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Effect of Low Temperature Thermo-Chemical Pretreatment of Dairy Waste Activated Sludge on the Performance of Microbial Fuel Cell

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This study investigates the influence of low temperature thermo-chemical pretreatment of diary waste activated sludge on the performance of microbial fuel cell. First, effect of sludge pretreatment was evaluated by Chemical Oxygen Demand (COD) solubilization and suspended solids (SS) reduction. At optimized condition (70°C for 24 hr), COD solubilization and SS reduction was 29% and 24% higher than control. Second, with 20 days operation at batch mode, H- type microbial fuel cell (MFC) was run with raw and pretreated sludge (external resistance - 300Ω). Low temperature thermo-chemical pretreatment improved the Total Chemical Oxygen Demand (TCOD) removal and SS reduction efficiency in the microbial fuel cell up to 54% and 43%, gaining an overall efficiency of 54% TCOD removal and 50% reduction in SS. The power density of the MFC had increased from $0.5 W/m^3$ (raw sludge) to $0.715 W/m^3$ (pretreated sludge). Thus, by combining this pretreatment with MFC, renewable energy could be generated from sludge in addition to treatment.

Keywords: waste activated sludge; sludge reduction; microbial fuel cell; solubilization; power density.

1. INTRODUCTION

Water management in the dairy industry is well documented, but effluent production and disposal remain a problematic issue for the dairy industry. Proper management of excess sludge is a big challenge to wastewater treatment operators because sludge handling and disposal accounts for up to 60% of total treatment plant operating costs [1]. Anaerobic digestion is of particular interest in sludge treatment since it can reduce the overall amount of sludge to be disposed, while producing an energy-rich biogas that can be valorized energetically. In order to improve the rate of hydrolysis and the anaerobic digestion performance, sludge disintegration was developed as a pre-treatment process to accelerate the anaerobic digestion and to increase the degree of stabilization. Various methods like Ultrasonic treatment [2], thermo-alkaline treatment [3], Fenton process [4] and biological hydrolysis with enzymes [5, 6] were investigated for sludge disintegration by several researchers in full-scale and lab-scale plants to bypass the rate limiting stage of hydrolysis.

The heat treatment of waste activated sludge was shown to be an effective pretreatment method for anaerobic digestion. Temperatures higher than 180°C lead to the production of recalcitrant soluble organics or toxic/inhibitory intermediates, hence reducing the biodegradability [7]. The only alternative to overcome this drawback is the application of low temperature treatment (< 100°C), and it is suggested as a biological predigestion step as it has an incremental effect over biogas production under thermophilic condition and significantly reduces the energy requirement and formation of refractory intermediates which are seen as a burden in high temperature pretreatments [3]. In thermo-chemical methods, an acid or base is added to solubilize the sludge. NaOH addition in combination with a low temperature (60°C) has led to 51% increase in biogas potential of dairy waste activated sludge [6]. Though pretreatment enhances anaerobic digestion, the latter still suffers practical hindrances such as longer retention time, vulnerability to shock loads etc. An alternative technology is needed to upgrade sludge reclamation and energy conversion. MFC can serve as such an alternative.

MFC are bio-electrochemical reactors in which microorganisms mediate the direct conversion of chemical energy stored in organic matter or bulk biomass into electrical energy. MFC have been run with various organic matters and waste such as glucose, organic matter in sewage [8], swine waste water [9], and manure sludge waste [10]. MFC research has documented effective COD removal efficiencies along with significant power densities [11]. Various modifications in the design of the fuel cells have resulted in increased performance efficiency. Among all other organic matter very few studies have reported that sludge can be used to run microbial fuel cell. Raw sludge degradation in MFC can be enhanced with sludge pretreatment, since soluble organics are readily utilized by microbes in MFC [12].

The objective of the current work is to study the effect of low temperature thermo-chemical pretreatment of dairy waste activated sludge in terms of solids reduction and solubilization, over the performance of MFC in a batch mode considering the power density, TCOD removal and sludge reduction efficiency.

2. MATERIALS AND METHODS

2.1. Sample collection and characteristics

Dairy waste activated sludge was collected from Aavin dairy effluent treatment plant at Ambathur, Chennai. The sludge was stored at 4°C. The dairy waste activated sludge had a total chemical oxygen demand (TCOD) of 12400 - 11800 mg/L, soluble chemical oxygen demand (SCOD) of 600 - 700 mg/L, pH of 6.9 - 7.2, total solids (TS) concentration of 13850 - 14000 mg/L, suspended solids (SS) concentration of 9900 - 10500 mg/L and volatile solids (VS) concentration of 6900 mg/L.

