STUDY ON THE INFLUENCE OF PRETREATMENT WITH ALKALI ON THE COMPOSITION AND ANAEROBIC DIGESTION CHARACTERISTICS OF EXCESS SLUDGE

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Abstract. Excess sludge was pretreated with NaOH in this study, and the changes in Total chemical oxygen demand, chemical oxygen demand, NH_4^+-N, volatile organic acids, protein and other indices before and after the pretreatments under different pH conditions were compared. The impact of pretreatment with alkali on the biogas production characteristics of excess sludge during anaerobic digestion was studied, which is beneficial for the pollution reduction and energy generation of excess sludge. The following results are obtained: 1) With the increase of pH during the pretreatment, the concentrations of soluble chemical oxygen demand and protein in the excess sludge increased. At pH 11 and 12, the soluble chemical oxygen demand of R_{Na11} and R_{Na12} samples was increased to 4044.19 ± 22.8 and 4154.2 ± 31.4 mg/L, respectively. The dissolution rates of soluble chemical oxygen demand were 70.15 and 72.05%, and the protein concentrations were 1212.5 ± 15.5 and 1945.3 ± 22.5 mg/L, respectively, increased by 899.5 and 1503.4%. 2) The biogas production efficiency of the excess sludge pretreated with alkali reached 28.5, 27.8, 29.6 and 31.9 ml/g VS in the anaerobic digestion, and the cumulative methane output was increased from 254.13 ml/g VS (untreated) to 269.7 ± 4.2, 275.5 ± 3, 282.4 ± 7.7, and 298.7 ± 6.3 ml/g VS, respectively. The methane concentrations in biogas were increased from 51.1 ± 3.7% (untreated) to 58.4 ± 6.6, 59.7 ± 4.9, 60.7 ± 4.5 and 61.4 ± 3.2%, respectively. In the last stages of the reactions, the concentrations of VFAs were maintained at a level of 345.5-375.5 mg/L, and the pH was maintained at a level of 7.3-7.5.
Keywords: *excess sludge, pretreatment with alkali, soluble organic component, anaerobic gas production efficiency, organic degradation*

Introduction

With the improvement of the treatment capacity of urban sewage treatment plants in China, the total output of excess sludge, a byproduct of this treatment process, is also increased year by year (Chen et al., 2022). In the year of 2020, the annual output of excess sludge exceeded 60 million tons (Chang et al., 2021). Currently, more than 60% of total excess sludge output of China is treated by simple landfill disposal (Ng et al., 2020), and about 23% of sludge is disposed of arbitrarily without any treatment (Rajagopal et al., 2017). Excess sludge contains a large amount of pathogenic bacteria, heavy metals, and toxic and harmful pollutants. If not effectively treated, it will be hazardous to the environment and even human life (Chen, 2005). Among the sludge treatment technologies, anaerobic digestion utilizes microorganisms to convert organics in sludge into biogas to reduce sludge volume and solid content, to avoid the odor of organics due to erosion reaction, to deactivate some pathogens, to turn waste into treasure, and to increase economic benefits (Zhan, 2009). However, in the process of anaerobic digestion,

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the protection effect of extracellular polymer and cell wall makes the hydrolysis rate of organic matter low, leading to problems such as long reaction time, a large pool volume, and a low biogas production rate. These problems limit the application and development of this technology. It has been reported that the hydrolysis reactions restrict the anaerobic digestion process of excess sludge (Li et al., 2016). The appropriate treatment of sludge can accelerate the destruction of sludge structure, and can promote the dissociation of cells and release of intracellular polymers. Thereby, the concentration of degradable organic compounds in sludge was increased, thereby improving the biodegradability of sludge, hydrolysis rate, and methane output (Siddique et al., 2017).

