Anaerobic Co-Digestion of Oil Refinery Wastewater with Bagasse; Evaluating and Modeling by Neural Network Algorithms and Mathematical Equations

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To survey the anaerobic co-digestion (AcoD) of oil refinery wastewater (ORWW) with sugarcane bagasse (SCB), six different AcoD compositions were evaluated. Results including cumulative biogas production (BGP), bio-methane contents (BMP), and soluble chemical oxygen demand (CODs) removal rate were experimentally obtained. The negligible BGP by ORWW mono-digestion revealed that it could not support any microbial activity. However, increasing the SCB ratio in the AcoD compositions led to increased BGP and BMP contents. By considering the statistical test ($LSD_{0.05}$) results for the kinetic parameters, the 1:4 ratio treatment was the most favorable AcoD composition. Moreover, the CODs removal rate from 22.34 ± 1.63% for the SCB mono-digestion was improved to 49.67 ± 0.38% for the 2:3 AcoD composition and BMP content from 54.12 ± 0.45% for the SCB mono-digestion was enhanced to 62.69 ± 1.22% for the 1:4 AcoD composition with 20% lower SCB usage. The results computed by applying three mathematical models determined that the modified Gompertz model provided the best fit. Also, implementing artificial neural network algorithms to model the BGP data revealed that the Back Propagation algorithm was the best suited for the experimental BGP data, with 0.6444 and 0.9658 for *MSE* and R^2, respectively.

Keywords: Anaerobic co-fermentation; Oil refinery wastewater; Sugar cane bagasse; Modeling; Bio-methane production

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ABBREVIATIONS

SCB: sugarcane bagasse; ORWW: oil refinery wastewater; AcoD: anaerobic co-digestion; AD: anaerobic digestion; TS: total solid; VS: volatile solid; TOC: total organic carbon; TN: total nitrogen; C/N: carbon/nitrogen; CODs: soluble chemical oxygen demand; BGP: cumulative biogas production; BMP: cumulative bio-methane production; TAN: total ammonia nitrogen; LSD: least significant difference test; ANN: artificial neural network; BPNN: back propagation ANN; GRNN: generalized regression ANN; RBFNN: radial base function ANN.

INTRODUCTION

Due to increased fossil fuel demand, a large volume of industrial wastewater is produced by the oil refinery industry. The combustion of fossil fuels has intensified climate change. The refining process for crude oil uses 1.6 gallons of water per gallon of crude oil (Coelho *et al.* 2006), which is responsible for a major share of aquatic pollution. To treat oily sludge and effluents of refining process, several techniques and pretreatments including chemical oxidation, centrifugation, adsorption, photo-Fenton, biological, and so forth were introduced (Diya'uddeen *et al.* 2011; Aljuboury *et al.* 2015; Siddique *et al.* 2015; Choromanski *et al.* 2016; Haak *et al.* 2016; Rastegar *et al.* 2011; Roy *et al.* 2016). The liquid part of residuals is oil refinery wastewater that is considerable and huge aquatic mixture. Managing petroleum and petrochemical wastewater can be categorized in three main interests including; (i) optimizing water consumption system, (ii) recycling the treated wastewater in the refining process, and (iii) treating wastewater and use it in agricultural farms and so on. Of the available techniques, anaerobic digestion (AD), as a biological pretreatment, is preferred and promotes affordability, energy recyclability, and improved waste management (Haak *et al.* 2016).

AD is an effective treatment for mass reduction of industrial wastes and recovery of their organic carbon as biogas (Roy *et al.* 2016; Horváth *et al.* 2016), which is considered a renewable and competitive energy resource. In addition, reducing natural sources of pollution and producing a lesser volume of biomass are benefits of using AD to treat waste and wastewater. The presence of toxins, detergents, petroleum hydrocarbons, and high volatile fatty acids in municipal and industrial wastewater prompts the application of co-digestion with nutrient-rich substrates such as livestock manures and agricultural residues. There are several applications of AcoD such as improving bio-methane production, providing proper nutrients to support microbial growth, and balancing C/N ratios, which is key for stabilizing the AD process (Rastegar *et al.* 2011; Siddique *et al.* 2015). Several studies have aimed at improving the AD process of ORWW through co-digestion with organic substrates including cow dung (Siddique *et al.* 2015), sugarcane molasses (Rastegar *et al.* 2011), and food wastes (Mehryar *et al.* 2016). However, the kinetic parameters of the AcoD process have not been critically evaluated.

Sugarcane bagasse (SCB) is the main solid waste produced in sugar factories. A portion of the SCB produced in the sugar manufacturing process is commonly burned in boilers as a fuel source (Talha *et al.* 2016). Some factories utilize natural gas or gasoline as their fuel. SCB has been used in boards, pulp and paper production, and animal feeding. However, few recent studies have been focused on the AD and AcoD of SCB (Talha *et al.* 2016; IME 2010; Janke *et al.* 2016). The major components of SCB (as a lignocellulosic material) are cellulose, hemicellulose, and lignin, which are of interest for AD fermentation (Talha *et al.* 2016; Matsakas *et al.* 2016). Matsakas *et al.* (2016) reported that the hydrolysis of lignocellulosic materials can be limited by several factors, including: (i) crystallinity of cellulose; (ii) degree of cellulose polymerization; (iii) level of hemicellulose and lignin contents; (iv) degree of hemicellulose acetylation; and (v) amount of accessible surface area (Matsakas *et al.* 2016). In fact, lignin covers the other two components and decreases their bio-digestibility, which has a negative effect on bio-methane production. In contrast, cellulose and hemicellulose are hydrocarbon polymers that can be simply hydrolyzed

(Sambusiti *et al.* 2013). Thus, contravention of lignin to increase SCB bio-digestibility is the key objective for mechanical, chemical, and thermochemical pretreatments (IME 2010; Sambusiti *et al.* 2013; Talha *et al.* 2016).

