Online measurement of alkalinity in anaerobic co-digestion using linear regression method

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Abstract: Alkalinity is a reliable indicator of process stability in anaerobic digestion system. Total alkalinity (TA) and partial alkalinity (PA) are usually monitored offline as indicators for the status of anaerobic digestion process. In order to online monitor TA and PA, the linear regression method was used as estimator to predict alkalinity via software sensor method. Parameters, namely, pH, oxidation and reduction potential (ORP), and electrical conductivity (EC), were used as input variables. EC was the most significant parameter with TA and PA. Multiple linear regression (MLR) models and simple linear regression models with EC were constructed to predict TA and PA in anaerobic co-digestion system. On the basis of the evaluation of prediction accuracy, the applications of linear regression models were better for monitoring PA than TA. MLR models provided higher accuracy for alkalinity prediction than simple linear regression models. The two MLR models based on single-phase anaerobic digestion system were also feasible to predict TA in anaerobic co-digestion systems. However, the accuracy of these models should be improved by calibrating for broad applications of linear regression method in online alkalinity measurement.

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1 Introduction

Anaerobic digestion is a common method applied in the treatment of organic wastes. The stability of anaerobic digestion process is considered the key point to maintain the methane production in the digester, specifically for the co-digestion system with various substrates. To observe unstable anaerobic digestion system early and prevent system failure, an efficient monitoring system should be developed. PH is one of the most fundamental parameters, but pH is less sensitive to the changes in the anaerobic digestion system. Thus, process status is not efficiently indicated based on pH[1]. Alkalinity has been proposed as another key parameter to control anaerobic digestion processes since 1964[2]. Palacios-Ruiz[3] found that alkalinity is a better indicator than pH for process control. Monitoring total alkalinity (TA) is beneficial to prevent a pH decrease in digesters[4,5], but partial alkalinity (PA) is more sensitive for imbalanced process detection than TA[6-9].

On the basis of the importance of monitoring

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alkalinity, online measurement of alkalinity was developed for application in the current monitoring systems. Different from the titration method for offline alkalinity measurement, an online titrimetric sensor with a pH probe[10] and an automated spectrophotometric system using pH indicator[9] were developed to measure alkalinity online. Although the measurement time of these two methods has been shortened to less than 5 min, the reduction of reagent consumption and real-time control of anaerobic digestion processes have not yet been achieved. The near infrared reflectance spectroscopy (NIRS) method via a calibration model and the software sensor method by mathematical models have also been proposed to monitor alkalinity[11-13]. Both of these methods could obtain the alkalinity values in real time. NIR spectrometer is additional necessary equipment for monitoring system using NIRS method. Furthermore, the software sensor method is a combination of hardware sensor and an internal software estimator. This method could be applied to predict the parameters that require expensive equipment or cannot be measured directly on the basis of related but less expensive measurements by online estimation[14,15]. Therefore, considering the realization of real-time control and the utilization of easily measured parameters, software sensor method combined with less expensive hardware sensor and simple software estimator can be easily developed. The use of multivariate sensor technologies has been recommended in many studies[16]. In previous studies, software sensor method was developed to predict TA from the anaerobic digester with single substrate. However, given the difficulty in achieving a nutrient balance in the anaerobic digestion system with single substrate, co-digestion has been increasingly developed to improve process performance in recent years. Anaerobic co-digestion systems are more stable than single-phase anaerobic digestion systems. Additionally, many types of organic wastes can be treated using co-digestion. Nevertheless, the characteristic of mixed substrates is more difficult to maintain within a suitable condition than single substrate, such as C/N, because of the difference in substrates. Thus, the software sensor method towards alkalinity measurement was developed in the present study for an anaerobic co-digestion system to promote the application of anaerobic co-digestion.