Treatment with alkali is the process of adding alkali to the sludge at room temperature to disrupt its structure and to promote the dissolution of organic matter (Gnaoui et al., 2020). Under the highly alkaline condition, the osmotic pressure of microbial cells is altered, so the cells swell and dissociate to release the intracellular substances. By treatment with alkali, some solid substances in sludge can be dissolved, and small-molecule soluble substances are generated. For instance, proteins, carbohydrates, and lipids are decomposed into amino acids, polysaccharides, fatty acids, etc. (Gnaoui et al., 2020). The effect of treatment with alkali is primarily determined by factors such as the alkali type, dosage, and treatment duration. Currently, the most common alkali for treatment is sodium hydroxide. Research studied the effects of a few of different alkalis (KOH, NaOH, $Ca(OH)_2$, and Na_2CO_3) on the properties of sludge (Su et al., 2013; Yao et al., 2016). Under the prerequisite of the same alkali dosage, the decomposition effect of sludge treated with sodium hydroxide was significantly better than sludge treated with other alkalis. The more alkali was added, the more obvious the decomposition effect of sludge was, and the greater the damage to the dewatering performance of sludge was. Research studied the impact of treatment with alkali on the anaerobic digestion process with sludge (Xie et al., 2014). The results showed that with the increase of alkali (NaOH) dosage, the decomposition rate of sludge gradually increased. When the dosage exceeded a certain value, the decomposition rate merely slowly increased, and the subsequent anaerobic digestion process would be affected, leading to the reduction of biogas output with sludge; In addition, the dewatering performance of sludge was deteriorated, greatly reducing the treatment efficiency. Research studied the effect of mixed alkalis on the decomposition effect and dewatering performance of sludge, and the results showed that the treatment with mixed alkalis had a significant promoting effect on the dissolution of organic matter in sludge and improvement of the dewatering performance (Su et al., 2013). To date, few studies have been reported on the change of composition of dissolved organic matter in sludge treated with alkali. In this paper, NaOH was employed to pretreat excess sludge, and the changes in Total chemical oxygen demand (TCOD), chemical oxygen demand (COD), NH_4^+-N, volatile organic acids (VFAs), proteins and other indicators before and after the pretreatments under different pH conditions were discussed to investigate the impact of pretreatment with alkali on the biogas production characteristics of anaerobic digestion with excess sludge, beneficial for the efficient anaerobic energy production with excess sludge.

Materials and methods

Apparatus

As shown in *Figure 1*, a self-designed anaerobic digestion reactor was used in this experiment. The apparatus consisted of two 1-L jars and a 1-L volumetric flask, which

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functioned as the raw-material digestion tank, biogas collector, and water collector. They were connected with anti-aging rubber pipes to compose the apparatus, of which the air tightness was checked after the assembly.

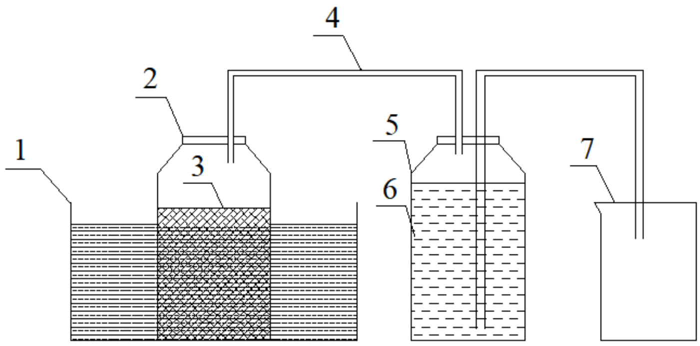

Figure 1. *Physical and schematic illustration of the apparatus. 1. Water bath 2. digestion-reaction bottle 3. mixture of excess sludge and acclimated sludge 4. air duct 5. biogas cylinder 6. distilled water 7. beaker*

Materials

Excess sludge

The excess sludge was acquired from the dehydrated sludge of the Northern Sewage Treatment Plant in Shenyang City. 5 kg of the sample was prepared, and all the sludge experimented was obtained from the sample to ensure the consistency. After sampling, the residual excess sludge was frozen and stored at -20°C. Before the experiment, the sample was placed at 4°C for 12 h for complete thaw.

Activated sludge

The anaerobic-digestion inoculation microorganisms were obtained from the anaerobic-digestion tank of the neighboring sewage treatment plant. The sludge was transferred to a large sealed plastic container at about 20℃. After returning to the laboratory, the sludge was cultured and domesticated at 37℃. In detail, 5 L of the activated sludge was placed in a 25-L sealed plastic barrel for cultivation at 37℃. The weights of dry matter of excess sludge and inoculated sludge were measured after drying in an oven at 105℃ for 24 h, and the content of organic matter was measured after calcination with a muffle furnace at 550℃ for 4 h. The primary parameters of the excess sludge and activated sludge are shown in *Table 1*.

Experimental procedures

Fifteen digestion reactors (1 L) were employed in the sequencing anaerobic-digestion experiment of excess sludge pretreated with alkali. 5 groups of experiments were performed, and each experiment was repeated three times. The mean value was taken as the real value. The detailed experimental conditions are shown in *Table 2*. 1000 g of excess sludge was placed in a 1000-mL jar, and 5 mol/L NaOH was added to adjust the pH to 9.0, 10.0, 11.0, and 12.0. After stirring, the samples were placed at 4°C in a refrigerator for 24 h. 100 g of the pretreated sample was placed in a 1-L jar in each

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group, and 300 mL of activated sludge as well as water was added until the total volume reached 1 L. These groups were labeled as R_{Na9}, R_{Na10}, R_{Na11}, and R_{Na12}. And, a control group containing excess sludge without alkali was labeled as R_{Na0}. After sealing with wax, these reactors were placed in a thermostatic water bath for incubation at 37℃ for 50 days.

