R2). The model describes the interaction among the parameters influencing the biogas yield by varying them concurrently. The biogas yield (Y) was modelled using (4).

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \tag{4}$$

Where; A, B and C are independent variables upon which Y is dependent, β0 is the constant term, β1, β2 and β3 are the linear coefficients, β12, β13 and β23 are interaction coefficients and β11, β22 and β33 are the quadratic coefficients.
Optimization of biogas yield was carried out using RSM. The optimum values of the process variables and the biogas yield were predicted by the statistical software Design Expert 7.0.0 software. The optimum conditions were used for the verification experiment to confirm the model developed; this was used to carry out the kinetic study of the process.

2.4. Kinetic study

The concentration of the IPW and PW in the slurry contained in the anaerobic bio-digesters were determined based on the chemical oxygen demand (COD) reduction throughout the duration of the verification experiment. The COD of the slurry was calculated using (5).

$$\text{COD}\left(\frac{\text{mg}}{\text{L}}\right) = \frac{(a-b)\times f}{v} \tag{5}$$

Where; *a* is potassium permanganate ($KMnO_4$) consumption by sample (in mL), *b* is $KMnO_4$ consumption by blank sample (in mL), *f* is titration factor of the $KMnO_4$ solution and *v* is the volume of sample (in mL). The experimental data obtained from the bio-digesters were checked for fitness using integrated form and half-life models as shown in Table 2.

Table 2: Kinetic Models and Half-Life for different Order of Reactions

Order of reaction (n)	Kinetic model	Integrated form	Half-life ($t_{1/2}$)
0	$r = \left(\frac{dS}{dt}\right) = k$	$S_t = S_o - kt$	$t_{1/2} = \left(\frac{1}{2k}\right) S_o$
1	$r = \left(\frac{dS}{dt}\right) = kS$	$\ln(S_t) = \ln(S_o) - kt$	$t_{1/2} = \left(\frac{\ln(2)}{k}\right)$
2	$r = \left(\frac{dS}{dt}\right) = kS^2$	$S_t^{-1} = S_o^{-1} + kt$	$t_{1/2} = \left(\frac{1}{kS_o}\right)$

r - rate of reaction, S_t - effluent concentration of slurry, S_o - influent concentration of slurry, dS - change in S, t - time, change in t and k - rate constant

The zero, first and second order kinetic models were tested for the residual substrate concentration reduction with time. The kinetic parameters for the reaction were determined by plotting suitable graphs and calculating the slope and the intercept using excel package. The kinetic model with the highest value of coefficient of determination (R^2) and lowest relative squared error (RSE) describes the model best.
The units of rate constants for the zero, first and second order kinetic models can be evaluated using (6).

$$\text{Rate constant (k)} = (\text{concentration of slurry})^{1-n}\,(\text{time})^{-1} \tag{6}$$

The RSE was used to compare the zero, first and second order models whose errors are measured in different units. The RSE of the models were evaluated using (7).

$$\text{Relative squared error (RSE)} = \frac{\sum_{i=1}^{n}(p_i - a_i)^2}{\sum_{i=1}^{n}(\bar{a} - a_i)^2} \times 100\% \tag{7}$$

Where; *a* is the actual value, *p* is the predicted value and $\bar{a}$ is the mean of actual value.

3. Result and Discussions

3.1. Characterization of Irish Potato and Poultry Wastes

The results of the characterization of IPW and PW are presented in Tables 3 and 4.

Table 3: Proximate Analysis of IPW and PW

Sample	pH	MC (%)	TS (%)	VS (%)	FS (%)
A (100% IPW)	6.00	13.80	86.20	63.34	36.66
B (100% PW)	8.80	22.30	77.70	73.87	26.13
C (50% IPW+50% PW)	7.40	13.70	86.30	63.38	36.62

MC - Moisture content, TS - Total solids, VS - Volatile solids, FS - Fixed solids, IPW - Irish potato waste and PW - Poultry waste.

