

Improving the Biodegradability of Rice Straw by Electrochemical Pretreatment

Shaohua Sun^a, Yuanyuan Zhang^a, Zhaoyang Yang^a, Chunmei Liu^b, Xiaoyu Zuo^{b*}, Yang Tang^c, Pingyu Wan^c,
Yanping Liu^b, Xiujin Li^b, Frederic Coulon^e, Qing Hu^{f,g}, Xiao Jin Yang^{a*}

^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, 15 Beisanhuan East Road, Chaoyang District, Beijing 100029, China

^b Beijing city environmental pollution control and Resource Reuse Engineering Center, Beijing University of Chemical Technology, 15 Beisanhuan East Road, Chaoyang District, Beijing 100029, China

^c National Fundamental Research Laboratory of New Hazardous Chemicals Assessment and Accident Analysis, Beijing University of Chemical Technology, Beijing, 100029, China

^e School of Water, Energy and Environment, Cranfield University, Cranfield MK43 0AL, UK

^f School of Environmental Science and Engineering, South University of Science and Technology, Shenzhen, Guangdong 518055, China.

^g Beijing Huanding Environmental Big Data Institute, No. 1 Wangzhuang Road, Beijing, 100083, China

Highlights

- Chemical and electrochemical pretreatments are investigated for rice straw anaerobic digestion;
- Electrochemical NaOH-H₂O₂ pretreatment improves the biogas production by 8-22%;
- A 5-h electrohydrolysis is equivalent to 3 days of NaOH-H₂O₂ chemical pretreatment;
- The biogas production with different pretreatments is predicted by modified Gompertz model.

Abstract

The efficacy of NaOH, alkaline hydrogen peroxide (NaOH-H₂O₂), electrochemically produced NaOH-H₂O₂ (eNaOH-H₂O₂) and electrohydrolysis (EH) pretreatments was investigated for anaerobic digestion of rice straw. The cumulative biogas production was enhanced by 8%, 22% and 14% in the NaOH-H₂O₂, eNaOH-H₂O₂ and EH relative to conventional NaOH pretreatment. The chemical and electrochemical pretreatments decreased the crystallinity of cellulose and created a porous surface vein. Electrochemical NaOH-H₂O₂ pretreatment is

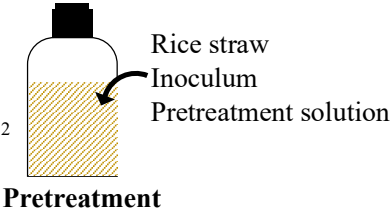
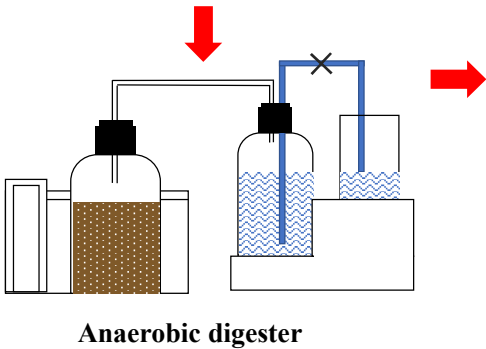
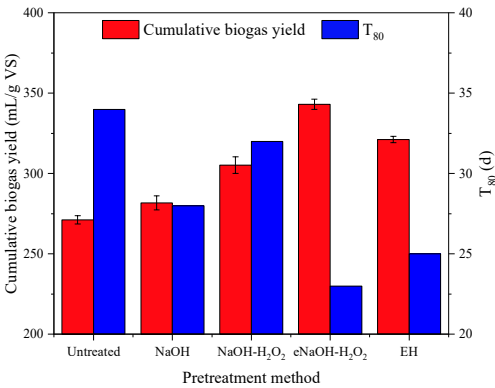
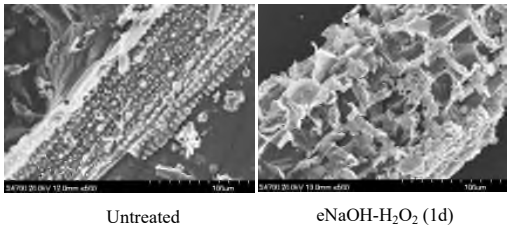
* Corresponding authors: zuoxxy@mail.buct.edu.cn; yangxj@mail.buct.edu.cn

efficient to promote microbial degradation of lignocellulose for biogas production while the risks associated with the transportation and storage of H_2O_2 are avoided. EH reduces the pretreatment time significantly and is a promising approach for utilizing rice straw biomass to produce renewable energy.

Graphical abstract

Four pretreatment methods:

- 1.NaOH
- 2.NaOH- H_2O_2
- 3.eNaOH- H_2O_2
- 4.EH



Main result

eNaOH- H_2O_2 : Electrochemically produced NaOH- H_2O_2
EH: Electrohydrolysis
 T_{80} : the time required to reach 80% of the total biogas production (T_{80})

Keywords: rice straw; pretreatment; anaerobic digestion; electrohydrolysis; electrolytic peroxide

1. Introduction

Rice straw (RS)* is one of the most abundant biomass resources available in China and southeastern Asia. RS is commonly used in anaerobic digestion (AD) to produce biogas [1]. RS consists of cellulose, hemicellulose and lignin, where crystalline microfibrils of cellulose are surrounded by amorphous hemicellulose, and both cellulose and hemicellulose are embedded in a matrix of lignin [2, 3]. Hydrolysis of lignocellulose is a limiting step for the AD process because its complex three-dimensional network is resistant to microbial degradation. Consequently, the AD efficiency is limited [4, 5]. Lignin, the dominant aromatic polymer in nature, has a highly cross-linked aromatic structure, containing aromatic, phenolic hydroxyl, and alcoholic hydroxyl groups and conjugated double bonds. Therefore, lignin readily reacts with many chemicals, including NaOH [6, 7].