The AD process, as an applicable and well-known treating method for waste management, is a pragmatic process for sustainable energy production. Modeling of this process has been the focus of several studies during the past decade (Huiliñir *et al.* 2014; Owamah and Izinyon 2015; Sridevi *et al.* 2014; Xie *et al.* 2016). Different modeling techniques had been applied in the previous studies to model the AD process outputs such as bio-methane production or VS removal. Xie *et al.* (2016) classified the applied mathematical models into five categories; (i) basic kinetic models including first order kinetic model, the modified Gompertz model, Haldane kinetic model, Transer function model and so forth; (ii) anaerobic digestion model No. 1 (ADM1); (iii) statistical models such as simple-centroid mixture design and central composite design (CCD); (iv) computational fluid dynamics (CFD) to study the flow and velocity, turbulence, rate of energy dissipation and so forth; and (v) other algorithm approaches including applying artificial neural network (ANN) with different architectures and algorithms to model the interrelationship between key variables (Xie *et al.* 2016). Besides the basic kinetic models, applying the ANN technique to model the AD process requires a minimum knowledge in the reaction mechanism. Thus, applying three different basic kinetic models and three different ANN algorithms have been applied to model the bio-methane production trends for AcoD of ORWW with SCB.

Several studies have aimed to improve the AD process of ORWW through co-digestion with organic substrates including cow dung (Siddique *et al.* 2015), sugarcane molasses (Rastegar *et al.* 2011), and food wastes (Mehryar *et al.* 2016). However, the kinetic parameters of the AcoD process have not been critically evaluated. Improving the ORWW fermentation process through co-digestion with rich-nutrient substrates such as dairy manures and organic wastes was the focus of several studies (Rastegar *et al.* 2011; Siddique *et al.* 2015; Haak *et al.* 2016; Mehryar *et al.* 2016). But their synergetic effects during AcoD process had not been evaluate through obtaining AcoD process parameters. In this research, the AcoD of ORWW with SCB was conducted, and the fermentation process was evaluated in terms of biogas production (BGP), bio-methane content (BMP), soluble chemical oxygen demand (CODs) removal rate, and retention time. Furthermore, the variation trends of AcoD process parameters during digestion period were obtained which are beneficial data to evaluate the AcoD of SCB with ORWW. Besides, semi-theoretical and theoretical modeling of BGP and BMP data using different mathematical equations and ANN algorithms was explored.

EXPERIMENTAL

Materials

Material collection

The inoculum of the anaerobically digested sewage sludge was collected from an active biogas plant, which was fed with pig manure from a local livestock farm in Pukou, Nanjing, China. To activate the collected sewage sludge and to remove the dissolved methane from it, glucose was fed into the sludge at a rate of 1.5 g/L per day at (35.0 ± 1.0)

°C for 1 month (Xi *et al.* 2014). The biogas production from mixed sludge with glucose was checked. At one week after its biogas production stoppage, the seed culture was thoroughly mixed, filtered through a screen with a pore size of 833 μm (Hassan *et al.* 2016) and then utilized as the inoculum. The ORWW was collected from the Jinlin SINOPEC oil refinery factory (Nanjing, Jiangsu, China). It may be noted that the applied ORWW in this research is the liquid residual of pre-treating oily sludge. This is the main part of waste mixtures from the oil refining process. Before disposing it to the environment and rivers, several pre-treating methods including solvent extraction, centrifugation, freeze/thaw, pyrolysis, and so forth are being utilized to treat oily sludge (Hu *et al.* 2013). However, the residual of pre-treated oily sludge, as oil refinery wastewater (ORWW), is potentially polluted and must be treated through oxidation, stabilization or biodegradation process.

The SCB used in this study was provided by Zhanjiang Huazi Land-Reclamation Sugar Industry Co. Ltd. (Guangdong, Zhanjiang, China) during the 2015 harvest season. The SCB was first air-dried and then oven-dried at 45 °C for 48 h. It was then milled with a grinder, sieved to pass a 5 mm sieve, and stored in plastic bags in a vented room until use.

Methods

Experimental setup and procedure

To conduct batch experiments of anaerobic co-digestion (AcoD) under mesophilic conditions (37.0 ±1.0 °C), 1-liter Erlenmeyer flasks were used as lab-scale anaerobic digesters, as described in Hassan *et al.* (2016). The working volume of each digester was 800 mL, including 400 mL of inoculum, which is the optimized amount to co-digest oil refinery wastewater with activated manure (Mehryar *et al.* 2016). To study the effect of AcoD of ORWW with SCB on their AD fermentation processes, six different ratios of ORWW:SCB were prepared at 5:0, 4:1, 3:2, 2:3, 1:4, and 0:5 and consequently termed as ORWW, treat-A, treat-B, treat-C, treat-D, and SCB, respectively. After feeding substrates and activated sludge (inoculums) to the digesters, 6% total solids (TS) were maintained in each digester. The contents of each digester were smoothly shaken manually for approximately 2 minutes per day prior to biogas volume measurements.

Physical and chemical analytics

The characteristics of the substrates and inoculum, including total solids (TS), volatile solids (VS), total organic carbon (TOC), total nitrogen (TN), carbon/nitrogen ratio (C/N ratio), and CODs were determined in accordance with standard methods (APHA 2006) and are reported in Table 1. The pH was directly measured from the liquid samples using a digital pH meter (FE20K, Mettler-Toledo, Greifensee, Switzerland). The CODs stabilization was calculated using Eq. 1 (Hassan *et al.* 2016),

$$CODs\ (\%) = \frac{CODs_i - CODs_f}{CODs_i} * 100 \tag{1}$$

where *i* and *f* indicate the initial and final CODs values during the digestion process, respectively. The total ammonia nitrogen (TAN) content was measured using an ammonia meter (Lianhua Tech. Co., Beijing, China), according to Hassan *et al.* (2016). Lignocellulosic characteristics of SCB were determined according to the Van Soest method (Talha *et al.* 2016) using a row fiber extractor machine (VELP Scientifica Company, Usmate (MB), Italy), which is based on sequential extraction under neutral and acid detergent fiber (NDF and ADF, respectively) followed by strong acid extraction (ADL) (Talha *et al.* 2016).

