SYNOPSIS

1. Preamble

Sustainable waste management practices play a critical role in minimizing environmental pollution and also promote the transformation towards a green society (Lee et al., 2014). Conventional waste management practices eliminate the potential advantage of waste as feedstock and also emit greenhouse gases. So in order to switch towards the environmental sustainability and biobased economy efficient waste management practices need to be developed embedded with resource recovery (Bonk et al., 2015; Venkata Mohan et al., 2016). Extensive scientific studies were being evaluated with the waste a resource to produce the value-added products apart from its remediation. Various solid, liquid and gaseous waste (CO_2) originating from municipal bodies, domestic (kitchen/food waste) and industrial could be used as a feedstock for biobased products synthesis (Puyol et al., 2017). Therefore, all major sectors, including environment expertise, industrialists and economist are pushing to recover and regain valuable products from waste resources (Marshall et al., 2013). It is important to explore individual and combined technologies to convert specific wastes to a wide spectrum of value-added products (Karmee, 2016; Venkata Mohan et al., 2016).

Apart from the solid waste, liquid waste is also one of the major waste which generated day to day human activities. Biological treatment of this wastewater generates huge quantities of waste activated sludge (WAS) and according to the estimates WAS production rate is 0.1-30.8 kg per person equivalent per year (Liu et al., 2017). Huge quantities of WAS is significantly increasing the disposal cost in the biological waste treatment process. In this context, proper WAS disposal practices are essential to avoid its further environmental contamination. Conventionally, WAS is being disposed off through landfills, incineration, and biomethanization. Landfilling requires big open lands and emits greenhouse gases and incineration necessitates high thermal energy inputs. In addition to the negative impacts on the environment, the potential use of WAS as a resource is also lost in these conventional practices (Salsabil et al., 2010). Alternatively, WAS could be used as a resource for sustainable biological processes and these are known as eco-friendly and economically reliable processes (Tao et al., 2016, Liu et al., 2017).

Renewable sugars and nutrient-rich hydrolysate extracted from the organic solid waste (OSW) could be considered as an alternative and potential resource biobased industries (Venkata Mohan et al., 2015). Acidogenic fermentation is emerging technology, which is compatible with various composite waste (high strength) biodegradation with concurrent production of biohydrogen (H_2) and volatile fatty acids (VFA) or short-chain carboxylic acids (SCA) (Wang et al., 2014; Venkata Mohan et al., 2016; Dahiya et al., 2015). VFA's are the soluble intermediate metabolic products of acidogenic fermentation and which are majorly composed of acetic acid (AA: C_2), propionic acid (PA: C_3) and butyric acid (BA: C_4) and valeric acid (IVA: C_5). Further, SCA's are considered as platform chemicals and act as building blocks for various high-value product synthesis including alcohols, ketones, esters, medium-chain fatty acids (caproic/capric acid), etc. (Lee et al., 2014). Medium-chain carboxylic acids (MCA) are the superior to VFA's as they have a longer hydrophobic carbon chain and low oxygen/carbon ratio, which increases the energy density and makes its separation simple (Steinbusch et al., 2011). MCA's are identified as C_6-C_{12} acids namely, caproic acid (C_6), Oenanthic acid (C_7), Caprylic acid (C_8), Pelargonic acid (C_9), and Capric acid (C_{10}). Among these acids, the biological production of caproic acid from VFA and alcohols utilizing chain elongation pathway is gaining perceptible interest. Besides this, VFA can be used as precursors for the production of biopolymers in an integrated process (Arslan et al., 2016). Biopolymers are the biodegradable polymers produced by microbiomes when subjected to stress conditions such as availability of excess carbon and limitation of nitrates and phosphates required for growth (Venkata Mohan and Reddy., 2013). Since their first report by Lemogine in 1926 (Anderson and Dawes., 1990), PHA's have attracted a great deal of attention due to their biodegradability, chemical-diversity, biocompatibility, and manufacture from renewable carbon resources. In order to enhance PHA production from wastes/wastewaters, many strategies have been proposed and of them, the integration of acidogenic fermentation with the aerobic process has emerged out as one of the viable strategy (Venkata Mohan et al., 2010). Acidogenic fermentation (AF) of wastes generates effluents that are rich in VFA need treatment prior to disposal (Dahiya et al., 2015). These VFAs can be effectively used as a source of carbon by aerobic bacteria for their growth and also their survival during carbon depleted conditions by storing these VFA as PHA (Reddy et al., 2012; Wu et al., 2016). Through this multiproduct approach, the intrinsic load of the waste can be reduced thereby reducing environmental pollution while obtaining products of high commercial interest (Reddy et al., 2013).