Table 1. *Main parameters of wet ground state of surplus sludge and activated sludge (Castelle et al., 2018)*

Parameters	Total solid (TS)/%	Volatile solid (VS)/%	pH	Total carton (TC)/%	Total nitrogen (TN)/%
Surplus sludge	13.49	68.55	6.43	36.07	5.13
Activated sludge	9.32	37.73	7.41	--	--

Table 2. *Experimental conditions for excess sludge pretreated with alkali (m/m, %)*

	R_{Na0}	R_{Na9}	R_{Na10}	R_{Na11}	R_{Na12}
Alkali type	--	NaOH	NaOH	NaOH	NaOH
pH	6.3	9	10	11	12

Monitoring methods

Monitoring of common indices

According to the "Analysis and Detection Methods for Water and Wastewater (Fourth Edition)" (Nazari et al., 2017), the SCOD, TCOD, NH_4^+-N, PO_4^{3-}, TS, VS, pH, alkalinity, and other indexes were determined with the methods and instruments shown in *Table 3*. The protein content in the sludge was determined by using the Lowry protein assay kit (Sun et al., 2016), and the polysaccharide content was determined by using the phenol- sulfuric-acid method (Elbeshbishy et al., 2011).

Table 3. *Main physicochemical characteristics and analytical methods*

Physical and chemical property	Analysis method	Instrument
TOCD	High-temperature rapid digestion	Water-quality analyzer
SCOD	High-temperature rapid digestion	Water-quality analyzer
NH_4^+-N	Colorimetry with the Nessler reagent	UV-Vis spectrophotometer
PO_4^{3-}	Molybdenum-antimony-ascorbic-acid spectroscopy	UV-Vis spectrophotometer
TS	Weighing	Blast drying oven
VS	Weighing	Muffle furnace
pH	Glass-electrode method	pH meter
Alkalinity	Titration with acid	Burette

Determination of volatile fatty acids

VFAs were determined by using gas chromatography (GC) with an FID detector. The analysis conditions are the following: initial column temperature = 120℃, 2 min; ramp rate = 10℃/min; terminal temperature = 180℃, 2 min. The sample was injected in a no-split mode, and the injection port and detector were at 200 and 220℃, respectively. The analysis took 10.6 min. A KB-Wax capillary column with a length of 30 m, film

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thickness of 1 μm, and inner diameter of 530 μm was employed. The sludge sample was treated by centrifugation at 8000 r/min for 5 min, and the supernatant was filtered with a 0.45-μm membrane. The filtrate was acidified with formic acid and then analyzed.

Detection method of biogas

The output of biogas was measured once a day according to the water expelled. The cumulative composition of biogas was detected by gas chromatography under these conditions: column: stainless-steel column (TDX-01 packing, 2 m × 3 mm) produced by the National Chromatographic Research and Analysis Center of Dalian Institute of Chemical Physics, Chinese Academy of Sciences; Detector: TCD; Carrier gas: 20 mL min^{-1} He; Current: 100 mA; Attenuation: 1; Detection temperature: 200℃; oven temperature: 180℃; Injection temperature: 200℃.

Data analysis

In the experiment, the physical and chemical indicators were measured in triplicate. The data was analyzed for significance and correlation using single-factor analysis of variance and multiple comparisons in SPSS v.18.0 software, evaluating the significant differences between each experimental treatment. The least significant difference method (LSD, a = 0.05) was used for multiple comparisons of the mean values. All data graphs were plotted using Origin-8.0.

Results and discussion

Impact of pretreatment with alkali on the excess sludge

Dissolution efficiency of Soluble chemical oxygen demand

During the treatment process, the dissolution rate of SCOD in sludge was calculated according to *Equation 1* (Farhat et al., 2018; Cui et al., 2002; Rajput et al., 2018).

$$\text{Dissolution rate }(\%) = \frac{SCOD_t - SCOD_0}{TCOD - SCOD_0} \times 100\% \qquad \text{(Eq.1)}$$

where $SCOD_t$ and $SCOD_0$ stand for the soluble chemical oxygen demand (mg/L) in the treated and untreated sludge; TCOD represents the total chemical oxygen demand (mg/L) in the original sludge.