Biogas measurements and composition analysis

During fermentation, the daily biogas production yield for each digester was measured using a liquid displacement method in which saturated $NaHCO_3$ solution was utilized as a displacing liquid (Mehryar *et al.* 2016). The process was continued until the daily biogas yield was lower than 1% of the previous cumulative yield. Biogas samples were taken periodically from the gas collection lines prior to the gas-holder flask and analyzed for composition (N_2, CH_4, and CO_2) using a gas chromatograph (GC 7820A, Agilent, Santa Clara, CA, USA) equipped with a PQ 80-100 mesh column and thermal conductivity detector (TCD). The operational conditions were 25 mL/min helium as the carrier gas, a detector temperature of 250 °C, and a column temperature of 90 °C. To calibrate the GC in prior to biogas composition analysis, the GC and its analytical software was calibrated by injecting two different standard gas samples which contained various percentages of N_2, CH_4 and CO_2.

Modeling the experimental BMP data

Previous studies applied several mathematical equations to model the BMP kinetics and determine the potential BMP of various substrates (Huiliñir *et al.* 2014; Owamah and Izinyon 2015). Besides, modeling the AD process trough modeling different process stages such as hydrolysis, acidogenesis and so forth were evaluated in previous literatures (Xie *et al.* 2016; Béline *et al.* 2017). Hence, three different and common mathematical equations including the modified Gompertz (Eq. 2), the Logistic function (Eq. 3), and the Transfer function (Eq. 4) models were applied to model the experimental BMP data. The model equations are as follows (Huiliñir *et al.* 2014; Owamah and Izinyon 2015),

$$Y = A \times exp\{-exp\left[\frac{\mu_m}{A} \times e \times (\lambda - t) + 1\right]\} \quad (2)$$

$$Y = \frac{A}{1+exp(\frac{4\times\mu_m\times(\lambda-t)}{A}+2)} \quad (3)$$

$$Y = A \times (1 - exp\left(-\frac{\mu_m(t-\lambda)}{A}\right)) \quad (4)$$

where A is the potential methane production (mL/gVS), μ_m is the maximum production rate of methane (mL/gVS.day), λ is the lag-phase (day), Y is the accumulated bio-methane at time t (mL/gVS), t is the measured time (day), and e is the base of natural logarithms (2.718282). The constants of the applied models were estimated using the MATLAB 8.1.0 (R2013a; the MathWorks, Inc., Natick, MA, USA) curve fit function. To evaluate the fittings, the co-efficient of determination (R^2) and the root mean squared error (*RMSE*) and mean absolute percentage error (*MAPE*) were calculated and compared.

Modeling the BGP using artificial neural network (ANN)

To model the BGP data using an artificial neural network (ANN), three different algorithms—Back Propagation ANN (BPNN), Generalized Regression ANN (GRNN), and Radial Basis Function (RBFNN)—were applied. A network architecture of 3-8-1 was applied for the three algorithms, corresponding to the number of neurons within the input, hidden, and output layers, respectively. The ANN consists of three layers: (*i*) an input layer that contains input neurons as independent parameters including the pH, TAN, and CODs values, (*ii*) an output layer that contains the output neuron, which is the dependent predicted process variable, or BGP for this study, and (*iii*) a hidden layer that transforms input neurons. Experimental data obtained from six digesters were divided into 2 sets of 42 samples as the training data set and 16 samples as the validation of the trained model. To evaluate and compare these three ANN algorithms, errors between the experimental and ANN model simulated data were determined. The regression coefficient (R^2) and mean square error (*MSE*) for training, testing and all data sets were calculated using Eq. 5 and Eq. 6 (Sridevi *et al.* 2014),

$$R^2 = 1 - \left(\sum_{i=1}^{n} \left(Y_{pi} - Y_i \right)^2 \Big/ \sum_{i=1}^{n} (Y_i - Y_{ave})^2 \right) \tag{5}$$

$$MSE = \frac{1}{n} \sum_{i=1}^{n} (Y_{pi} - Y_i)^2 \tag{6}$$

where n gives the number of samples, Y_{pi} is the predicted value, Y_i is the experimental value, and Y_{ave} is the mean of Y_i. All error performance calculations and ANN trainings were conducted in MATLAB 8.1.0 (R2013a; the MathWorks, Inc., Natick, MA, USA).

Statistical analysis

A complete randomized design was utilized to examine the effect of various mixing ratios of ORWW with SCB on process parameters including BGP, BMP, CODs removal rate, retention time, and bio-methane content of BGP. All AcoD experiments (including biogas production yield and produced biogas composition) and analytical parameters (including pH, CODs, TAN and FAN) were obtained by triplicates. And obtained data were analyzed by analysis of variance (ANOVA) using Statistix 8.1 software (Tallahassee, FL, USA). When the F-test indicated statistical significance at the P = 0.05 probability level, treatment means were separated by the least significant difference ($LSD_{0.05}$) test.

RESULTS AND DISCUSSION

Chemical Compositions

The physicochemical characteristics of the applied substrates are presented in Table 1. The estimated characteristics illustrate that the ORWW contained low amounts of the proper organic nutrients needed to support microbial activities and improve the fermentation process. Moreover, its C/N ratio was 83.33/1, which is outside of the favored range for anaerobic fermentation (Ahn *et al.* 2010). The chemical characteristics of SCB and inoculum confirmed their superior ability to support the fermentation process compared with ORWW. Therefore, the respective AcoD process with ORWW can be favorable and beneficial. AcoD of various substrates can be used for diluting toxic compounds, providing proper nutrients for microbial activities, improving buffer capacity, and preventing ammonia inhibition (Ahn *et al.* 2010; Siddique *et al.* 2015; Talha *et al.* 2016). Compared with other substrates, the inoculum contained more TN to provide the requirements of the microbial communities. However, the SCB was the nourish-rich substrate that enabled the microbial activities to pass the adaptation phase.

