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Enhancing biomethane potential of pulp and paper sludge through disperser mediated polyhydroxyalkanoates

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ABSTRACT

In the present study, the extraction of polyester like polyhydroxyalkanoates (PHAs) from enzymes extracted sludge was investigated by varying extraction time and chloroform – sodium hypochlorite dosage. Maximum of 874 mg/g of PHAs was achieved at an optimum extraction time of 120 min and chloroform – sodium hypochlorite dosage of 30% v/v. The characteristics of derived PHAs were examined using Fourier transform infrared (FTIR) spectroscopy and Nuclear magnetic resonance (^{1}H NMR) spectroscopy. Then, the effect of derived PHAs dosage on biomethane production from pulp and paper mill secondary clarifier (PPSC) sludge was studied. Higher amount of biomethane production was observed to be 174 L/(kg VS) at 35 mg of PHAs dosage when compared to other dosage. To further enhance biomethane production, disperser pretreatment method was carried out by optimization of specific energy. At optimum specific energy of 8547 kJ/kg TS, the maximum solubilization rate and suspended solids (SS) reduction were found respectively to be 19% and 15.8%. Then, biomethane assay was conducted on disperser pretreated sludge, disperser pretreated sludge with optimized PHAs dosage (35 mg) and control sludge. Among these, disperser mediated PHAs method exhibited maximal biomethane production and was observed to be 267 L/(kg VS). Hence, PHAs based sludge treatment method can be implemented in sludge management studies by retrieval of value added product and PHAs canbe used to enhance biomethane production sustainably.

1. Introduction

The rapid growth of industrial activities increases day by day to meet the human necessities by exploitation of natural resources [1]. Paper industry is a water exhaustive industry in terms of water usage for pulp processing and paper production occupying third position in the world [2]. Even with the advanced operational procedures, about 20–100 m^3 of fresh water is used to produce 1 ton of paper resulting in enormous quantum effluent generation [3]. As per environmental regulations, paper industry is forced to treat its effluent to meet pollution control board standards before discharging into water bodies [4]. In general, activated sludge process is the common treatment method adopted for reducing the organic content of pulp and paper mill effluent and it also discharges an inevitable product such as waste activated sludge which should be treated before disposal to avert the impact of secondary pollutant on ecosystem [5,6]. Campos et al. [7] reported that management of activated sludge contributes 50–60% of operating cost of effluent treatment plant. Thus, many researchers focus on retrieval value added product from sludge as raw material. PHAs is one such product extracted from activated sludge and the same can be used as stimulant in digestion process to enhance biogas production.

PHAs are polyesters produced by heterotrophic organisms under unstable nutrient conditions during liquid fermentation process. PHAs have the potential alternate for conventional plastics namely polypropylene or polyethylene because of its biocompatibility, easily biodegradable and versatile thermal properties [8]. PHAs is a biomaterial extensively used for making of food packing material, plastic films and also used in medical field for controlled drug delivery, treatment of cartilage tissues, fibrous ligament and bone joints [9]. Recently, Wang et al. [10] reported that commercial PHAs can be easily degraded and used as a substrate for acidogenic microbes to enrich biohydrogen production in batch fermentation study. The cost of commercial PHAs is very expensive due to carbon source utilization, screening and culturing of microbes in sterile condition, extraction and purification of product [8]. The cost limitations can be overcome by extraction of PHAs from activated sludge. Wang et al. [11] reported that 30–40% of PHAs (dry weight) content was accumulated in sludge biomass of waste water treatment plant. PHAs extraction solvents such as methylene chloride, trichloromethane and chloropropanes were used to derive PHAs from plant source and subsequently PHAs was decolorized with ozone (O_3)

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assisted treatment as reported by Ni et al. [12].

Anaerobic digestion is an economic and eco-friendly technology for treating enormous amount of waste sludge from municipal and industrial treatment plant. This sustainable technology has the ability to reduce sludge volume by disintegration of complex organic substance into renewable fuel called as biogas (50–70% methane gas). Hence, it is applied for sludge treatment to reduce the overall treatment plant operating cost. However, it has constraints such as hydrolytic phase is the rate limiting step and higher time course for sludge matrix disintegration during digestion process. Various sludge pretreatment methods such as sonication treatment [13], multihydrolytic enzymes [14], microwave treatment [15], ozone treatment [16] and chemical treatment [17] were studied for bypassing these limitations. Among these treatment methods, mechanical treatment method has the potential to solubilize the organic substances, leading to the enhancement in efficacy of anaerobic digestion process. Disperser is a prominent mechanical method used for microbial cell wall disruption. Wuytack et al. [18] stated that disperser is mainly used in food industry to stabilize the food material and dairy product emulsions and it has opened up many industrial application sectors. Recently, disperser was reported to be used in sludge disintegration causing a changes both in the rate and extent of waste sludge disintegration in the digestion process [19]. Disperser assisted sludge pretreatment is based on lysis of intact microbial cell and then cytoplasm release into the liquid phase by the function of shear force, turbulence, cavitation and pressure ramp. It has several merits over the other sludge flocs disintegration methods, including effective cell lysis, no chemical changes, easy handling and high disintegration efficacy as reported by Li et al. [20]. Till date, no attempt has been made to enhance the biomethane production from pulp and paper mill sludge using disperser mediated PHAs method. Thus, the objectives of the present work are to (i) study the effect of extraction time and chloroform- sodium hypochlorite dosage on PHAs extraction (ii) perform the characterization of extracted PHAs using FTIR and NMR analysis (iii) evaluate the effect of PHAs dosage on biomethane potential (iv) investigate the effect of disperser pretreatment time and rpm on organic matter release (v) study the effect of disperser specific energy on solubilization rate and biomolecule release (vi) investigate the impact of disperser pretreated sludge and disperser pretreated sludge with optimized PHAs on biomethane production.

