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Impact of Fe_3O_4 Nanoparticles on Methane Production from Anaerobic Digestion and Kinetic Analysis

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Abstract: *Anaerobic digestion (AD) is one of the most widely used processes to stabilize waste sewage sludge and produce biogas as renewable energy. This study investigated the effects of Fe_3O_4 NPs at different concentrations (0,100 and 300 mg/L) on AD. 100mg/L Fe_3O_4 NPs could increase gas production by 21.9% and reach the highest methane content of 66.75%. In addition, 100 mg/L Fe_3O_4 kept pH at an appropriate level. Scanning electron microscope (SEM) was used to study the changes in surface morphology in sludge. The dynamics of cumulative biogas production and daily biogas production were studied by using the Logistic model and modified Gompertz model respectively. Other indices also had changed in the whole process, which in the end lead to the variation of biogas production. These results suggested that Fe_3O_4 NPs could increase microbial activity and relevant enzyme activities, caused changes and transitions between different phases in the system.*

Keywords: *anaerobic digestion, Fe_3O_4 NPs, sludge, biogas production, microorganism*

1. Introduction

Due to the wide application of nanomaterials, which inevitably enter into the environment [1], the nanomaterials present in the wastewater were adsorbed by the sludge, finally trapped in sludge [2]. Anaerobic digestion (AD) is an effective technique to treat solid waste and convert it into biogas consisting of carbon dioxide and methane. This biogas can be used as heating value or biomethane of the replacement to natural gas [3]. Therefore, using anaerobic digestion can solve the problem of energy shortage in the world.

The AD is the cleanest and effective method to treat waste sludge, it referred to that in the absence of oxygen and microbial metabolism, through the degrading organic substances and produce clean combustible gases such as hydrogen and methanee [4] but there are so many limiting factors in the anaerobic digestion process that lead to a decrease in gas production, such as *p*H, temperature, oxidation-reduction potential and also the methanogens which have high environmental requirements. With the development of nanotechnology, more and more engineering nanomaterials (ENMs) were incorporated into industrial and daily productss [5], main environmental release pathway for ENMs was most likely through wastewater treatment plant whatever ends in wastewater bound to sludge through agglomeration, aggregation and settling mechanisms [6, 7]. The traditional anaerobic digestion process has the characteristics of a long reaction cycle, low biogas production and low methane content in biogas, so adding additives to promote gas production has become a research hotspot.

Studies had shown that nanomaterials promote anaerobic digestion of gas production. For example, nanoscale zero valent iron（NZVI）improved anaerobic digestion of gas production by promoting cell lysis and methanogen activity [8]. The Ag nanoparticles (NPs) can be combined with sulfides and mercapto complexes in sludge to reduce hydrogen sulfide in biogas and alleviate the inhibition of anaerobic digestion [9]. Therefore, NPs can accelerate the hydrolysis process of anaerobic digestion, increase the yield and quality of biogas, and thus realize the resource utilization of sludge [10]. Fe_3O_4 NPs as an anti-spinel cubic crystal material, due to unique physicochemical properties such as high specific surface area, superparamagnetic, high biocompatibility and easy surface modification, widely

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Revista de Chimie
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used in bio-medical, catalyst carrier, microwave absorption material and environmental repair and other fields [11]. The addition of Fe_3O_4 NPs into the AD reactor will increase the degradation of organic matter, increase the production of methane, that solving the difficulty of sludge treatment and increasing the new energy methane.

In this study, the effect of different concentrations of Fe_3O_4 NPs on AD of sludge was investigated, and an effective method to increase the gas production of anaerobic digestion was found.

2. Materials and methods

2.1. Fe_3O_4 NPs characterization

The Fe_3O_4 NPs were obtained from the previous work [12]. As shown in Figure 1, the size of Fe_3O_4 NPs was 40-60 nm. It shapes in agglomerates, has a large surface area, and has great contact with sludge for AD.

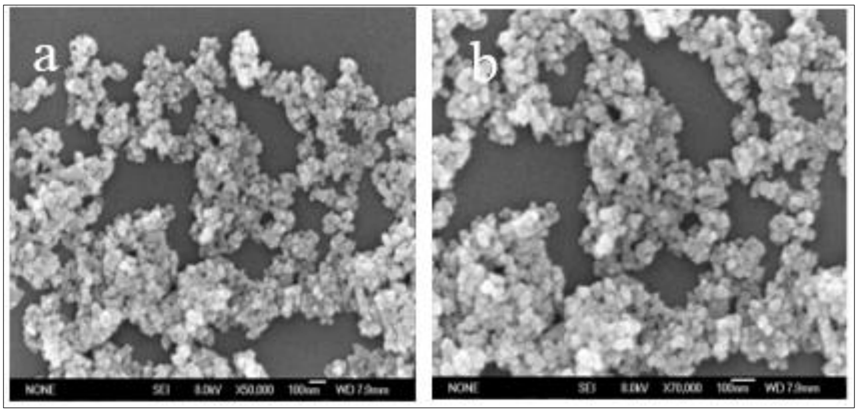

Figure 1. SEM of Fe_3O_4 NPs (a) X 50000, (b) X 70000

2.2. Sludge characteristics

The waste activated sludge used in this study was obtained from the secondary sedimentation tank of a municipal wastewater treatment plant in Qingdao, China. The sludge was concentrated by settling at 24 h, and storage at 4°C before use. The substrate was made up of the raw sludge at the solid-liquid ratio of 8%. The inoculum was cultivated by the substrate with a C: N:P ratio of 500:5:1. The compound consisted of 300 mL substrate and 200 mL inoculum. The characteristics of substrate inoculum and compound are compared in Table1.

