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Effect of magnetite powder on anaerobic co-digestion of pig manure and wheat straw

Yanzi Wang [a,c], Guangxin Ren [b,c,*], Tong Zhang [b,c], Shuzhen Zou [b,c], Chunlan Mao [b,c], Xiaojiao Wang [b,c]

[a] College of Forestry, Northwest A&F University, Yangling 712100, Shannxi, China
[b] College of Agronomy, Northwest A&F University, Yangling 712100, Shannxi, China
[c] Research Center of Recycle Agricultural Engineering and Technology of Shannxi Province, Yangling 712100, Shannxi, China

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ABSTRACT

This study investigated the effects of different amounts of magnetite powder (i.e., 0 g, 1.5 g, 3 g, 4.5 g, 6 g) on the anaerobic co-digestion of pig manure (PM) and wheat straw (WS). The variations in pH, alkalinity, cellulase activity (CEA), dehydrogenase activity (DHA) and methane production, were analyzed by phases. Correlation of the activities of the two enzymes with methane production was also analyzed, and the Gompertz model was used to evaluate the efficiency of anaerobic digestion (AD) with the addition of magnetite powder. The results showed that magnetite powder had significant effects on the anaerobic co-digestion of PM and WS. The maximum total methane production with the addition of 3 g of magnetite powder was 195 mL/g total solids (TS), an increase of 72.1%. The CEA and DHA increased with magnetite powder in the ranges of 1.5–4.5 g, 1.5–6 g, respectively, while the methane production showed a better correlation with DHA than with CEA. Using the Gompertz model, the efficiency of AD was optimal when adding 3 g magnetite powder, with higher methane production potential (206 mL/g TS), shorter lag-phase time (14.9 d) and shorter AD period (44 d).

1. Introduction

With the development of the economy and the expansion of industrialization, the demand for energy, including renewable energy, is growing rapidly. It has been widely accepted that biogas production plays an important role in energy supply. In China, about 809 million tons of crop straw and 1629 million tons of animal manure are collected as biogas resources every year (Zhang et al., 2015b). Anaerobic digestion (AD) is an efficient way of converting wastes, such as crop straws, poultry and livestock manure, into energy sources, and is of great significance in solving certain resource and environmental problems (Jiang et al., 2011; Wei et al., 2014).

The technology is advancing steadily, and previous studies paid more attention to the factors in AD, such as different raw materials, the ratio of materials, C/N, initial pH, and alkaline treatment (Zhang et al., 2013, 2014, 2015a; Song et al., 2013; Wang et al., 2014; Lin et al., 2015). In recent years, the techniques of molecular cloning, high throughput sequencing, metagenome or metaproteome have been applied to reveal the microbial community. The use of them has shown the distribution of populations and dominant communities in AD (Angelika et al., 2013; Jun et al., 2014; Li et al., 2016), which is taken as an exploratory method on the mechanism of AD. However, the goal of attaining a greater understanding of AD is still driving the efficiency of the technology. Currently, biogas production in China comes from two primary sources: rural household digesters and medium-to- large biogas projects. It is essential for China's national conditions sustainability that both models develop simultaneously (Song et al., 2014). However, the method promoted to rural households must be simple to operate and low cost. If the method is complex, it will not be readily accepted by farmers. Therefore, it is essential to continue to explore for a simple and easy method of operation.

The growth and propagation of microorganisms capable of AD require the involvement of trace elements, particularly Fe, Co, Ni, Cu, Zn, Se, W and Mo, which are key constituents of the enzyme systems of several methanogens (Scherer et al., 1983). They are usually important components of coenzymes, agons, and cofactors of AD enzyme systems that have significant regulatory effects on the methane production stage (Mudhoo and Kumar, 2013). Insufficient supply of trace elements will affect the bioconversion efficiency, and render an AD system unable to function normally (Lo et al., 2012). The use of additions like active minerals that contain metal elements can enhance biogas production through

* Corresponding author at: College of Agronomy, NO. 37 Mailbox, South Campus of Northwest A&F University, Yangling, Shaanxi 712100, China.
E-mail address: rengx@nwsuaf.edu.cn (G. Ren).

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influencing the microorganic and enzymatic transformation of the AD process (Dohanyos et al., 1997; Milan et al., 2003; Parawira, 2012; Chai et al., 2013). However, due to the complexity of accessing trace element additives and the lack of knowledge in regard to dosages, it is inconvenient and impractical for use by rural households. In comparison, adding trace elements in mineral form can not only provide mixed trace elements, but is also simpler to operate and easier to popularize. At present, the required amounts of trace elements in mineral form in AD of different solid wastes have not been studied sufficiently (Liu et al., 2014, 2015).

Magnetite powder contains several types of metals, particularly for Fe, Co, Ni and K, which are considered essential nutrients for methanogens. Adding it into the AD is economical and easy to operate (Demirel and Scherer, 2011). Liu et al. (2015) found that the addition of magnetite produced conditions beneficial to AD. But the efficiency of AD on addition of magnetite has not been evaluated to date. Kinetics models have been proven to be a useful tool to describe and evaluate the performance of the AD process (Zhang et al., 2010). Thus, such models can be tried in the evaluation of the efficiency of AD following the addition of magnetite powder. Moreover, as a bridge between the biological community and the AD products, enzymes play an important role in the process of AD. Thus, the impact of magnetite on some enzyme activity and the relationship between enzyme activity and methane production ought to be explored.