2.2. Low temperature thermo-chemical pretreatment

The low temperature thermo-chemical pretreatment was carried out at 50, 60, 70, 80 and 90°C in order to enhance solubilization of particulate material, as well as enzymatic hydrolysis. In this work, the effect of pretreatment time was evaluated by taking samples at different pretreatment times (7, 9, 12, 24, 36 and 48 hr) in order to study the combined effect.

Batch reactors containing 1L of sludge were submersed in a thermostatic bath at various temperatures (50, 60, 70, 80 and 90°C) during 7, 9, 12, 24, 36 and 48 hr. The sludge in the reactor was kept in suspension by a slow-speed stirrer (Digital overhead IKA RW 20, Germany), to ensure temperature homogeneity. For the waste activated sludge studied, the pH was adjusted to 11 using 1N NaOH. pH 11 was selected to restrict the final pH of the treatment to less than 8 [13]. Even though, sodium hydroxide decrease the dewaterability of the sludge, the choice of this alkaline agent was made from different studies indicated that, for anaerobic digestion, pretreatment with NaOH was more efficient than using other alkaline agents. The negative influence of sodium hydroxide over sludge dewaterability is reduced when it is combined with other treatment methods such as microwave and thermal [14]. Dewaterability of the sodium hydroxide pretreated sludge can be improved by the subsequent sludge management using lime.