Table 1. Characteristics of the raw sludge and alkaline pretreated sludge

Parameters	Substrate	Inoculum	Compound
pH	7.82	6.68	7.34
TCOD (mg/L)	34256±310.58	28206±188.13	16154±123.54
SCOD (mg/L)	1928±23.13	1428±16.52	1628±18.74
TS/%	6.399	6.471	6.523
VS/%	3.156	3.315	3.101
NH_3-N (mg/L)	615±26.23	1749±29.46	1161±19.84

2.3. AD and experimental design

AD reactor used for the experiment was shown in Figure 2. Three dosages (0, 100, 300mg/L) of Fe_3O_4 NPs were added to the reactors. Each reactor was inflated with nitrogen gas for about 5 min to assure anaerobic condition before starting the experiment. All of the reactors were then kept in the water bath under mesophilic conditions (35±1°C). Biogas volume was daily recorded by reading water displacement inside the calibrate glass cylinder which was connected to the reactor.

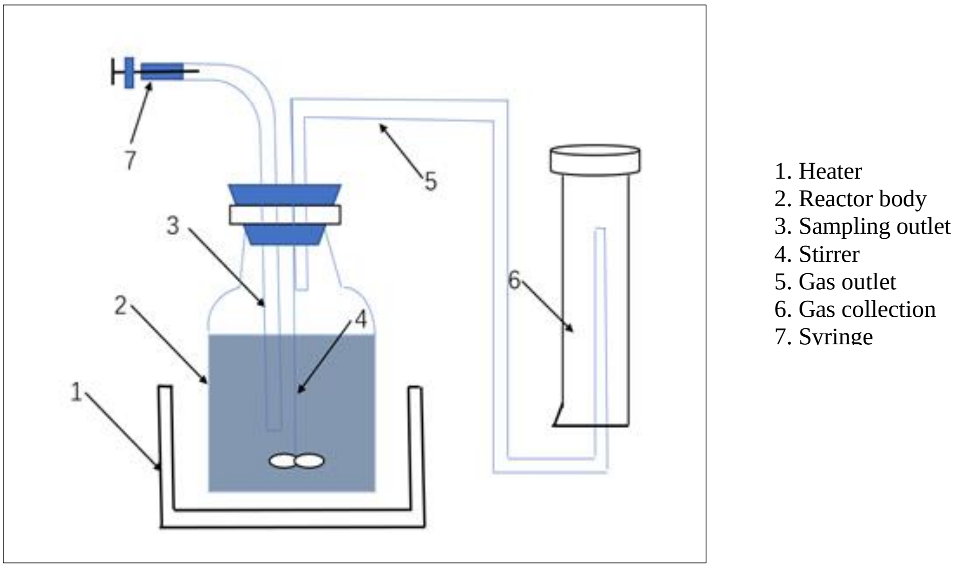

Figure 2. Reactors of AD

2.4. Analytical methods

The physical and chemical parameters volatile solid (VS), total solid (TS), ammonia nitrogen (NH_3-N), and COD were determined according to standard methods [13].

The soluble COD (SCOD) was measured after centrifuging at 3000rpm for 20 min and filtering the supernatant through membranes with the mesh size of 0.45mm.

The composition of the biogas was analyzed with the gas chromatograph (Shimadzu, GC-14C/TCD, Japan) equipped with the thermal conductivity detector (TCD) [14]. The use of carrier gas for hydrogen set the column temperature at 80°C, the thermal conductivity at 150°C. The sample temperature was 150°C, the carrier gas flow rate was 60 mL/min, and the bridge current was 80 mA.

The concentrations of VFAs, including acetate, propionate, butyrate, were determined using another GC (Shimadzu, GC-2010/FID, Japan) equipped with a flame ionization detector (FID). The measurement parameters are as follows: a detector for the FID detector, using DB-FFAP capillary column specifications for the 30mm ID×0.53mm ID×1.0 μL, capillary column flow rate adjusted to 2.77 mL/min. According to 5:1 split into the sample, each injection 1μm, retention time 3.5 min, import, detector, oven temperature were set to 230°C, 230°C, 70°C, and then 20°C/min temperature rise to 180 after holding for 5 min.