Table 1. Characteristics of the Applied Substrates and Inoculum

Characteristics	SCB	ORWW	Inoculum
TS (%)	58.90 ± 0.01[b]	1.73 ± 0.03	2.51 ± 0.10
VS (% of TS)	97.59 ± 0.00	2.69 ± 0.70	49.35 ± 1.00
TOC (g/Kg of TS)	55.05 ± 1.79	175.60 ± 1.39	36.81 ± 4.30
TN (g/Kg of TS)	1.86 ± 0.42	2.10 ± 0.11	2.04 ± 0.20
C/N ratio	29.64/1	83.33/1	17.71/1
Hemicellulose (%)	32.29 ± 0.49	ND	ND
Cellulose (%)	35.61 ± 2.78	ND	ND
Lignin (%)	22.56 ± 2.93	ND	ND

[a] not detected; [b] mean ± standard deviation

Biogas Production at Different AcoD Mixtures

The variation trends of the daily BGP and their BMP content *vs.* digestion period for the different AcoD compositions are depicted in Fig. 1(a-e). Biogas production began on the first day of fermentation. The digester containing SCB and inoculum produced the maximum yield of BGP during the first ten days, while other compositions had their peak BGP production on the 10th day of digestion. In general, each set had one peak in the first ten days, and another peak was observed before the twentieth day. Talha *et al.* (2016) reported that these two peaks were from two periods of biogas production. The first period could be due to degradation of the soluble sugar of the present substrates in the bio-digesters. The cellulose and hemicellulose decomposition caused the second period of biogas production about ten days after the first peak (Talha *et al.* 2016). Small peaks of biogas production were obtained because of provisional volatile fatty acid (VFA) accumulation or time differences between VFA production and its consumption by bacteria (Zhang *et al.* 2013). In contrast with the digesters treat-A, treat-B, treat-C, treat-D, and SCB (alone), the digester containing ORWW (alone) did not support the fermentation process, and this digester produced negligible biogas. This observation could be due to several factors such as low proper nutrient content and/or inadaptability of the microorganisms with the present substrates (Haak *et al.* 2016; Mehryar *et al.* 2016). The cumulative bio-methane production trends for the different AcoD mixtures are represented in Fig. 1 (a-e). Figure 2-a and Table 2 represent the cumulative BGP and its bio-methane content. The treat-B produced 129.37 ± 8.58 mL/gVS and 60.84 ± 15.55 mL/gVS as a cumulative BGP and BMP, respectively, which is not significantly different from that of treat-C. Thus, treat-B and treat-C produced the same cumulative BGP and BMP when using 20% less SCB.

Table 2. $LSD_{0.05}$ Analysis of Kinetic Parameters for Different AcoD Treatments

Parameters Treatments	Retention Time (day)	CODs % Reduction	Cumulative BGP (mL/gVS)	Cumulative BMP (mL/gVS)
ORWW	3.00 ± 0.00[c]	0.00 ± 0.00[c]	8.83 ± 2.89[d]	1.00 ± 071[d]
treat-A	34.00 ± 4.51[b*]	33.10 ± 9.79[b]	105.43 ± 5.94[c]	40.87 ± 1.93[c]
treat-B	34.00 ± 1.53[b]	29.48 ± 5.93[b]	129.37 ± 8.58[bc]	60.84 ± 15.55[b]
treat-C	34.00 ± 2.65[b]	49.67 ± 0.38[a]	142.22 ± 12.49[b]	66.10 ± 6.22[b]
treat-D	34.00 ± 1.53[b]	30.89 ± 6.71[b]	154.72 ± 10.17[ab]	97.13 ± 8.24[a]
SCB	39.67 ± 0.94[a]	22.34 ± 1.63[b]	177.32 ± 4.24[a]	95.95 ± 1.94[a]