2.3. Microbial fuel cell setup and operation

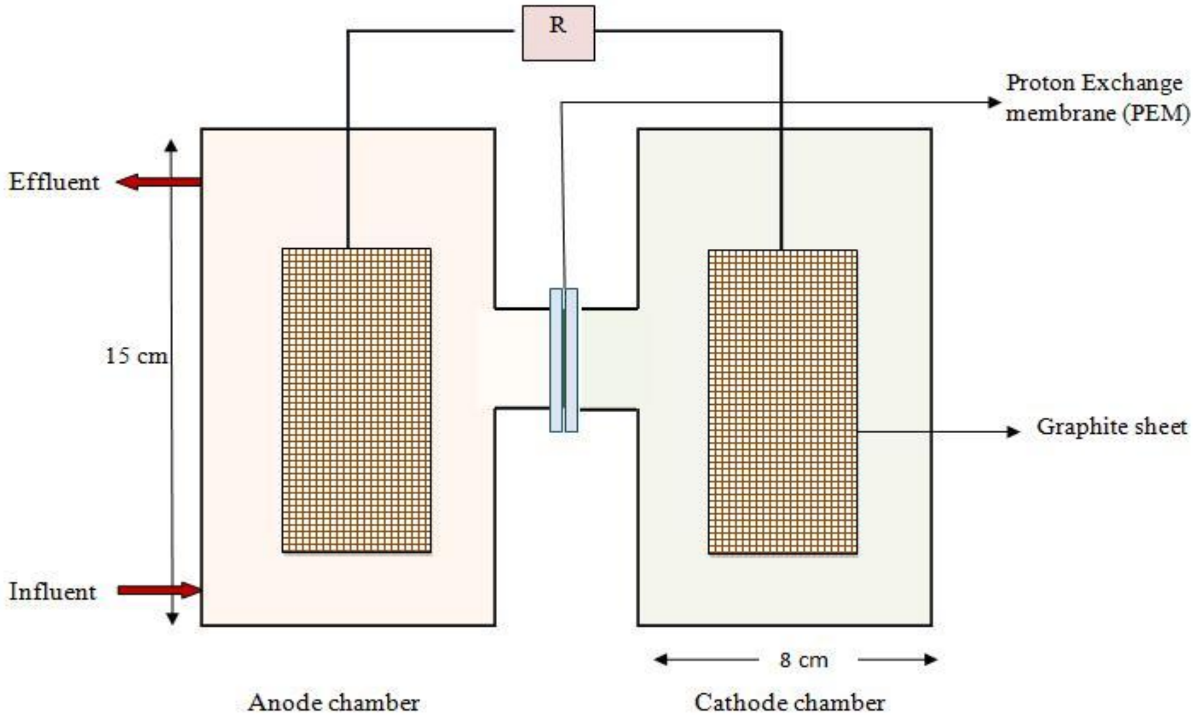

Figure 1. Schematic representation of the microbial fuel cell

Two H - Type MFCs were constructed as described in a previous paper [15]. The anode and cathode chambers were connected through a proton exchange membrane (Nafion) and the total and working volume of each chamber were 750 mL and 600 mL, respectively as shown in Figure 1. The anode and cathode electrodes consisted of uncoated graphite sheet of dimension 13 × 8cm, yielding an effective anode surface area of 208 cm^2. The distance between the electrodes was approximately 10 cm. Dissolved oxygen (DO) was used as the final electron acceptor in the cathode chamber and its concentration was maintained at 4 to 5 mg/L. Raw sludge (control) and thermo-chemical pretreated sludge (experimental) was used anode fuel and was mixed homogenously using a magnetic stirrer to ensure effective mixing. The initial pH was adjusted to 7.0. MFC experiments were conducted at batch mode and at room temperature.

2.4. Analytical Parameters

The following parameters were analyzed before and after thermo-chemical treatment: Total Solids (TS), SS, COD, Carbohydrate concentration, Protein concentration and pH as detailed in APHA [16]. Soluble protein concentration was determined on total sludge and on the supernatant using the Lowry method [17]. Carbohydrate concentration was determined on total sludge and on the supernatant using the anthrone method [18]. COD solubilisation was calculated as follows (Equation (1)).

$$SCOD = \frac{(SCOD_{after\ pretreatment} - SCOD_{before\ pretreatment})}{SCOD_{after\ pretreatment}} X\,100 \qquad (1)$$

2.5. Electrochemical analysis

Voltage production of the microbial fuel cell was measured using digital multimeter. By ohms law (I = V/R, where I = Current (A), V= Voltage (V) and R = Resistance (Ω),) the load, voltage and current were measured and calculated. Internal resistance of MFC was measured from the slope plotted with voltage versus current. Polarization curve for the fuel cell was determined by varying the external resistance from 10-3000 Ω. The power density of the MFC was presented in terms of anode volume [19], rather than anode surface since power generation had to be evaluated based on the fuel characteristics than the electrode characteristics. The columbic efficiency of the batch mode MFC was calculated as stated by Logan [20].

3. RESULTS AND DISCUSSION

3.1. Low temperature thermo-chemical pretreatment

In this study, low temperature thermo-chemical pretreatment of waste activated sludge was performed to improve the treatment efficiency. The control was performed using both raw and pretreated WAS. The treatment was performed for different temperature and treatment time. The expected effect of the thermo-chemical treatment of sludge was an increase in soluble materials, with interest focused on COD solubilization and SS reduction, thus enhancing hydrolysis. The experiments were conducted in triplicate and the average of the values was presented in the manuscript. However the deviations among the trials have been represented in the figures.

3.2. COD solubilization and SCOD release

The pretreatment was done to improve the bioavailability of sludge particulate material. COD solubilization and SCOD release were considered the main parameter for evaluation of sludge particulate material, and it enables an evaluation of the maximum level of sludge solubilization. The optimization of time and temperature for COD solubilization during low temperature thermo-chemical pretreatment is shown in Figure 2a. From the figure, it is evident that, as the treatment time was increased from 7 to 24 hr, an increase in COD solubilization was observed. This may be due to the disruption of chemical bonds in cell walls and membranes by thermo-chemical treatment. Therefore intracellular organic material is released to the liquid phase and increases the SCOD [21]. As reaction time increases from 24 to 48 hr, SCOD was found to be decreased. The fall in SCOD after 24 hr could be due to the occurrence of refractory compounds catalyzed by the thermal energy over prolonged period of treatment. Similar effect was observed in previous studies. Thus, for the waste activated sludge sample, a treatment time of 24 hr was found to be the optimum. Likewise at 50°C, the COD solubilization was found to be 22%. However at 60, 70, 80 and 90°C, the temperature plays a major role in enhancing COD solubilization and it was found to be 25, 29, 30 and 33% respectively. From the above, it is clear that temperature above 70°C doesn't help in solubilizing the excess sludge. Similar positive effect of temperature over COD solubilization was documented, but for a higher temperature and shorter time duration [22].