Alkaline pretreatment is important in the destruction of lignocellulose biomass for its utilization, such as wheat straw and sugarcane bagasse [8-10] and NaOH pretreatment has been widely employed to improve the

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List of Abbreviations

Abbreviation	Description
RS	Rice straw
AD	Anaerobic digestion
NaOH-H ₂ O ₂	Alkaline hydrogen peroxide
eNaOH-H ₂ O ₂	Electrochemically produced NaOH-H ₂ O ₂
EH	Electrohydrolysis
T ₈₀	The time required to reach 80% of the total biogas production
SEM	Scanning electron microscopy
XRD	X-ray diffraction
HPW	High-purity water
VFAs	Volatile fatty acids
TS	Total solid
VS	Volatile solid
GC	Gas chromatograph
TCD	Thermal conductivity detector
FID	Flame ionization detector
CrI	Crystallinity index
TMY	Theoretical methane yield
B _d	Biodegradability
EMY	Experimental methane yield
B ₀	Maximal methane yield or the methane yield potential
μ _m	Maximum methane production rate
λ	Lag phase time
AN	Ammonia nitrogen

accessibility of RS and thereby biogas production efficiency [11, 12]. NaOH pretreatment improves the biodegradability of lignocellulose biomass by disrupting the lignin structure and breaking the linkage between lignin and the other carbohydrate fractions (i.e., depolymerization) [13, 14], thus making the carbohydrates in the hetero-matrix more accessible by swelling, solvation and saponification [15]. Chemical oxidation is another important process for lignin biomass destruction and depolymerization [16-18]. Of the different oxidative chemicals, H_2O_2 has found widespread applications as a green oxidative chemical and bleaching agent in the paper and cellulose industry [19]. H_2O_2 pretreatment can break the cell wall of RS and thus increase the accessibility of cellulose and hemicellulose to anaerobic microorganisms for improving biogas production [20, 21]. However, H_2O_2 pretreatment requires a relatively long time to break down the lignin, primarily because H_2O_2 does not possess swelling, solvation, and saponification properties. Therefore, the combined use of NaOH and H_2O_2 as pretreatment was reported to improve the biogas production of agricultural crop stalks, corn stover and rice straw [22-26]. Nevertheless, the safety risk in transportation and storage of H_2O_2 is a serious concern.

The electrochemical generation of alkali-peroxide is a well-established process by electrolyzing alkaline solution [27], which readily provides on-site preparation of NaOH- H_2O_2 , thus avoiding the transportation and storage of H_2O_2 and associated safety risks. Importantly, electrochemically generated NaOH- H_2O_2 (eNaOH- H_2O_2) contains oxidative radicals ($\cdot\text{OH}$, $\cdot\text{O}_2^-$) [27-31] and it was found that these radicals can promote the destruction and depolymerization of lignocellulose [32, 33]. To the best of our knowledge, no studies regarding the use of eNaOH- H_2O_2 pretreatment for biogas production of RS anaerobic digestion have been reported. Alternatively, electrohydrolysis (EH) was reported to depolymerize lignin, where C-C bonds and C-O-C bonds are cleaved synergistically by direct anodic oxidation [32, 34] and a combined effect of ohmic heating, electrophoresis and electro-osmosis [35, 36]. Indeed, the cumulative methane yield of RS was improved by 31.4%-42.4% using EH pretreatment [37, 38]. The electrochemical pretreatment can breakdown lignin and lignocellulose, exposing cellulose and hemicellulose for microbial utilization. However, large electrical resistance and the loss of volatile fatty acids (VFAs) caused by ohmic heating are the limitations of the EH pretreatment. Therefore, it is of interest to compare eNaOH- H_2O_2 and EH with NaOH- H_2O_2 for anaerobic digestion biogas production from RS. Unpretreated and conventional NaOH pretreated RS were investigated as counterparts. The pretreatment performance was evaluated by the production of biogas and methane and the time required to reach 80% of the total biogas production (T_{80}). Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses were used to characterize the structural changes of RS after pretreatment and anaerobic digestion. The modified Gompertz model [39, 40] was examined to predict cumulative methane yield

for different pretreatment methods.

2 Materials and methods

2.1 Chemicals, pretreatment solutions, rice straw and inoculum

NaOH pellets (analytical grade) and hydrogen peroxide solution (30% wt, analytical grade) were purchased from the Aladdin company. High-purity water (HPW, $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used for the preparation of pretreatment solutions. NaOH (2% w/v)-H₂O₂ (6 % v/v) solutions were prepared by dissolving 2 g NaOH pellets and 6 mL hydrogen peroxide in 100 mL HPW. RS was collected from Tianjin, China, dried naturally, cut to 30-40 mm and then ground to 20 mesh (0.85 mm) using a grinder (Zhengde YSW-180, China). Anaerobic sludge samples collected from Xiaohongmen municipal wastewater treatment plant in Beijing were settled for 24 h in dark and cool conditions. The supernatant was decanted and the settlement was screened using a 1 mm sieve to remove impurities. The sieved suspension was used as the inoculum for anaerobic digestion.

2.2 Electrochemical preparation of NaOH-H₂O₂

The electrochemical preparation of NaOH-H₂O₂ solutions is illustrated in Figure 1. A two-chamber electrolytic cell consisting of an anode chamber (filled 200 mL 6M NaOH solution), a cation-exchange membrane and a cathode chamber (200 mL) was constructed for the preparation of NaOH-H₂O₂. A carbon cloth (40 × 25 mm) and the same size of titanium ruthenium plate were used for cathode and anode, respectively. The distance between the two electrodes was 30 mm and a cation-exchange membrane (CJDDMC-1, Heifei Chemjoy Polymer Materials Co., Ltd, China) was inserted. O₂ and HPW were pumped into the cathode chamber at a flow rate of 30 mL/min and 1 mL/min, respectively. A voltage of 5 V was applied using an electrochemical workstation (Shanghai Chenhua CHI760e, China) and the current density was set at 100 mA/cm². The electrochemically generated NaOH-H₂O₂ was termed as eNaOH-H₂O₂.