The concentration of SCOD is usually taken to evaluate the effect of pre-treatment. The SCOD concentration in sludge reflects the content of soluble organic matter in sludge. The dissolution rate of SCOD reflects the effect of pre-treatment of excess sludge. The higher the dissolution rate of SCOD is, the better the pre-treatment effect of sludge is. *Figure 2* shows the variation of SCOD concentration after 24 h of pre-treatment with 5 mol/L NaOH under different pH conditions. With the increase of pH, the concentration of SCOD in the excess sludge increased. Under the weakly alkaline condition of pH 9, the dissolution effect of SCOD in the R_{Na9} sample was not obvious, and the SCOD was increased from 1746.2 ± 11.6 in the R_{Na0} sample to 2538.97 ± 9.6 mg/L. The SCOD concentration was increased by 45.4%, and the dissolution rate of SCOD was 30.29%. Under the condition of pH 10, the SCOD of R_{Na10} sample was increased to 3306.1 ± 13.9 mg/L, the SCOD concentration was

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increased by 69.6%, and the SCOD dissolution rate was 44.04%. Under the condition of pH 11, the SCOD of R_{Na11} sample was increased to 4044.19 ± 22.8 mg/L, the SCOD concentration was increased by 131.6%, and the SCOD dissolution rate reached 70.15%. Under the condition of pH 12, the SCOD of R_{Na12} sample was increased to 4154.2 ± 31.4 mg/L, the SCOD concentration was increased by 137.9%, and the SCOD dissolution rate reached 72.05%.

Most of the organic matter in excess sludge is intracellular substances, and the cell wall can protect cells, which are difficult to be destroyed under mild pH conditions, thereby inhibiting the hydrolysis of excess sludge. With the treatment with alkali, the cellular structure inside the sludge can be destroyed to a certain extent at room temperature, promoting the dissolution of organic matter. Under the condition of pH 9-12, with the increase of pH in the pretreatment procedure, the SCOD concentration in the sludge increased. At pH 11, the SCOD of the R_{Na11} sample was increased to 4044.19 ± 22.8 mg/L, and the dissolution rate of SCOD reached 70.15%. The highly alkaline condition altered the osmotic pressure of microbial cells, leading to the swelling and breaking of cells. Therefore, a few solid substances, such as proteins, carbohydrates and lipids, released from the cells can be converted into small-molecule soluble substances amino acids, polysaccharides, fatty acids, and so on. At pH 12, the treatment effect was similar to that in the R_{Na11} group, indicating that the quantity of SCOD could not always increase with the increase of alkali dosage. Instead, the quantity of SCOD was kept constant eventually. It can also be understood that when the alkalinity reaches a certain degree, the dissolution of organic matter in the remaining sludge also reaches a stable state, researcher Li (Li et al., 2016) also reported the same conclusion. This indicates that at high pH values, the decomposition effect of sludge was very evident, but the increase in SCOD was gradually attenuated with the increase of pH. Therefore, the pH condition of 12 may be preferable for the treatment with alkali (Li et al., 2016).

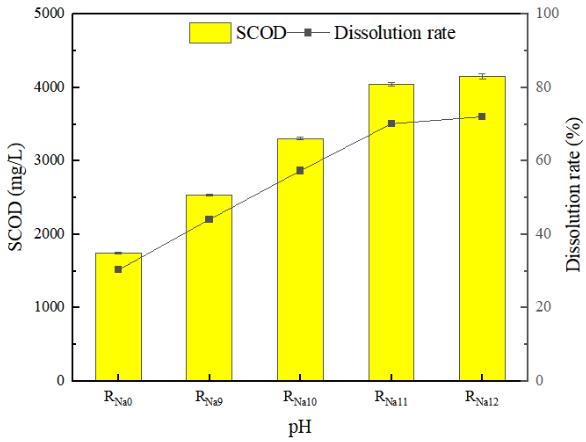

Figure 2. *Change in SCOD of excess sludge pretreated under different pH conditions*

Dissolution efficiency of protein and ammonia nitrogen in the excess sludge

Figure 3 shows the changes in protein and ammonia-nitrogen concentrations after pretreating with 5 mol/L NaOH under different pH conditions. With the increase of pH, the protein concentration in the sludge increased. Under the weakly alkaline condition

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of pH 9, the protein dissolution effect in the supernatant of excess sludge was poor: the concentration was only increased from 114.5 ± 4.3 mg/L (control group) to 233.5 ± 11.2 mg/L. The reasons are the following: On the one hand, the organic matter inside the excess sludge was difficult to destroy under the weakly alkaline condition, resulting in the dissolution of only a small amount of protein; On the other hand, the microbial activity in the sludge was not significantly weakened under the weakly alkaline condition of pH 9. The microorganisms had high biological activity and utilized proteins as their nutrients, resulting in the low concentration of protein in the sludge. With the continuous increase of pH, the concentration of protein in the sludge was significantly increased. Under the conditions of pH 11 and 12, the protein concentrations of R_{Na11} and R_{Na12} samples were 1212.5 ± 15.5 and 1945.3 ± 22.5 mg/L, respectively, increased by 899.5 and 1503.4%. Meanwhile, the protein concentration in the sludge accounted for 65.4% of the SCOD concentration, indicating that the organic matter in the sludge was easily dissolved in the form of proteins under the highly alkaline conditions.