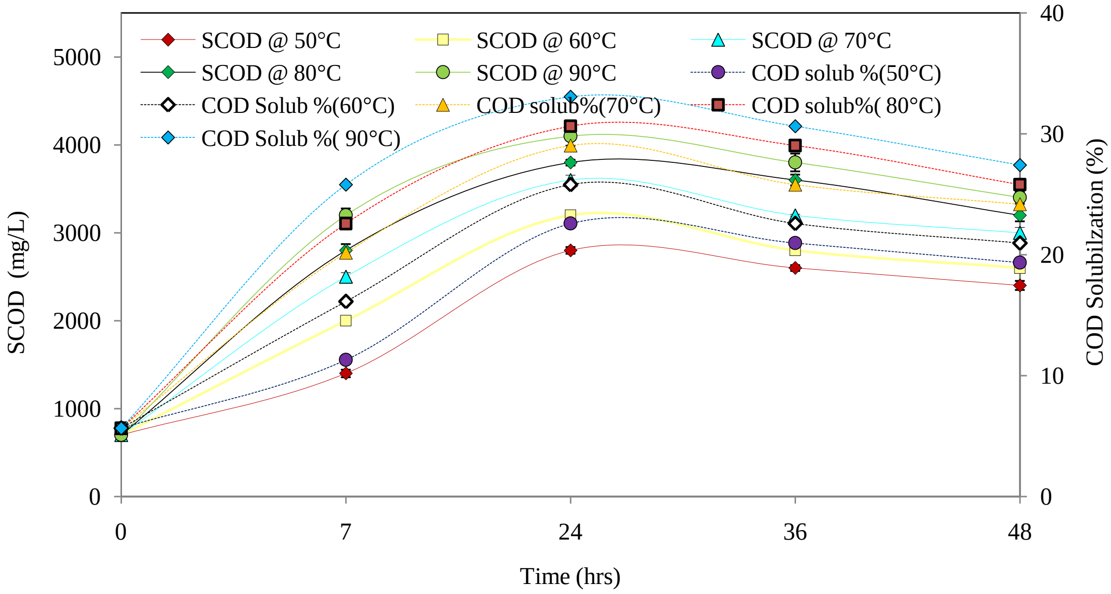

Figure 2a. Optimization of time and temperature during low temperature thermo-chemical pretreatment for COD solubilization

Thus, considering energy generation, low temperature thermo-chemical treatment (70°C) was considered to be an optimum condition for rupturing cell membranes. The study is carried out at low temperature range of 50 to 80°C which is less intense when compared to high temperatures. The effect of time thus had a higher impact than the temperature when studies were carried over longer durations and in low temperature range [3]. Though the solubilization doesn't show a rapid rise, but the overall solubilization for the treatment is satisfactory.

3.3. SS reduction

SS reduction is an indication of sludge stability, and it is used for assessing the effectiveness of a process in stabilizing sludge [23]. The optimization of time and temperature for SS reduction during low temperature thermo-chemical pretreatment is shown in Figure 2b. From the figure, it is evident that, as the treatment time was increased from 7 to 24 hr, an increase in SS reduction was observed. The main reason for mass reduction of sludge during the thermo-chemical pretreatment might be to rupture the cell wall and to release of extracellular and intracellular matter. Thus, it is evident that at 70°C with pH 11, COD solubilization and SS reduction was found to be 29 and 24% respectively, which might be regarded as a threshold for the pre-digestion step.

