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Hydrothermal pretreatment for biogas production from anaerobic digestion of antibiotic mycelial residue

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HIGHLIGHTS

- Hydrothermal pretreatment eliminated the hindrance of residual antibiotics.
- Anaerobic digestion performance was much improved for hydrothermally treated MAR.
- The optimal hydrothermal pretreatment condition was 120 °C for 60 min.
- The highest methane yield reached 290 ml/g VS.

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ABSTRACT

This paper aims at investigating the effect of hydrothermal pretreatment on anaerobic digestion of antibiotic mycelial residue (AMR) for biogas production based on batch laboratory experiments. The pretreatment temperature and time varied from 80 to 180 °C and from 0 to 60 min, respectively. The results show that the hydrothermal pretreatment could degrade the organic particulates in AMR into soluble and even small-molecule substances to significantly improve the anaerobic digestibility of AMR and greatly facilitate biogas production. The biogas yield increased with increasing pretreatment temperature and time when the temperature was not higher than 120 °C, and a higher temperature did not significantly facilitate the biogas production and even lead to a lower biogas yield, especially when the pretreatment temperature time was excessively long. The hydrothermal pretreatment at 120 °C for 60 min gave the best digestion performance, and the corresponding methane and biogas yields reached 290 and 446 ml/g VS, respectively.

1. Introduction

China has become the largest producer of antibiotics in the world and the production of antibiotics in 2009 was about 150 thousand tons, accounting for 70 wt.% of the total global production [1]. Thus, millions of tons of various antibiotics mycelial residues (AMRs) are being produced each year in China and their safe disposal/use has become a big impending problem. As one kind of solid wastes from the production of antibiotics, the AMRs mainly consist of mycelia, remaining substrate, intermediate metabolite as well as residual antibiotics due to incomplete extraction of the objective medicines. These wastes have been used for fertilizer or animal feedstuff after drying, but they have been listed as one of "national hazardous wastes" in 2008 because the residual antibiotics can easily accumulate in animals' bodies to cause drug resistance. Therefore, the AMRs must be handled according to the regulations for hazardous wastes [2].

Usually, incineration is the most efficient way to achieve the goals of reducing amount and safe disposal of hazardous wastes, but this has to require an expensive combustion equipment and suffers a high energy consumption for drying AMRs with excessively high moisture contents (79–92 wt.%) [3]. Such high moisture contents also hinder the use of landfill for disposing AMRs due to its bad operation safety. In addition, direct landfill of AMRs rich in organic matters is apt to cause secondary pollution to ground water; meanwhile this also wastes the organic ingredients in the AMRs as nutrients, which are mainly proteins and saccharides. Now there is not yet any effective or low energy-consumption method available to dispose or utilize AMRs, and this has brought out heavy pressure on the manufacturers of antibiotics.

Anaerobic digestion, as an environment-friendly waste treatment method, can not only reduce the amount of biomass waste but also convert the waste into biogas as a kind of important

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renewable fuel. A lot of studies have proven that anaerobic digestion technology can be employed to successfully deal with many kinds of solid biomass wastes including industrial bioprocess residues [4,5], municipal sludge [6] and so on.

Of the four fundamental steps involved in anaerobic digestion, which are hydrolysis, acidogenesis, acetogenesis and methanogenesis, the first step – hydrolysis is well recognized as the rate-limiting step for digestion [7,8]. Without material pretreatment, the biogas yield and digestion time are usually remarkably lower and longer than those with material pretreatment, respectively, due to hydrolysis of big organic particles and large organic molecules taking place to a less extent [9,10]. Therefore, various pretreatment methods including hydrothermal and alkaline methods and their combination [11–13] have been extensively tested to overcome the limiting action of hydrolysis. Among the pretreatment technologies, the hydrothermal technology emplies compressed hot water as the reaction medium, and has exhibited many unparallel advantages in converting biomass wastes for their reuse [14].