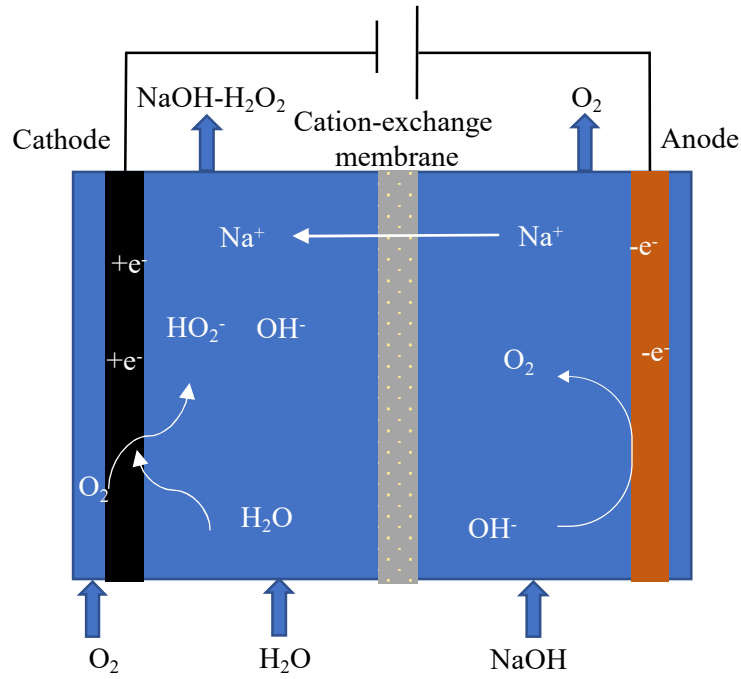


Figure 1. The diagram of electrolytic cell for producing eNaOH-H₂O₂ electrolyte

2.2 RS pretreatment

RS powders were mixed with pretreatment solution (NaOH, NaOH-H₂O₂, eNaOH-H₂O₂) in a 500 mL glass bottle and the mixtures were purged with nitrogen for 5-10 min. The bottle was placed in a temperature-controlled water bath at 35 ± 1 °C for 3 days. The mass to volume ratio of RS over pretreatment solution was 1:6 (20 g TS/120 mL). A negative control was also conducted using HPW instead of chemical solutions. Blank control (inoculum only) was not conducted because the biogas production from inoculum is negligible [41, 42]. For EH pretreatment, the cation-exchange membrane was removed and RS powders (20 g TS) were placed between the two electrodes and the electrolyte solution was 400 mL 2% (w/v) NaOH solution. The current intensity of 1.5 A was applied at a voltage of 5 V for 5 h. The temperature of the electrolytic cell was maintained at 35 ± 1 °C.

2.3 Anaerobic digestion of RS

After the pretreatment (NaOH, NaOH-H₂O₂, eNaOH-H₂O₂ and EH), the inoculum suspension of 100 mL (6g VS) was added to the digestion bottle followed by HPW to make up to 400 mL. The bottle was shaken to mix up and the pH of the solution was adjusted to 7. The anaerobic digestion was maintained at 35 ± 1 °C for 43 days and the volume of biogas production was measured by water drainage using measuring cylinder. Triplicates were carried out for each anaerobic digestion.

2.3. Analytical methods

TS and VS of the RS and inoculum were determined according to the standard methods for the Examination of Water and Wastewater[43]. The pH value was measured by a pH meter (Mettler Toledo, USA). Alkalinity was tested using a 0.1 M HCl titration method and represented in the manner of g equivalent $\text{CaCO}_3 \cdot \text{L}^{-1}$. Elemental composition (C, H, N, and S) of the RS was obtained by an elemental analyzer [44]. The content of oxygen was determined by assuming $\text{C} + \text{H} + \text{O} + \text{N} = 99.5\%$ on a VS basis. The cellulose, hemicellulose, and lignin contents were obtained according to the Van Soest method using an A2000 fiber analyzer (ANKOM, USA).

The methane contents of biogas samples were analyzed using a gas chromatograph (GC) (BeiFenRuiLi SP-2100, Beijing, China) equipped with a molecular sieve (TDX-01) and a thermal conductivity detector (TCD). An Alltech carbospher column was used. The column head pressure was maintained at 350 kPa. The temperatures of the oven, injector port, and TCD were 140, 150, and 150 °C, respectively. The carrier gas was argon, and the flow rate was 30 mL/min. A standard gas (BeiFenRuiLi Co., Beijing, China) composed of 10.02% hydrogen, 4.98% nitrogen, 50.10% methane, and 34.90% carbon dioxide were used for the calibration of the system. The content of VFA was determined using gas chromatography (GC2014, Shimadzu, Japan). It was equipped with a flame ionization detector (FID) and a DB-WAX123-7032 capillary column. Nitrogen was used as the carrier gas. The operational temperatures of the injector and detector were both maintained at 250 °C, and the temperature of column was increased from 100 to 180 °C at a rate of 5 °C / min.

SEM was used to analyze the morphology of the RS. Observing the material under a 10 kV acceleration voltage, the 500-times image obtained intuitively reflects the RS fiber's structural changes and interface conditions. The changes in the crystallinity of unpretreated and treated RS were investigated by XRD. Scans in a region of 2θ from 5 to 90° at a speed of 5°/min [45] were performed. The crystallinity index (CrI) was determined by Eq. (1) [46] as follows.

$$\text{CrI}(\%) = [(I_{002} - I_{18.0^\circ})/I_{002}] \times 100 \quad (1)$$

where CrI represents the crystallinity index (%), I_{002} represents the maximal scattered intensity at the main peak at approximately 22°, and $I_{18.0^\circ}$ represents the amorphous zone scattered intensity at 2θ of 18.0°.

2.4 Data analysis

Theoretical methane yield (TMY) was calculated based on the element content using the Buswell–Mueller

[47]:

$$\begin{aligned}
& C_n H_a O_b N_c + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{4} \right) H_2O \\
& \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8} \right) CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3c}{8} \right) CO_2 \\
& + cNH_3 \\
& TMY \left(\frac{mL CH_4}{g VS} \right) = \frac{22.4 \times 1000 \times \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8} \right)}{(12n + a + 16b + 14c)} \quad (2)
\end{aligned}$$

The anaerobic biodegradability (B_d) of the substrate was calculated based on the experimental methane yield (EMY) and the TMY according to Eq. (3) [48].

$$B_d = \frac{EMY}{TMY} \quad (3)$$

The cumulative methane yield was predicted using the modified Gompertz model (Eq. 4), which has been widely employed for methane production [49, 50]

$$B = B_0 \exp \left\{ -\exp \left[\frac{\mu_m e}{B_0} (\lambda - t) + 1 \right] \right\} \quad (4)$$

where B represents the cumulative methane yield (mL/g VS); B_0 is the maximal methane yield or the methane yield potential (mL/g VS); μ_m is the maximum methane production rate (mL/(gVS·d)); λ represents the lag phase time (d); t refers to the AD time (d); and e is equal to 2.72.

Data processing and graphing were completed using Origin 8.0 (OriginLab, USA).

3 Results and discussion

3.1 Effect of pretreatment time on pH

The physicochemical properties, surface structure and morphology of lignocellulose vary with pretreatment time during the process of pretreatment where the pH variation of the system is an important indicator [51]. As shown in Figure 2, the pH of NaOH, NaOH-H₂O₂ and eNaOH-H₂O₂ pretreatment systems decreases significantly from 9-10 to 5-6 within 2 days of pretreatment and then stabilizes at 4.92-5.48. This is the result of neutralization by acids produced by the hydrolysis of RS during the pretreatment. Therefore, a 3-day pretreatment is employed for these three methods in this study. The pH approached neutral in 5 h of the EH pretreatment and then the pH increased with further increasing the EH pretreatment time. Therefore, the EH pretreatment of 5 h was set in this work.