2.5. Kinetic analysis

Kinetic analysis of AD was used two kinetic models: Logistic model, modified Gompertz model (Formula 3-1 and 3-2) [15]. The Logistic model assumes that the gas production was directly proportional to the gas generated, the maximum gas generated rate and the gas generated potential, which could adapt to the rapid growth in the initial stage and finally reach a stable level [16]. The classic sigmoidal curve describing microbial growth was shown by the modified Gompertz model, and biogas production was usually assumed to be a function of microbial growth [17]. Based on the experimental data, two models were used to determine the maximum gas production potential, the maximum gas production rate (R_m) and the lag time (λ). All experimental results were used in the three kinetic models for analysis. The model formula is as follows:

$$P = \frac{P_{max}}{1+\exp\left[\frac{4R_{max}(\lambda-t)}{P_{max}}+2\right]} \quad (1)$$

$$P = P_{max} \times \exp\left\{-\exp\left[\frac{R_{max} \times 2.718}{P_{max}}(\lambda - t) + 1\right]\right\} \quad (2)$$

To evaluate the kinetic model, the kinetic parameters were analyzed by correlation (R^2), root mean square error (RMSE) [18] and final prediction error (FPE) [19]. The formula was as follows:

$$R^2 = \frac{\sum_{i=1}^{n}(z_i - \bar{z})(w_i - \bar{w})}{\sqrt{\sum_{i=1}^{n}(z_i - \bar{z})^2 \sum_{i=1}^{n}(w_i - \bar{w})^2}} \quad (3)$$

$$RMSE = \sqrt[2]{\frac{1}{n}\sum_{i=1}^{n}(z_i - w_i)^2} \quad (4)$$

$$FPE = \frac{1+p/n}{1-p/n} \times \frac{1}{n} \times \sum_{i=1}^{n}\frac{1}{2}\left(\frac{z_i - w_i}{z_i}\right)^2 \quad (5)$$

while P(t) is the cumulative gas production; Pmax is the maximum gas production potential value; Rm is the maximum gas production rate; λ, t_0 is the lag time. t is the anaerobic digestion time. z_i is the experimental value, w_i is the predicted value, n is the experimental samples, p is the degree of freedom.

3. Results and discussions

3.1 Effect of Fe_3O_4 NPs on biogas production

3.1.1 Daily and cumulative biogas production

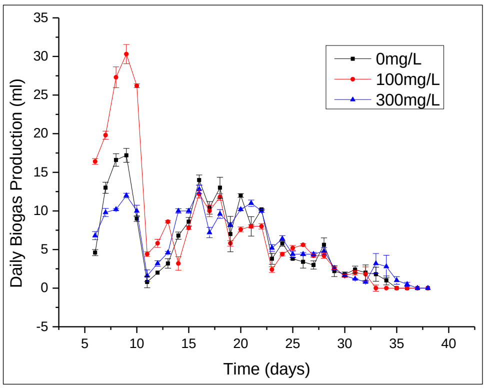

Figure 3. Variation of daily biogas production

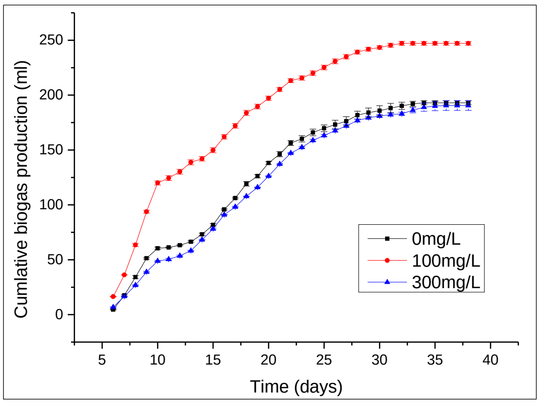

Figure 4. The variation of cumulative biogas production

Figure 3 showed the variation of daily biogas production. In the first nine days, biogas production increased quickly because of the sufficient substrate and the better use of macromolecular organic matters in the early process of AD [20]. The daily biogas production of the three experimental groups reached the maximum value on the 9th day, the biogas production of the control group was 17.2mL, and the biogas production of the 100mg/L Fe_3O_4 NPs group was 30.3 L and higher than that of the control group. The lowest daily gas production in the 300mg/L Fe_3O_4 NPs group was 12 mL. The change of cumulative biogas production was the same as that of daily biogas production. From Figure 4, when the concentrations of Fe_3O_4 NPs increased from 100 mg/L to 300 mg/L, cumulative biogas production reduced from 247.2 mL to 190.5 mL. It suggested that adding an appropriate concentration of Fe_3O_4 NPs could increase biogas production at about 21.9% while adding excess Fe_3O_4 NPs had no significant effect on cumulative biogas production.

The results showed that 100 mg/L Fe_3O_4 NPs could promote AD, which made the biogas increase. But when the Fe_3O_4 NPs over 300 mg/L, it inhibited the generation of biogas. It was due to the excess of Fe_3O_4 NPs would be adsorbed on the surface of sludge, inhibit the microorganisms secret the enzymes, finally reduce the biogas [12].