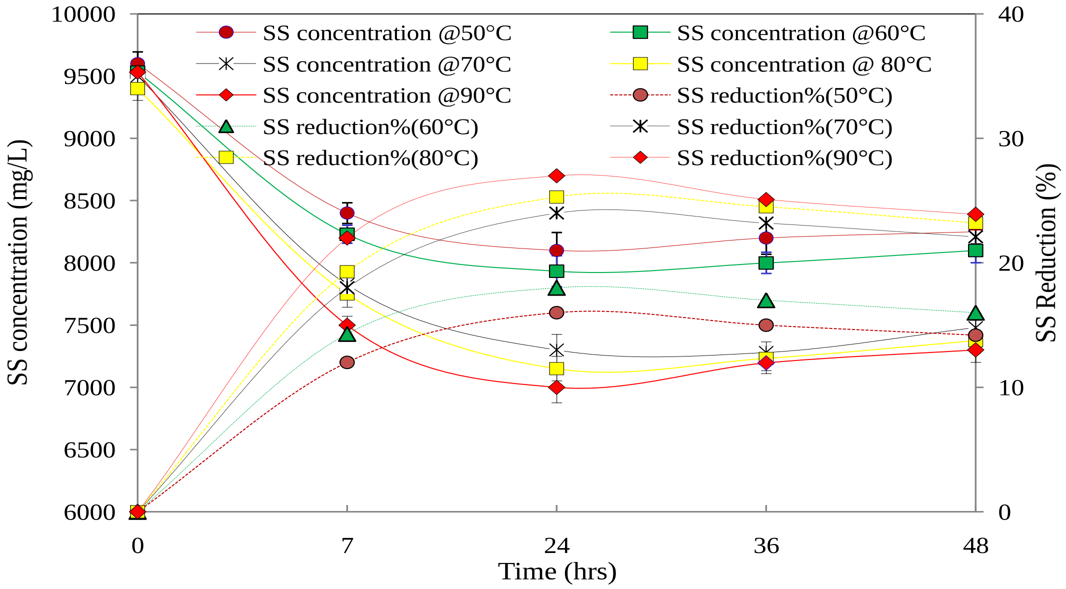

Figure 2b. Optimization of time and temperature during low temperature thermo-chemical pretreatment for SS reduction

3.4. Soluble Carbohydrate and Protein release

Cell lysis releases protein content into the medium is the first stage of floc disintegration. Proteins are the principal constituents of organisms, and they contain carbon, which are a common organic substance as well as hydrogen, oxygen and nitrogen. For this reason, it was considered that as the level of soluble protein increased, the efficiency of anaerobic digestion would be improved. Due to thermo-chemical treatment, solids were solubilized, especially organic solids. The proteins and carbohydrates release for the samples is presented in Figure 3. Moreover, it was found that the protein and carbohydrate release increases linearly with temperature. Thus, 70°C with pH 11 is significant for protein and carbohydrates release, since energy utilization is minimum at this temperature. According to Liu and Fang [24], during the sludge treatment with NaOH, protein is released more compared to carbohydrate and this result is similar to that obtained in the present study. The protein releases presented in the figure are the sums of protein released from EPS as well as the cell lysis. Hence protein concentration is more than carbohydrate.

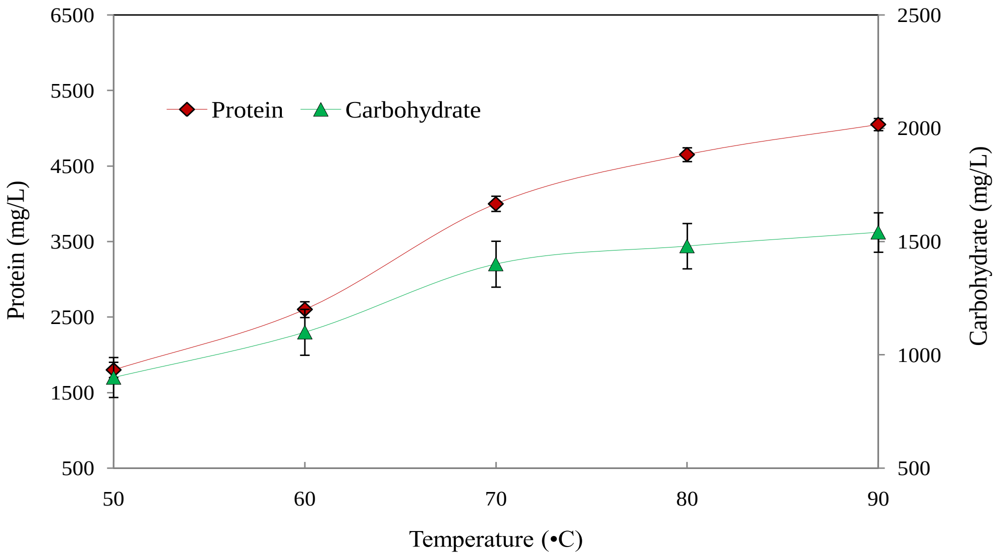

Figure 3. Effect of low temperature thermo-chemical pretreatment on protein and carbohydrate release

3.5. Effect of low temperature pretreatment on electricity generation in MFC and coulombic efficiency

The microbial fuel cell was acclimatized for 30 days with dairy waste activated sludge. The MFC got stabilized after 20 days with a stable open circuit voltage of 0.680V. The control test was run in open circuit condition with raw (non-pretreated) and pretreated sludge. It was considered as a typical anaerobic digestion. The open circuit voltage during the control test was found to be 0.686V. Anaerobic digestion in the anode chamber had resulted in 31% of TCOD removal at the end of 20 days. In addition to COD removal, the sludge was efficiently degraded resulting in 20% reduction in SS concentration.