Table 4: Ultimate Analysis of IPW and PW

Sample	Carbon (C)	Hydrogen (H)	Nitrogen (N)	Sulphur (S)	Oxygen (O)	C/N ratio
A (100% IPW)	46.39	7.68	1.30	0.19	44.44	35.57:1
B (100% PW)	48.32	6.29	2.28	0.28	42.83	21.15:1
C (50% IPW+50% PW)	49.25	7.14	1.52	0.17	41.92	32.43:1

C/N - Carbon to Nitrogen ratio.

Table 3 presents the proximate analysis of samples A, B and C. It can be seen that sample B had the highest percentage volatile solids, followed by sample C, then sample A. The high percentage volatile solids of sample B can be attributed to high biodegradable materials in PW as a result of high intake of digestible materials [21]. The higher value of volatile solids in sample C compared to A can be attributed to proper mixing of the IPW and PW [22].

The pH values of samples A, B and C were 6.0, 8.8 and 7.4 respectively. The pH value of sample C was adequate and within the limits required for biogas production [13]; while the pH values of samples A and B were inadequate and not within the limits for biogas production and there is the need for pH adjustment [21]. The pH values of samples A and B are far from the optimum pH of biogas production of 7.0 but can be adjusted to make the wastes suitable for effective biogas production using sodium hydroxide (NaOH) and hydrochloric acid (HCl) respectively [6].

In addition, it can be seen from Table 4 that the C/N ratios obtained for samples A and C were out of range of the standard ratio (20-30:1) for optimum biogas production [9]. On the other hand, the C/N ratio for sample B fell within the range required for biogas production of 20-30:1 [9]. Therefore, C/N ratio was not a limiting factor in sample B. On the other hand, C/N ratios were limiting factor to optimal biogas production in samples A and C [22].

3.2. Optimization of biogas production

The optimal levels for the independent variables and the effect of their interaction on biogas production were conducted in fifteen (15) experiments using the Box-Behnken design (BBD) of response surface methodology (RSM). Table 5 shows the experimental conditions (initial pH value, solids concentration and waste ratio) and the biogas yield (experimental and predicted) obtained from the process optimization of biogas production.

Table 5: Experimental Conditions and Biogas Yield

		Factor			Biogas yield (Y)	
Std	Run	A: Initial pH value	B: Solids concentration (%)	C: Waste ratio (IPW:PW) (%)	Experimental (%)	Predicted (%)
1	3	6	5	50	16.26	15.85
2	6	8	5	50	18.10	18.40
3	13	6	15	50	17.02	16.73
4	11	8	15	50	19.01	19.42
5	7	6	10	0	14.29	14.79
6	8	8	10	0	16.74	16.53
7	10	6	10	100	13.45	13.66
8	9	8	10	100	17.66	17.16
9	12	7	5	0	16.27	16.18
10	4	7	15	0	15.45	15.25
11	5	7	5	100	13.84	14.04
12	15	7	15	100	16.80	16.89
13	1	7	10	50	19.50	19.50
14	14	7	10	50	19.50	19.50
15	2	7	10	50	19.50	19.50

Table 5 shows the fifteen experimental runs sorted using standard order of the three factors (initial pH 6-8, solids concentration 5-15% and waste ratio 0:100 to 100:0%) varied at three levels with their corresponding experimental and predicted biogas yields. The minimum and maximum values for experimental and predicted biogas yields were 13.45-19.50% and 13.66-19.50% respectively. [23] evaluated biogas yield of 17% from cow dung and watermelon peels which falls within the range of biogas yield in this present study.

The values obtained from the experimental design were subjected to response analysis to evaluate the relationship between initial pH (A), solids concentration (B) and waste mix ratio (C). By applying multiple regression analysis on the experimental data, the second order polynomial equation was derived to explain the biogas yield. Thus, the equation obtained based on mathematical regression models for biogas yield (Y) fitted in terms of actual factors is as follows.

$$\begin{aligned} Y = & -39.65125 + 14.49875A + 0.59275B + 0.017550C + 7.5\times10^{-3}AB + 8.8\times10^{-3}AC \\ & + 3.78\times10^{-3}BC - 0.97875A^2 - 0.03695B^2 - 1.1945\times10^{-3}C^2 \end{aligned} \tag{8}$$

Where; A, B and C are initial pH value, solids concentration and waste ratio respectively.

