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Process characteristics of hydrothermal treatment of antibiotic residue for solid biofuel

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HIGHLIGHTS

- Hydrothermal treatment (HT) was performed for two kinds of antibiotic residues (ARs).
- HT greatly improved the dewaterability of solid matters to produce biofuel at about 50% solid recovery ratio.
- HT transferred more than 50% nitrogen in solid matters of AR into liquid of HT process.
- HT almost completely decomposed the residual antibiotics in AR.
- The liquid from HT has high COD to be potentially suitable for anaerobic digestion.

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ABSTRACT

Hydrothermal treatment (HT) of environmentally and healthily hazardous antibiotic residue (AR) was performed in a laboratory batch autoclave to investigate the feasibility of solid biofuel production and to understand some characteristics of the HT process. The results showed that HT remarkably improved the dewaterability of the tested residues. For ARa with a lower content of saccharides, the optimal HT conditions were shown to be at 200 °C for 30 min, under which a solid biofuel with a water content of 47.6 wt.% was obtained at a solid recovery ratio of 42.5%. For ARb with a higher content of saccharides, a lower optimal HT temperature of 180 °C was required, to attain a similar solid content but at a lower solid recovery ratio. The nitrogen content in the solid biofuel from ARa was lowered to 5.8 wt.%, implying 68% removal of nitrogen from the solid of the raw residue. The removed nitrogen was mostly transferred into the HT liquid as ammonia nitrogen. Additionally, almost all the antibiotics in the tested ARs were decomposed during HT. Hydrothermal technology was thus proved to be promising for recycling ARs to make clean bioenergy and meanwhile to realize the thorough safe treatment of ARs.

1. Introduction

The fermentative biowastes usually contain a fairly large proportion of water and are difficult to be mechanically dewatered because the water mostly exists in the "bound" form or inside the mycelial cells, which brings about great difficulties in their transportation, innocent treatment and disposal/resource reuse. Certainly, drying is alternative for dewatering the fermentative biowastes but usually consumes large quantities of energy. Especially, antibiotic residues (ARs), one typical kind of biowastes from fermentative processes for producing antibiotics, are produced with an estimated annual yield of 10 million tons just in China which is producing and exporting majority of antibiotic medicines, and invariably contain antibiotic valences that are apt to cause serious environmental pollution and even to threaten the health of human beings and animals. Following other countries, China recently includes antibiotic residues in the list of dangerous wastes, and henceforth requires their innocent treatment and disposal before discharge them. Evidently, the antibiotics resided in ARs have unavoidably negative impacts on the microorganisms frequently present in biochemical processes of wastewater treatment, and the conventional wastewater treatment systems have been testified by us to be unsuitable for treating and disposing ARs. It is also the fact that the residual antibiotics cannot be safely disposed in wastewater treatment process. Except for energy-consuming drying followed by various incineration processes,

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there are no effective and high-efficiency technologies available for the treatment and utilization of ARs. This heavily perplexes the manufacturers of antibiotic medicines, especially after the dominant utilization way of ARs as animal feed or feed additives are rigidly forbidden by the newly established environment protection law. A new technical method is thus in urgent need for solving the pollution and toxic problems associated with ARs and also for utilizing this kind of biowastes. Based on our knowledge about the new law, combusting ARs seem be recommended as the disposal method, which will generate dual benefits both in environmental safety and resource reuse. Consequently, the key problem is turned to the above difficulty of high efficient dewatering of ARs with low energy consumption.

Hydrothermal technology employs hot compressed water as the solvent, which avoids water evaporation when heated and is thus expected to consume less energy than thermolysis involving steam vaporization [1]. In addition, hot compressed hot water has also many particular properties, which can greatly facilitate reactions of organic matters occurring in water [2]. Hydrothermal technology is considered to be promising for treating biomass and biowastes including bioprocess residues with high water contents [3,4]. Moreover, hydrothermal treatment (HT) under mild conditions has been testified to be effective for handling municipal sludge which is rich in water and pollutant components [5,6], to facilitate its reduction in volume and even energy recovery. via HT, viscous organic matters outside the mycelial cells, can be hydrolysed or thermally decomposed to disaggregate the cell aggregates that are called ''supra-colloids''. In turn, the majority of the ''bound water'', including the interstitial water, vicinal water (adhesive water and capillary water) and even intercellular water, can be transformed into free water and thus significantly improve the mechanical dewaterability of the material [7]. Noticeably, the cost as well as energy consumption for HT is also estimated to be attractively low in comparison with the other evaporative dewatering technologies [8,9].