Many parameter measurements during anaerobic digestion process can be performed by using simple electrodes. These parameters, such as pH, oxidation and reduction potential (ORP), and electrical conductivity (EC) are easily monitored using simple electrodes, which are inexpensive to be calibrated and cleaned regularly. In anaerobic digestion processes, alkalinity is a parameter related to buffer capacity, which is influenced by carbonate, ammonium, phosphate, VFA and sulfide subsystem. The buffering concentration of each subsystem was analyzed based on pH ranges[17]. In addition, ORP is a measure of redox potential and can be used to define the condition of biochemical reactions[18]. An increase in ORP values inhibits the level of anaerobic digestion performance[19]. EC is defined as the ability of a solution to conduct electrical current. This parameter is proportional to the ionic concentrations in the solution[12]. Ionic concentration in anaerobic digestion processes depends mainly on VFA and carbonate/bicarbonate concentration[20]. Thus, carbonate/bicarbonate concentrations could be estimated by means of EC. According to their effects on alkalinity, pH, ORP and EC could be used as input variables to predict alkalinity via mathematical models.

Considering the development of anaerobic co-digestion, samples for alkalinity analysis were obtained from a continuous co-digestion system fed with cow manure, corn straw, and fruit and vegetable waste (FVW) at laboratory scale. Software sensor method was combined with the dataset of pH, ORP, EC and linear regression models, and used to predict TA in previous studies. With the development of TA determination via software sensor method, linear regression models were constructed to predict both TA and PA from the data of pH, ORP and EC in this study. The application of linear regression models for TA and PA prediction was evaluated by the accuracy of predicted values. The models constructed for alkalinity prediction from an anaerobic co-digestion system could be helpful for the development of software sensor method. These models are also beneficial to realize online measurement of alkalinity and thereby maintain the stability of anaerobic digestion system.

2 Materials and methods

2.1 Substrates

In the anaerobic co-digestion system, cow manure was the main substrate. Corn straw and FVW were used as the co-substrates. Cow manure was sourced from two dairy farms in Beijing, and corn straw was collected from corn fields. FVW was obtained from a fruit and vegetable market at the University of Science and Technology Beijing. Corn straw and FVW were shredded into small sizes (about 5 mm) and then homogenized. Cow manure and FVW were stored at −20°C, whereas corn straw was stored at room temperature. The characteristics of substrates are shown in Table 1.

Table 1 Characteristics of substrates in the anaerobic co-digestion system

Substrate	TS/%	VS/%	C/N
Cow manure 1	19.57	70.97	17.42
Cow manure 2	20.02	49.25	18.18
Corn straw	85.47	94.91	53.88
Fruit and vegetable waste	7.56	91.46	10.70

2.2 Digester and operating conditions

A continuous stirred tank reactor (CSTR) with 8 L working volume was used. The digester was operated at mesophilic temperature ((38±1)°C) with a stable mixing rate of 100±1 r/min. The digester operation consisted of three stages. The hydraulic retention time of all the stages was 20 d. The digester was purged and then fed once a day at the same organic loading rate (OLR) of 3.0 g VS/(L·d), and the mixing ratios of cow manure: corn straw: FVW based on VS contents during stages 1, 2 and 3 were 40:20:1, 15:5:1 and 15:5:1, respectively. The mixing ratio was changed from stage 1 to stage 2 to improve the treatment of cow manure and FVW. From stage 2 to stage 3, the source of cow manure was changed from cow manure 1 to cow manure 2. With the change of mixed substrates, various data of process performance were obtained for constructing prediction model.

2.3 Analytical methods

Total solids (TS) and volatile solids (VS) were measured according to standard methods[21]. The online measurements of temperature, pH and ORP were carried out using the temperature, pH and ORP meters installed in the digester, respectively. EC was measured by a conductivity meter (HQ14d, HACH, USA) offline. Alkalinity was measured as per titration method.

Samples for alkalinity measurement were centrifuged at 8000 r/min for 5 min. The supernatants were maintained prior to titration. TA was measured by potentiometric titration method. The samples reached the specified pH end-point at 4.3[21] after the addition of 0.1 mol/L hydrochloric acid. The TA values were determined by the volume of samples and acid. PA was measured by two end-point titrations. The samples for PA measurement were titrated with 0.1 mol/L sulfuric acid at pH 5.75[22].