Ammonia nitrogen is generated from the hydrolysis of proteins, and a high concentration of ammonia nitrogen indicates a large quantity of proteins undergoing hydrolysis and acidification. *Figure 3* shows the variation of ammonia nitrogen concentration. Under the alkaline conditions, the ammonia-nitrogen concentration in the sludge was significantly increased. The variation characteristics of ammonia nitrogen are different from the dissolution rules of soluble proteins. With the increase of pH, the ammonia-nitrogen concentration in sludge increased in the first place, and then it decreased. At pH 10, the ammonia-nitrogen concentration reached a maximum of 243.6 ± 9.1 mg/L. With the further increase of pH, the concentration of ammonia nitrogen gradually declined, but the minimum was still greater than the ammonia-nitrogen concentration in the supernatant under the condition of pH 9, because the microbial structure was not obviously destroyed under the condition of pH 10. A large amount of soluble protein-type organic matter was decomposed by hydrolysis-acidification bacteria, resulting in the high concentration of ammonia nitrogen in the solution. With the increase of alkalinity, the hydrolysis of proteins was inhibited, resulting in the gradual decrease in the concentration of ammonia nitrogen in the sludge. In addition, at high pH, ammonia nitrogen in the solution is prone to be released in the form of NH_3 (Jin et al., 2016).

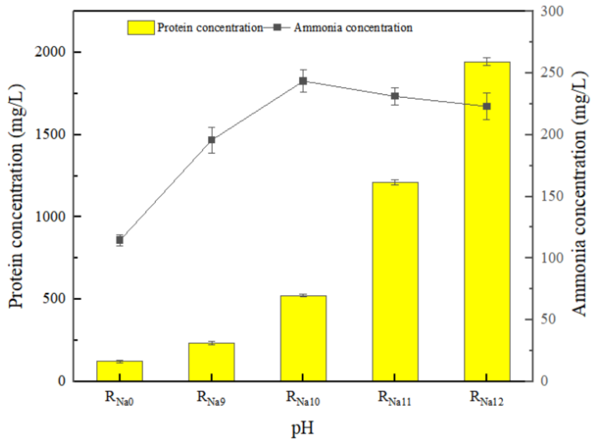

Figure 3. *Changes in protein and ammonia-nitrogen concentrations in the excess sludge pretreated under different pH conditions*

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Leaching of volatile fatty acids in the excess sludge

Volatile fatty acids (VFAs) are composed of acetic acid, propionic acid, isobutyric acid, n-butyric acid, isovaleric acid, and n-valeric acid, and the changes in their ratios reflect the hydrolysis degree of sludge (Ruffino et al., 2016). *Figure 4* shows the variation of concentrations and composition of volatile fatty acids in the excess sludge after the pretreatment with alkali under different pH conditions. The volatile fatty acids in the excess sludge primarily included acetic acid, propionic acid, and valeric acid. Except for R_{Na9}, these three acids accounted for 76.32-78.35% of the total TVFAs in the R_{Na10}, R_{Na11}, and R_{Na12} groups, and acetic acid was the most abundant component. After the pretreatment with alkali, the ratio of acetic acid in TVFAs was increased from 38.24% (R_{Na0}) to 50.70-53.90%. In the R_{Na9} group, acetic and propionic acids only accounted for 42.44% of TVFAs, mainly because the low amount of dissolved organic matter at pH 9 led to the fact that the dissolution rate was lower than consumption rate of acetic and propionic acids. Therefore, the contents of acetic and propionic acids were low. From this point of view, it can be deduced that the microorganisms in the sludge participated in active life activities, and consumed a large amount of small-molecule organic compounds such as acetic and propionic acids. Research suggested that during the anaerobic digestion process, acetic, propionic and butyric acids could be generated from the fermentation of proteins, polysaccharides, lipids and macromolecular volatile acids, and the formation of valeric acid was related to the fermentation of protein (Chen et al., 2007). After the hydrolysis with alkali, proteins were the primary SCOD components in the sludge. Therefore, the ratios of valeric acid in the organic acids of all the sludge groups were higher than those of butyric acid.