From the polarization curve (Figure 4), the internal resistance of the fuel cell was found to be 270 Ω closer to the external resistance of 300Ω at which maximum power density had occurred. Furthermore, it can be observed that, the MFC had removed 11% more TCOD than the typical anaerobic digestion test, resulting in 42% of TCOD removal. The MFC reactions had also degraded sludge efficiently resulting in 34% of SS reduction. An increment of 14% in SS reduction compared to the control test indicates that the MFC reactions could degrade more sludge than anaerobic digestion. In loaded condition, the anode respiring bacteria utilizes the organic matter in sludge for electricity generation through reduction at the anode surface. When the maximum equivalent electron transfer rate increases, the demand for substrate increases and hence sludge gets more degraded.

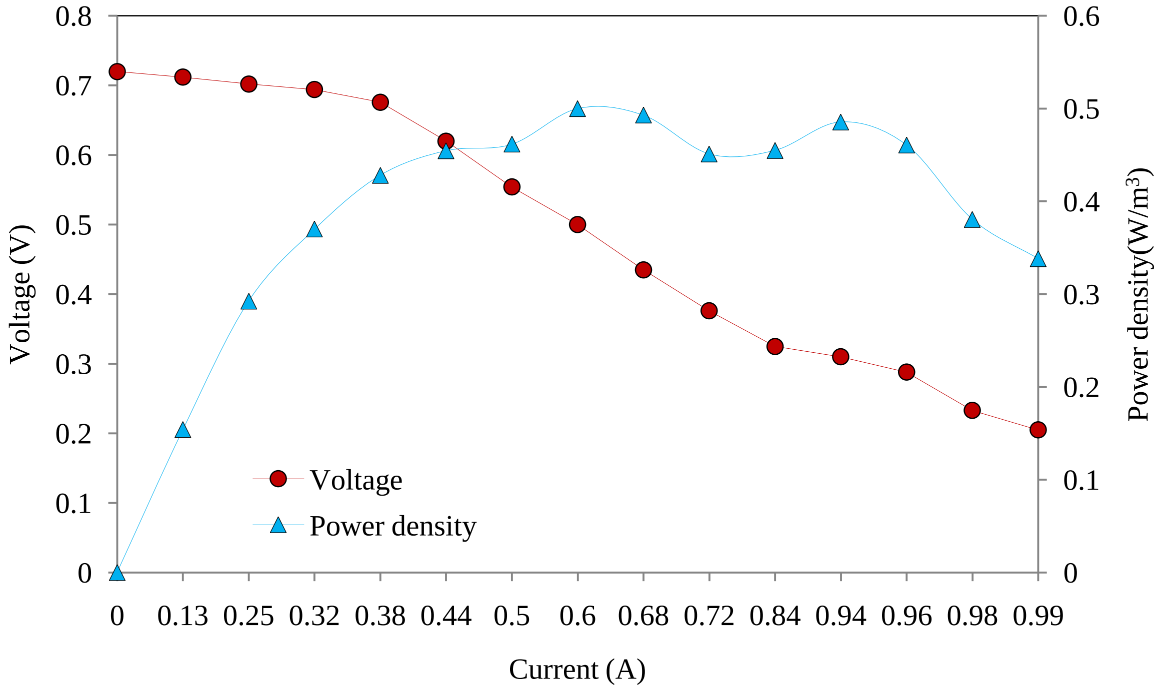

Figure 4. Polarization curve depicting power density as function of voltage and current (10 to 3000 Ω)

After sludge was pretreated by low temperature thermo-chemical treatment, the pretreated sludge was introduced into the subsequent dual-chamber MFC for further degradation and simultaneous electricity generation. Solubilized sludge had a final pH of 8.6, which was neutralized to 7 and was introduced into MFC, working at resistance of 300 Ω for 20 days. Sludge pretreatment had enhanced both TCOD removal efficiency and sludge reduction. The pretreated sludge run under open circuit condition showed 50% TCOD removal and 40% SS reduction. It was observed that in Figure 5, 54% of TCOD was removed in MFC run under closed circuit with pretreated sludge. This might be attributed to the thermo-chemical pretreatment that has led to the release of soluble cellular organics. The simple and solubilised substrates are reported to be easily degraded in MFC [25]. Earlier ultrasonic pretreatment had resulted in 50.3% rise in TCOD removal in MFC [26]. The fuel cell reactions with pretreated sludge had degraded an excess of 11% suspended solids.