In the potentiometric titration, the titration system was composed of a pH electrode (HI9125, HANNA, Italy), a cylinder magnet, and a magnetic stirrer. Each pH end-point was measured for 30 s to improve the titration accuracy. All titrations in this study were performed in triplicate.

2.4 Statistical analysis

Correlation analysis of all the parameters (i.e., pH, ORP, EC, TA and PA) was conducted with SPSS Statistics for Windows Version 21 (2012, IBM Corp.) to determine the relationship between the observed and predicted parameters.

Multiple linear regression (MLR) method is widely applied for multivariate data analysis. Regression models were established with MLR analysis. The significance of each input variable could also be determined based on the *t*-statistic and *p*-value. According to their effects on alkalinity, pH, ORP and EC were selected as the input variables, and the outputs were TA and PA. All programs for modeling were implemented in Microsoft® Excel.

Standard error of estimate (SEE) was calculated by using Equation (1) to evaluate regression models based on the number of input variables, predicted values, and observed values. The accuracy of each prediction model was evaluated by calculating the Bias, mean absolute error (MAE), and root mean square error (RMSE) between predicted and observed values. Calculation equations of the indexes are shown in Equations (2)-(4):

$$SEE = \sqrt{\frac{1}{(n-k-1)}\sum_{i=1}^{n}(P_i - O_i)^2} \quad (1)$$

$$Bias = \frac{1}{n}\sum_{i=1}^{n}(P_i - O_i) \quad (2)$$

$$MAE = \frac{1}{n}\sum_{i=1}^{n}\left|P_i - O_i\right| \quad (3)$$

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(P_i - O_i)^2} \quad (4)$$

where, n is the number of output samples; k is the number of input variables; and P_i and O_i are the predicted and observed values, respectively.

3 Results and discussion

3.1 Correlation between alkalinity and input parameters

The use of simple electrodes allowed the inexpensive measurement of pH, ORP and EC online. Therefore, these three parameters were selected as the input parameters to predict alkalinity via software sensor method. On the basis of total 60 datasets of parameter measurements, the correlation between alkalinity and input parameters was analyzed. The correlation results in Table 2 showed that all input parameters were significantly correlated with alkalinity. EC and pH were positively correlated with alkalinity. On the contrary, a negative correlation was observed between alkalinity and ORP. The correlation results showed that the buffer system was functioning with decreasing alkalinity to maintain the stability of anaerobic digestion system. The values of TA and PA were both increased with an increase in the EC value or ionic concentration. All the ORP values were negative in the anaerobic co-digestion system, which meant a reduction state of system. However, an increase in ORP values was related to a tendency of oxidation reactions in anaerobic digestion system, which may contribute to a decrease in alkalinity.

Among the input parameters, the most significant correlation was observed between alkalinity and EC. The coefficients of TA and PA were 0.983 and 0.985, respectively. The results indicated that alkalinity was most sensitive to the change of ionic concentrations, which could be determined by EC value.

Table 2 Correlation coefficient matrix of the parameters for pH, ORP, EC, TA, and PA

	pH	ORP	EC	TA	PA
pH		–0.891*	0.954	0.953	0.952
ORP	–0.891		–0.930	–0.927	–0.933
EC	0.954	–0.930		0.983	0.985
TA	0.953	–0.927	0.983		0.999
PA	0.952	–0.933	0.985	0.999	

Note: * All data were at 0.01 significant correlation in double sides.