Both ARs and municipal sludge are fermentative process wastes and are somewhat similar to each other in composition, for example, a large proportion of mycelia. Therefore, HT is also supposed to effect on dewatering ARs for energy recovery. However, differences do exist between ARs and municipal sludge, so the feasibility of HT of ARs needs to be verified and its adaptability meticulously studied before carrying out practical applications. The properties of the solid products from HT of ARs also need to be evaluated for use as a good biofuel. In this article, the process characteristics of HT is investigated with respect to ARs to prove the effectiveness of hydrothermal technology for safe disposal of the ARs as well as for making the residues into biofuel that can be converted into bioenergy.

2. Materials and methods

2.1. Materials

The tested two antibiotic residues (ARs), denoted as ARa and ARb, were supplied from two Chinese biopharmaceutical factories in Hebei province in which fermentation with corn starch, bean protein and other additives as the substrate are carried out for producing cephalosporin C (CPC), bulk drug for various types of β-lactam antibiotics. Because of their different technical processes employed for CPC production, the two ARs contained different amounts of mycelia and substrates. As shown in Table 1, the ARa had the higher contents of volatile suspended solids (VSS) and extracellular polymeric substances (EPS) but a lower total saccharide content. The used CPC–Na sample for testing the possibility of destroying antibiotics via HT was supplied from Heibei Zhongrun Pharmaceutical CO., Ltd. All other chemicals used in this study are commercially available analytical agents, except for the standard matters used for GC and HPLC analyses.

2.2. Hydrothermal experiment

All experiments for HT of ARs were conducted in a batch autoclave that had an inner volume of 1.0 L and an inner diameter of 70 mm. Fig. 1 shows a schematic diagram of the experimental apparatus. The autoclave was heated by a detachable heating jacket that was controlled by a PID interfaced with a thermocouple mounted inside the autoclave body. A stainless steel vessel with 700 ml in volume and 68 mm in outer diameter was used to load the treated materials. The vessel was only 2 mm thinner than the inner diameter of the autoclave in order to get an efficient heat transfer from the autoclave wall to the inside reactor and also to minimize the material loss during HT for accurate product collection. Actually, viscous products after HT tended to adhere to the high-temperature inner wall of the autoclave if the internal vessel was not employed, which would undoubtedly cause an incomplete collection of the products for analysis. A stirrer was equipped coaxially along the center of the autoclave body and driven by an adjustable motor. The autoclave could be reversed for discharging the tested material and its resulting product inside the internal vessel.

The HT experiment was typically started by charging a desired amount of the tested material into the stainless steel vessel, and the vessel was in turn inserted into the autoclave. A given amount of deionized water was then added to the gap between the outer wall of the vessel and the inner wall of the autoclave (any excessive water might overflow into the vessel). Subsequently, enough argon gas was used to purge the autoclave to replace the air inside the autoclave. In succession, the autoclave was sealed immediately after stopping the purging and was heated at about 3 °C min^{-1} to a preset temperature and then kept there for a desired duration to implement HT. During the HT process, the material inside the reactor was agitated by a stirrer at 120 RPM. A duration of zero means that the autoclave was cooled immediately after it was heated to the preset temperature. At last, the autoclave including the built-in vessel was naturally cooled by terminating the heating for the autoclave.

Unless particularly specified, the autoclave was cooled typically to 60 °C (taking 60–90 min, depending on the HT temperature and room temperature). It was then unsealed to collect the gas and liquid products. This was done by first opening the valve on the effluent line of the autoclave to lower its inner gas pressure and meanwhile to release the gaseous product. For runs with flash evaporation at 160 °C (taking 0–30 min to cool the autoclave to this temperature, depending on the HT temperature and room temperature), steam was included in the gaseous product. The effluent gas usually passed through a condenser to strip its moisture and subsequently an absorption dryer to get the dry non-condensable gas that was collected into a gas bag for GC analysis. When the pressure in the autoclave was lowered to room pressure, the sealing cover of the autoclave was opened to take the internal vessel out. Then, the water in the autoclave was poured into the vessel, and the vessel was further washed for complete collection of the liquid product as well as the solid residue.

Subsequently, the collected liquid product, which tended to contain char for HT at excessively high temperatures, was subjected to centrifugal separation at a separating factor of 600 for 5 min. The centrifugal machine was filter type one fitted with 200-mesh filter cloth. Both the centrifugate and the remaining solid were collected for quantitative analysis. The solid obtained after centrifugation was referred to as solid biofuel in the study, and its recovery ratio was estimated as the percentage of the mass