Combined MgO nanoparticle and microwave pre-treatment on biogas increase from Enteromorpha during anaerobic digestion

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Abstract. This study evaluated the anaerobic digestion of MgO metal-oxide nanoparticles combined with microwave pretreatment to increase biogas production from microalgae. The result shows the maximum total biogas yield of 342ml and 320ml were achieved by the MW pretreatment of 800W, 4min +15mg/L MgO NPs group and 600W, 6min +5mg/L MgO NPs group, which are 1.38 and 1.30 times compared to control, respectively. The influence of metallic oxide (MgO) NPs and MW pretreatment on anaerobic digestion of Enteromorpha resulted in significant increase in cumulative biogas production. The modified Gompertz equation and Logistic function model were used to simulate the nanoparticle-enhanced anaerobic digestion process, which demonstrate that the modified Gompertz equation can better simulate the fermentation process of microalgae.

1. Introduction
Due to the increase of the world's population and the rapid development of industrialization, traditional non-renewable energy sources such as oil, natural gas and coal are rapidly being consumed [1]. Energy consumption and environment sustainability is also getting more and more attention in the environment pollution, such as energy saving methods for refrigeration rooms [2], power consumption [3, 4], energy conversion[5, 6]. The use of these energy sources usually increases the load of carbon dioxide in the atmosphere, causing enormous damage to the environment [7]. Anaerobic digestion (AD) is considered a promising technique for converting organic matter into valuable energy sources, i.e., methane and hydrogen. Organic substrates can be destroyed and degraded by bacteria in the absence of oxygen to produce biogas as the main by-product[8].

In addition to conventional organic waste for the production of bioenergy, microalgae from natural algal blooms or in large quantities are considered to be one of the potential raw materials for biogas production by the AD[9]. Enteromorpha is one of the sources of pollution that often causes red tides, which is rich in organic matter such as proteins and carbohydrates and can be anaerobically degraded by microorganisms. However, their high resistance and hard cell walls limit the hydrolysis process so that microorganism is not easy to obtain intracellular carbohydrates, proteins and the like. Therefore, the use
of some necessary pretreatment techniques to break the protection of the cell wall makes it easier for bacteria to come into contact with intracellular organic matter[10]. Compared to conventional heating methods, MW pretreatment supplies higher heating efficiency through microwave and direct interaction with algal cell walls and disrupts the structure of the algal cell wall[11].

Mineral elements are needed in the growth process of microorganisms. Trace metals play an important role in the AD process. It has been reported that trace metals are essential for the synthesis of key enzymes and can increase the activity of microorganisms involved in AD[12]. Nanoparticles have a high surface to volume ratio that provides a reaction point for chemical reactions in the AD process. Trace metals as nanoparticles are added to increase the efficiency of the AD and the degradation of microalgae.

Our recent study[12] researched the effects of metal nanoparticles Ni and Co on microalgae (Enteromorpha) during AD process, which revealed that the use of NPs in Enteromorpha during hydrolysis had a similar effect as the non-treated substrate. The purpose of this study was to investigate the effects of combined with MW pretreatment of intestinal morph and MgO NPs. The established predictive model can also be used to confirm the experimental results of this work to estimate the biogas produced during the AD.

2. Materials and methods

2.1. Raw material
Anaerobic sludge was purchased from Wenchang Wastewater Treatment Plant in Harbin, Heilongjiang Province, China. The total suspended solids (TSS) of the sludge was 5,120 mg / L, while the volatile suspended solids (VSS) was 2,031 mg / L. The Enteromorpha was obtained from the Institute of Hydrobiology of The Chinese Academy of Science, Wuhan, China. MgO is metallic-oxide NPs. NPs were purchased from China Metallurgical Research Institute, Beijing. The average particle diameter of the metal nanoparticle is less than 100nm.

2.2. Experimental procedure
The MW pretreatment was performed prior to AD using a domestic Panasonic microwave oven (1180 W). The MW pretreatment condition was liquid:solid of 20:1[12]. The laboratory glass bottles (working volume 500 ml) were used as bioreactors. The bioreactor is sealed with a rubber stopper. Nitrogen gas was purged through a digester for 5 min at the beginning to create anaerobic conditions[8, 13]. The digester was maintained at a temperature of 37 °C and a mixing speed of 150 rpm[14].

2.3. Analytical methods
Total Solids (TS) and Volatile Solids (VS) were assessed as per the standard methods[15, 16]. Samples were collected from a gas-tight bottle using a medical syringe with a long needle and then transferred to a small tube with a rubber stopper to avoid gas loss. The amount of biogas produced was measured twice a day.

