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Application of nano-scale transition metal carbides as accelerants in anaerobic digestion

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ABSTRACT

Four types of nano-scale transition metal carbides (HfC, SiC, TiC, and WC), used as accelerants in anaerobic digestion (AD) with cattle manure, were investigated through batch experiments under mesophilic conditions (37 ± 1 °C). The AD system with four carbide accelerants showed a higher biogas yield (463–499 mL/g TS), chemical oxygen demand (COD) degradation rate (58.62–78.90%) and total Kjeldahl nitrogen (TKN) concentrations (905.0–1077.0 mg/L) as compared with control check (CK, 294 mL/g TS, 46.99%, 290 mg/L). All of the digestate samples from the AD systems using four carbide accelerants showed not only higher degradation of organic compounds during thermal analysis, but also stronger fertilizer values. The use of transition metal compounds (TMCs) as accelerants in AD can efficiently improve the conversion of waste resources into biogas and fertilizers, which can potentially open new avenues for the use of TMCs in upcoming research on biomass energy.

Introduction

With the rapid increase of large-scale animal husbandry in China, large quantities of livestock manure are produced, which have heavily polluted the ecological environment. Potential pollutants, resulted from decomposing livestock manure including pathogens, nutrients, ammonia, and greenhouse gas emissions, increase the biological oxygen demand [1–5]. Livestock manure contains a large amount of organic matter that can be effectively utilized by anaerobic digestion (AD), in which complex organic matter can be converted into methane by microorganisms under oxygen-free conditions [6,7]. Methane is a clean and cost-effective fuel, making it a cheaper alternative to fossil fuels. The use of methane can vastly improve the sustainability of energy production [8,9].

Although AD can be used as an effective technical strategy to reduce environmental pollution from livestock manure, there still remain some problems that need to be resolved. Firstly, livestock manure may not degrade easily during the process of AD because it contains a large amount of crude fiber, such as hemicelluloses, cellulose, and lignin [2,10]. Secondly, livestock manure contains a certain amount of crude fatty acids, the accumulation of which has a negative effect on the operational stability of AD. In order to solve these problems, researchers introduced some biological materials as accelerants to the AD system, including microbes [11,12], alkaline [13], microelements [14], enzymes [15], adsorbents [16], chelating agents [17], and bacterium [18]. For example, Wan et al. [14] found that with the increase of Fe^{2+} concentration in 100, 250, and 500 mg/L in the AD systems, the biogas production of AD systems increased by 48.7, 52.1, and 54.8%, respectively. Fang et al. [13] found that a higher alkaline

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dosage within 0–0.05 mol/L resulted in a greater enhancement in AD systems, with the optimal alkaline dosage being 0.04 mol/L. Xi et al. [9] reported that 1 mg/L heme was added into the AD reactor, resulting in that the cumulative methane yield (257.4 mL/g TS) increased by 20.6% as compared with the control group (213.5 mL/g TS). Romano et al. [19] found that the rate of biogas production was significantly affected as the enzymes were used to pre-treat wheatgrass prior to AD or added during the hydrolysis stage of a two stage digester. Shen et al. [20] found that pine biochar and white oak biochar resulted in an average methane content of up to 92.3% and 89.8%, respectively, during AD of sludge at mesophilic temperature. Thus, these additives can vastly improve biogas and methane production in AD systems.

Nano-structured transition metal compounds (TMCs), due to their distinctive structure and unique properties, have been widely applied in different catalytic fields, such as organic matter decomposition, pollution control, fuel cells, capacitor, biosensors, hydrogen generation, energy storage, and solar cells [21–25]. To improve the degradation efficiency of AD systems and enhance biogas production, adding accelerant to AD is an effective technical strategy. TMCs, such as TiO_2, SiO_2, ZnO, CuO, and Fe_3O_4, have so far been applied to AD systems [21,26–28]. The addition of TiO_2 and SiO_2 into the reactor does not produce a significant effect on the AD system [21]. On the contrary, adding ZnO and CuO into the AD reactors inhibits hydrolysis, acidification, and methanation of the AD systems, resulting in a decreased cumulative biogas production [27,28]. Interestingly, the addition of 20 mg/L Fe_3O_4 as an accelerant into the AD reactor resulted in enhanced cumulative biogas production by 1.7 times [26]. Adding $FeCl_2$ (500 mg/L) as an accelerant into the AD system increased biogas production by 54.8% [14]. The degradation activity of cattail (140% and 122%) after adding $CuCl_2$ (2.4 mg/L) and $CdCl_2$ (1.6 mg/L) into the AD systems are higher than that of the control group (control group = 100%), respectively [29]. This means that it is particularly important to seek suitable TMCs as accelerants for improving the AD environment in order to realize the maximized potential of waste biomass resources. However, the investigation of TMCs as accelerants in the AD system is still in the nascent stage.