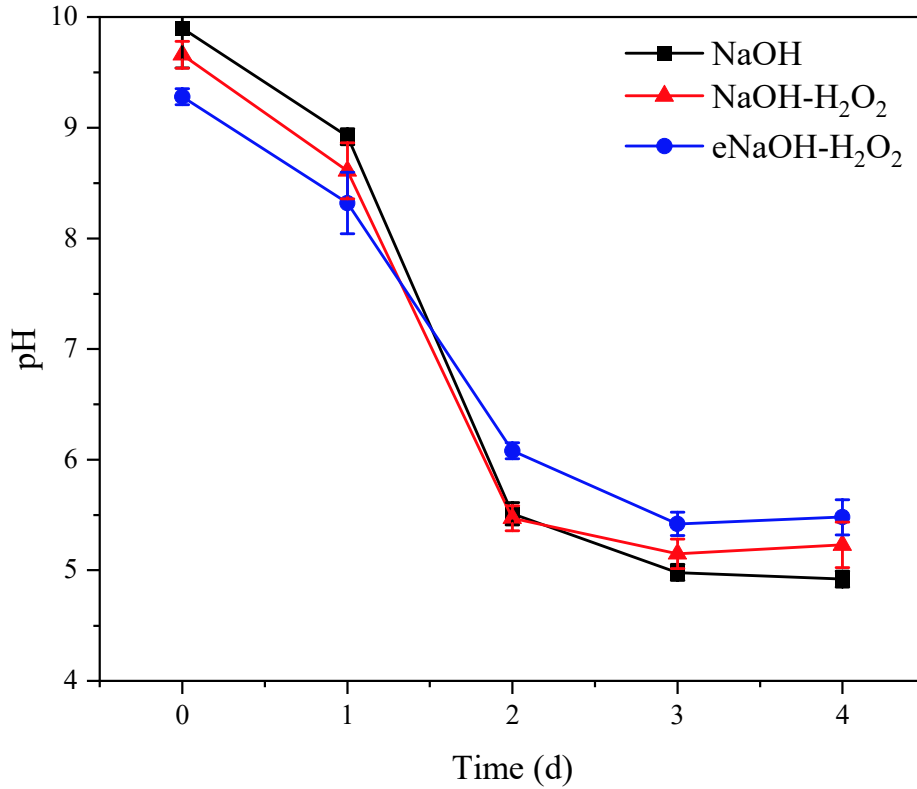


Figure 2. The pH profile of NaOH, NaOH-H₂O₂ and eNaOH-H₂O₂ pretreatment systems with time.

3.2 The effect of pretreatment on biogas production

The biogas production from unpretreated, NaOH, NaOH-H₂O₂, eNaOH-H₂O₂ and EH pretreated RS is shown in Fig. 2. Three to four peaks in the daily biogas production are observed (Figure 3a) and the daily biogas production ceases on the 3rd-5th day indicating the inhibition of the anaerobic digestion, the length of which is 8, 7, 5, 3 and 2 days for unpretreated, NaOH, NaOH-H₂O₂, eNaOH-H₂O₂ and EH groups, respectively. The inhibition of methanogenic activity and reduction of methane production are caused by the accumulation of VFAs in the fermentation of RS [52, 53].

The chemical formula of RS used in this study was determined as C_{100.9}H_{155.2}O_{71.4}N₁, and the chemical compositions of RS and inoculum are shown in Table 1. Therefore, the theoretical methane production is estimated as 458 mLCH₄/g VS. The highest peak of biogas production by eNaOH-H₂O₂ group is same with EH group but 15 days ahead of unpretreated group and 7 days earlier than the NaOH-H₂O₂ group. The majority of biogas production is between 20 and 33 days of anaerobic digestion (Figure 3b) and the cumulative biogas production was 271, 282, 305, 343, and 321 mL/g VS for unpretreated, NaOH, NaOH-H₂O₂, eNaOH-H₂O₂, and EH groups, respectively. Daily methane yield and cumulative methane yield are given in Figure 3 c, d. Clearly, NaOH pretreatment improves methane production as compared to unpretreated RS and this observation is in

agreement with previous studies [12]. Adding H₂O₂ to NaOH further increases methane production while the eNaOH-H₂O₂ pretreatment results in 5 % higher methane production than NaOH-H₂O₂. The total methane yields of NaOH-H₂O₂, eNaOH-H₂O₂, and EH groups were 9%, 15%, and 15% more than that of NaOH group, respectively.

Table 1. The chemical composition of RS and inoculum.

Parameter	Content (%)	
	RS	Inoculum
Total solid (TS)	93	7
Volatile solid (VS)	84	5
VS/TS	90	71
Cellulose	40	ND
Hemicellulose	30	ND
Lignin	11	ND
C	43	23
N	1	2
O	41	ND
H	6	ND
S	ND	ND