With the increase of pH, the concentration of volatile organic acids in the sludge showed a volcanic trend. At pH 10, the content of volatile fatty acids in the sludge reached a maximum, and the dissolution rate of volatile fatty acids in the sludge was greater than the consumption rate; With the further increase of pH, the concentration of TVFAs in the sludge gradually decreased. Research suggested that this was because the activity of hydrolysis-acidification bacteria in sludge declined or even disappeared with the enhancement of alkalinity (Chen et al., 2007). The soluble organic matter in the sludge could not be decomposed by hydrolysis-acidification bacteria, resulting in the gradual decrease of VFA content in the sludge and accumulation of soluble organic matter.

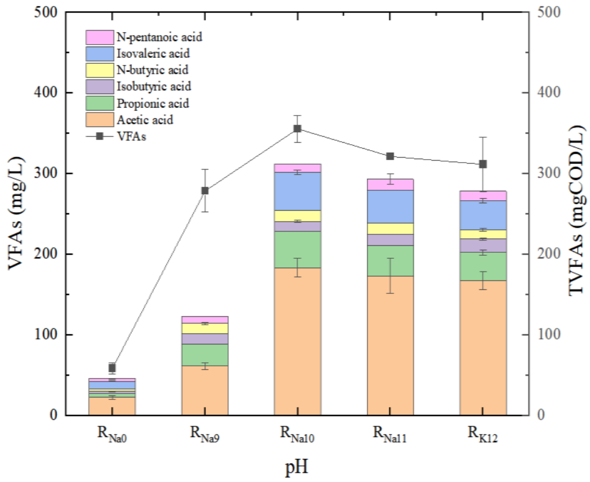

Figure 4. *Changes in VFAs in the excess sludge pretreated under different pH conditions*

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Effect of pretreatment with alkali on the anaerobic digestion with excess sludge

Biogas production characteristics

Figure 5 and *Table 4* present the changes in methane production efficiency, cumulative biogas and methane output, biogas concentration, and other parameters after the pretreatment with alkali. The cumulative biogas output and cumulative methane output of control group R_{Na0} were 498.2 ± 8.7 and 254.1 ± 4.7 ml/g VS, respectively. The methane concentration in biogas reached 51.1 ± 3.7%, and the concentrations of carbon dioxide and other gases were 44.3 ± 1.5% and 4.6 ± 0.6%, respectively.

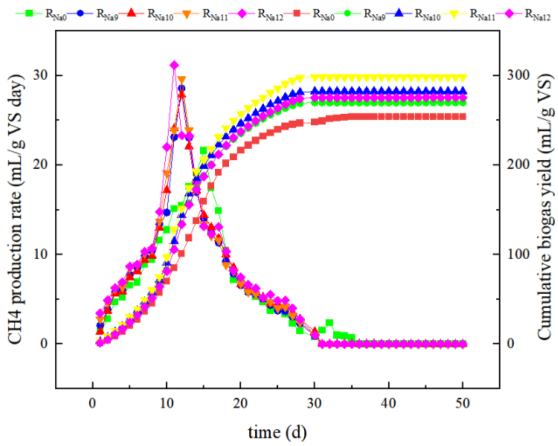

Figure 5. *Changes in methane production efficiency and cumulative methane output of excess sludge pretreated under different pH conditions*

Table 4. *Output and concentration of biogas, CH_4 and CO_2 during the anaerobic digestion processes*

Group	Cumulative biogas output (ml/g VS)	Cumulative CH_4 output (ml/g VS)	Concentration of methane (%)	Concentration of carbon dioxide (%)	Concentration of other biogases (%)
R_{Na0}	498.2 ± 8.7	254.1 ± 4.7	51.1 ± 3.7	44.3 ± 1.5	4.6 ± 0.6
R_{Na9}	458.3 ± 9.8	269.7 ± 4.2	58.4 ± 6.6	35.3 ± 1.6	6.3 ± 0.5
R_{Na10}	461.8 ± 11.3	275.5 ± 3.5	59.7 ± 4.9	32.5 ± 1.7	7.8 ± 0.6
R_{Na11}	470.1 ± 11.9	282.4 ± 7.7	60.7 ± 4.5	32.1 ± 2.1	7.3 ± 0.1
R_{Na12}	486.4 ± 11.7	298.7 ± 6.3	61.4 ± 3.2	32.2 ± 2.7	6.4 ± 0.5