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3.1.2. The methane content percentage

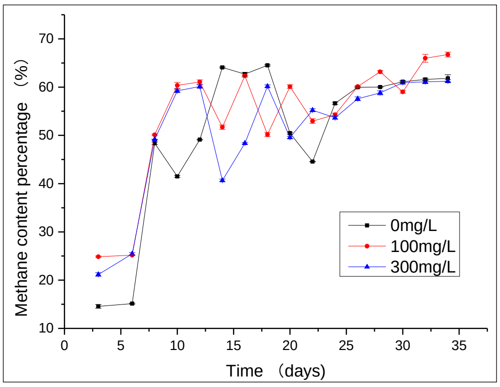

Figure 5. The variation of methane content percentage

Figure 5 showed the methane content percentage of AD with different concentrations of Fe_3O_4 NPs. The methane content of the three experimental groups was low in the first 6 days and remained stable. At the same time, the organic acid had low accumulation, the methanogens did not have sufficient substrate to use. After the 6th day, the methane content percentage entered a rapid increase stage and reached the maximum on the 18th day, the methane content percentage was 64.52%, 66.75% and 61.21% when the Fe_3O_4 NPs concentration was 0, 100, 300 mg/L respectively. The addition of Fe_3O_4 NPs would produce Fe^{2+}, combine with S^{2-} to form a precipitate, reducing the inhibitory effect of S^{2-} and H_2S on methanogens. Therefore, the 100 mg/L Fe_3O_4 NPs group had the highest methane content. After the 6th day, the CH_4 content began to rise, and the acetic acid-type methanogens began to decompose acetic acid to produce CH_4 [21].

3.2. The liquid phase effect on anaerobic digestion

3.2.1. The variation of NH_3-N, *p*H and VFAs

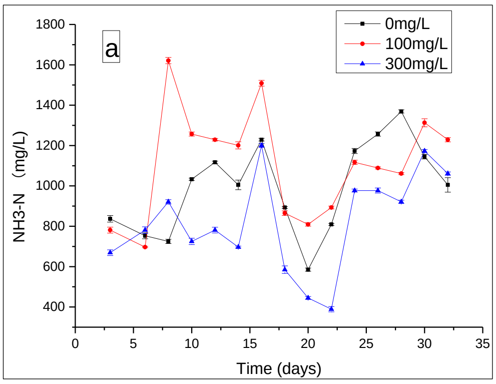

Figure 6. The variation of NH_3-N

NH_3-N was the product resulting from AD and was sometimes regarded as a potential inhibitor during AD [22]. As shown from Figure 6, in the first 6 days, the control group and the experiment with 100mg/L Fe_3O_4 NPs had the same trend, two groups both decreased and reached 753 mg/L and 697 mg/L, respectively. The concentration of ammonia nitrogen decreased in the early stage because ammonia nitrogen was an important nitrogen source for microorganisms, which use ammonia nitrogen for growth. In contrast, the 300 mg/L Fe_3O_4 NPs group was increased to 781 mg/L, this was because Fe_3O_4 NPs accelerate the resolve of organic matter. After the 8th day, the concentration of NH_3-N of the 100 mg/L Fe_3O_4 NPs group increased sharply and reach a maximum concentration of 1621 mg/L. With the accumulation of NH_3-N, biogas production decreased. Figure 6 showed that the addition of an appropriate concentration of Fe_3O_4 NPs could keep ammonia nitrogen at an appropriate level, which was conducive to the survival of methanogens and further improved biogas production.

3.2.2. The variation of *p*H

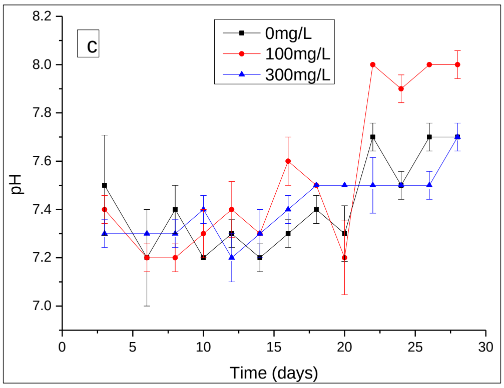

Figure 7. The variation of *p*H

The *p*H buffer system in AD was necessary to ensure that the production of methane was under the proper *p*H condition [23]. The *p*H of the experiment was able to approximate the progress of acidification of organic matter was also reflected and the measured *p*H was shown in Figure 7. In this experiment, the *p*H of all experimental groups in the 20 days changed with a range of 7.2-7.6 which was the optimal growth and metabolism range of methanogens. On the 21st day, the *p*H of the 100 mg/L Fe_3O_4 NPs groups suddenly increased, reached the highest *p*H of 8.0, exceeding the normal *p*H range, and the biogas production decreased at the same time. As an important environmental factor in AD, *p*H not only affects the activity of microbial enzymes but also determines the components of volatile fatty acids in AD, thus affecting the efficiency of AD and biogas production.