The hydrolysis reaction enhanced by thermo-chemical sludge pretreatment had promoted effective degradation of the sludge biomass. Sterilization and base treatment had earlier resulted in remarkable sludge reductions of 32.8% and 25.5% in microbial fuel cell [26]. The overall efficiency of the study, combining the pretreatment and fuel cell reactions regarding organic removal was found to be 54% with respect to the TCOD and 50% with respect to sludge degradation. Coulombic efficiency of a system was determined by substrate concentration and circuit resistance [8]. Coulombic efficiency of the batch mode MFC utilizing pretreated dairy waste activated sludge was found to be around 9%. The low coulombic efficiency of the MFC might be due to the predominance of methanogenic bacteria than exo - electrogens (electrochemically active bacteria). Min *et al* [9] had reported only 5% columbic efficiency for waste water. Decrease in columbic efficiency in case of complex organics are attributed to the competitive electronic sinks co existing with the fuel cell reactions [27].

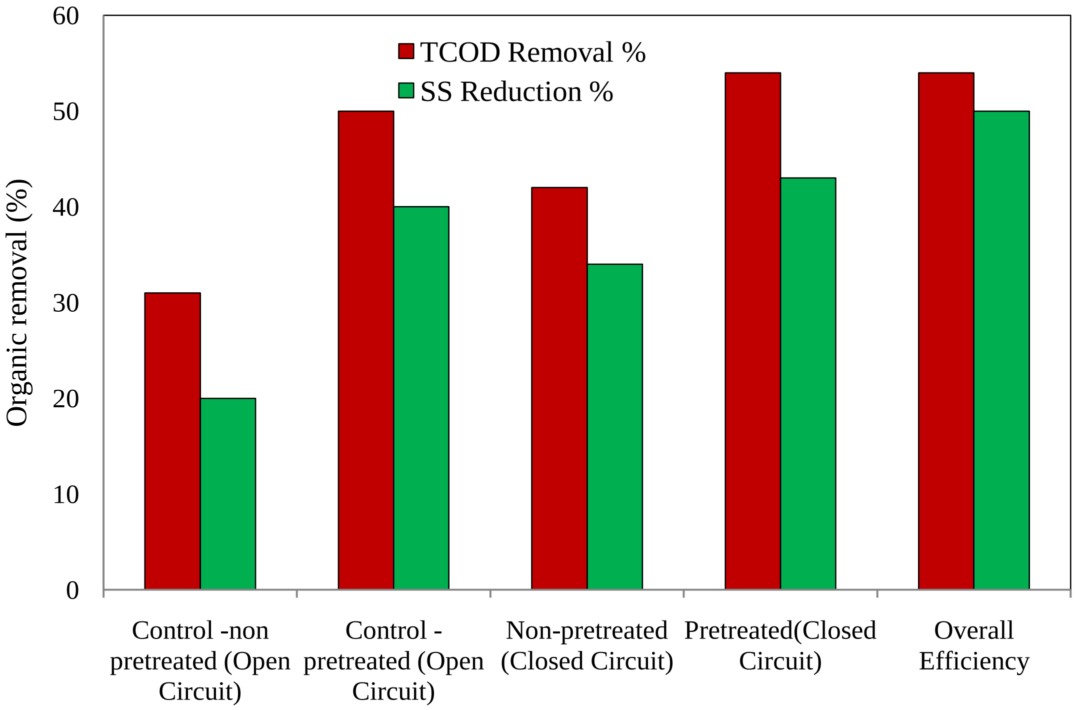

Figure 5. Organic removal at different conditions in Microbial fuel cell

3.6. Effect of low temperature thermo-chemical pretreatment on power density

At an external resistance of 300 Ω the power density with raw sludge was 0.5W/m^3. This was mainly due to the sludge organics and the action of anode respiring bacteria. It could be noted in Figure 6, as the MFC treatment gets extended, assisted with sludge pretreatment, the power density raised up to 0.715W/m^3. The rise in power density was due to the fact that, pretreatment had solubilized the sludge and the substrate was easily utilized by the exo-electrogenic bacteria. Power density had increased when sludge was subjected to individual thermal and alkaline pretreatment. Base pretreatment had provided around 50% increase than the thermal treatment at high temperature. In the current study the synergetic effect of temperature and alkali has been exploited for better results. The addition of base increases the ionic strength which may also increase electricity production [8].

