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Using calcium peroxide (CaO_2) as a mediator to accelerate tetracycline removal and improve methane production during co-digestion of corn straw and chicken manure

Shan-Fei Fu[a,b], Kai-Qiang Chen[a,b], Hua Zou[a,b,*], Jia-Xing Xu[c,*], Yi Zheng[d], Qing-Fu Wang[e,*]

[a] School of Environment and Civil Engineering, Jiangnan University, Wuxi, Jiangsu Province 214122, PR China
[b] Jiangsu Key Laboratory of Anaerobic Biotechnology, Jiangnan University, Wuxi, Jiangsu Province 214122, PR China
[c] Jiangsu Key Laboratory for Biomass-Based Energy and Enzyme Technology, Huaiyin Normal University, Huaian, Jiangsu Province 223300, PR China
[d] Department of Environmental Engineering and Earth Sciences, Clemson University, 342 Computer Court, Anderson, SC 29625, USA
[e] Key Laboratory of Rubber-Plastic, Ministry of Education, Qingdao University of Science and Technology, Qingdao, Shandong Province, PR China

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ABSTRACT

Antibiotics have been widely detected in livestock waste. The removal of antibiotics from livestock waste before they are exposed to the environment is crucial. Anaerobic digestion (AD) is an effective technique to deal with livestock waste. However, tetracycline was found to inhibit the AD process. In this research, effects of CaO_2 addition on the tetracycline removal and methane production during the co-digestion of corn straw and chicken manure were investigated. Results showed the presence of tetracycline in AD system reduced methane yield by 8.8%. Addition of CaO_2 at the dose of 0.032 g/g TVS (total volatile solid of substrate and inoculum) improved methane yield by 4.8% and shortened lag-phase by more than 2 days. Using CaO_2 also accelerated the removal of tetracycline, therefore mitigated its inhibition effect. The microbial communities of the co-digestion system were also affected by tetracycline/CaO_2 addition. The addition of tetracycline especially CaO_2 led to increased relative abundance of microorganisms associated with complex substrate degradation. This study indicated that using CaO_2 is a promising way to accelerate tetracycline removal and improve methane production during AD of antibiotic-containing organic wastes.

1. Introduction

Antibiotics are natural or synthetic physiologically active substances, which are widely used to promote growth [1], reduce the mortality and morbidity of diseases caused by bacteria [2,3]. However, the utilization of antibiotics has resulted in many issues. For instance, the overuse and misuse of antibiotics have contributed to a rise in bacterial resistance [4], and the release of antibiotics to soil and water environment has been discovered to cause phylogenetic structure alteration, resistance expansion, and ecological function disturbance in the micro-ecosystem [5,6]. During the utilization of antibiotics, considerable amounts of antibiotics remain unchanged and are excreted into urine and feces and discharged to the environment [7]. The detected concentrations of antibiotics in wastewater, groundwater and sewage sludge ranged from 0.1 to 100 μg/L [8]. It can be up to milligram per liter in the manufacturing industry wastewater [9].

The natural degradation efficiency of antibiotics in environment is rather low. Therefore, the discharged antibiotics can remain intact in the environments for a long time, resulting in antibiotic resistance problem [10,11]. In Europe, approximate 25,000 people die from bacterial infections every year due to antibiotic resistance [12]. As the largest antibiotic production country in the world, China is facing a grand challenge associated with the misuse of antibiotics. In China, about 46% of all the produced antibiotics has been used by the livestock industry, which resulted in 29,000 to 87,000 tons of antibiotic residues annually in livestock waste [13,14]. Livestock waste has been widely used as feedstock for anaerobic digestion (AD) [15,16]. Therefore, the antibiotics in livestock waste could be a concern during the AD of livestock waste. On the other hand, digestates produced during the AD were also widely used as organic fertilizer [17]. If the fertilizer containing antibiotics was used, it may alter soil microbial constitution and function, as well as lead to antibiotic resistant genes problems [18]. One of efficient ways to deal with these problems could be the removal of the antibiotics existing in the livestock waste before they are discharged into the environment. Therefore, it is essential to study the removal of antibiotics during AD process and eliminate the antibiotics

* Corresponding authors at: School of Environment and Civil Engineering, Jiangnan University, Wuxi, Jiangsu Province 214122, PR China (H. Zou).
E-mail addresses: fusf@jiangnan.edu.cn (S.-F. Fu), zouhua@jiangnan.edu.cn (H. Zou).