Figure 5 shows that the maximum daily biogas output in the R_{Na0} group without pretreatment with alkali took place on the 15th day, and the biogas production efficiency was 21.6 ml/g VS. After pretreatment with alkali, the cumulative methane output and biogas production efficiency were improved in the anaerobic digestion. The maximum daily biogas output of the R_{Na9}, R_{Na10}, and R_{Na11} groups took place, earlier, on the 12th day, and that of the R_{Na12} group took place, earlier, on the 11th day. The biogas production efficiency of the four groups with excess sludge pretreated was 28.5, 27.8, 29.6, and 31.9 ml/g VS, respectively. The cumulative methane output was increased from 254.13 ml/g VS (control group) to 269.7 ± 4.2, 275.5 ± 3, 282.4 ± 7.7, and 298.7 ± 6.3 ml/g VS, respectively. The methane concentration in the biogas was also increased from 51.1 ± 3.7% (control group) to 58.4 ± 6.6, 59.7 ± 4.9, 60.7 ± 4.5, and 61.4 ± 3.2%, respectively.

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The cumulative methane output, biogas production efficiency, and methane concentration in the biogas of anaerobic digestion of excess sludge pretreated with alkali were obviously improved, mainly because the macromolecular structure inside the sludge was destroyed to a certain extent under the alkaline conditions, thereby promoting the breaking of chemical bonds in insoluble macromolecular organic substances for hydrolysis. The concentrations of soluble organic substances such as sugars, proteins, and VFAs in the fermentation broth were increased, and hydrolysis was promoted, preparing hydrolysis products for the archaea to give methane in the later stage. With the increase of alkali concentration and pH, the promoting effect for hydrolysis got better. Therefore, the pretreatment with alkali improved the anaerobic-digestion efficiency of excess sludge, which is consistent with the result reported: The ester bonds in the composite of lignin and carbohydrate could be broken by NaOH, and thereby the cellulose was released from the encapsulation of lignin (Atelge et al., 2020). It is precisely because of these changes that the excess sludge was hydrolyzed and acidified by the anaerobic microorganisms. The effective decomposition was promoted, so the cumulative biogas output and biogas production efficiency of anaerobic digestion were improved.

Volatile organic acids concentration and pH

The profiles of VFAs concentrations and pH during the anaerobic digestion processes of excess sludge treated with alkali are shown in *Figures 6* and *7*. Volatile fatty acids (VFAs) are the primary hydrolysis-acidification products, and play an important role in anaerobic digestion (Svensson et al., 2018). The variation principles of TVFAs in the excess sludge in all the groups over time exhibited the same volcanic trend. The concentration of TVFAs in the R_{Na0} control group reached its maximum, 348.9 mg/L, on the 15th day. Then, the concentration gradually declined. At the end of the reactions, the concentration of TVFAs was 105.4 mg/L. In the other four groups treated with alkali, the concentration of TVFAs reached their maximums on the 12th day, and the concentration of TVFAs was positively correlated with the pH. The concentration of TVFAs in the R_{Na12} group, 1288.6 mg/L, was the highest among these groups, and the concentration of VFAs leveled off at 345.5-375.5 mg/L at the end of the reactions. Hydrolysis and acidification are the key factors limiting anaerobic digestion, and the hydrolysis-acidification rate also determines the efficiency of biogas production. Under different pH conditions, the pretreatment with alkali promoted the hydrolysis of excess sludge, increased the concentration of organic acids in the sludge, and thereby the hydrolysis and acidification were favored, providing substrate for the production of methane in the later stage. From this point of view, it is speculated that the microorganisms underwent active life activities at this stage. This point of view explains the biogas production laws during this period: The faster the consumption of organic acids is, the faster the biogas production is.

The change in pH has a significant impact on the activity of microorganisms during anaerobic digestion. The preferential pH ranges for different microorganisms as well as their sensitivity to pH are varied. Methanogenic bacteria are sensitive to pH, with a preferential pH range of 7.2 to 7.4 (Kang et al., 2019). *Figure 7* shows the changes in pH during the anaerobic digestion processes of excess sludge after the pretreatment with alkali. The pretreatment altered the initial pH of excess sludge as well as the pH variation rules during the anaerobic-digestion processes. During the 50-day anaerobic digestion processes, the pH of R_{Na0} control group showed a concave profile, and the pH reached a minimum of 5.1 on the 15th day. Then, the pH was gradually increased, and

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leveled off at 6.3 at the end of the reactions. The pH of the R_{Na0} control group showed a concave profile during the 50-day anaerobic-digestion process, because the organic matter in the excess sludge was decomposed by hydrolytic microorganisms to produce small-molecule organic acids, leading to the decrease of pH in the reaction system. In the later stage, these small-molecule organic acids were converted into methane by archaea, and the consumption of organic acids led to the increase of pH in the system.