The statistical significance of the second order polynomial equation was checked by Analysis of Variance (ANOVA), F-value and p-value as shown in Tables 6 and 7.

Table 6: Regression Model and Analysis of Variance (ANOVA)

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F
Model	56.59	9	6.29	26.27	0.0011
A-Initial pH value	13.76	1	13.76	57.46	0.0006

B-Solids concentration	1.81	1	1.81	7.58	0.0402
C-Waste ratio	0.13	1	0.13	0.52	0.5023
AB	5.625×10-3	1	5.625×10-3	0.023	0.8842
AC	0.77	1	0.77	3.23	0.1320
BC	3.57	1	3.57	14.92	0.0118
A^2	3.54	1	3.54	14.78	0.0121
B^2	3.15	1	3.15	13.16	0.0151
C^2	32.93	1	32.93	137.55	< 0.0001
Residual	1.20	5	0.24		
Lack of fit	1.20	3	0.40		
Pure error	0.000	2	0.000		
Cor total	57.79	14			

Table 7: Model Fitness Summary

Parameter	Value
Std. dev.	0.49
Mean	16.89
C.V. (%)	2.90
PRESS (predicted residual sum of squares)	19.15
R-squared (%)	97.93
Adj R-squared (%)	94.20
Pred R-squared (%)	66.86
Adeq precision	14.622

From Table 6, it can be seen that the F-value of 26.27 and p-value of 0.0011 implies the model is significant. The p-value represents the significance of the variables in which the smaller the p-value, the higher the significance of each variable. The p-value was less than 0.05 which indicated the model terms are significant. For biogas yield, the fit of the polynomial model was also expressed by the coefficient of determination (R^2) which was found as 97.93%. The R^2 value indicated a measure of variability in the observed response values which could be described by independent factors of the model. The linear model terms of initial pH value (A) and solids concentration (B) were significant (p<0.05) and waste ratio (C) was insignificant (p>0.05). The interactive model terms for AB and AC were found to be insignificant (p>0.05) and BC was significant (p<0.05). The quadratic model terms of A^2, B^2 and C^2 were significant (p<0.05) indicating that three variables had an individual effect on biogas yield.

It can be seen in Table 7 that the adequate precision (Adeq Precision) value of 14.622 indicated an adequate signal because it measures the signal to noise ratio and the ratio greater than 4 is desirable. This model can be used to navigate the design space. Here the adjusted coefficient of determination (Adj R-Squared) value of 94.20% was also very high, which indicate the higher significance of the model. The predicted coefficient of determination (Pred R-Squared) value of 66.86% indicates the poor agreement between the observed and predicted values. The difference between the Adj R-Squared and Pred R-Squared was 27.34% which should not be greater than 20%, otherwise there may be a problem with either the data or the model [24]. The higher value of coefficient of variation (CV) gives lower reliability of the experiment but here a lower value of 2.90% indicated a high degree of precision and a good deal of reliability of the experimental values [25]. This model has high mean, low standard deviation and predicted residual sum of squares (PRESS) values of 16.89, 0.49 and 19.15 that were significant respectively.

Optimization was performed to investigate the optimum experimental conditions and biogas yield. It determines the optimum desirability depending on the “goals” set for each of the factors and response [26] & [27]. In this study, the goal for initial pH, solids concentration and waste ratio were set to “in range”, whereas the goal for biogas yield was set to “maximize”. The main reason why biogas yield was set to maximize was that the yield from a process needs to be maximum because it is the main product of the process. The desired goal of the model was to maximize biogas yield to achieve highest biogas production. The constraints were the experimental conditions and biogas yield for the model optimization as shown in Table 8.

Table 8: Constraints for Experimental Conditions and Biogas Yield

Name	Goal	Lower limit	Upper limit
Initial pH value	in range	6	8
Solids concentration (%)	in range	5	15
Waste ratio (%)	in range	0	100
Biogas yield (%)	maximize	13.45	19.50

The verification experiment indicates that the maximum biogas yield was obtained when the values of each parameter were set as the optimum values as shown in Table 9. It implies that the strategy to optimize the experimental conditions and to obtain the maximum biogas yield using RSM for the biogas production in this study was successful at the highest desirability of 1.00.