3.2.3. The variation of VFAs

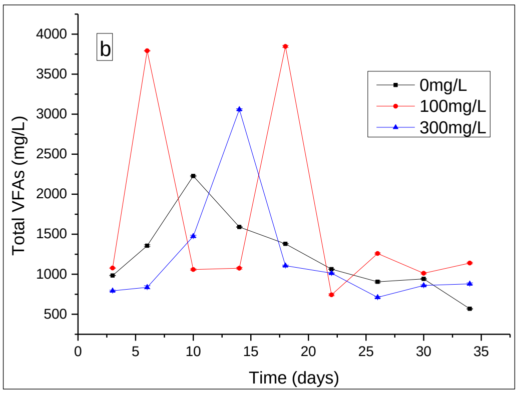

Figure 8. The variation of VFAs

It could be seen from Figure 8 that VFAs of the three experimental groups began to increase and reached the maximum value in the early stage. The maximum values of 0 mg/L, 100 mg/L, 300 mg/L Fe_3O_4 NPs groups were 2226.8 mg/L, 3792.5 mg/L, 3060 mg/L respectively.

The VFAs concentration of the three groups showed the same trend from 18 to 22 d, and the VFAs concentration decreased sharply and reached the lowest, and the concentration at this time was similar to that at the beginning of AD. It was due to a large number of refractory organic cells broken and the organic acid began degradation [24], saw formula below. The VFAs degradation rate in the control group was relatively slow, indicating that the addition of Fe_3O_4 NPs promoted the generation and degradation of VFAs, thus increasing gas production.

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (6)$$

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3.2.4. The relationship of NH_3-N, *p*H and VFAs

Previous reports have suggested that high NH_3-N concentration acts as a buffer for VFAs acidification [25]. The ratio of NH_3-N to acids would determine the buffering capacity in AD, and it was likely that the high NH_3-N concentrations as alkalinity were able to buffer higher VFAs concentration before the *p*H fell to a level which methanogenesis was inhibited [26]. Therefore, it is very important to maintain the balance between NH_3-N and VFAs to ensure the environment required for biological growth and increase biogas production. In the early stages of AD, organic matters in the sludge were first hydrolyzed into water-soluble organic matter and then acidified. The acidified products were acetic acid, propionic acid, butyric acid and other VFAs [27]. In 22-25 days, the experimental groups appeared the concentration of NH_3-N increased, but the concentration of volatile fatty acids decreased, although the acetic acetate produced has been consumed by the methanogens, the ammonia had an inhibition to this stage, so the biogas production was a slip, consistent with the study of [28]. At 22-25 days, the concentration of NH_3-N increased in all experimental groups, but the concentration of volatile fatty acids decreased, and the *p*H value remained unchanged, indicating that the addition of Fe_3O_4 NPs was beneficial to improve the ability of methanogens to balance high concentrations of NH_3-N and VFAs.

3.3. Solid phase effect on AD
3.3.1. SEM

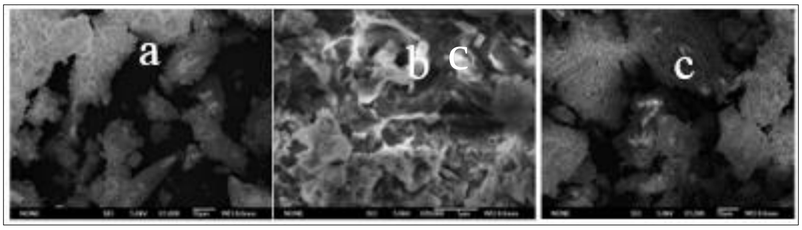
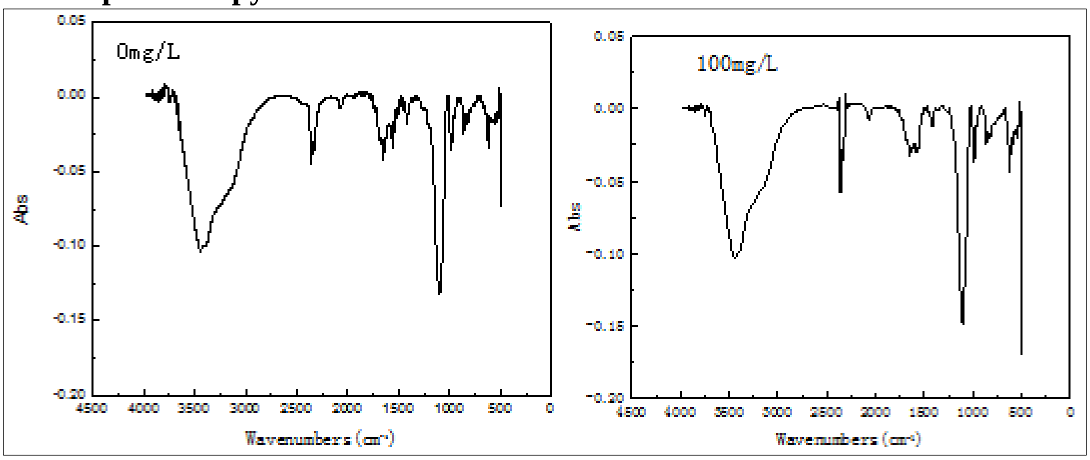


Figure 9. SEM images of 0 mg/L Fe_3O_4 NPs (a) and 100 mg/L Fe_3O_4 NPs (b) and 200 mg/L Fe_3O_4 NPs (c)

The SEM was used to observe the microstructure of sludge with and without Fe_3O_4 NPs. As can be seen from Figure 7, the sludge structure was relatively loose before Fe_3O_4 NPs was added, while after Fe_3O_4 NPs was added, the sludge structure was relatively dense and sludge flocculation can be seen. It could be seen that the sludge porosity of the 100 mg/L Fe_3O_4 NPs group was lower than that of the other two groups, which proved that the addition of an appropriate amount of Fe_3O_4 NPs could increase the contact area between microorganisms and sludge. The Fe_3O_4 NPs were adsorbed to microorganisms on the surface, thereby increasing their metabolic activity and accelerating methane production.