3.2 Development of linear regression models for alkalinity prediction

Alkalinity data collected from the anaerobic co-digestion system consisted of a set of 60 data points. During the anaerobic co-digestion process, the operation was composed of three stages, with the change in mixing ratios and source of cow manure. The 60 data points were obtained from the three stages. The number of collected data points was 30, 16 and 14 for stages 1, 2 and 3, respectively. Considering the representative of each stage, the data points selected for modeling for stages 1, 2 and 3 were 20, 11 and 9, respectively. The other data points were selected for model validation. Therefore, 40 of the 60 data points were utilized to develop linear regression models for predicting alkalinity, and 20 were used for model validation. Table 3 shows the maximum, minimum, and mean values of pH, ORP, EC, TA and PA for modeling and model validation. The multiple regression results (Figure 1) showed that two MLR models with pH, ORP and EC for predicting TA and PA were obtained, as shown in Equations (5) and (6). The MLR model for PA prediction presented a slightly higher coefficient of determination (R^2) and adjusted R^2, and a lower SEE between the observed and predicted values, compared with the regression result of the MLR model for TA prediction. Moreover, according to MLR analysis, EC was the most significant factor among all the input variables with a considerably higher t-statistic and lower p-value than other variables. The values of t-statistic and p-value for EC were 6.23 and 3.47E-07 in the TA prediction model, and 6.57 and 1.2E-07 in the PA prediction model, respectively. Therefore, EC was considered the most important parameter for alkalinity prediction based on correlation and MLR analyses.

Given the importance of EC, a simple linear regression model with EC was constructed to predict alkalinity with Equations (7) and (8). The models for predicting TA and PA by EC were feasible based on the regression results shown in Figure 2. However, the comparison of regression results between MLR and simple linear regression models showed the good performances of regression models with the increase in input parameter number. Such good performance was indicated by the high R^2 and adjusted R^2 and low SEE.

$$TA=-12717.57+506.36\times EC+1378.58\times pH-7.43\times ORP \tag{5}$$

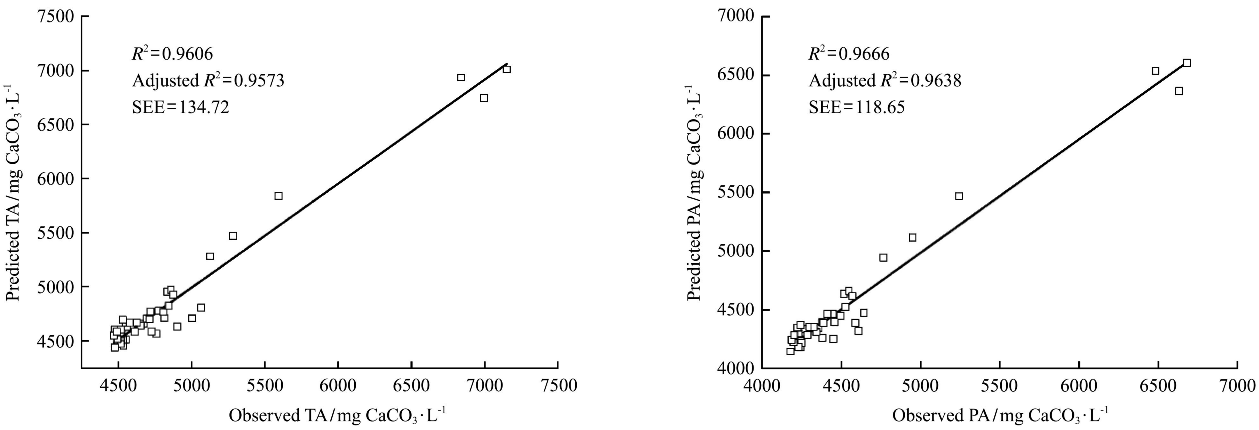
$$PA=-13708.48+470.91\times EC+1132.38\times pH-11.97\times ORP \tag{6}$$

