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Optimization and characterization of hydrochar produced from microwave hydrothermal carbonization of fish waste

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ABSTRACT

Fish processing results in large amounts of solid and liquid wastes that are unsustainably dumped into oceans and landfills. Alternative sustainable technologies that completely utilize seafood wastes are needed. Hydrothermal carbonization (HTC) that converts moisture-rich biomass into hydrochar is mostly employed for pure lignocellulosic biowaste. However, the suitability of HTC for pure non-lignocellulosic waste is unknown. Here, for the first time, a response surface design guided optimization of microwave hydrothermal carbonization (MHTC) process parameters, holding temperature (150–210 °C) and time (90–120 min), showed that a temperature of approximately 200 °C and a time of approximately 119 min yielded maximal hydrochar (~34%). The atomic carbon and ash content, and calorific value of hydrochar were approximately 25–57%, 20–28%, and 19–24.5 MJ/kg respectively, depending on the MHTC operating conditions. Taken together, these results confirm that MHTC produces hydrochar from fish waste of quality comparable to one produced from certain lignocellulosic, sewage and municipal wastes. Therefore, this strategy presents an exciting alternative technology that can be used either independently or in combination with other valorization techniques to completely utilize fish wastes irrespective of their quality.

1. Introduction

The sustainable management of waste from the seafood-processing sector is a global problem. Seafood including fish needs to be processed to extend its shelf life owing to its highly perishable nature. During fish processing, the commercially unattractive parts of the fish such as viscera, fins, scales, heads, and carcasses are wasted. Global fish production as reported by an FAO factsheet was ~167 million tonnes (live weight) in 2014 (FAO, 2016), of which ~146 million tonnes was allocated for human consumption and the remaining (21 million tonnes) for fish oil and meal production (FAO, 2016). However, using an estimation from a previous study that 45% of the live weight of fish is regarded as waste (Rai et al., 2015), about 75 million tonnes of fish waste would have been produced in 2014. This frightening scenario is true even in the developed countries such as the U.S where it was reported recently that 40–47% of the seafood supply is lost (Love et al., 2015). Fish waste from the processing industry is a mixture of solid and liquid wastes. Solid matter consists of the aforementioned tissues, while the liquid phase includes blood-water and sticky-water that are high in proteinaceous compounds and oils (Islam et al., 2004). Most of these wastes are disposed of in oceans or landfills thus making the environment susceptible to algal blooms (Berdalet et al., 2016), thereby endangering the local ecosystem (Berdalet et al., 2016).

Some of the current ways of utilizing these wastes include bioactive extraction (Menon and Lele, 2015), fishmeal (Arvanitoyannis and Kassaveti, 2008b), oil (Arvanitoyannis and Kassaveti, 2008b) and silage (Arvanitoyannis and Kassaveti, 2008b) production. Fish meal is a highly concentrated nutritious feed supplement obtained from fresh fish or fish waste that is rich in protein, minerals and vitamins. Fish meal production has been proposed as one of the ways to manage fish waste and has been commercialized in several countries. However, a recent study has found that most of the fish meal plants use fresh fish that can be directly consumed by humans to produce high-quality fish meal (Cashion et al., 2017). In addition to this, fish meal plants produce effluents that have a higher contaminant load as compared to the

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Abbreviations: HTC, hydrothermal carbonization; MHTC, microwave hydrothermal carbonization; FBGU, fungal beta-glucan units; DoE, design of experiment; RSM, response surface design methodology; CCD, central composite design; SEM, scanning electron microscopy; FTIR, Fourier Transform Infrared spectroscopy; HHV, high heating value; EEF, Energy Enrichment Factor.

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effluents produced by fish processing plants (Arvanitoyannis and Kassaveti, 2008a; Jamieson et al., 2017; TEAM, 2003). Fish silage, a liquid product obtained by the liquefaction of whole fish or fish waste, has been used as a feed supplement in animal husbandry. Fish silage, despite utilizing whole waste is often associated with disagreeable odor and may limit its use in high proportion for feed formulations (TEAM, 2003). Ensilaging produces silage of high moisture content, up to 80%, making it difficult to handle and store (TEAM, 2003). For these reasons, fish meal is preferred more as a feed supplement than silage. Despite the disadvantages associated with these processes, they offer clear environmental benefits as they have reduced the amount of fish waste that needs handling by 30% (Hardy and Tacon, 2002). However, most of the aforementioned processes do not use the fish waste completely and thus leave behind or generate new waste, which needs to be further managed (Arvanitoyannis and Kassaveti, 2008b; Cashion et al., 2017; Hardy and Tacon, 2002; TEAM, 2003). For instance, in the fish meal plants, blood water and sticky water are generated as effluents (TEAM, 2003). For these reasons, fishmeal and oil plants have been shown to exhibit adverse effects on the environment similar to that produced by incineration, composting, and landfilling of fish waste (Lopes et al., 2015). Considering these drawbacks, there is a dire need for additional or supplemental technological practices to better utilize seafood waste including blood and sticky water and wastes that have started degrading.