[*] mean ± standard deviation

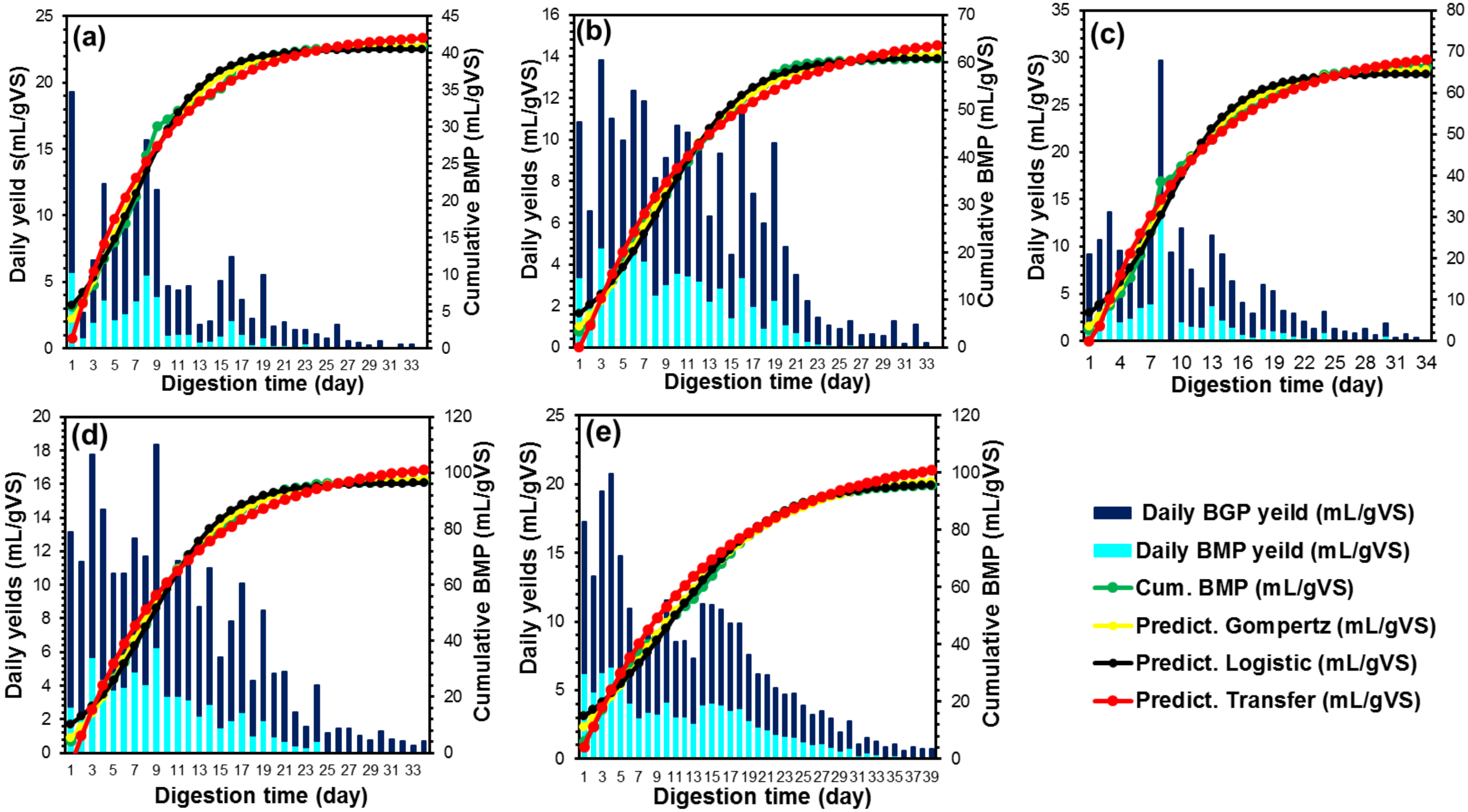

Fig. 1. Daily biogas and bio-methane production yields (BGP and BMP), experimental and predicted data of cumulative BMP for (a) treat-A, (b) treat-B, (c) treat-C, (d) treat-D, and (e) SCB.

Comparing the experimental results of treat-D to that of SCB alone, the cumulative BGP was the same, but the BMP content was higher with lower SCB consumption, suggesting the beneficial effect of applying AcoD on ORWW fermentation. The results confirmed that by decreasing the SCB portion in the AcoD mixtures, the cumulative BGP and BMP decreased non-linearly. The experimental results of 1:4 AcoD composition also confirmed the benefits of lower SCB consumption with higher biogas and bio-methane production. Several applications for SCB waste already exist, such as fuel for boilers, animal feed, and composting (IME 2010; Janke *et al.* 2016; Talha *et al.* 2016), while the end use of ORWW is to release it to rivers after purification decreases its toxicity (Zhang *et al.* 2015). By applying AcoD to these two substrates, a portion of SCB, which is a valuable waste material, can be replaced by ORWW (as a malnourished substrate), which does not have more environmental friendly applications. And the produced biogas as the main product of this AcoD process and other by-products, including liquid fraction of digested effluent as usable water for irrigation and solid fraction of digested effluent as a fertilizer, can increase the added value of these substrates.

CODs, pH and TAN Profiles During AcoD Period

By continuing the AD process, a substrate's polluting indexes, such as CODs and VS, can be decreased, which is one of the benefits of the AD process. The CODs is the most important parameter used to evaluate the AcoD process for waste-activated sludge or wastewater with the other organic substrates such as dairy manure (Hassan *et al.* 2016). In the present research, the CODs value was measured every three days, and the results are shown in Fig. 2-b. When increasing the SCB proportion in the AcoD mixtures, the CODs peaks became predominant (except with SCB treatment). Other AcoD treatments did not support the same conclusion for CODs removal. AD is a multi-stage process that is divided into hydrolysis, acidogenesis, and breaking of long chain polymers like carbohydrates (cellulose, hemicelluloses, starch, *etc.*), oils and fats, and proteins to monomers, sugars, fatty acids, and amino acids, respectively (Kothari *et al.* 2014). This process converts the available nutrients to the edible and expendable forms for the microbial community, supporting their activities to continue the AD process. The CODs values increase by surpassing the hydrolysis stage. Growing methanogenic bacteria and consuming converted nutrients through the third and fourth stages of the AD process leads to bio-methane and carbon dioxide production (Fang *et al.* 2014) as well as CODs reduction. The estimated CODs variation trends (Fig. 2-b) clearly illustrate these processes and activities. The CODs removal rates for the different AcoD treatments are represented in Table 2. The highest CODs removal rate was 49.67 ± 0.38% for treat-C, which achieved a 122.34% improvement in the CODs removal rate compared to control treatments. Generally, the CODs removal rates for the different AcoD compositions were higher than that of mono digested ORWW and SCB. This result showed that utilizing the AcoD technique improves CODs removal efficiency. The present experimental results agreed with previous reported results for trends in CODs removal (Hassan *et al.* 2016; Mehryar *et al.* 2016; Talha *et al.* 2016).

The pH is one of the most important operational parameters that efficiently improves or prevents the AD process. Different pH ranges that are considered proper and healthy for the AD process are mentioned in previous studies (Ahn *et al.* 2010; Zhang *et al.* 2014); the discrepancies could be due to differences in the required pH for the various microorganisms present in the anaerobic digesters. Zhang *et al.* (2014) reported that a pH range of 4.0 to 8.5 is the comprehensive range for fermentation bacteria growth, while the optimum or preferred range for methanogenic archaea is limited to the range of 6.5 to 7.2. However, Ahn *et al.* (2010) confirmed that the pH range of 6.5 to 8.5 is suitable in achieving a normal and healthy AD system. As Fig. 3-a illustrates, the pH for all experiments were in the range of 7.02 ± 0.05 to 7.70 ± 0.10, which proved suitable for the stability and quality of the anaerobic fermentation process. During initiation of the digestion period, the pH in all digesters declined but started to increase after five to seven days. VFA production decreases the pH and consumption of the produced VFA; methanogenic bacteria increase the pH (Ahn *et al.* 2010). Biogas production is the first and main result of consuming VFA in the methanogenesis stage of AD.