3.3.2. Infrared spectroscopy



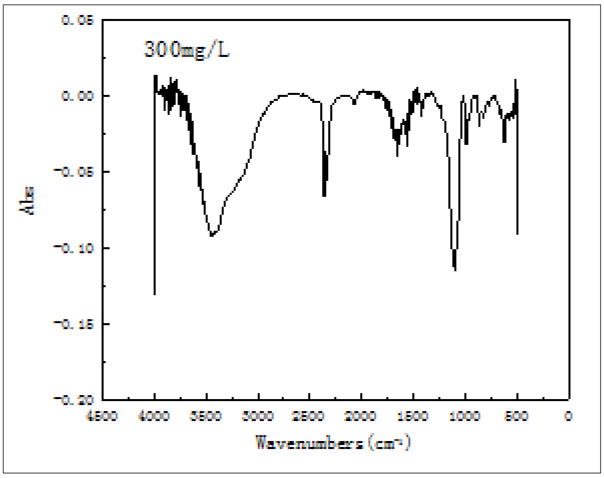


Figure 10. The FT-IR spectra of solid products with Different concentrations of Fe_3O_4

The infrared spectra showed that there were similar peaks in the three experimental groups, but the peak value was different, which indicated that the addition of Fe_3O_4 NPs affected the AD process. It could be seen from Figure 10 that between 3600-3300 cm^{-1}, may be caused by -NH and -OH, the material content of the infrared spectra was proportional to the intensity of the absorption peak, and the 300mg/L Fe_3O_4 NPs group had the lowest content, because of the high concentration of Fe_3O_4 NPs hinder the formation of acid. Between 1015-1200cm^{-1}, due to the alcohol substance, the highest concentration was found in the experiment with 100mg/L Fe_3O_4 NPs, and the lowest found in the experiment with 300mg/L Fe_3O_4 NPs, indicating that the addition of Fe_3O_4 NPs improves the hydrolysis of macromolecular organic compounds into small molecules. The bands approximately at 1558 cm^{-1} were mainly assigned to N-H bending [29, 30]. The infrared absorption peak at 1558 cm^{-1} was narrowed and the 100mg/L Fe_3O_4 NPs groups had the lowest value, indicating that Fe_3O_4 NPs could inhibit the production of NH_3-N, so the biogas production was higher. Therefore, 100mg/L Fe_3O_4 NPs could improve the process of AD.