Different from the control group, the pH of the other four groups pretreated with alkali was relatively high at the initial stages. With the proceeding of anaerobic-digestion reactions, the pH gradually decreased. The change in pH was principally attributed to the effects of organic acids, amphoteric proteins, and other substances. At the early stage of anaerobic digestion, organic acids were generated due to the decomposition of organic matter by acidification bacteria, and thereby the concentration of VFAs in the digestion system was increased and pH of the system declined. Later, due to the effects of amphoteric proteins and alkaline substances such as ammonia nitrogen, the pH increased and then leveled off. At the end of the reactions, the pH was maintained at the level of 7.3-7.5, which was very favorable to the biological activity of methanogenic archaea, resulting in the higher methane concentration in the groups pretreated with alkali compared to the control group.

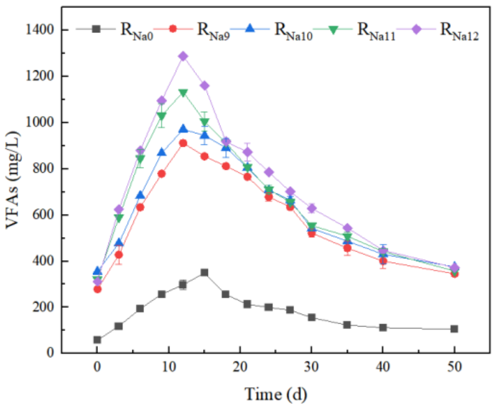

Figure 6. *Changes in VFAs during the anaerobic digestion of excess sludge pretreated under different pH conditions*

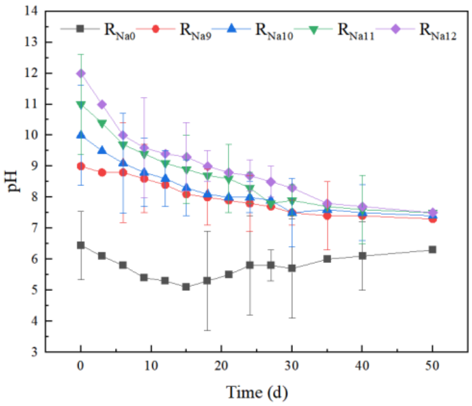

Figure 7. *Changes in pH during the anaerobic digestion of excess sludge pretreated under different pH conditions*

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Conclusion

(1) With the increase of pH during the pretreatment procedure with alkali, the concentrations of SCOD and protein in the excess sludge increased. At pH 10, 11, and 12, the SCOD of R_{Na10}, R_{Na11}, and R_{Na12} groups was increased to 3306.1 ± 13.9, 4044.19 ± 22.8, and 4154.2 ± 31.4 mg/L, respectively, and the dissolution rates of SCOD reached 69.6, 70.15, and 72.05%, respectively. At pH 11 and 12, the protein concentrations of R_{Na11} and R_{Na12} groups were 1212.5 ± 15.5 and 1945.3 ± 22.5 mg/L, respectively, with increase of 899.5 and 1503.4%.

(2) The cumulative methane biogas output and biogas production efficiency of the excess sludge pretreated with alkali in the anaerobic digestion processes were improved. The maximum daily biogas output of R_{Na9}, R_{Na10}, and R_{Na11} groups took place, earlier, on the 12th day, and the maximum daily biogas output of R_{Na12} group took place, earlier, on the 11th day. The biogas production efficiency of the pretreated excess sludge in these four groups was 28.5, 27.8, 29.6, and 31.9 ml/g VS, respectively. The cumulative methane output was increased from 254.13 ml/g VS (untreated) to 269.7 ± 4.2, 275.5 ± 3, 282.4 ± 7.7, and 298.7 ± 6.3 ml/g VS, respectively. The methane biogas concentrations in the biogas were also increased from 51.1 ± 3.7% (untreated) to 58.4 ± 6.6, 59.7 ± 4.9, 60.7 ± 4.5, and 61.4 ± 3.2%, respectively.

(3) During the anaerobic-digestion processes, the concentration of TVFAs and pH in the R_{Na0} control group reached their maximum values of 348.9 mg/L and 5.1 mg/L on the 15th day of the reactions. Then, the concentration of TVFAs decreased while pH was elevated. At the end of the reactions, the concentration of TVFAs and pH were 105.4 mg/L and 6.3 respectively. The concentrations of TVFAs in the other four groups pretreated with alkali reached their maximum values on the 12th day of the reactions. Among these four groups, the concentration of TVFAs in the R_{Na12} group was the highest, 1288.6 mg/L. At the end of the reactions, the concentration of VFAs leveled off at 345.5-375.5 mg/L, and the pH leveled off at 7.3-7.5.

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