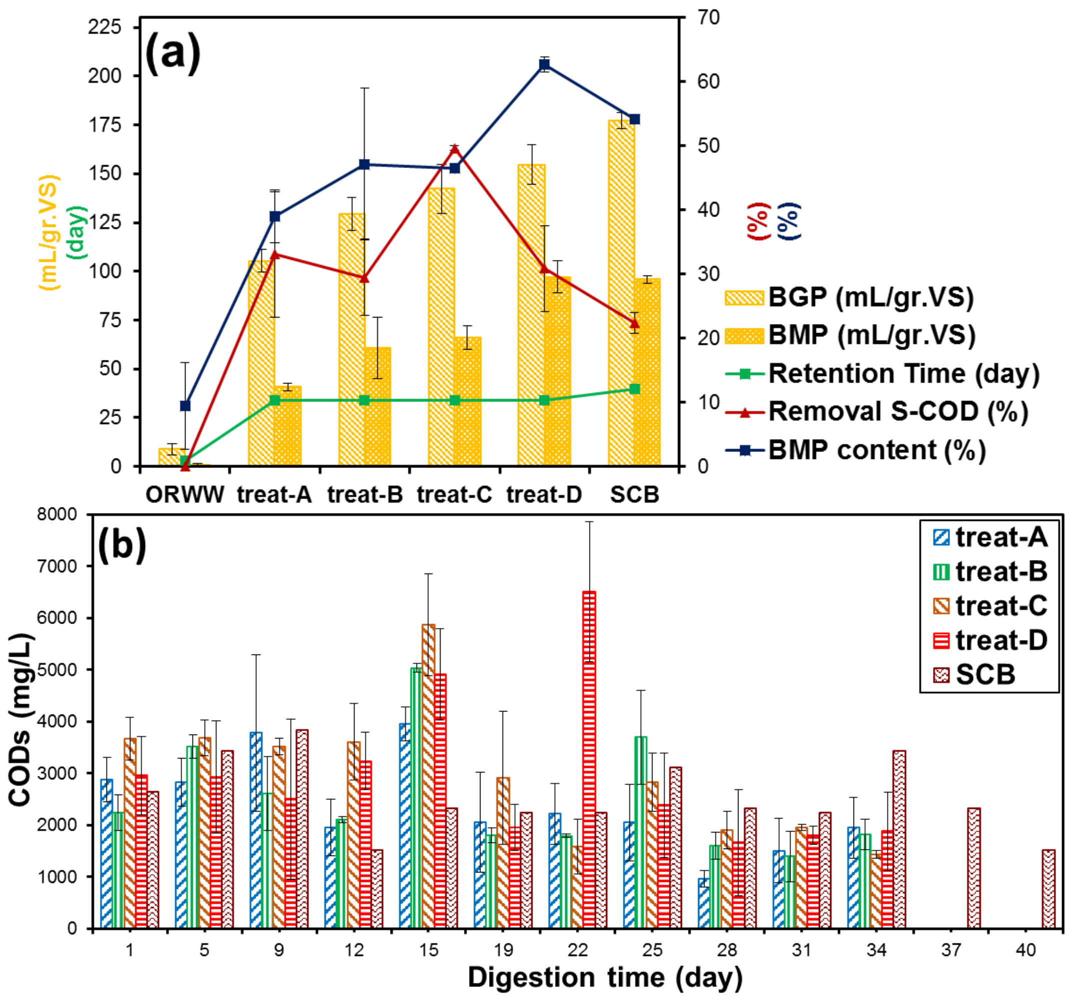

Fig. 2. (a) The kinetic parameters of the AcoD process, and (b) temporal CODs variation profiles for the different AcoD treatments.

Several components are necessary for microorganism growth in AD such as ammonia, volatile fatty acids (VFA) *etc.*, as well as acting as an inhibitor at high concentration levels (Chen *et al.* 2014). As some of the vital factors in the AD process, ammonia (NH_3) and ammonium (NH_4^+) are the products of the digestion process of proteins, urea, and nucleic acids (Mehryar *et al.* 2016). In previous reports, different suitable ammonia ranges are reported because of different process conditions such as pH, temperature, and utilized substrate characteristics such as C/N ratio. Chen *et al.* (2014) reported that several studies demonstrated a wide range of critical TAN and FAN, which was classified on the basis of different pH and temperature values. For the pH range of 6.8 to 7.8 at a temperature of 35 °C, a wide range of 1445 to 7000 mg/L for the critical TAN is illustrated, which inhibits 50 to 100% of bio-methane production (Chen *et al.* 2014). The TAN trends for the different AcoD compositions are depicted in Fig. 3-b. The comprehensive range of TAN variations was from 226.50 ± 9.02 mg/L to 1010.67 ± 260.87 mg/L. Except for the ORWW treatment (control digesters), the TAN concentrations for all other treatments were in the non-toxic range and provided the proper conditions to reach to a stable fermentation process. The applied substrates in the current study (ORWW and SCB) are carbon-rich materials. These types of the waste materials are good options for co-digesting with protein reach substrates such as manures. As the TAN variation trends demonstrated, these materials have good potential to optimize the C/N ratio in the digesters and cause ammonia dilution or prohibit its negative effect on the bio-methane production.