2.4. Mathematical Kinetic Models
Using the improved Gompertz model equation Eq.1 and Logistic function model Eq.2, the calculation and comparison of biogas production kinetics in algae biomass digestion under different pretreatment conditions were modeled[13].

\[
B = B_p \exp \left( - \exp \left( \frac{MBPR \cdot 2.7183}{B_p} \cdot (BPDT - t) + 1 \right) \right) \quad (1)
\]

\[
B = \frac{B_p}{1 + \exp \left( \frac{MBPR \cdot BPDT - t}{B_p} + 1 \right)} \quad (2)
\]
Where, \( B \) = Cumulative biogas volume at digestion time \( t \) (ml); \( BP \), Biogas production potential (ml); \( MBPR \), Maximum biogas production rate (ml/h); \( BPDT \), Biogas production delay time (hrs); \( t \) = Total digestion time (hrs).

In order to find out which model closely matches the experimental data, we performed a second-order Akaike Information Criterion (AIC) test. The lower the value of AIC, the better the fitting and predictive ability of the model. For each model, the AIC value and the Akaike weight value are calculated using Eq.3 and Eq.4:

\[
AIC = \begin{cases} 
N \ln \frac{RSS}{N}, & \text{when } \frac{N}{K} \geq 40 \\
N \ln \frac{RSS}{N} + 2K + \frac{2K(K+1)}{N-K-T}, & \text{when } \frac{N}{K} < 40 
\end{cases} 
\quad (3)
\]

Akaike’s weight = \( \frac{e^{-0.5\Delta AIC}}{1 + e^{-0.5\Delta AIC}} \) \quad (4)

Where: \( N \) = Number of points; \( RSS \) = Residual sum of square; \( K \) = Number of model parameters; \( \Delta AIC \) = The relative difference between two AIC values.

3. Results and discussion

3.1. Influence of nanoparticles and MW pretreatment on biogas production

Figure 1 (a) illustrates the cumulative biogas production during AD of microalgae. Obviously, most treatments increase biogas production compared to control samples. MW pretreatment of 800W, 4min + 15mg/L MgO NPs group obtain the maximum biogas production of 342ml. An increase in biogas production of 1.38, 1.18 and 1.12 times by the MW pretreatment of 800W, 4min +15mg/L MgO NPs, the MW pretreatment of 800W, 6min +10mg/L MgO NPs and the MW pretreatment of 800W, 4min +5mg/L MgO NPs, respectively. The time that the test group reached the same cumulative gas production was greatly shortened compared to the control group. The maximum cumulative gas production of the control group was reached, and the time of the MW pretreatment of 800W, 4min +15mg/L MgO NPs was 40 hours earlier, indicating that the AD process was greatly accelerated by the pretreatment and the addition of nanoparticles.

Figure 1 (b) illustrates the different pretreatment time of MW pretreatment in 600W power and the concentration of MgO NPs produced an almost similar trend of cumulative biogas production. The maximum total biogas production of 320ml was obtained by the MW pretreatment of 600W, 6min +5mg/L MgO NPs group, which is 1.30 times compared to the control group.

Table 1. Parameters of the modified Gompertz model

| Parameter       | Control | 800W, 2min, MgO(10mg/L) | 800W, 4min, MgO(15mg/L) | 800W, 4min, MgO(15mg/L) | 800W, 6min, MgO(10mg/L) |
|-----------------|---------|-------------------------|-------------------------|-------------------------|-------------------------|
| BP (ml)         | 602.355 | 214.045                 | 352.353                 | 527.689                 | 324.692                 |
| MBPR (ml/hr)    | 2.74    | 2.34                    | 2.83                    | 3.38                    | 3.44                    |
| BPDT (Hrs)      | 1.01    | 1.45                    | 0.40                    | 0.46                    | 0.50                    |
| \( R^2 \)       | 0.97072 | 0.98119                 | 0.99322                 | 0.99746                 | 0.98544                 |
| PBY(ml)         | 254.76  | 197.65                  | 271.62                  | 343.90                  | 284.77                  |
| MBY (ml)        | 247     | 198                     | 277                     | 342                     | 292                     |
| Dif             | 3.14    | 0.17                    | 1.98                    | 0.55                    | 2.53                    |
Table 2. Parameters of Logistic Function model

| Parameter | Control | 800W, 2min, MgO(10mg/L) | 800W, 4min, MgO(5mg/L) | 800W, 4min, MgO(15mg/L) | 800W, 6min, MgO(10mg/L) |
|-----------|---------|-------------------------|------------------------|-------------------------|-------------------------|
| BP (ml)   | 356.582 | 198.608                 | 298.085                | 400.169                 | 289.923                 |
| MBPR (ml/hr) | 2.82   | 2.42                    | 3.02                   | 3.68                    | 3.69                    |
| BPDT (Hrs) | 1.06   | 1.19                    | 0.57                   | 0.66                    | 0.65                    |
| \( R^2 \) | 0.96927 | 0.98595                 | 0.98601                | 0.9966                  | 0.9819                  |
| PBY (ml)  | 253.64  | 193.61                  | 268.14                 | 339.46                  | 278.10                  |
| MBY (ml)  | 247     | 198                     | 277                    | 342                     | 292                     |
| Dif       | 2.68    | 2.26                    | 3.30                   | 0.74                    | 4.99                    |