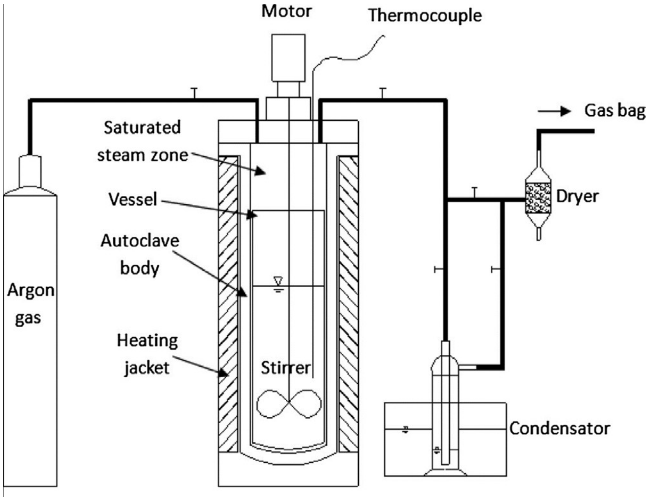
For fermentative biowastes (taking municipal sludges for instance), they are rich in bio-flocs with a polymeric network structure formed by many kinds of microorganisms, organic and inorganic compounds via the agglomeration of extracellular polymeric substances (EPSs) that are mainly carbohydrates, proteins, lipids and volatile fatty acids [15]. When being subjected to hydrothermal pretreatment, the network structure of the bio-flocs in municipal sludge can be disintegrated to generate small organic particles and soluble organic substances, and at the same time the cell wall can be ruptured to spill out the intracellular soluble substances under high-temperature and high-pressure conditions [14]. The biodegradability was thus significantly enhanced. The higher degradability is apt to lead to a higher biogas yield via anaerobic digestion [16]. On the premise verified by us that antibiotic valences left in AMRs can be thoroughly eliminated by hydrothermal treatment under mild conditions [17], we have proposed a process for recovery of biogas from AMRs by combining anaerobic digestion and hydrothermal pretreatment, after considering the similarity of AMRs and municipal sludge in composition and physio-chemical properties.

This work is devoted to investigating the effect of hydrothermal pretreatment on anaerobic digestion of AMRs. The tested pretreatment temperature and time varied from 80 °C to 180 °C and from 0 min to 60 min, respectively. The other tested parameters about digestion substrate included pH value, total ammonia nitrogen (NH_4^+-N) concentration and solid solubilization characterized by chemical oxygen demand (COD) and suspended solid (SS). The tests were performed before and after hydrothermal pretreatment to reveal the effect of hydrothermal pretreatment on anaerobic digestion of AMRs in terms of methane and biogas yields.

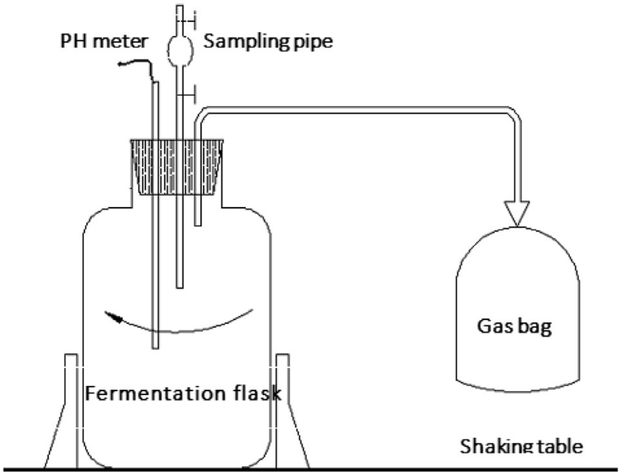
2. Materials and methods

2.1. Hydrothermal and digestion tests

All hydrothermal treatment experiments for AMR were performed in an electrically heated stainless steel autoclave shown in Fig. 1(a). The autoclave has an inner volume of 1.0 L and an inner diameter of 70 mm, inside which an internal stainless steel vessel of 750 ml in inner volume and 68 mm in inner diameter was used as the actual reactor for hydrothermal treatment test. There was a motor stirrer mounted in the inner vessel to agitate the material there during pretreatment. The autoclave was connected to an Argon cylinder for circumstance purge. A thermocouple was immersed into the inner reactor to monitor the reactant temperature.



(a) Experimental hydrothermal pretreatment equipment.



(b) Constant temperature incubator

Fig. 1. Schematic diagrams of the adopted experimental apparatus for (a) hydrothermal pretreatment and (b) anaerobic digestion.

The typical procedure of hydrothermal test [17] was started with loading 400 g raw AMR and further 80 g deionized water (the water addition ratio being 20 wt.%) into the reactor vessel. After inserting the reactor vessel into the autoclave and sealing the autoclave, the hydrothermal treatment was implemented through in succession, heating the loaded material to a preset temperature, keeping it for a given slot of time, terminating heating, cooling the autoclave to room temperature by an electric fan, releasing pressure of the equipment to atmosphere pressure and finally opening the autoclave to collect products. The continuous stirring at 120 ± 2 R/M avoided any serious temperature gradient inside the reactor. The liquid product was collected into a glass bottle and in turn kept at 4 °C in a fridge for its use as the digestion substrate. The hydrothermal pretreatment temperature varied from 80 °C to 180 °C, and the pretreating time at such temperatures was 0, 30 or 60 min. Here, 0 min (exactly requiring about 10 s for operation) means the termination of heating and meanwhile the start of cooling once the reactor reached the preset temperature. The heating rate for the autoclave was averagely 2.5–3 °C/min, and the required heating time varied in 30–80 min depending on the preset HT temperature. Similarly, the time for cooling the tested material to room temperature was about 40–70 min and also varied with the HT temperature. The highest and