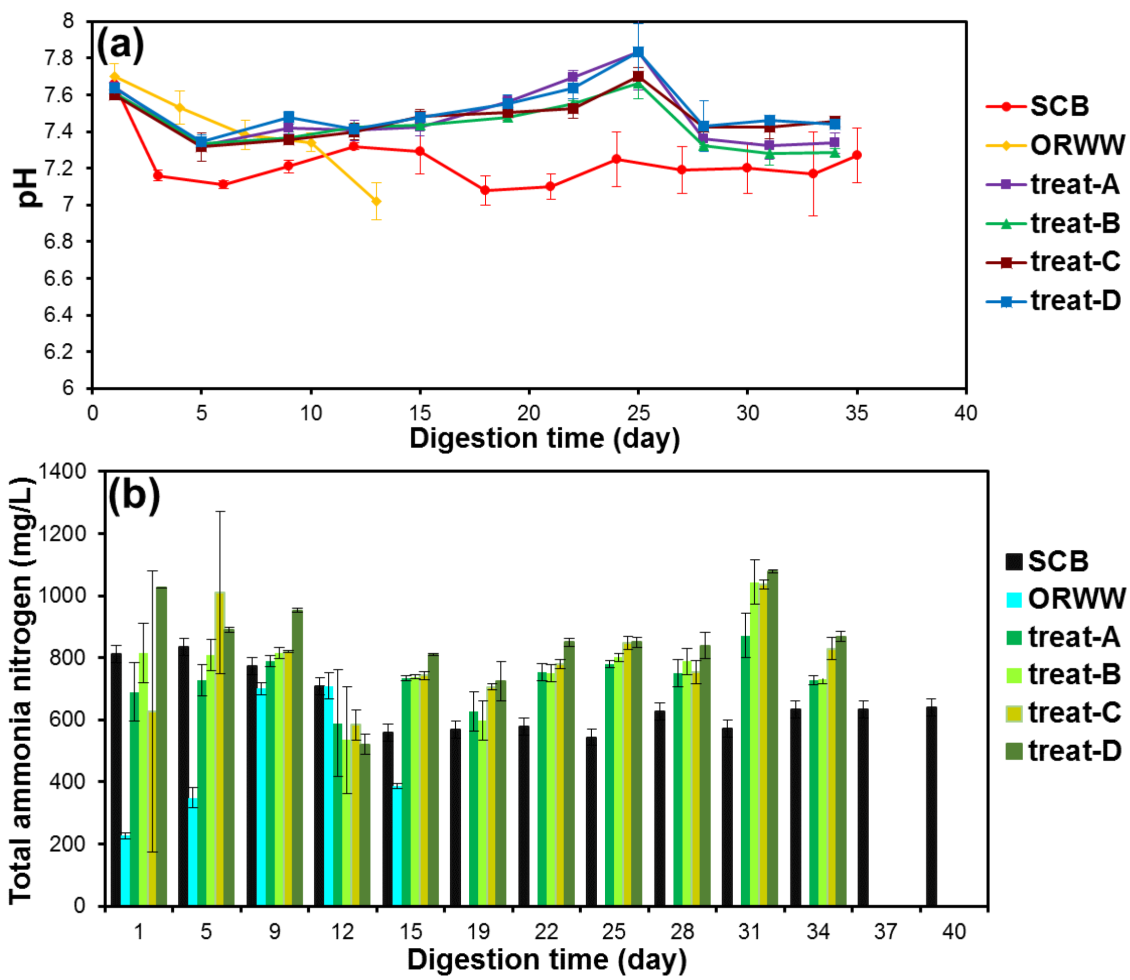

Fig. 3. The variation trends of (a) pH, and (b) total ammonia nitrogen (TAN) profiles for different AcoD treatment during the digestion period

Modeling the BMP Kinetics by Applying Mathematical Equations

Applying mathematical equations to model the BMP kinetics is useful in obtaining modeling parameters such as the potential methane production (*A*) and the maximum rate of methane production (μ_m)., which are advantageous indexes for evaluating different AcoD compositions. The computed values of model parameters and evaluating indexes (R^2, *MAPE* and *RMSE*) are presented in Table 3. The fitting data curves are depicted in Fig. 1 (a-e). The R^2 values between experimental data and fitted data of the modified Gompertz model range from 0.994 to 0.999 for different AcoD mixtures. The estimated values for R^2, *MAPE* and *RMSE* revealed that the other two applied models did not fit as well as the modified Gompertz model. Their fitting with the experimental data yielded almost the same R^2. However, larger *MAPE* and *RMSE* values compared with the modified Gompertz model were observed. The estimated values for R^2 and *RMSE* revealed that the other two applied models did not fit as well with the experimental data with almost the same R^2 but larger *RMSE* values compared with the modified Gompertz model. Thus, the best fit was observed with the modified Gompertz model, which confirmed previous research that demonstrated this model fits experimental BMP data well (Huiliñir *et al.* 2014; Owamah and Izinyon 2015).

Table 3. Computed Values of Model Parameters for the Different AcoD Mixtures

Model Name	Model Parameters	AcoD Mixtures Compositions				
		treat-A	treat-B	treat-C	treat-D	SCB
Modified Gompertz model	A	41.030	62.160	65.870	98.210	99.050
	μ_m	3.295	4.143	4.868	7.121	4.432
	λ	0.308	0.896	1.407	1.325	-0.755
	R^2	0.994	0.998	0.994	0.999	0.996
	MAPE	3.051	3.510	3.887	2.754	4.933
	RMSE	0.940	0.962	1.672	0.884	1.822
Logistic function model	A	40.440	60.950	64.610	96.390	96.260
	μ_m	3.140	3.979	4.961	6.898	4.264
	λ	0.316	1.025	1.499	1.499	-0.716
	R^2	0.992	0.995	0.986	0.995	0.994
	MAPE	3.006	7.359	10.805	8.180	7.231
	RMSE	1.083	1.358	2.546	2.054	2.261
Transfer function model	A	42.720	66.510	70.800	104.9	107.600
	μ_m	5.310	6.356	7.146	10.63	7.071
	λ	0.751	1.228	1.467	1.416	0.443
	R^2	0.981	0.988	0.987	0.987	0.992
	MAPE	6.999	7.084	9.391	10.937	5.179
	RMSE	1.631	2.128	2.454	3.423	2.475