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in digestates. In order to mitigate the risk of antibiotics inhibition on AD process, methods that benefit the removal of antibiotics during the AD should be developed.

Calcium peroxide (CaO_2) has been widely used in agriculture, aquiculture and pharmaceuticals. It has also been used for contaminant degradation by means of its oxidative capability [19,20]. In our previous studies, CaO_2 has also been proved to be an efficient mediator to improve the AD performance [21]. CaO_2 can react with water and release oxygen/$Ca(OH)_2$ as resultants, while generating hydrogen peroxide (H_2O_2) and hydroxyl radical ($^{\cdot}OH$) as intermediates [22]. According to such features, CaO_2 is expected to be a potential mediator to accelerate the removal of antibiotics during the AD process.

This research was conducted to study the effects of limited CaO_2 addition on the anaerobic co-digestion of corn straw and chicken manure and the anaerobic removal of tetracycline antibiotics. In addition, tetracycline removal in the sterile water with/without CaO_2 addition was also examined as controls. The implementation of this study would provide an easy and practical solution to improve the AD performance and accelerate the removal of antibiotics during the AD of antibiotic-containing organic wastes.

2. Materials and methods

2.1. Substrates and inoculum

Substrates used in this study were corn straw and chicken manure, which were obtained from cornfield in Pingdu (Qingdao, China) and a chicken farm in Pingdu (Qingdao, China), respectively. The inoculum for AD in this research was mesophilic sludge (i.e., 35 °C) collected from a 500-m^3 biogas digester (Pingdu, Qingdao, China) which has used corn straw as a substrate. The collected sludge was stored in a refrigerator at 4 °C until used. Before AD, the sludge was pre-activated in a shaking water bath at 37 °C for two days. The characteristics of substrates and inoculum were shown in Table 1

2.2. Anaerobic co-digestion of corn straw and chicken manure

Triplicate mesophilic (37 °C) anaerobic co-digestions of corn straw and chicken manure were conducted in 300-mL glass bottles with working volume of 200 mL. The TS loading of the AD process was 4% (w/v). The mass ratio of corn straw and chicken manure was fixed at 3:1 (based on VS) according to the study of Li et al. [23]. As one of the major antibiotic groups, tetracycline antibiotics were the most often used around the world [24,25]. In this study, tetracycline hydrochloride (Shanghai Macklin Biochemical Co., Ltd, China) was selected as a typical antibiotic to investigate the impact of antibiotic on the AD performance. The concentration of tetracycline hydrochloride in the fermentation system was set at 25 mg/L. The CaO_2 dose in this study was 32 mg/g TVS (total VS of substrate and inoculum), which was selected based on our previous study [21]. The anaerobic co-digestion of corn straw and chicken manure was carried out in 6 different scenarios as described in Table 2.

Biogas volume was measured by water replacement method and the methane content in biogas was measured with a gas chromatograph (SP 6890, Shandong Lunan Inc., China). The gas chromatograph was equipped with a Porapak Q stainless steel analytical column (180-cm long and 3-mm outer diameter) and a thermal conductivity detector. The temperatures of the injector, detector and oven were 50, 100 and 80 °C, respectively. Argon was used as carrier gas.

Table 1
Characteristics of substrates and inoculum.