3.3.3. Thermogravimetric analysis

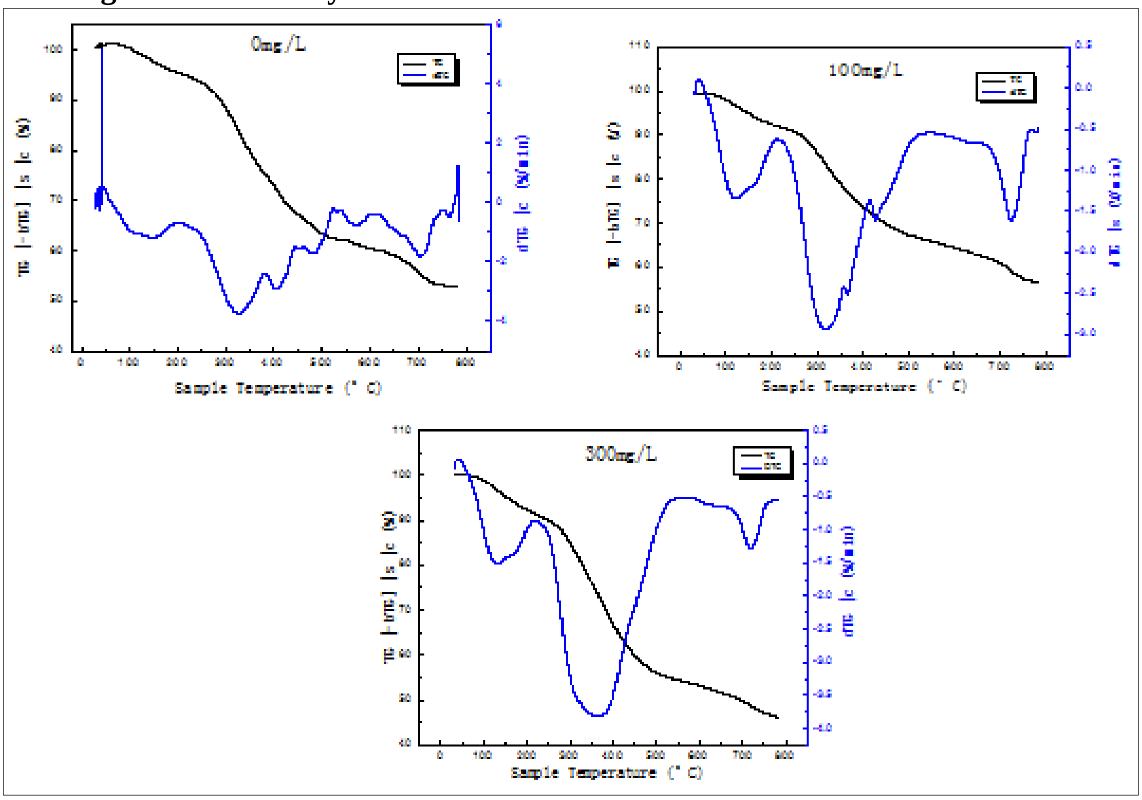


Figure 11. Thermogravimetric analysis of sludge without 0 mg/L,100 mg/L and 300 mg/L Fe_3O_4 NPs

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The TG and weight loss rate (DTG) curves of the raw sludge and the sludge treated with Fe_3O_4 NPS showed that the trend of TG and DTG curves were similar, but there were also some differences. The similarities were that there were three stages of weight loss. The first stage was the precipitation of water, which was mainly caused by the loss of free water and bound water in the sludge, and the trend of the three groups was similar. The second stage was the decomposition and volatilization of organic matter, in this stage, protein and carbohydrate pyrolysis conversion, as can be seen from the figure, the experiment with 300 mg/L Fe_3O_4 NPs dropped the fastest, and the experiment with 100 mg/L Fe_3O_4 NPs changed the slowest. Therefore, the appropriate addition of Fe_3O_4 NPs could promote the decomposition of protein, while excessive Fe_3O_4 NPs would reduce the activity of microbial decomposition of organic matter and lead to the increase of protein and other macromolecular organic matter content. The final stage was the decomposition and charring of residual organic matter, and the last remaining was ash and fixed carbon, and it can be seen that the experiment with 100 mg/L Fe_3O_4 NPs remained the most, it indicated that adding an appropriate amount of Fe_3O_4 NPs can promote the activity of microorganisms so that more organic matter converts into inorganic.

3.4. Kinetic analysis

3.4.1. Logistic model

Fit the cumulative gas production with the Logistic model. According to the kinetic parameters (Table 2) and fitting curve (Figure 12) estimated by the Logistic model, the maximum gas production potential, the maximum gas production rate (R_m) and the lag time (λ) were obtained.

Table 2 showed the kinetic parameters calculated from the Logistic equation. The lag time was between 1.4 to 2.9 days. The correlation modified (R^2) values for the three samples (0 mg/L, 100 mg/L and 300 mg/L Fe_3O_4 groups were 0.87, 0.84, 0.91, respectively. The correlation coefficient (R_2) values showed that the experimental results could be fitted with the Logistic model. And the 300 mg/L Fe_3O_4 groups had the highest R^2(0.91), but the 100 mg/L Fe_3O_4 groups had the lowest R^2(0.84). The 100 mg/L Fe_3O_4 groups had the highest value of FPE (0.04) and the 0 mg/L Fe_3O_4 groups had the lowest value of FPE (0.0072). Therefore, the Logistic model could accurately reflect the cumulative biogas production of AD and the 300 mg/L group had a better with the logic model. Figure 12 showed the comparison of predicted and daily biogas production values for the three samples. When the concentration of Fe_3O_4 NPs was 0, 100 and 300 mg/L, the corresponding maximum gas production were 191, 215 and 186 N mL g^{-1} VS, respectively. Compared with the blank group, the gas production of the 100 mg/L Fe_3O_4 NPs experimental group increased by 12.5%, while the 300 mg/L Fe_3O_4 NPs experimental group inhibited the anaerobic digestion, decreased the gas production. The experimental results showed that the model fitting results were consistent with the experimental results, and the addition of 100 mg/L Fe_3O_4 NPs could promote the performance of anaerobic digestion gas production.

Table 2. Parameters of Logistic model

Logistic model	Cumulative gas production (N mL g^{-1} VS)	Maximum gas production potential (N mL g^{-1} VS)	R_m (mL$d^{-1}g^{-1}$ VS)	λ	R^2	RMSE	FPE
0 mg/L	193	192	6.3	2.1	0.87	1.66	0.0072
100 mg/L	247.2	215.8	7.3	2.9	0.84	4.45	0.04
300 mg/L	190.5	186	6.2	1.4	0.91	1.85	0.0089