ND: not determined; VS/TS: the ratio of VS to TS

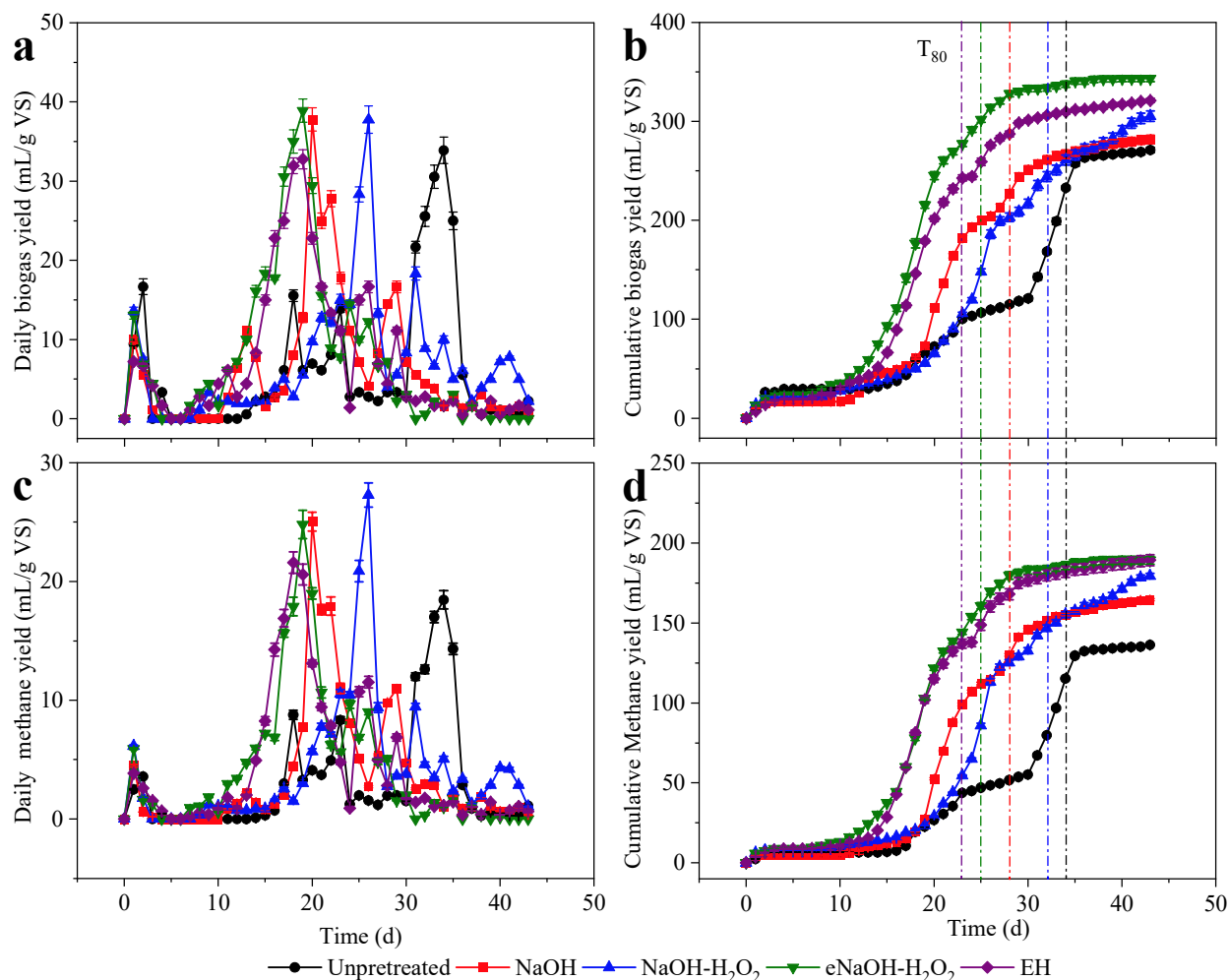


Figure 3. The biogas production from anaerobic digestion of unpretreated RS and pretreated by NaOH, NaOH-H₂O₂, eNaOH-H₂O₂ and EH.

The removal efficiencies of TS and VS are typical indicators for the biodegradability of biomass anaerobic digestion [54]. In this study, the final removal efficiencies of TS and VS from RS anaerobic digestion are 33 and 51%, 43 and 51%, 40 and 53%, and 40% and 55% by NaOH, NaOH-H₂O₂, eNaOH-H₂O₂ and EH pretreatment, respectively. TS removal efficiencies in NaOH-H₂O₂, eNaOH-H₂O₂ and EH pretreatment groups are 7-10 % higher than that with NaOH pretreatment while VS removal efficiencies are all most the same among these four pretreatments. B_d is another important indicator of the biodegradability of RS and the B_d values with the different pretreatments are shown in Table 2. Clearly, NaOH pretreatment improves the biodegradability of RS while NaOH-H₂O₂ and electrochemical pretreatments further improves it, resulting higher methane production yield.

Table 2. T_{80} , biogas and methane production yield and TS and VS removal efficiencies of anaerobic digestion of RS with different pretreatments

Pretreatment	Biogas yield (mL/g VS)	EMY (mL/g VS)	T_{80} (d)	B_d (%)	TS removal (%)	VS removal (%)
Unpretreated	271	136	34	30	25	40
NaOH	282	165	28	36	33	51
NaOH-H ₂ O ₂	305	179	32	39	43	51
eNaOH-H ₂ O ₂	343	189	25	41	40	53
EH	321	189	23	41	40	55

The anaerobic digestion time when biogas production achieves 80% of the maximum production (T_{80}) is the technical digestion time[55]. The total anaerobic digestion time was set for 43 days in this study and the T_{80} of unpretreated RS anaerobic digestion was 34 days. NaOH pretreatment shortens T_{80} by 6 days and eNaOH-H₂O₂ and EH pretreatment reduce T_{80} by 9 and 11 days. It is noted that the NaOH-H₂O₂ pretreatment's T_{80} is 4 days longer than the NaOH pretreatment. This is most likely caused by the inhibition of residual H₂O₂ on the methanogenesis process. Microbial inhibition by H₂O₂ is well recognized and the populations of methanogenic archaea are significantly reduced by high concentrations of H₂O₂ in bioenergy production from palm oil mill effluent by anaerobic co-digestion process[56]. As for the eNaOH-H₂O₂ pretreatment, the impurities introduced during the preparation process may catalyze the decomposition of H₂O₂, resulting in less residual H₂O₂ in the system. The stability of eNaOH-H₂O₂ and the effect of its storage time will be discussed later.

The stability of RS anaerobic digestion is evaluated by the system parameters of pH, VFAs, ammonia nitrogen (AN) and alkalinity (Table 3). The pH values of 6.9-7.4 are in the optimal range of anaerobic digestion and the VFAs concentrations are all well below the threshold of 1500 mg·L⁻¹ for a healthy anaerobic digestion system [57]. The AN concentration of 268-1570 mg·L⁻¹ in the effluents after the digestion is significantly lower than the inhibition limit of 4000 mg·L⁻¹ for methanogenesis. The alkalinity of unpretreated system is 4832 mg CaCO₃·L⁻¹ and that of 5579-6155 mg CaCO₃·L⁻¹ indicates the strong capacity of pretreated systems to buffer the acidification.

Table 3. pH, VFAs, ammonia nitrogen (AN) and alkalinity of untreated and pretreated systems

Pretreatment	pH	AN (mg·L ⁻¹)	Alkalinity (CaCO ₃ ·L ⁻¹)	VFAs (mg·L ⁻¹)
Untreated	6.5	1570	4832	510
NaOH	7.4	1193	5579	440
NaOH-H ₂ O ₂	6.9	989	6014	209
eNaOH-H ₂ O ₂	7.2	523	5861	153
EH	7.1	268	6155	80

3.3 Kinetic modeling

The modified Gompertz model is used to describe the dynamics of the AD process of corn stover[58] and Figure 4 shows the experimental and modeling results for methane yield of RS anaerobic digestion. The fitting parameters (B_0 , λ and μ_m) are summarized in Table 4. The R^2 values of 0.986-0.994 indicate that the experimental data fit well with the modified Gompertz model for the four pretreatments. The eNaOH-H₂O₂ pretreatment has the highest B_0 and μ_m and lowest λ , indicating the best performance of eNaOH-H₂O₂ pretreatment for methane production from RS anaerobic digestion.