The low power density of the fuel cell has to be attributed to the high internal resistance of the cell and low reduction kinetics at the cathode. Studies which used DO as final electron acceptor have reported low current profiles. Use of uncoated graphite had also influenced the power density [28]. Thus, these results indicated that low temperature thermo-chemical pretreatment could enhance organic matter removal as well as electricity generation by MFC.

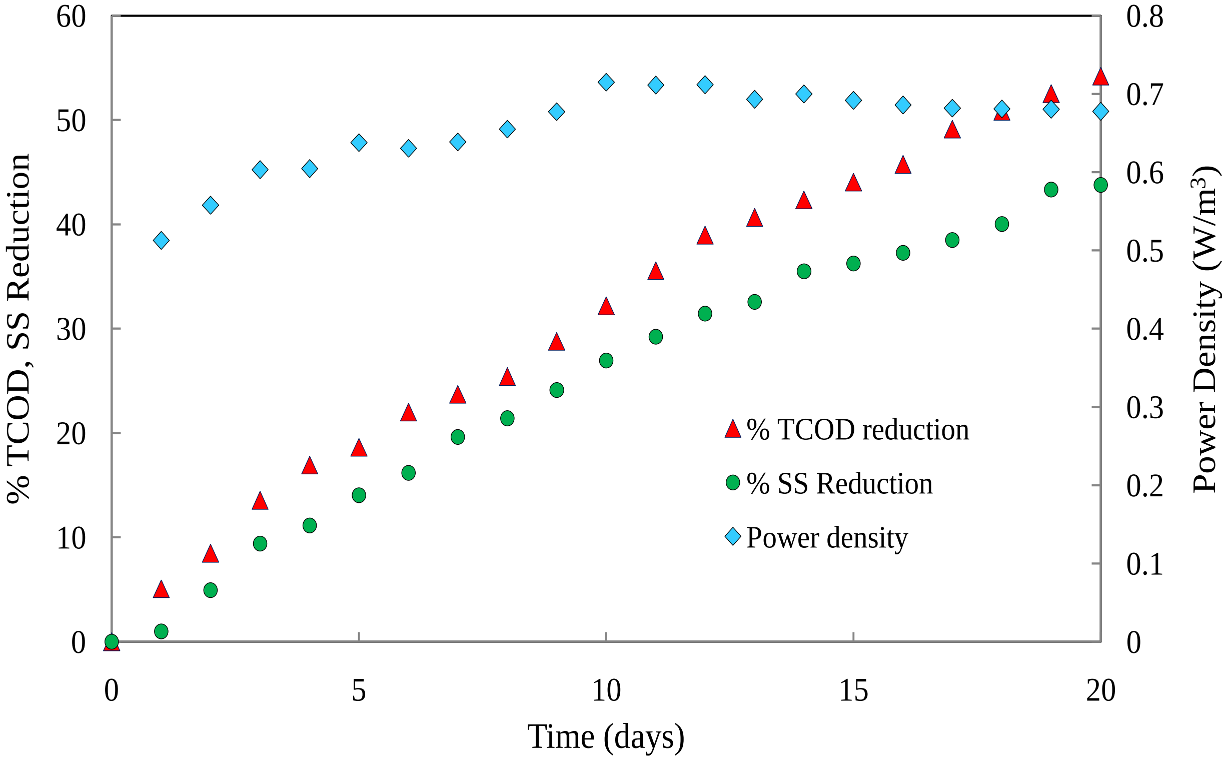

Figure 6. Effect of pretreatment over power density, TCOD and SS Removal

4. CONCLUSIONS

Based on the study of low temperature thermo-chemical pretreatment on sludge degradation and electricity generation by MFC, conclusions could be drawn as follows.

- At 70°C with pH 11, the pretreatment yielded 29% COD solubilization and 24% reduction in SS.
- The pretreatment improved the TCOD removal and SS reduction efficiency in microbial fuel cell up to 54% and 43%, gaining an overall efficiency of 54% TCOD removal and 50% SS reduction. The power density had increased from $0.5 W/m^3$ to $0.715 W/m^3$.
- Thus, by combining this pretreatment with MFC, renewable energy could be generated from sludge in addition to treatment.

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