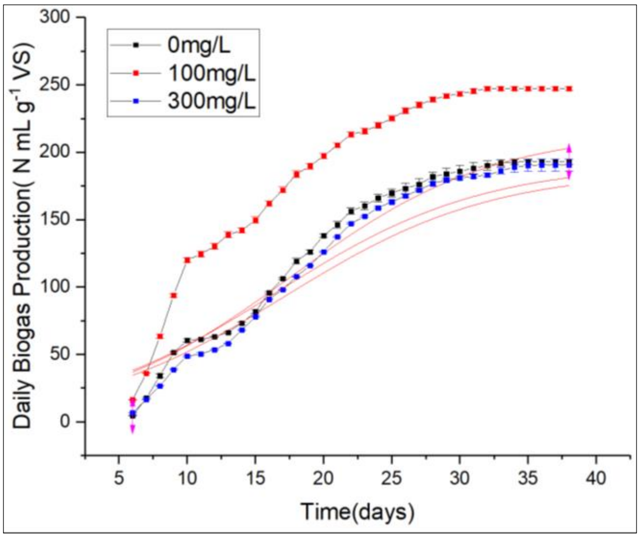

Figure 12. Daily biogas production-experimental and Logistic model

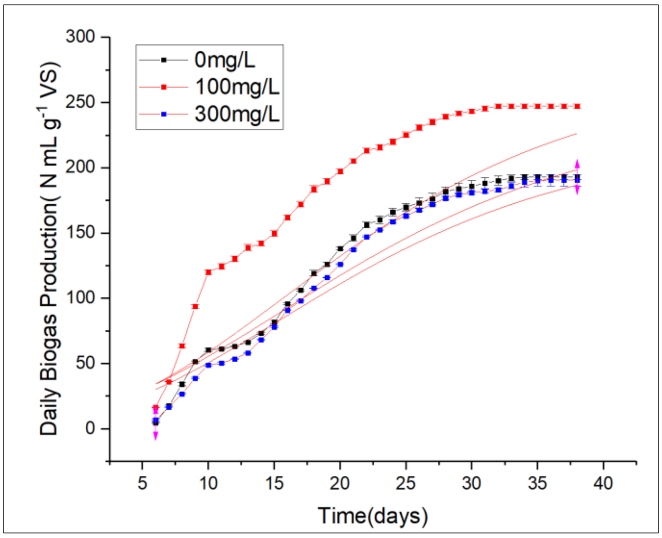

Figure 13. Daily biogas production-experimental and modified Gompertz model

3.4.2. Modified Gompertz model

The Daily biogas production was fitted with the Modified Gompertz model. The regression analysis of the Modified Gompertz model (Table 3) showed that the results were in good agreement with the experimental data of all stages. The lag time was between 1.4 to 2.4 days. The correlation modified (R^2) values for the three samples (0 mg/L, 100 mg/L and 300 mg/L Fe_3O_4 groups were 0.9, 0.89 and 0.92, respectively. The 300 mg/L Fe_3O_4 groups had the highest R^2(0.92), but the 100 mg/L Fe_3O_4 groups had the lowest R^2(0.89). The 0 mg/L Fe_3O_4 groups had the highest value of FPE (0.13) and the 300 mg/L Fe_3O_4 groups had the lowest value of FPE (0.047).

Figure 13 showed the comparison of predicted and daily biogas production values for the three samples. The results demonstrated the feasibility of applying the modified Gompertz model to develop the kinetic model of cumulative biogas production due to the high correlation coefficient (R^2=0.89-0.92), and low FPE (0.047-0.013) and RMSE (4.25-7.07), indicated a strong linear relationship between the experimental data and the model.

It could be shown that the value of the correlation coefficient of the Logistic model was lower than that of the modified Gompertz model. Root mean square error (RMSE) and Final Prediction Error (FPE) of the modified Gompertz model fitted well for the kinetic study of the AD process. Therefore, the modified Gompertz model was more suitable for the evaluation of AD kinetic study.

Table 3. Parameters of Modified Gompertz model

Improved Gompertz model	Cumulative gas production (N mL g^{-1} VS)	Maximum gas production potential (N mL g^{-1} VS)	R_m (mL$d^{-1}g^{-1}$ VS)	λ	R^2	RMSE	FPE
0 mg/L	193	243	6.3	1.9	0.9	7.07	0.13
100 mg/L	247.2	273	7.5	2.4	0.89	5.1	0.053
300 mg/L	190.5	223	6.2	1.4	0.92	4.25	0.047

4. Conclusions

In this study, the effects of different concentrations of Fe_3O_4 NPs on the yield of COD, VFAs, NH_4-N In this study, the effects of different concentrations of Fe_3O_4 NPs on the yield of COD, VFAs, NH_4-N and biogas in the process of AD were analyzed, and it was proved that Fe_3O_4 NPs could promote the AD. The results showed that 100mg/L Fe_3O_4 NPs was the best additive concentration, which could increase gas production by 21.9% and reached the highest methane content of 66.75%. The analysis of the kinetic model showed that the model results were consistent with the actual biogas production change. The modified Gompertz model had the best fitting effect. Through the analysis of the solid phase and liquid phase material changes, it was found that as the AD progressed, the solid phase and the substance in the liquid phase were finally converted to the gas phase. At the same time, 100mg/L Fe_3O_4 NPs could maintain the three-phase balance, kept the substance concentration in an appropriate range, and promote the production of biogas.

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