Waste valorization is the process of transforming organic-rich substrate into valuable products like, renewable chemicals, biofuels, and materials. The globe is tuning the magnitude of the waste management problems and has been working towards the development of advanced waste remediation technologies with resource recovery as the main goal (Amulya et al., 2015; Venkata Mohan et al., 2016). On the other hand, there is a platform exists for the devotement of sustainable technologies that could follow the ‘trash to cash’ concept by producing industrially important chemicals, materials, and fuels which will reduce the dependency on fossil-based fuels and products but also help in addressing the environmental sustainable remediation issues (Bing et al., 2016; Chen et al., 2016). Concept of biorefinery analogous to today’s petroleum refineries is also showing interest. Biorefinery systems work by utilizing bio-based feedstock to produce a range of bio-products like fuel, platform chemical, animal feeds, etc. in a closed-loop approach (Pradel et al., 2016; Pleissner et al., 2016; Venkata Mohan et al., 2016). Many scientists working with waste believe that it contains potentially huge amount of energy to replace a major fraction of the global energy crisis if it can be economically converted to sustainable energy forms (Kannengiesser et al., 2016).

2. Rationale of the Study

Organic municipal solid waste per capita generation in major Indian cities ranges from 0.2 Kg to 0.6 Kg, out of which the about 90-95% is being dumped as waste (Dube et al., 2014;Venkata Mohan et al., 2018). The calorific value of Indian solid waste is between 600 and 800 Kcal/Kg and the density of which is in between 330 and 560 Kg/m^3. Organic solid waste (OSW) is conventionally disposing of through landfilling, incineration and biomethanization. Landfilling requires large open lands and emits the greenhouse gases into the environment. Further, the process of incineration requires high thermal energy input and releases the secondary pollutants into the environment. In addition, these conventional disposal practices are eliminating the potential of OSW and are no longer sustainable due to its high economic inputs and negative impacts on the environment. Alternatively, sustainable biological conversion is an eco-friendly process and economically reliable (Lee et al., 2014). The heterogenic composition of OSW and embedded polysaccharide content in it does not suit its direct supplementation as a biological substrate. Studies were reported with various individual pretreatment methods to harness the maximum sugars from OSW like physical (thermal conversion, sonication), chemical (acid, base), enzymatic (amylase, cellulases, mixture of enzymes) (Ho et al., 2013, Hernández et al., 2015, Hafid et al., 2015, Shokrkar et al., 2018). Each individual method has its own advantages and disadvantages, wherein the physical method is easy to operate but the resulting sugar yields are lower. On the other side, chemical method is suitable for effective degradation of polysaccharides, but the acid or base concentrations need to be optimized to avoid the formation of the inhibitor and moreover, the resulting sugar yields are lower. Advantageously, enzymatic hydrolysis is more specific towards the carbohydrate depolymerization with no/low inhibitors formation, but the major concerns of this method is the requirement for longer reaction time apart from the high cost of enzymes (Lee et al., 2013). Therefore, there is a need to develop an effective pretreatment method for maximum sugar extraction from OSW and its entirety utilization as a renewable resource. Since the selection of an appropriate pretreatment method largely depends on the composition of waste. Additionally, optimization of biological process is pre-requisite to maximize the process efficiency and to obtain higher yields. In this context, experimental were evaluated to harness the maximum sugars from OSW followed by its effective utilization in the subsequent biological processes for the production of various biobased products such as biohydrogen, short-chain carboxylic acids, medium-chain carboxylic acids, biopolymers and bioethanol in the integrated multiproduct approach.

3. Scope of the Research

The present study comprehensively evaluates the renewable resource potential of organic solid waste for the production of various biobased products such as reducing sugars, short-chain carboxylic acids, biohydrogen, medium-chain carboxylic acids, biopolymers, bioethanol and struvite in a closed-loop approach. With the existing scope in the literature, the experiments were designed and evaluated with the following objectives.

- Effective strategy for organic solid waste (OSW) pretreatment for maximizing sugar solubilization using various individual and combined methods like physical, chemical, physicochemical, enzymatic and bio-electrohydrolysis.
- Evaluation of waste-derived renewable sugars as main feedstock in the fermentation process towards the production of short-chain carboxylic acids (C_2-C_5), biohydrogen (Bio-H_2) and bioethanol

- Integrated utilization of SCA as a carbon source for the production of biopolymers (PHA: polyhydroxyalkanoates) and medium-chain carboxylic acids (MCA: C_6-C_{10}) in the secondary biological process.
- Evaluation of biorefinery process with multiproduct valorization design in a circular loop

Renewable sugars obtained from the organic solid waste was used as a substrate for the production of short-chain carboxylic acids (C_2-C_5), biohydrogen (Bio-H_2), medium-chain carboxylic acids (C_6-C_{10}), biopolymers (PHA), bioethanol and struvite in the biorefinery framework. Organic fractions present in waste could replace the fossil based raw materials for the synthesis of biobased products in the biorefinery approach. These renewable products have a good commercial interest and also the production of which using waste reduces the carbon load on the environment. Although it would be presumptuous to believe that waste will be able to completely meet the world's energy needs, it is still achievable if a coalesced approach to recycle and reuse waste is developed, wherein the waste coming from one industry or sector becomes the raw material for another. However, this leads to the development of the biobased circular economy with less environmental impact and an utmost generation of bioenergy and other bio-based products. In line with the above mentioned facts, to address the entirety use of organic solid waste the present study strategically designed and evaluated in the multiproduct approach with the integrated cascading approach.