In order to investigate the effect of magnetite powder on the process and efficiency of AD, batch experiments were conducted under mesophilic conditions using magnetite powder with common raw materials (i.e., pig manure and wheat straw). The variations of pH, alkalinity, cellulose enzyme activity (CEA), dehydrogenase activity (DHA) and methane production were investigated, and the correlation between methane yield and the activities of enzymes were analyzed. This might be the first attempt to evaluate the efficiency of AD with added magnetite powder using the Gompertz model, as well as to explore the trends in CEA and DHA.

2. Materials and methods

2.1. Feedstock and inoculums

WS was collected from test fields of Northwest A&F University in Yangling, China, which was naturally dried, and cut into 2–3 cm pieces by a food grinder. PM was collected from a local pig farm, while AD sludge from a normally running biogas digester in a local village was used as inoculum. The basic characteristics of WS, PM and inoculum used in the study are shown in Table 1. Natural magnetite powder (not distilled) was obtained from Panzhihua of Sichuan Province, China. It was prepared by crushing and sieving to a particle sizes range of 0.5–1.0 mm, which was then washed with deionized water and dried in an oven at 105 °C for 12 h. The major and trace element composition of the magnetite was determined by atomic absorption spectroscopy (Hitachi-Z 5000, Japan) (Table 2).

Table 2
Major and trace element composition of the magnetite.

Element (%)	%
Fe	16.59 ± 0.04
K	8.11 ± 0.02
Zn	6.90 ± 0.04
Ca	6.05 ± 0.02
Mg	1.02 ± 0.01
Co	$3.91 \times 10^{-3} \pm 5.28 \times 10^{-5}$
Cu	$2.07 \times 10^{-3} \pm 2.94 \times 10^{-5}$
Ni	$1.88 \times 10^{-3} \pm 2.36 \times 10^{-5}$

2.2. Experimental design

The digestion tests were conducted according to the method described by Wang et al. (2012). All experiments were conducted for 51 days at 35 °C, and the mixing ratio of PM and WS was 1:1 (TS). The reactions were conducted in 1 L ground flasks with working volumes of 700 g, including 200 g of inoculum and 500 g digesting materials, and with the total solid concentration of 8%. According to the characteristics of PM, WS and inoculum in Table 1, the inoculum-to substrate ratio (ISR) was 14.84/41.16 g TS. Different amounts of magnetite powder (i.e., 0 g, 1.5 g, 3 g, 4.5 g, 6 g) (i.e., 0 g, 0.027 g, 0.054 g, 0.080 g, 0.107 g per 1 g of TS) were separately added into the bioreactors, which were labeled as M0, M1.5, M3, M4.5 and M6, respectively. M0 was the control group without magnetite powder. Consistency of the characters of material, to a certain extent M0 can represent the methane potential of the substrate in the study. Each treatment was repeated three times.

All experiments were performed with sunlight-dark conditions in transparent reactors using natural sunlight. All reactors were tightly closed with rubber septa and screw caps. The head space of each reactor was flushed with nitrogen gas for approximately three min to assure anaerobic conditions prior to the start of tests. Constant-temperature was maintained using a water circulator. All reactors were shaken manually for about one min daily prior to measurement of biogas volume. Generally, the digester with best biogas production of the triplicate was sampled and kept unchanged. All parameters were measured three times except for methane production. After each sampling, the same amount of tap water was added to restore working volumes (Yin et al., 2015).

2.3. Analytical techniques and statistical method

Total solids (TS), volatile solids (VS), total organic carbon (TC), total Kjeldahl nitrogen (TN) and total alkalinity were measured according to the procedures described in the Standard Methods (1998). Biogas volume was recorded every day by the water displacement method, and the methane proportion was determined by a biogas analyzer (Gasboard-3200p, Wuhan). Cellulose enzyme activity (CEA) was measured every 5 days by 3,5-dinitrosalicylic acid (DNS) colorimetry. A color reaction occurs when DNS is mixed with sugars produced in enzymatic reactions under certain conditions, and the absorbance (OD value) can be measured by a

Table 1
Characteristics of PM, WS and inoculum.

Substrates	pH	TC (%)	TN (%)	C/N	TS (%)	VS[a] (%)
PM	6.5 ± 0.03	36.28 ± 0.25	4.19 ± 0.09	8.66 ± 0.18	11.02 ± 0.04	82.31 ± 1.12
WS	ND[b]	35.26 ± 0.27	0.79 ± 0.11	44.63 ± 0.48	91.20 ± 0.21	92.88 ± 0.62
Inoculum	7.62 ± 0.02	36.11 ± 0.46	1.75 ± 0.02	20.63 ± 0.13	7.42 ± 0.11	70.09 ± 0.47

Note: TC, TN, C/N, TS and VS denote for total carbon, total nitrogen, carbon/nitrogen ratio, total solids and volatile solids, respectively.
[a] Dry basis.
[b] Not determined.