Table 4 Parameters of the modified Gompertz models by different pretreatment methods.

Pretreatment	Modified Gompertz model			R^2
	B_0 (mL/g VS)	λ (d)	μ_m (mL/(gVS·d))	
NaOH	164.40±2.06	16.03±0.28	13.22±0.59	0.994
NaOH-H ₂ O ₂	182.52±4.87	16.31±0.45	11.48±0.70	0.986
eNaOH-H ₂ O ₂	191.86±2.07	11.44±0.29	15.41±0.69	0.993
EH	187.95±1.89	11.64±0.26	14.72±0.59	0.994

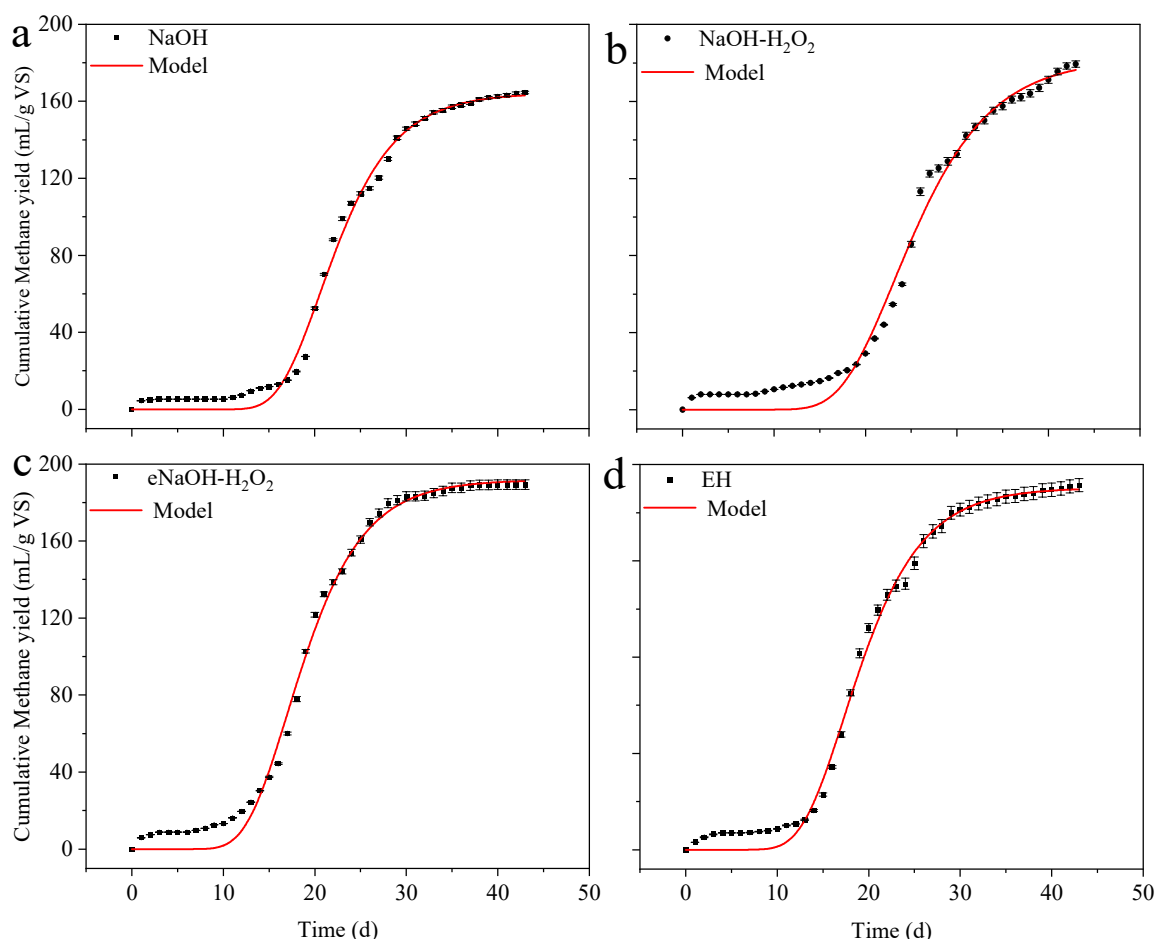


Figure 4. Biogas and methane production of anaerobic digestion of RS pretreated by a, NaOH, b, NaOH-H₂O₂, c, eNaOH-H₂O₂ and d, EH and the prediction by modified Gompertz model

3.4 SEM and XRD characterization of RS

Figure 5 shows the surface morphologies of untreated, NaOH, NaOH-H₂O₂, eNaOH-H₂O₂ and EH pretreated RS in SEM photographs. Clearly, surface morphologies of RS become porous, cracked, loose and/or fibrous after pretreatment and these changes are likely caused by the fragmentation of hemicellulose and lignin [59]. It was considered that the lignin, cellulose and hemicellulose of the lignocellulose was physically isolated to some extent by the pretreatment of NaOH, NaOH-H₂O₂, eNaOH-H₂O₂ and EH and the biogas production improvement is more likely related to the changes of “physical structures” of the lignocellulose. The cellulose and lignocellulose crystallinity of RS is estimated from the XRD diffraction peaks at the 2θ angle of 16° and 23° and it is 67.3%, 66.5%, 68.2%, 73.5% and 71.4% for untreated and pretreated by NaOH-H₂O₂, eNaOH-H₂O₂, and EH treatment, respectively. The crystalline structural change of lignocellulose is likely the result of removal of noncellulosic polysaccharides and the dissolution of amorphous zones. The changes in surface morphologies and crystallinity promote the bacteria to interact with cellulose and hemicellulose and enhance

anaerobic digestion. Pretreatment has been extensively employed to improve the anaerobic digestion of agricultural crop stalks, corn stover and rice straw [22-26].