$$TA\_EC=400.17+639.09\times EC \tag{7}$$

$$PA\_EC=265.78+612.74\times EC \tag{8}$$

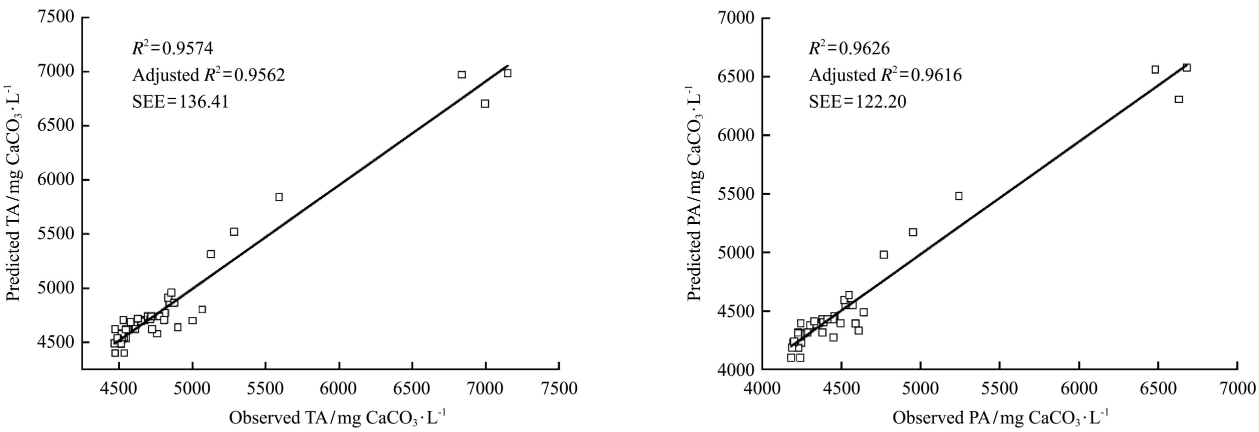
Table 3 Characteristics of data for modeling and validation

		pH	ORP/mV	EC/mS·cm^{-1}	TA/mg $CaCO_3$·L^{-1}	PA/mg $CaCO_3$·L^{-1}
Model 40 points	Maximum	7.27	–578	10.30	7150.00	6680.00
	Minimum	6.96	–604	6.26	4469.17	4181.67
	Mean	7.04	–585	7.03	4893.46	4573.77
Validation 20 points	Maximum	7.29	–579	10.41	7275.83	6826.67
	Minimum	6.97	–604	6.30	4476.67	4200.00
	Mean	7.05	–585	7.14	4950.75	4631.96



a. Model for total alkalinity prediction b. Model for partial alkalinity prediction

Figure 1 Regression of alkalinity prediction by pH, ORP and EC



a. Model for total alkalinity prediction b. Model for partial alkalinity prediction

Figure 2 Regression of alkalinity prediction by EC

3.3 Validation of linear regression models for alkalinity prediction

In addition to the MLR model shown in Equation (5), Ward et al.[11] and Argyropoulos[13] also proposed MLR models (Equations (9) and (10), respectively) for TA prediction. The simple linear regression and MLR models for TA and PA prediction were validated to evaluate the prediction performance. The accuracy of predicted values was evaluated by R^2, MAE, Bias and RMSE between predicted and observed values. Table 4 shows validation results. The comparison of predicted TA and PA values from the models constructed showed that application of linear regression model was better for PA than TA, with higher R^2 and lower MAE, Bias and RMSE. Considering the validation results of simple linear regression and MLR models, the values of evaluation indexes showed that MLR model provided a higher accuracy in alkalinity prediction than simple linear regression model. The values of Bias from simple linear regression models were at a low level, which was only 9.65 and 6.03 mg $CaCO_3$/L for TA and PA prediction, respectively. The positive Bias values showed that predicted values were higher than the observed values on average.

All predicted values of TA from TA_W and TA_A models were lower than the observed values according to the values of MAE and Bias. These observations could also be found in the predicted values shown in Figure 3. Although Ward's and Argyropoulos' models were feasible to predict the alkalinity from an anaerobic co-digestion system with high R^2, the accuracy of models was not satisfactory because of relatively high MAE, Bias, and RMSE.

$$TA\_W=(-7965+373.46\times EC+1483\times pH+0.459\times ORP)/1.22 \quad (9)$$

$$TA\_A=(-8906+384.2\times EC+1678\times pH+1.998\times ORP)/1.22 \quad (10)$$

where, 1.22 is the conversion factor for alkalinity in the form of $CaCO_3$ and HCO_3^-.