Hydrothermal carbonization (HTC) is the process of converting biomass into carbonaceous material at a relatively low temperature (150–250 °C) and elevated pressure under wet conditions. As this process takes place in an aqueous reaction medium, wet biomass can be carbonized without an energy intensive pre-drying step like in the case of dry pyrolysis (Libra et al., 2011). Conventionally, HTC methods employ temperature gradients (conduction and convection) for heat transfer. However, possible limitations of these methods include longer processing times and uneven heating. Microwaves on the other hand heat the material from within as they work on the principle of dielectric heating. The high moisture content of the raw seafood waste is favourable as the water molecules readily couple with the electromagnetic field resulting in microwave dielectric heating. Therefore, microwaves help address the shortcomings of conventional heating methods that suffer from longer residence times, non-selective/superficial heating, and the less controllable nature of the heating process (Nüchter et al., 2004).

HTC process is predominantly used for plant derived agricultural wastes and lignocellulosic wastes (Lynam et al., 2015; Reza, 2011). Adaptation of mixed waste streams, i.e. mixture of lignocellulosic and non-lignocellulosic waste such as municipal waste (Reza et al., 2016), human biowaste (Afolabi et al., 2015), food waste (Kaushik et al., 2014), and sewage sludge (Afolabi et al., 2015) is gaining increasing attention. However, the suitability of microwave hydrothermal carbonization (MHTC) to produce good quality hydrochar from a pure non-lignocellulosic waste such as fish waste has not been explored. In this paper, for the first time, we have optimized the MHTC process conditions for the production of maximal yield of hydrochar from enzymatically pre-treated fish waste. Further, we have analyzed the chemical, material, energy, and morphological properties of the fish waste hydrochar to facilitate the prediction of its potential applications.

2. Materials and methods

2.1. Sample preparation

Fish waste comprising of heads, tails, viscera, fins, and scales from a variety of fishes including northern anchovy, salmon, and cod were obtained fresh from the local market, stored, and processed as previously described (Kannan et al., 2015).

2.2. Enzymatic hydrolysis

Previous studies have shown that enzymatic hydrolysis is a critical pre-treatment step prior to MHTC of fish waste (Kannan et al., 2015). Raw fish waste subjected to MHTC without any pre-treatment produced no hydrochar (Kannan et al., 2015). Enzymatic hydrolysis was carried out using three commercial enzymes namely Viscozyme (catalog no.: V2010), lipase (catalog no.: L0777), and protease (catalog no.: P4860) as previously described (Kannan et al., 2015). Briefly, 20 g of minced fish waste was homogenized with a food-grade blender. The enzyme cocktail (20%, w/w of each enzyme) was then added to the homogenized waste in the ratio of 1:1:1 (Viscozyme: Protease: Lipase; w/w/w). Then the digestion was carried out in a laboratory incubator/shaker at ~40 °C with rotation at 120 rpm for a period of 6 h. The enzyme concentration of 20% w/w, enzyme ratio of 1:1:1, and treatment time of 6 h were found to be the optimal conditions that resulted in the maximal digestion of the fish waste ((Kannan et al., 2015) and Supplementary data Fig. S1).

2.3. Microwave hydrothermal carbonization

MHTC was performed using the Mini-WAVE Digestion Module (SCP Science, Canada) that operates at a frequency of 2.45 GHz as previously described (Kannan et al., 2015). The product of MHTC process was then subjected to vacuum filtration to separate the solid fraction (i.e., wet hydrochar) from the liquid, biocrude liquor. The wet hydrochar was then oven-dried at 105 °C for 24 h to produce dry hydrochar. The yield of the hydrochar was calculated on dry basis.

$$Hydrochar\ Yield\ (\%) = \frac{Mass\ of\ hydrochar\ (dry\ basis)}{Mass\ of\ waste\ before\ pre\text{-}treatment\ (dry\ basis)} \times 100 \tag{1}$$

2.4. MHTC optimization protocol

For optimizing the MHTC process parameters namely, holding temperature, holding time, and biomass-water index (ratio of wet weight of biomass (g) to weight of water (g)), we first performed an initial screening study to determine the significant parameters that affected the hydrochar yield. We found that hydrochar yield was significantly affected by the holding temperature and holding time. Hydrochar yield was indifferent to biomass-water index. For a detailed description of the results, please refer to the supplementary data file (see Supplementary data Fig. S2). Therefore, biomass-water index is excluded from further optimization studies.

To further optimize the MHTC parameters namely, holding temperature and time, we employed a central composite design (CCD). As the central composite design (CCD) renders an even distribution of the experimental points, it can be used in response surface methodology (RSM) to implement the design of experiment (DoE) approach to optimize the process parameters of MHTC. This type of optimization study is fast and efficient as it minimizes the number of experiments and thus renders effective utilization of the resources. For our experimental setup, CCD design involves the use of two-level factorial design with 2^k factorial points, 2 k axial points and n center points; where k is the number of factors. For holding temperature, the minimal and maximal levels (−1, 1) were set to 150 °C and 210 °C. For the holding time, the maximal and

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