Characteristics	Corn straw	Chicken manure	Inoculum
Moisture content (%)	4.4 ± 0.09	11.4 ± 0.14	93.7 ± 0.02
Total solid (TS, %)	95.6 ± 0.09	88.6 ± 0.14	6.3 ± 0.02
Volatile solid (VS, % of TS)	88.2 ± 0.19	64.2 ± 0.93	78.7 ± 0.05
C (% of TS)	39.94 ± 0.44	31.05 ± 3.17	–
N (% of TS)	1.06 ± 0.23	2.18 ± 0.32	–
H (% of TS)	4.2 ± 0.10	3.76 ± 0.51	–
C/N	27.28 ± 3.38	14.22 ± 0.77	–

Note: "–" means this parameter was not tested.

2.3. Effect of CaO_2 addition on the removal of tetracycline hydrochloride in sterile water

Removal performances of tetracycline hydrochloride in sterile water with and without the addition of CaO_2 were conducted in 300-mL glass bottles with working volume of 200 mL. Prior to the test, the bottles and distilled water were firstly autoclaved for sterilization. Tetracycline hydrochloride was then added to the bottles aseptically to achieve the concentration of 25 mg/L. In investigating the effect of CaO_2 on the removal of tetracycline hydrochloride, CaO_2 was added into the bottles with the same total amount used in the 3rd scenario (T2) described in Section 2.2.

2.4. Analysis of tetracycline hydrochloride concentration

To measure the tetracycline hydrochloride concentration in the liquid phase, the samples were firstly centrifuged at 10,000 rpm for 5 min, and the supernatants were filtered through 0.45 μm glass microfiber paper. The filtrates were collected for the analysis of tetracycline hydrochloride concentration on a high performance liquid chromatography (Aglient HPLC 1200 series) with a UV detector at the wavelength of 355 nm. The mobile phase for this analysis was the mixture of oxalic acid, acetonitrile and methyl alcohol at the ratio of 76:16:8 (v/v/v) with the pH of 2.5.

For the analysis of tetracycline hydrochloride absorbed by the solid, 1 g solid (wet weight, digestate collected after AD using centrifugation method) was added into a 10-mL glass tube together with 3 mL EDTA-Mcllvaine buffer for tetracycline hydrochloride extraction. The EDTA-Mcllvaine buffer contained 0.05 mol/L of EDTA, 0.06 mol/L of Na_2HPO_4 and 0.08 mol/L of citric acid, and the pH was adjusted to 4.0 using 2 M NaOH and 2 M HCl. After the mixture was sonicated for 10 min, the suspension was centrifuged at 10,000 rpm for 5 min. The supernatant was filtered through a 0.45 μm glass microfiber paper. This extraction process was repeated 3 times. All the collected supernatant filtrates were combined and passed through prewashed SPE (Solid Phase Extraction, Supelco, USA). The SPE was prewashed using 3 mL methanol and followed by 3 mL distilled water, respectively. And then eluted with 5 mL distilled water, followed by 5 mL oxalic acid (0.01 mol/L) solution in methanol. All the eluents were combined and dried by N_2 stripping. The dried residue was dissolved in 1 mL of the mixture of oxalic acid, acetonitrile and methyl alcohol (76:16:8, v/v/v) at pH = 2.5, which was finally subjected to the measurement of tetracycline hydrochloride using the aforementioned HPLC method.

2.5. Data analysis

In this study, modified Gomperz equation $P(t) = P\exp\left\{-\exp\left[\frac{R_m e}{P}(\lambda - t) + 1\right]\right\}$ was employed to analyze the methane production characteristics. In this equation, $P(t)$, P, R_m, λ, and t represent the cumulative methane yield at time t (mL/g VS), maximum methane production potential (mL/g VS), maximum methane production rate (mL/g VS-d), the span of lag-phase (d), and the duration of the assay (d), respectively [26,27].

The degradation characteristics of tetracycline hydrochloride was analyzed using first-order kinetics equation $C_t = C \times \exp(-k \times t)$ [28], where C_t is the concentration of tetracycline hydrochloride at time t (mg/L), C is the initial concentration of tetracycline hydrochloride (mg/L), t is the process operation time (d), and k is the degradation