Very recently, Nb-based compounds (NbO_2, $Nb_{3.49}N_{4.56}O_{0.44}$, and NbN) as AD accelerants were investigated in the AD system [30]. Nb-based compounds can greatly improve the AD environment, increase the substrate utilization, and minimize the hazards of the digestate. Compared with the control check (CK, 409.2 mL/g VS and 29.55%), substantially higher cumulative biogas production (437.1–522.7 mL/g VS), and chemical oxygen demand (COD) removal rates (56.08–65.19%) were achieved using Nb-based accelerants in the AD system. Besides, Nb-based compounds used as accelerants improved the degradation of organic compounds in the AD system. To further clarify the role of TMCs as accelerants in improving the environment of AD systems, in the present work, we investigated the effect of four transition metal carbides (HfC, SiC, TiC, and WC) as accelerants on the AD environment, including biogas production, pH, COD degradation rate, total Kjeldahl nitrogen (TKN), and the degradation of organic compounds of the digestate and fertilizer analysis. To the best of our knowledge, the application of nanostructured carbides in AD systems has not been reported in the previous literature.

Materials and methods

Substrate and inoculum

Cattle manure, used as a substrate, was collected from a large-scale farm located in Xi'an city, China. The inoculum (activated sludge) was obtained from the activated sludge treatment system at the municipal wastewater treatment plant in Xi'an, China. Both fresh cattle manure and activated sludge were homogenized and stored at 4 °C, prior to the experiment. The characteristics of substrate and inoculum used for the experiment are shown in Table 1.

Accelerants

Four carbides (HfC, SiC, TiC, and WC) with the purity of higher than 99.5% were used as accelerants in this experiment. SiC with an average size of 40 nm, and TiC nanopowder with an average size of 70 nm were purchased from Kaier (Hefei, China) and Chaowei (Shanghai, China), respectively. HfC nanopowder (average size: 300 nm) and WC nanopowder (average size: 400 nm) were purchased from Aladdin (Shanghai, China).

Experimental set-up

A batch experiment was carried out to evaluate biogas production in the laboratory. The schematic diagram of the experimental equipment is shown in Fig. 1. The digestion temperature was maintained at 37 ± 1 °C, using a homothermal water bath. The AD was performed in glass reactors that have a capacity of 500 mL and a working volume of 400 mL. The feeding inlet was sealed with a rubber bung, in which a gas outlet was created. Based on the four types of carbides, this experiment was conducted on four experimental groups and a CK. In the CK, cattle manure, sewage sludge, and urea was added. Urea purchased from Yinfeng

Table 1 – Characteristics of cattle manure and sewage sludge.

Parameters	Cattle manure	Sewage sludge
Total solids (TS), TS (%)	15.95	5.01
Volatile solids (VS), VS (%)	12.35	3.99
Volatile solids/total solids (VS/TS), VS/TS (%)	77.43	79.64
pH	5.5	7.2
Total chemical oxygen demand (TCOD), TCOD (mg/g)	91.4	4.14
Ammonia nitrogen (NH_3–N), NH_3–N (mg/g)	0.477	–
Soluble phosphorus (SP), SP (mg/g)	0.516	–
Total carbon (TC), TC (% TS)	8.64	–
Total nitrogen (TN), TN (% TS)	1.05	–
Total carbon/total nitrogen (TC/TN), TC/TN	8.23	–

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