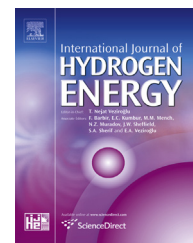


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Sequential hydrogen and methane production with simultaneous treatment of dairy industry wastewater: Bioenergy profit approach

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ABSTRACT

A sequential study for hydrogen and methane production with pollutants reduction from dairy industry wastewater (DIWW) was conducted using bacterial strain of *Enterobacter aerogens* and methanogenic bacteria of cow dung. Among the different selected concentrations of DIWW viz: 25%, 50%, 75% and 100%, the 75% concentration depicted the best feasibility for biomass growth rate (0.21 h^{-1}) as well as hydrogen ($105 \text{ ml H}_2/\text{g-Chemical Oxygen Demand (COD)}$) and $0.562 \text{ L-H}_2 \text{ L}^{-1} \text{ DIWW}$) and methane ($190 \text{ CH}_4 \text{ ml/g-COD}$ and $0.59 \text{ L CH}_4 \text{ L}^{-1}\text{-FDIWW}$) production with the selected substrate. Experimental results were tested with various kinetic models viz. (Monod, Moser, Hanes–woolf and Eadie–Hofstee) to observe substrate utilization and growth pattern of bacteria. Hanes equation ($R^2 = 0.95$) was the best fitted model observed in the present study. Economic Assessment of produced energy ($0.22\$/\text{m}^3 \text{ DIWW}$ and $0.336\$/\text{m}^3\text{-FDIWW}$) illustrates the selected pathway has the viability of the system for treatment simultaneous with bioenergy production.

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Introduction

Dairy industry has global importance due to its essential contribution in human nutrition with high economic opportunities. This industry is a large economic driver globally, which represent about \$330 billion and is expected to grow \$400 billion by 2015 [1]. The rise in number of dairy industry has also increased the wastewater load for instance a typical dairy industry in European Union generates approximates $180,000 \text{ m}^3$ of waste effluent annually [2].

Because of strong environmental legislation, industries with solid, liquid or gaseous waste discharges are bound to

employ economic feasible and effective waste treatment before final discharge at permissible level [3]. Most of the industries installed treatment process at the source for separation of pollutants, which reduce the quantity of wastewater. In dairy industry, processing of various dairy products (yogurt, cheese, butter, milk, ice cream, etc.) and cleaning at place are major source for wastewater generation.

Dairy industry effluent characteristics are mainly influenced by climatic condition, operating condition, types of cleaning in place and wastewater management practices [4]. Among the key parameters characterizing these waste, dairy wastewater shows relatively a high Biological oxygen demand (BOD) and Chemical oxygen demand (COD) with a range of

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0.3–5.9 g L⁻¹ and, 1–10 g L⁻¹, respectively [5]. In addition, presence of fat content (0.1–10.6 kg m⁻³), suspended solid (0.1–22 kg m⁻³) and nutrients (N and P) also contribute in the contamination level [5].

Most of the organic matter (99%) present in dairy industry wastewater is biodegradable [7]. The conventional biological treatment of such wastewater involved with incomplete degradation of organic fraction, which causes odour and act as breeding ground for pathogens and insects [6]. Thus, a cost effective biological treatment process with efficient degradation potential is strongly needed for management of huge load from dairy industry wastewater. This sustainable way of dairy wastewater treatment can be achieved by adopting the integrated approach of wastewater treatment and energy production simultaneously. In this context two phase anaerobic digestion process offer more benefits (more energy recovery, high degradation) in compare to the conventional anaerobic digestion process [7–9].

Anaerobic digestion for treatment of industrial waste has been applied since a long time [10,11]. However, the same process is potentially applied for bioenergy production too. Therefore, anaerobic digestion process has potential to solve the global issue of energy crisis, which has been raised due to depletion in petroleum products [12]. The loading capacity in any anaerobic biological wastewater treatment system completely depends on the amount of active bacterial biomass present in wastewater. Hoogwijk et al. [13] assessed the potential supply of biomass from various categories of waste and suggested that organic waste and biomaterial have higher potential for biomass supply than other waste. So, the growth of bacterial biomass is secondary product in any system, because the synthesis of bacterial biomass primarily occurs from organic precursors with some inorganic nutrients. The net effect is to move organic matter from one pool to another. Hence, high rate/highly potential anaerobic reactors are those which retain biomass for periods longer than retention times.