A: the BMP potential; μ_m: the maximum rate of the BMP; λ: the lag-phase; R^2: the co-efficient of determination; *RMSE*: root mean squared error; *MAPE*: mean absolute percentage error

Huilinir *et al.* (2014) reported that the modified Gompertz model and Logistic function are proper equations for modeling sigmoidal kinetics, while the Transfer function provides a better fit of the first-order curves which state the maximum rate of BMP at the beginning of digestion period and decreasing steeply until the end of fermentation process (Huiliñir *et al.* 2014). The computed results for μ_m proves that treat-D has the maximum rate of methane production among all AcoD mixtures. This result confirmed the results discussed in the last section. The model parameters illustrated that the cumulative BMP volumes of treat-D and SCB were approximately equal to that of the experiment, while the SCB portion in the digester treat-D was 20% lower than that for digester SCB. The application of the AcoD technique determined that treat-D is the optimum mixing ratio with the same BGP volume, higher BMP content, and CODs removal rate with a shorter retention time compared with the control digesters (ORWW and SCB treatments).

Implementation of the Artificial Neural Networks (ANN) Modeling

Three different ANN algorithms (BPNN, GRNN, and RBFNN) were applied to model the BGP data. The error performance parameters (R^2 and *MSE*) are represented in Table 4. The experimental and predicted BGP data are shown in Fig. 4. The fit data illustrated that the RBFNN could not predict the experimental data well. On the other hand, the R^2 values for BPNN and GRNN confirmed that these algorithms could predict the BGP near the experimental data. Similar R^2 values were obtained by other researchers (Sridevi *et al.* 2014), who applied the BPNN algorithm to model bio-hydrogen production.

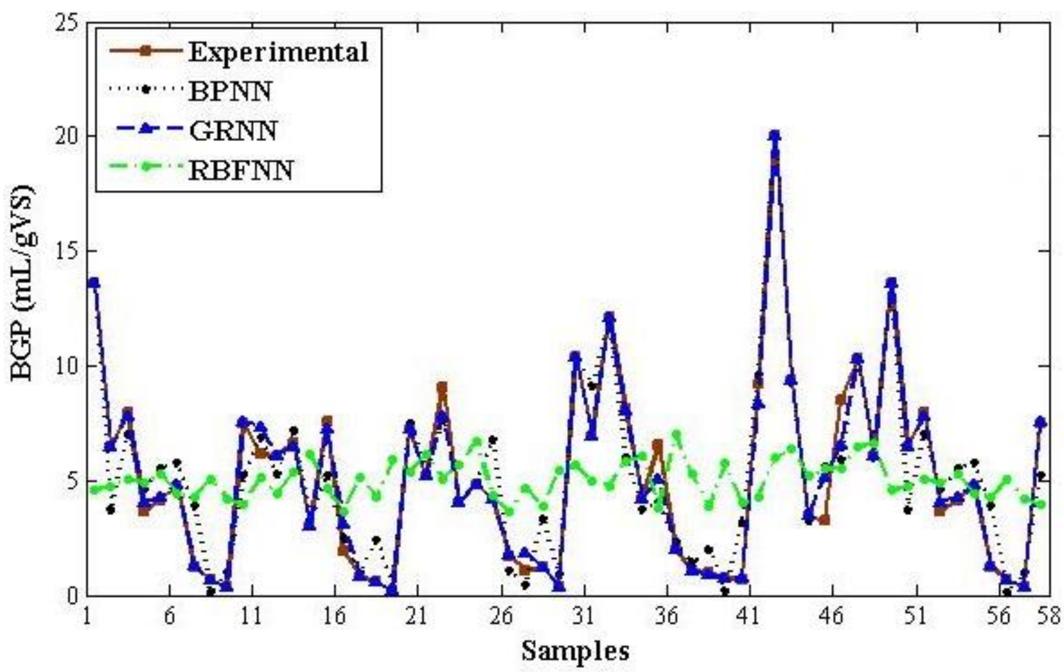

Fig. 4. Experimental and fitting biogas production (BGP) yield with using three different neural network algorithms. BPNN: back propagation neural network; GRNN: Generalized regression neural network; RBF: Radial basis function neural network

Table 4. Error Performance Parameters for Different ANN Algorithms

Parameters / ANN Algorithms	*Training*		*Testing*		*All*	
	R^2	*MSE*	R^2	*MSE*	R^2	*MSE*
BPNN	0.9769	7.4666	0.6214	16.6026	0.9658	7.5946
GRNN	0.9819	32.2324	0.7896	5.1637	0.9463	42.6910
RBFNN	0.0391	14.9092	0.0064	5.8034	0.0446	15.8674

MSE: Means squared error; R^2: the co-efficient of determination

CONCLUSIONS

1. The AcoD compositions confirmed that SCB is a superior co-substrate to improve the AD process of ORWW. The 1:4 AcoD composition delivered the same BGP volume with a higher BMP content. BGP was enhanced with 20% less SCB consumption.
2. Applying the AcoD technique improved the CODs removal rate from 22.34 ± 1.63% for the SCB mono-digestion to 49.67 ± 0.38% for the 2:3 AcoD composition of ORWW with SCB.
3. Modeling the experimental BMP data using various mathematical equations illustrated that the modified Gompertz model satisfactorily fit the experimental data. The computed values of μ_m showed that the 1:4 AcoD composition has the maximum rate of the methane production and therefore was the optimum AcoD ratio.
4. Utilizing three different ANN algorithms (including BPNN, GRNN, and RBFNN) for modeling the BGP volume confirmed that the BPNN algorithm with 3-8-1 designed architecture is the most accurate fitting of experimental BGP data.
5. Surveying TAN variation trends during the digestion period revealed the potential of this mixture (ORWW with SCB) to AcoD with protein-rich substrates like dairy manures.

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