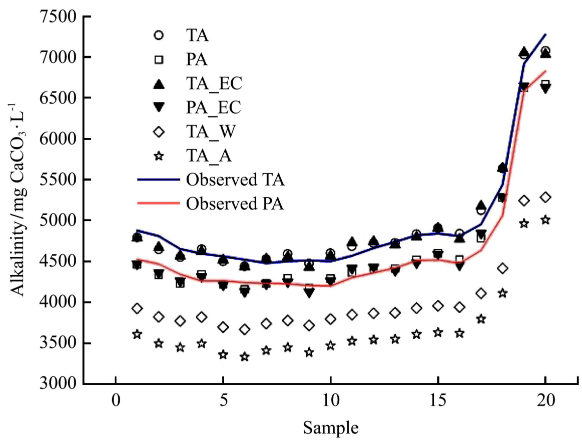


Figure 3 Prediction results of total alkalinity and partial alkalinity using linear regression models

Table 4 Validation results of linear regression models for TA and PA prediction

Predicted alkalinity	R^2	MAE /mg $CaCO_3 \cdot L^{-1}$	Bias /mg $CaCO_3 \cdot L^{-1}$	RMSE /mg $CaCO_3 \cdot L^{-1}$
TA	0.9807	89.73	16.03	110.99
PA	0.9833	76.22	11.89	93.83
TA_EC	0.9763	96.43	9.65	115.82
PA_EC	0.9794	82.25	6.03	103.32
TA_W	0.9799	942.53	-942.53	993.09
TA_A	0.9795	1262.12	-1262.12	1297.09

3.4 Comparison of different MLR models for total alkalinity prediction

MLR models provided a higher accuracy for alkalinity prediction than simple linear regression models according to the analysis in Section 3.3. Ward's and Argyropoulos' models for TA prediction were constructed based on anaerobic digestion systems with single substrates, but Equation (5) was developed to predict TA in anaerobic co-digestion system. Given the difference in substrates, two MLR models established in previous studies should be calibrated to improve the prediction accuracy in an anaerobic co-digestion system. Furthermore, the ratios of predicted values from different models were calculated to promote the application of MLR model towards online measurement of alkalinity. Table 5 shows that the ratios of TA_W to TA, TA_A to TA, and TA_W to TA_A were 0.81±0.02, 0.74±0.01 and 1.09±0.01, respectively. The ratio of TA_W to TA_A showed that although these two models were constructed based on the anaerobic digestion system with different single substrates, their predicted values were similar. Moreover, the value of relative standard deviation (RSD) was at the lowest level (0.92%).

Table 5 Comparison of predicted values from different MLR models

Ratio	Mean	Standard deviation	Relative standard deviation/%
TA_W / TA	0.81	0.02	2.47
TA_A / TA	0.74	0.01	1.35
TA_W / TA_A	1.09	0.01	0.92

The RSD values for the ratios of TA_W to TA and TA_A to TA were 2.47% and 1.35%, respectively. The RSD values were higher than the RSD for the ratio of TA_W to TA_A, which may be caused by the number change of substrates. Nonetheless, considering the low standard deviation and relative standard deviation, a transformation is feasible among different MLR models based on the ratios. The ratios could be helpful in calibrating the existing models on their coefficients.

4 Conclusions

Linear regression method was applied to predict alkalinity by using a dataset of pH, ORP, and EC. This software sensor method was developed towards online measurement of alkalinity in anaerobic co-digestion system. The following findings can be concluded based on the experiments and analysis:

1) EC and pH are positively correlated with alkalinity, but ORP is negatively correlated with alkalinity. The most significant correlation is between EC and alkalinity.

2) According to the results of MLR analysis, EC is the most significant factor on the change of alkalinity. Given the importance of EC, the simple linear regression model is preferred to predict alkalinity by EC.

3) The applications of simple linear regression and MLR models are better for predicting PA than TA. MLR models presented a higher accuracy in alkalinity prediction than simple linear regression models based on the values of R^2, MAE and RMSE.

4) The MLR models based on single-phase anaerobic digestion system were feasible to predict TA in anaerobic co-digestion system. However, the accuracy of these models was not satisfactory. On the basis of the ratios calculated from the predicted values of different MLR models, the existing models could be calibrated with a coefficient.

5) A large amount of data from different anaerobic co-digestion systems under different conditions are needed in future research to further develop the existing MLR model for broad applications with improved accuracy in the field of online alkalinity measurement.

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