



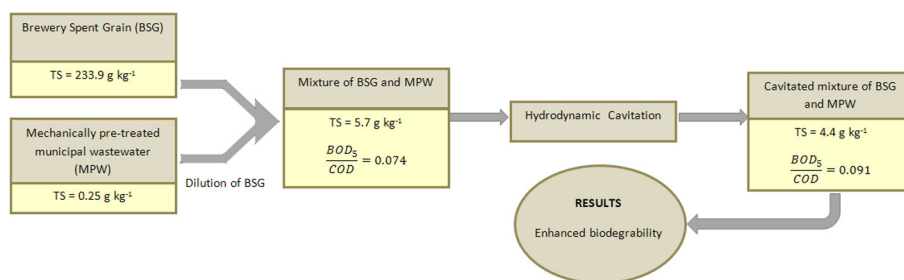
Hydrodynamic cavitation of brewery spent grain diluted by wastewater

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HIGHLIGHTS

- The BSG biodegradability index increased via cavitation from 0.074 to 0.091.
- Solubilization of carbohydrates occurred with related monosaccharides release of 87%.
- Enhanced biodegradability was attributed to the physical cavitation effects.
- FT-IR/PAS analysis did not reveal the formation of new compounds via cavitation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 July 2016

Received in revised form 27 October 2016

Accepted 30 October 2016

Available online 1 November 2016

Keywords:

Hydrodynamic cavitation

Brewery spent grain

BSG pretreatment

Enhanced biodegradability

Carbohydrate solubilization

FT-IR/PAS analysis

ABSTRACT

This study examined the influence of hydrodynamic cavitation on the biodegradability and composition of brewery spent grain diluted by mechanically pre-treated municipal wastewater. An orifice plate with a conical concentric hole (3/10 mm as an inlet/outlet diameter) was used as the constriction in the cavitation device; the corresponding cavitation number was 0.036. Hydrodynamic cavitation was applied at an inlet pressure of 7 bar, maintaining 30 recirculation passes through the cavitation zone. As a result, the concentration of soluble organic compounds (expressed as soluble chemical oxygen demand), BOD₅ value, and BOD₅/COD ratio increased. The BOD₅/COD ratio was enhanced from 0.074 to 0.091, indicating improved biodegradability of the brewery spent grain. Moreover, solubilization of carbohydrates occurred, as confirmed by the hemicellulose removal with a related monosaccharides release of 87%. On the other hand, the COD value and the concentrations of both total solids and volatile solids decreased significantly, revealing the effective destruction of complex organic compounds via cavitation.

Additionally, Fourier transform infrared photoacoustic spectroscopy analysis was conducted to check the findings. It confirmed that hydrodynamic cavitation did not lead to the formation of new compounds that would interfere with the biological treatment of the brewery spent grain diluted by mechanically pre-treated wastewater.

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Abbreviations: BI, biodegradability index (i.e. BOD₅/COD ratio); BSG, brewery spent grain; C, cellulose; FT-IR/PAS, Fourier transform infrared photoacoustic spectroscopy; HC, hemicellulose; HD, hydrodynamic cavitation; LG, lignocellulose; MPW, mechanically pre-treated wastewater; MS, monosaccharides; P, protein; PPH, phenolic compounds; PPPM, polysaccharides, phenolic compounds, proteins, and monosaccharides; SEM, scanning electron microscopy.

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1. Introduction

Brewery spent grain (BSG) is the main by-product of the brewing process, corresponding to approximately 85% of the total residues generated from the raw materials. Worldwide, BSG is produced annually in large quantities – more than 30 million tonnes [1]. It is a widely available and low- or no-cost organic resource

with potentially high nutritional value. This lignocellulosic solid fraction remains after the mashing of the barley malt and the separation of the wort. It includes cellulose (around 17–25%), hemicelluloses (28–35%) – particularly arabinoxylans – and lignin (7–28%). In addition to fibers, it contains highly concentrated proteins (15–24%), monosaccharides (xylose, glucose, and arabinose), lipids, vitamins (choline, niacin, pantothenic acid, riboflavin, and others), minerals (high amounts of calcium, magnesium, silicon, and phosphorus are reported), and amino acids [2]. Brewery spent grain is also rich in phenolic compounds, particularly ferulic and *p*-coumaric acids [3]. Because of its high moisture content (typically more than 75%), the amount of fermentable sugars, and the presence of resident microflora, BSG is very unstable and susceptible to microbial growth, hence its rapid degradation. In order to prolong its storage time, several methods were proposed: mixing BSG with water and formic or benzoic acid, oven drying at temperatures below 60 °C, using superheated steam, or a membrane filter press with vacuum drying [4]. The most common method is oven drying, which reduces the BSG volume and retains its chemical identity. However, high investment and operational costs must be expected in all cases.

Brewery spent grain can be considered as a valuable resource for various applications. These include animal and human nutrition, energy and biofuel production, metal adsorption, production of bricks, charcoal, and paper, cultivation of microorganisms, enzyme production, yeast immobilization, and the generation of added-value products such as lactic, ferulic, and *p*-coumaric acids, xylitol, and pullulan [2,4,5–10]. In spite of this diversity, animal feeding still remains a major strategy for BSG use.