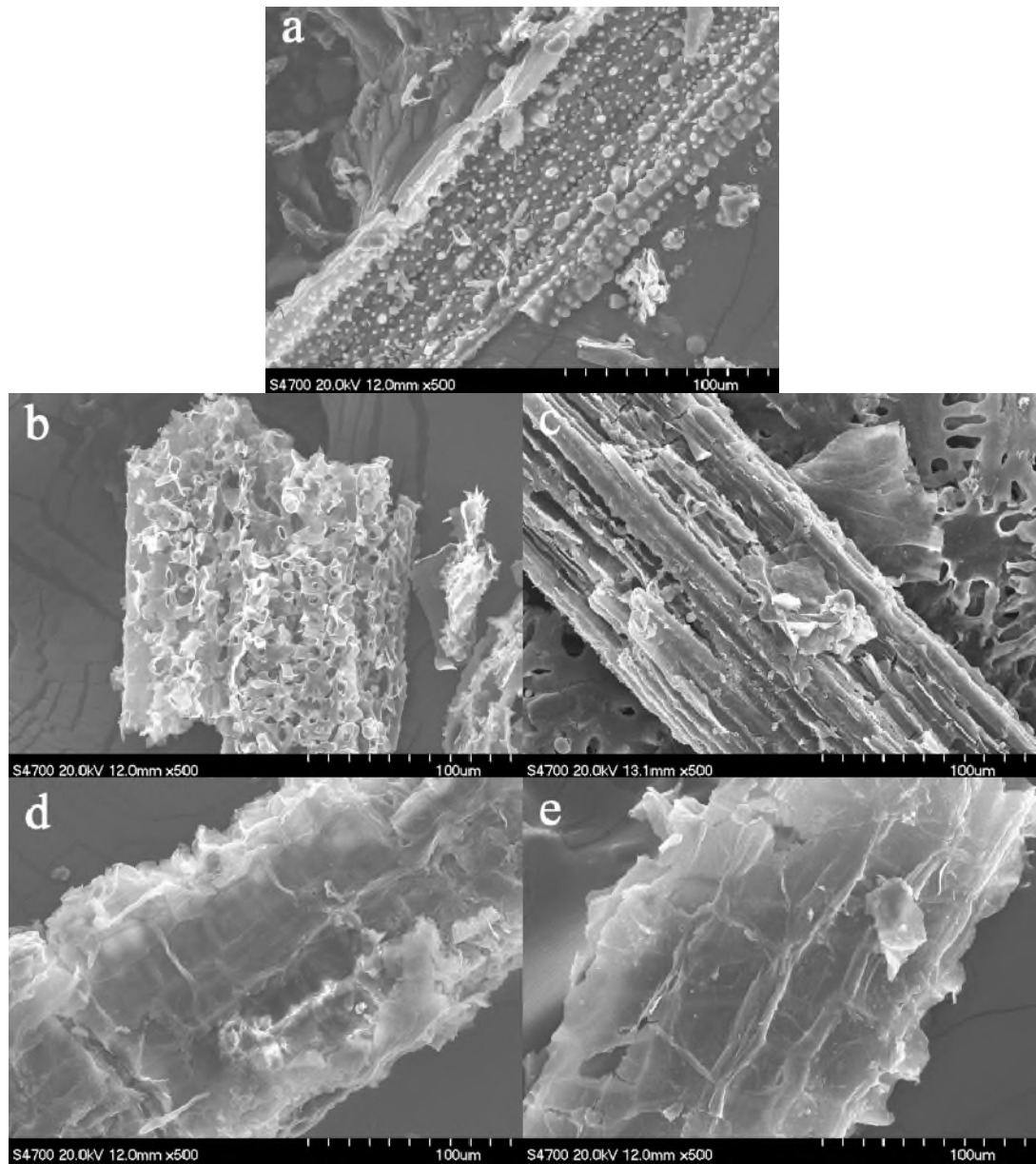
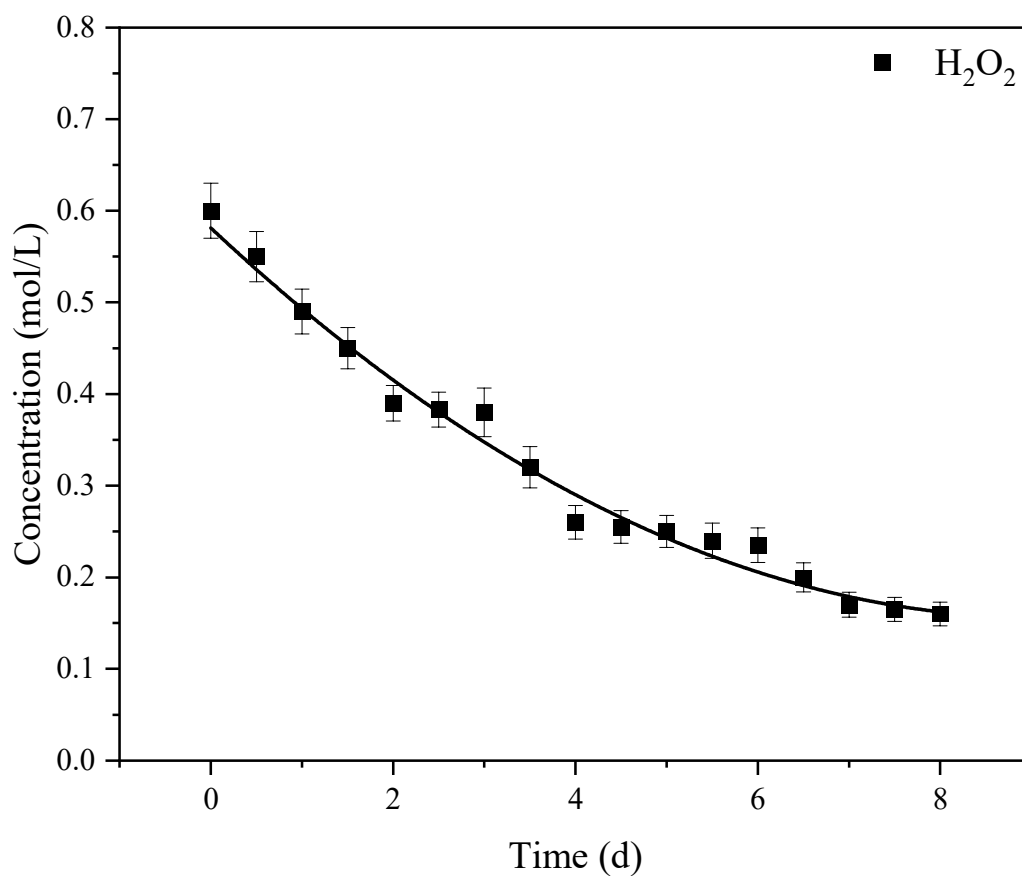


Figure 5. SEM images of RS: a, unpretreated; b, NaOH; c, NaOH-H₂O₂; d, eNaOH-H₂O₂; e, EH pretreated.