Table 9: Optimum values for Experimental Conditions and Biogas Yield

Solutions number	Initial pH value	Solids concentration (%)	Waste ratio (%)	Biogas yield (%)	Desirability
1	7.28	9.85	45.47	19.7512	1.000 Selected
2	7.41	10.41	45.37	19.8672	1.000
3	7.76	8.87	51.78	19.7669	1.000
4	7.49	8.32	43.35	19.6136	1.000
5	7.40	12.38	67.10	19.7133	1.000

The verification experiment produced 19.85% of biogas yield at optimal conditions of initial pH value 7.28, solids concentration (w/v) 9.85% and waste ratio (45.47%) i.e. IPW:PW approximately (45:55%) within 35 days’ retention time. This also confirms that the biodegradation conditions which are initial pH value, solids concentration and waste ratio improved the anaerobic digestion process. The optimum initial pH value of 7.28 was close to the initial pH value of 7.11 obtained from the co-digestion of food waste and PW manure as reported by [13] & [28]. Also, the optimum value of solids concentration of 9.85% closely agreed with the value of 10% obtained from food waste by [17]. The optimum value of waste ratio of 45:55 agreed with the equal blending of cow and elephant dungs in the ratio of 50:50 by [6]. In addition, the optimum biogas yield of 19.75% agreed with the biogas yield of 17% from cow dung and watermelon peels as reported by [23].

3.3. Kinetics of Biogas Production

Figures 1-3 shows the plots of zero, first and second order kinetic models of the experimental data respectively.

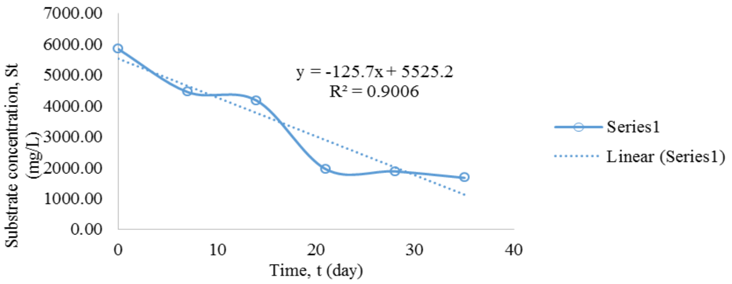

Figure 1: Substrate Concentration versus Time for Zero order

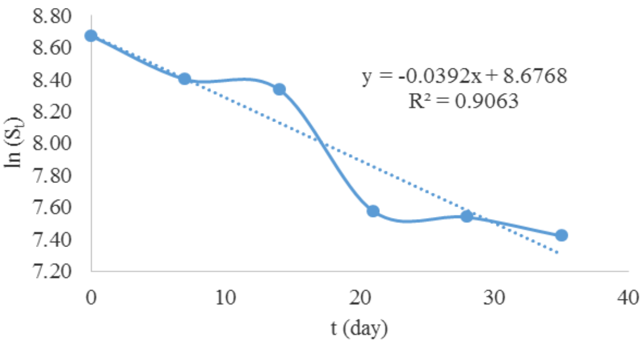

Figure 2: ln (S_t) versus Time for First order

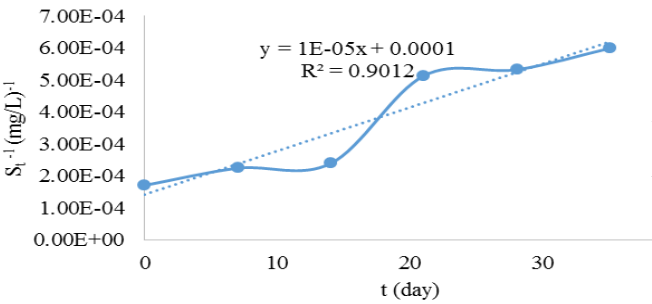

Figure 3: S_t^{-1} versus Time for Second order

From Figures 1-3 the developed models are thus:
$y_1 = -125.7x + 5525.2$
(for zero order)
$y_2 = -0.0392x + 8.6768$
(for first order)
$y_3 = 0.00001x + 0.0001$
(for second order)
Where; y_1 is the predicted substrate concentration at time t (S_{tp}), $y_2 = \ln (S_{tp})$, $y_3 = S_{tp}^{-1}$ and x = t. The kinetic parameters evaluated from the developed models are presented in Table 10.