Importantly, the high content of potentially renewable energy that exceeds 300 mL CH₄ per g of total solids added (TS) and a C/N ratio of less than 25 mark BSG as a valuable substrate or co-substrate for anaerobic digestion [11]. In order to enhance the hydrolysis rate, improve the BSG biodegradability and digestibility, and thus omit the limitations of the bioconversion of lignocellulosic matter, several pretreatments have recently been proposed. Their essential aim is to decrease the size of the particles, break down cell wall structures, and reduce cellulose crystallinity [12]. The attributable methods involve mechanical, biological (by enzymes and fungi), chemical (alkaline or acidic), and thermal treatments, or a combination of these [13–17]. Frequently, a step prior to the other treatments is mechanical disintegration via wet or dry milling. Applying such a stage provides an increased particle surface available for microbial colonization and ensures effective carbohydrate solubilization [18,19], enhancing the efficiency of the subsequent treatments.

Among the physicochemical methods, hydrodynamic cavitation (HD) has actually been shown to be a promising way of breaking down complex organic chemicals and degrading bio-refractory pollutants [20]. In general, cavitation (regarded as an advanced oxidation process) means a particular phenomenon that occurs inside a liquid when subjected to changes in the pressure field over time and distance. It is hydrodynamically generated by the passage of the liquid through constrictions, such as orifice plates, curved channels, and Venturi or throttling valves, and also as a result of the motion of bodies in a liquid caused by rotating equipment. Hydrodynamic cavitation consists of the formation, growth, and subsequent collapse of micro-bubbles or cavities, occurring over an extremely small time interval (milliseconds) and releasing large magnitudes of energy at the site of transformation [21]. The cavities are formed at the constriction, where liquid pressure falls below the vapor pressure at a given liquid temperature. In the downstream of the cavitation device, these cavities collapse inducing local supercritical conditions that include temperatures in the order of 10,000 degrees Kelvin and pressures up to a GPa. Consequently, the intensification of various operations occurs, involving

mechanisms like thermal decomposition, shockwaves, shear forces, pressure gradients, and the reaction of hydroxyl radicals and reactive hydrogen atoms (formed after hemolytic cleavage of water molecules) with the pollutant [21–24]. The main factors influencing the intensity of cavitation include the cavitating geometry (structural characteristics of the reactor, size and shape of the cavitation orifice), operating parameters (flow rate, inlet pressure, number of recirculation passes through cavitation zone), and liquid properties (viscosity, density, surface tension, dissolved gas and solid particle content, liquid temperature) [25,26]. Moreover, cavitation number is determined to characterize the intensity of cavitation in hydraulic device [27]. The results of the treatment and the energy efficiency depend on the cumulative effect of the parameters mentioned. Hence, their optimization is required every time.

Currently, a lot of attention is being paid to investigating hydrodynamic cavitation as a tool of water and wastewater disinfection [28,29], microalgal cell disruption [30,31], cyanobacterial bloom removal [32], disintegration of activated sludge prior to anaerobic digestion [33–35] and degradation of various organic compounds such as pharmaceutical residues [36,37], polymers [38,39], phenols [40], and humic substances [41]. Special focus has been placed on studying hybrid systems based on synergism between hydrodynamic cavitation and other advanced oxidation processes, such as Fenton chemistry, ozonation, photocatalytic oxidation, and the use of hydrogen peroxide or sodium hypochlorite [42–44]. Recent findings in this area have revealed a higher degradation efficiency compared to individual HD in terms of different recalcitrant compounds, i.e. pesticides [45,46], pharmaceuticals [47] and dyes [48–50]. However, most of the studies concerned the removal of only one specific pollutant (rarely mixtures) and also in matrices far less complex than wastewater [23]. With reference to HD applications, the subject has rarely been considered regarding the delignification of matter [51,52] or the enhancement of biodegradability of lignocellulosic material prior to anaerobic digestion or co-digestion [53]. These issues have been investigated only for wheat straw. Accordingly, it seems worthwhile to study the usefulness of hydrodynamic cavitation in terms of BSG pretreatment. To do so, the BSG needs to be diluted by a liquid that would minimize its excessively high TS content to a level appropriate for the cavitation device and pump. From sustainable development considerations, the suitable liquids could include municipal wastewater, some industrial sewage, and fluid waste, but not water.

The present study examines the advisability of the application of using hydrodynamic cavitation as a pretreatment technique for improving the biodegradability of BSG prior to its anaerobic digestion. Because of the cavitation device requirements, the substrate was diluted by mechanically pre-treated (pre-settled) municipal wastewater to decrease the TS content (i.e. solid particle content of the medium). Structural modifications were assessed using scanning electron microscopy (SEM). A Fourier transform infrared photoacoustic spectroscopy analysis (FT-IR/PAS) was also carried out to evaluate the influence of hydrodynamic cavitation on the possible formation of new compounds that could interfere with the subsequent biological treatment.

2. Materials and methods

2.1. Materials

Wastewater, which was a medium for suspending the BSG, was sourced from the municipal wastewater treatment plant in Lublin (Poland). In order to reduce the TS content, the wastewater was taken as mechanically pre-treated (pre-settled) sewage from a bioreactor inlet chamber and transported immediately (within half

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