3.5 The stability of eNaOH-H₂O₂ and the effect of its storage time

The concentration of H₂O₂ in a fresh eNaOH-H₂O₂ solution sample decreases gradually with storage time and a loss of 37% H₂O₂ is observed over a period of 3 days storage under ambient temperatures and protection from light (Figure 6). The effect of eNaOH-H₂O₂ storage time on anaerobic digestion was investigated (Figure 7 and Table 5). Overall, the performance of biogas and methane production is similar among the pretreatment with fresh (0 days), 1-day and 2-day stored eNaOH-H₂O₂ despite that a slightly higher cumulative biogas and

278 methane production is observed in the 1 and 2-day stored eNaOH-H₂O₂ pretreatments.



279
280 Figure 6. The change of H₂O₂ concentration in electrochemically produced NaOH-H₂O₂ solution at room
281 temperature
282

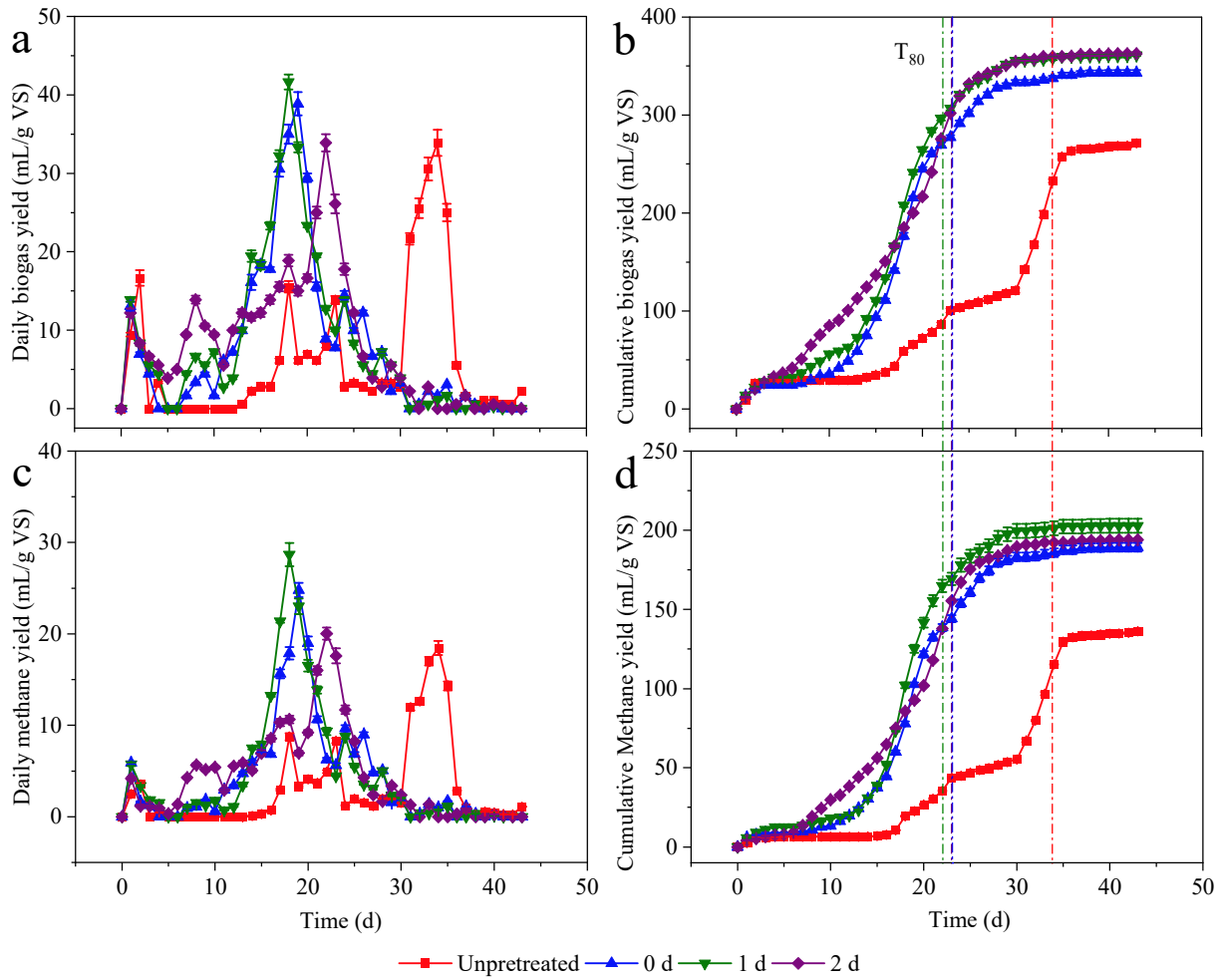


Figure 7. The biogas and methane production performance of anaerobic digestion of RS unpretreated and pretreated by fresh, 1-day and 2-day stored eNaOH-H₂O₂ solutions.

Table 5 T_{80} , biogas and methane production yield and TS and VS removal efficiencies of anaerobic digestion of RS unpretreated and pretreated by fresh, 1-day and 2-day stored eNaOH-H₂O₂ solutions

Pretreatment	T_{80} (d)	EMY (mL/g VS)	B_d (%)	TS removal (%)	VS removal (%)
eNaOH-H ₂ O ₂ (0 d)	23	189	37	40	54
eNaOH-H ₂ O ₂ (1 d)	22	203	40	48	58
eNaOH-H ₂ O ₂ (2 d)	23	194	38	45	55

4. Conclusion

This study confirms that conventional NaOH pretreatment improves the biogas production performance of rice straw by anaerobic digestion and demonstrates that adding H₂O₂ to NaOH further improves the performance

and that electrochemically produced NaOH-H₂O₂ and electrohydrolysis (EH) pretreatments are viable approaches to enhance the performance of rice straw's anaerobic digestion. The T₈₀ of eNaOH-H₂O₂ and EH pretreatments are shortened by 3-5 days and the cumulative biogas production of NaOH-H₂O₂, eNaOH-H₂O₂ and EH pretreatments are increased by 8-22% relative to the NaOH pretreatment. The concentration of H₂O₂ in the eNaOH-H₂O₂ solution decreases by 37% upon 2 days of storage under ambient conditions, but no significant differences in biogas and methane production are observed among fresh, 1-day and 2-day stored eNaOH-H₂O₂ pretreatments. The eNaOH-H₂O₂ pretreatment presents high methane production efficiency while eliminating the safety risks associated with H₂O₂ transportation and storage.

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AUTHOR INFORMATION

Corresponding Author

*E-mail: zuoxy@mail.buct.edu.cn; yangxj@mail.buct.edu.cn

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