Table 10: Evaluated Kinetic Parameters and Model Fitness Check

Kinetic model	Rate constant (k) Value	Unit	Half-life $t_{1/2}$ (day)	S_o mg.L^{-1}	R^2 (%)	RSE (%)
Zero order	125.70	mg.L^{-1}.day^{-1}	21.98	5525.20	90.06	9.94
First order	0.0393	day^{-1}	17.68	5865.25	90.63	9.63
Second order	0.00001	L.mg^{-1}.day^{-1}	10.00	10000.0	90.12	53.95

Initial substrate concentration (S_o), coefficient of determination (R^2) and relative squared error (RSE)

The rate constant (k) represents a measure of the wastes biodegradation rate and the half-life ($t_{1/2}$) indicates the length of time it takes to degrade half the concentration of the organic wastes [29] & [30]. The higher the value of k, the higher or faster is the rate of biodegradation and consequently the lower is the half-life of the waste for first order kinetic model [31] & [32]. The zero, first and second order kinetic models were used to assess the dynamics of the biodegradation process and how close the models fitted the experimental data.
From Table 10, the biodegradation rate constant of 125.70 mg.L^{-1}.day^{-1} and half-life of 21.98 days for the zero order model, indicated that at optimal conditions, 125.70 mg.L^{-1} of IPW and PW slurry per day degrades and it takes 21.98 days for the initial substrate concentration of 5525.20 mg.L^{-1} to reduce to half its value. Similarly, the first order model with biodegradation rate constant of 0.0392 day^{-1} and half-life of 17.68 days, indicates that 0.0392 mg.L^{-1} of 1 mg.L^{-1} IPW and PW slurry per day degrade and it takes 17.68 days for the initial substrate concentration of 5865.25 mg.L^{-1} to reduce to half its value. The same explanation applies to the second order model.
In addition, from the same table, the first order kinetic model gives the smallest RSE value of 9.63% and has the largest R^2 value of 90.63%, which implies that the first order kinetic model describes the kinetic data best followed by the zero order and the least is the second order. Most of the previous studies revealed that the substrate degradation and subsequent biogas production follows the first order kinetic [30] & [33]. Therefore, in this study, the first order kinetic model can be used to describe the COD reduction from slurry of IPW and PW.

4. Conclusions

Optimization and kinetic of biogas production from the anaerobic degradation of two mixtures of wastes (IPW and PW) was investigated. Firstly, the characterization shows that the waste mixtures produced good substrate for biogas production; giving 63-74% volatile solids and 21-36% carbon to nitrogen ratio. RSM was used to design and model the process, in which a predictive model was developed to predict the yield of the biogas production. The model had F-value of 26.27 and p-value of 0.0011 indicating that the model is significant. The fit of the polynomial model was expressed by the coefficient of determination of 97.93% which indicated a measure of variability in the observed response values described by independent factors of the model. Optimization outcome gave initial pH value of 7.28, solids concentration of 9.85% and waste ratio (IPW:PW) of 45:55 with biogas yield of 19.75%. In addition, the verification experiment produced 19.85% of biogas yield at the optimal conditions. Furthermore, the kinetic study revealed that first order kinetic model describes the biogas production best with rate constant and half-life of 0.0392 day^{-1} and 17.68 days having coefficient of determination and relative squared error of 90.61 and 9.63% respectively. Therefore, the kinetic and optimization parameters obtained can be used to design a bio-digester, monitor the substrate concentration as reaction progresses and simulate the anaerobic digestion of IPW and PW.

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