4. Summary of Results

The pervasiveness of organic solid waste (OSW) and the energy content embodied in it makes waste one of the most potential and affordable feedstocks for the production of multiple biobased products. This will address the dual challenges, resource scarcity and increasing energy demand. Usually, the composition of waste is dissimilar, based on its material distribution and origin the pretreatment method will differ. The obtained result from the study illustrates the influence of various pretreatment methods based on the origin of OSW. Hybrid (PSC) pretreatment strategy with dilute acids (H_2SO_4/HCl) resulted in relatively higher RS solubilization from vegetable waste and deoiled algal biomass sugar solubilization. On the other side, waste activated sludge (WAS) pretreatment showed the good organic and nutrient solubilization with alkaline-catalyzed conditions pretreatment than corresponding acid-catalyzed method. Specifically, WAS alkaline catalyzed conditions facilitated the leaching of the cell wall and thus resulted effective disintegration of WAS with increased soluble COD concentration. However, the combination of physical and chemical methods (physicochemical) with acid/alkaline-catalyzed conditions induced good sugar solubilization than the consequent individual methods. Additionally, WAS pretreatment with novel alkaline bioelectrohydrolysis system (BES) also resulted in good SCOD solubilization and resulted the sludge flocs disintegration. On the contrary, low SCOD solubilization resulted in non-electrochemical control system (AnT). FE-SEM morphological examination was supported well with the WAS refractory structure degradation and the EDX analysis showed the changes in elemental composition with the course of pretreatment.

Acidogenic fermentation of waste derived renewable sugars as a substrate for the production of biohydrogen and short-chain carboxylic acids (VFA: C_2-C_5) resulted the good yields. The experiments were studied at various redox conditions such as pH-4, 6, 7 and 10. Higher biohydrogen and VFA production resulted at pH-6 condition (H_2; 1.22 l and VFA: 0.62 g VFA/g RS) than corresponding other experimental variations. Operational pH showed a marked influence on the production and compositional distribution of biogas and VFA. Higher AA concentration in systems operated with pH-6, 10 and 7 contributed to higher DOA, while in the case of pH-4 system BA contributed a major fraction of DOA. Fermentation time also played a key role in the governance of VFA profiles. Specifically, in the case of pH-7 condition, longer retention time consumes the accumulated VFA towards methane production. On the other side, lower retention time (48 h) wrapped further VFA consumption towards the methane in all the pH conditions. First-order kinetic models were studied to fermentative biobased products synthesis to understand the stable process performance under practical conditions.

Besides, the resulted VFA was also reutilized as a substrate in the integrated biological processes for medium-chain carboxylic acids and biopolymers production due to its simple organic nature. Medium-chain carboxylic acids (MCA) are the superior to VFAs as they have a longer hydrophobic carbon chain and low oxygen/carbon ratio, which increases the energy density and makes its separation simple. MCA are majorly composed of C_6-C_{12} namely, Caproic acid (C6), Oenanthic acid (C7), Caprylic acid (C8), Pelargonic acid (C9), and Capric acid (C10). Among these acids, the biological production of caproic acid from short-chain acids/ VFAs and alcohols utilizing chain elongation pathway is studied using VFA as an electron acceptor and ethanol as an electron donor. The obtained results showed the good yields (4.73 g/l) than the corresponding hydrogen as an electron donor. Additionally, the utilization of VFA as a substrate for biopolymer production (PHA: polyhydroxyalkanoates) also resulted in good yields than renewable sugars.

Enriched mixed microbial cultures were used for PHA production, wherein PHA producing bacteria was examined using a fluorescent microscopy, flow cytometry and confocal microscope with Nile blue staining. Thereafter, the characterization of extracted PHA was studied using NMR, FT-IR, XPS, XRD and thermal analysis. These obtained results showed the structural correlation with polyhydroxybutyrate (PHB). Thereafter, PHB films were prepared using acetic acid as a casting agent and which resulted in good high-quality films than conventional chloroform films. Acetic acid is relatively safe and cost-effective solvent which can bring down the cost of film preparation and wider the application of PHB films in the medical applications. Additionally, to increase the strength of the extracted PHB, nanocellulose composites were prepared by using different concentrations of PHB. The obtained PHB nanocellulose composite film showed a higher strength than individual PHB.

The energy crisis, escalating crude oil prices and environmental aberrations upsurge the need for potential renewable fuels like bioethanol. The 3G ethanol produced from deoiled algal biomass (DAB) residue is gaining interest owing to the sustainable supply of the feed and the possibility of waste valorization. Subsequent utilization of DAB derived sugars showed the significant variations in the bioethanol production, wherein in higher bioethanol production was found at pH 5.5 followed by pH 5.0 and pH 6.0. In addition, struvite was also produced from organic rich hydrolysate resulted from the WAS. Struvite is known as a phosphate fertilizer with a crystalline solid structure composed of magnesium, ammonium and phosphorus ($Mg.NH_4PO_4.6H_2O$). The precipitated struvite yield was 0.18 g/L which resulted at most suitable pH 9.0 to 9.5. The FTIR structural analysis of struvite revealed a broad asymmetric band in between 3600 and 2200 cm^{-1}, which can be attributed to O-H and N-H stretching vibrations.