Remarks: BP, Biogas production potential; MBPR, Maximum biogas production rate; BPDT, Biogas production delay time; \( R^2 \), Correlation Coefficient, PBY, Predicted biogas yield, MBY, Measured biogas yield, Dif, Difference between measured and predicted biogas yield.

Figure 1. Cumulative biogas production (a) effect of 800 W MW power, (b) effect of 600 W MW power, (c) effect of 400 W MW power with different pretreatment time and different MgO NPs concentration

The algal cell wall is composed of an outer layer and an inner layer. In the initial phase of AD, combined NPs and MW pretreatment methods dissolve the outer layer of the cell wall to release glycoproteins, carbohydrates and cellulose. MW pretreatment increases the rate of cell cracking, which increases the impact on biogas production. MW pretreatment hydrolyzes glycosidic bonds in carbohydrates and polysaccharides, thereby biodegrading complex polysaccharides into simple sugars. Later, the dissolution of the inner layer of the cell wall was due to the attack of NP. NP hydrolyzes cellulose into simpler oligosaccharides such as cellobiose and celloextrin. Figure 1 (c) shows that the MW pretreatment power is lower than that of the upper two groups, which is not enough to cause great damage to the cell wall, and the NPs and microorganisms cannot be fully contacted with intracellular substances. Therefore, the cumulative gas production is not significantly different from the control group.

To the best of the authors' knowledge, the first study analyzed the combined effects of microwave pretreatment and metal oxide NPs on the AD of microalgae. Cumulative biogas production (Figure 1) shows that combining MW pretreatment with metal oxide NPs can have a significant impact on biogas production by dissolving algae cell walls.
Table 3. Results for Akaike’s Information Criterion (AIC) Test

| Model                        | RSS       | N   | AIC   | Akaike Weight |
|------------------------------|-----------|-----|-------|---------------|
| Modified Gompertz Model      | 1360.80908| 10  | 65.1325 | 0.5604        |
| Logistic Function Model      | 1428.52121| 10  | 65.6181 | 0.4396        |

Remarks: RSS, the Residual sum of the square; N, Number of Points; AIC, Akaike’s Information Criterion.

3.2. Mathematical Kinetic Models

Figure 2 and Figure 3 shows predicted versus all the experimental groups and the biogas production cumulative biogas production. The results obtained from the kinetic studies are given in Table 1 and Table 2, respectively. While using the modified Gompertz model, maximum biogas production rate (MBPR) for the control group was 2.74 ml/hr. For all 800W MW pretreatment of 2min MgO(10mg/L), 4min MgO(10mg/L), 4min MgO(15mg/L) and 6min MgO(10mg/L), the MBPR found to be 2.34, 2.83, 3.83, and 3.44 ml/hr, respectively. Similarly, for the Logistic model, the MBPR for the control group, 800W MW pretreatment of 2 min MgO(10mg/L), 4 min MgO(10mg/L), 4 min MgO(15mg/L) and 6 min MgO(10mg/L) were 2.82, 2.42, 3.02, 3.68 and 3.69 ml/hr, respectively. Determined by the kinetic model, the combined effect of MW pretreatment and NPs increased biogas production rate and reduced lag phase time relative to the untreated control group. The reduction in the hysteresis phase is caused by microwave pretreatment of the early hydrolysis of the algal cell wall in the first stage of AD. The
correlation coefficient for the modified Gompertz model and Logistic Function model were above 97.07% and 96.92%, respectively. This shows that both models are very consistent with the experimental data. Table 3 shows the obtained results for the Akaike Information Criterion (AIC) test. The AIC test indicates that the modified Gompertz model has a lower AIC value and is therefore a more suitable model.

4. Conclusion
The influence of metallic oxide (MgO) NPs on anaerobic digestion of Enteromorpha resulted in significant increase in cumulative biogas production. The cumulative enhancement in biogas yield for the MW pretreatment of 800W, 4min +15mg/L MgO NPs group and 600W, 6min +5mg/L MgO NPs group, was 38.5%, 30.01%, respectively. The presented results show robustness of MgO NPs with anaerobic digestion of microalgae (Enteromorpha) for enhancement in biogas yield. Experimental data was further modeled by improved Gompertz and Logistic function models. The AIC test emphasizes that the modified Gompertz model is almost matched to the experimental data.

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