2. Materials and methods

2.1. Pulp and paper mill sludge sample collection and characterization

The sludge sample was collected from secondary clarifier of pulp and paper mill effluent treatment plant with the capacity of 23,000 m^3/day situated at Pallipalayam, India. The collected sludge sample was kept in deep freezer at 4 °C for further usage in experiments. Then, the characterization of pulp and paper mill secondary clarifier (PPSC) sludge sample was performed as per the standard procedures [21] and is presented in Table 1.

Table 1
Characteristics of PPSC sludge sample.

Parameters	Value
pH	7.1 ± 0.4
TS (mg/L)	23400 ± 64
VS (mg/L)	16237 ± 178
TSS (mg/L)	21148 ± 115
COD (mg/L)	19150 ± 230
SCOD (mg/L)	145 ± 25
Soluble carbohydrate (mg/L)	154 ± 10
Soluble protein (mg/L)	527 ± 18
DNA (mg/L)	1.2 ± 0.1
C/N ratio	18

PPSC – Pulp and paper mill secondary clarifier, TS – Total solids, VS – Volatile solids, TSS – Total suspended solids, COD – Chemical oxygen demand, SCOD – Soluble COD, C/N ratio – Carbon/Nitrogen ratio.

2.2. Effect of extraction time and chloroform-sodium hypochlorite dosage for PHAs extraction

150 g of enzymes extracted sludge [22] was taken in six 200 mL beakers and to which different dosage of chloroform-sodium hypochlorite solvent (5%, 10%, 20%, 30%, 40% and 50% v/v) were added and labelled as P1, P2, P3, P4, P5 and P6 respectively. Then, magnetic stirring was performed with varying extraction time from 2 to 180 min. The stirred sample was centrifuged at 6000*g* for 5 min to separate precipitate followed by washing with methanol reagent (2% v/v) and drying at 30 °C. For decolourization, the extracted PHAs was dissolved in chloroform and mixed with activated carbon (0.5 g/g PHAs) followed by stirring for 25 min at 65 °C. Finally, the sample was centrifuged to remove activated carbon, and vacuum evaporated to recuperate the solvent [12]. The same PHAs extraction procedure was repeated for the samples P2, P3, P4, P5 and P6. The extraction of PHAs was carried out in triplicate.

2.3. Characterization of extracted PHAs

2.3.1. FTIR analysis

The extracted PHAs (40 mg) sample was dissolved in 800 µl of chloroform solvent, to which potassium bromide pellets were added and the resulting mixture was compressed to make salt disc. The prepared salt disc was subjected to FTIR spectroscopy (Model- Spectrum Two, Supplier-Perkin Elmer and Spectral resolution- 0.5 cm^{-1}) and then infrared (IR) spectra of the salt disc was recorded in the corresponding wave number between 400 and 4000 cm^{-1} [23].

2.3.2. NMR analysis

7 mg of PHAs was dissolved in 1 mL chloroform solvent with 0.1% v/v tetramethylsilane. Then, the sample was subjected to ^1H NMR analysis by Bruker Avance III spectrophotometer at a frequency of 500 MHz. The PHAs chemical shifts (δ) were reported in ppm scale as illustrated by Higuchi-Takeuchi et al. [24].

2.4. Efect of PHAs dosage on biomethane gas production

Batch experiment was conducted in nine Wheaton media lab bottles (WNML), each with working capacity of 500 mL WNML bottles were fed with 270 mL of PPSC sludge and different dosage of PHAs (5, 10, 15, 20, 25, 30, 35, 40 and 45 mg) were added into WNML bottles and marked as G1, G2, G3, G4, G5, G6, G7, G8 and G9 respectively. Anaerobic digested sludge collected from municipal anaerobic digester plant located at Thanjavur, India was used as inoculum. The working volume ratio of PPSC sludge to inoculum was taken as 9:1. All WNML bottles were flushed with N_2 (nitrogen gas) for 40 s to ensure the anaerobic condition. Then, WNML bottles were made airtight with a rubber septum, sealed and kept in orbital shaker with agitation speed of 150 rpm at 37 ± 2 °C for 30 days. Biomethane was measured using a sterile syringe inserted onto the rubber septum [25]. The effect of PHAs dosage on biomethane potential was conducted in triplicate. Modified Gompertz Eq. (1) was used to predict the biomethane gas generation and kinetics of biomethane gas production as suggested by Kavitha et al. [26].

$$M_t = M * \exp[-\exp\{R_{max}/M * \exp(\gamma - t) + 1\}] \tag{1}$$

where M_t indicates cumulative biomethane gas produced in mL at time (t), M represents biomethane gas production potential (L/kg VS), R_{max} implies maximum biomethane gas production rate (L/kg VS d) and γ indicates lag phase (days).