Hydrogen is considered as a clean energy source without any kind of emissions [14]. There are wide applications of hydrogen as fuel in vehicle as well as for electricity generation via fuel cells [15]. Different studies reported by the various researchers enlisted it as a key component for developing a clean and sustainable energy system by integration of hydrogen production process with promising technologies [16]. The integrated sequential hydrogen and methane can be applied for most of all types of organic waste including industrial waste from different industries [17–19]. Integration of pollution reduction with generation of bioenergy (biohydrogen and methane) in a two phase process can be adopted which is a supplementary/auxiliary approach in wastewater treatment. Integrated approach not only reduces the capital cost of process but also provide high energy recovery from the substrates [20–22].

The efficiency of microorganism for remediation of wastewater depends on substrate utilization pattern, which can be expressed through kinetic studies. Microbial kinetics of substrate utilization (biomass) with value of kinetic coefficient provides key information in treatment of wastewater [22]. Various microorganisms including bacteria and algae are known to facilitate biohydrogen production with waste

treatment in anaerobic conditions by utilizing the available carbon source in the medium it grows.

Some of the upstream and downstream technologies like selection of bacterial culture and their efficiency for bioenergy production and treatment, respectively, still suffering from the drawbacks of best culture with suitable substrate and low treatment options, limiting the feasibility of these integrated approaches. This study thus, presents a new approach for two phase study using dairy industry wastewater for hydrogen (H₂) production in first phase with treatment option simultaneously and methane (CH₄) production in second phase under anaerobic conditions. Moreover *E. aerogens* and cow dung were used to convert substrate into hydrogen and methane, respectively and pollution reduction rates were determined on the basis of chemical oxygen demand. Kinetic coefficient for bacterial for growth and substrate utilization were also compared in both phases of the experimental study. Economical assessment also evaluated for the selected bio-process route. The aim of present work is to develop a low-cost and effective treatment technology for industrial wastewater with bioenergy production. Despite of marked development in integrated wastewater and energy generation process, various drawbacks in upstream (Screening of microbial strain) and downstream process (treatment and energy recovery) have limited these technologies only up to lab scale. These drawbacks involve lack of best culture with suitable substrate and lesser treatment efficiency. The present work provides a new sight for sustainable energy and environment management with development of an integrated experimental plan to examine the potential of organic waste materials present as an environmental discards and its use for bioenergy options (hydrogen and methane) for clean future fuel.

Materials and methods

Collection and characterization of dairy industry wastewater (DIWW)

The dairy industry wastewater (pH, 6.2; TS, 2200 mg L⁻¹; Chloride, 385 mg L⁻¹; Nitrate, 66.4 mg L⁻¹; Nitrite, 0.94 mg L⁻¹; Ammonia, 24 mg L⁻¹; Phosphate, 21 mg L⁻¹; Sulphate, 137 mg L⁻¹; BOD, 320 mg L⁻¹ and COD, 11,200 mg L⁻¹) was collected from the dairy industry, India using composite sampling methodology. Collected dairy wastewater samples were stored at 4 °C to prevent its degradation and filtered through 1 mm sieve to remove larger particles, if any. Preservation and characterization of samples were carried out by following the standard methodology as prescribed in APHA [23]. Each parametric analysis was carried out in triplicate. The industry has capacity to process about 150,000 L/day milk and utilizes about 1200 m³/d of fresh water in processing of various products. The industry discharges about 480 m³/d of wastewater i.e. 60% of the total water used in dairy processing products.

Preparation of inoculums

Pure bacterial culture of *Enterobacter aerogens* (MTCC no.8100) was procured from Microbial Technology Culture Centre

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