Production of Bio-Diesel from Dairy Waste Scum

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Abstract-Dairy factory waste scums are increasingly being considered a valuable resource. However, these wastes may also contain contaminants, natural or artificial, that may adversely affect the land or water to which they are discharged. The study investigates the potential of using dairy waste scum as a feed stock for bio-diesel production. Present study optimized the parameters involved in the alkali catalysed Trans esterification process of dairy waste scum oil. The effects of methanol to oil ratio, temperature and amount of KOH were investigated. A study was conducted to evaluate the capability of production of biodiesel from consortium of native microalgae culture in dairy farm treated waste water. Native algal strains were isolated from dairy farm waste waters collection tank (untreated wastewater) as well as from holding tank (treated wastewater). The consortium members were selected on the basis of fluorescence response after treating with Nile red reagent. Preliminary studies of two commercial and consortium often native strains of algae showed good growth in waste waters. A consortium of native strains was found capable to remove more than 98% nutrients from treated waste water. The biomass production and lipid content of consortium cultivated in treated waste water were 153.54t ha-1 year-1 and 16.89%, respectively. 72.70% of algal lipid obtained from consortium could be converted into biodiesel. The present study found that bio-diesel from dairy waste scum is quite suitable as an alternative to petroleum diesel with recommended fuel properties as per ASTM standards. By using dairy waste scum as a feed stock for bio diesel and the environmental impact related to the disposal of dairy scum

Keywords: Environment,Bio-Diesel,Dairy Waste Scum, Extraction of Lipids

1. INTRODUCTION

Bio-fuel is one of the most promising renewable fuels as it is biodegradable, less toxic than fossil fuel and has low emission profile. However, now-a-days the competitive potential of bio-diesel is limited due to high cost of common lipid feedstock such as soybean, canola, rapeseed, sunflower, palm and coconut oils which constitutes 70-85% of the overall bio-diesel production cost, strongly influencing the final price of the biofuel. Thus, there is a need to find an alternative source for the production of biofuel which is cheaper and readily available in large quantities.

In contrast, dairy waste activated sludge has been used for the production of biofuel. The production of bio-diesel from sludge poses great challenges for fast commercialization.

The dairy Waste Activated Sludge (secondary sludge) formed during the treatment process of dairy wastes are collected and used for biofuel production. Ethanol and bio-diesel are the major biofuel in the production. Environmental technologies are those that reduce pollution. They also include changes in the production process, such as energy efficiency, which leads to reduce environmental impacts. The extraction of lipids from dairy sludge generates bio-diesel as renewable energy without any harmful impacts. The biofuel production is one of the smartest technologies that deliver benefits to multiple interests, including improved economy, and a positive impact on environment and government policiesUnsupervised learning algorithms, such as clustering algorithms, have been identify patterns and anomalies data. These algorithms can group similar water samples together and detect outliers that may indicate pollution events. By analyzing the patterns and trends in water quality data, unsupervised learning algorithms can provide valuable insights into the overall pollution status of a water body.

Biofuel is commonly advocated as a cost-effective and environmentally benign alternative to petroleum and other fossil fuels, particularly within the context of rising petroleum prices and increased concern over the contributions made by fossil fuels to global warming. Many critics express concerns about the scope of the expansion of certain biofuels because of the economic and environmental costs associated with the refining process and the potential removal of vast areas of arable land from food production.water samples significantly outnumbers the other. Class imbalance can lead wrong estimates.

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II. LITERATURE SURVEY

Literatures were reviewed about the effects of various pretreatment of sludge, bio-fuel production from sludge. Bio-fuels are being considered as successors to petroleum in vehicles. A different pretreatment method for sludge has been surveyed in the Literature.

The low overall biodegradation efficiency of the sludge solids and long retention times (20-30 days) result in only moderate efficiencies. Thermal, chemical, biological, microwave and mechanical processes, as well as combinations of these, cause the disintegration of sludge cells permitting the release of intracellular matter that becomes more accessible to anaerobic microorganisms. This chapter will provide a series of literature reviews concerning optimum conditions to obtain enhanced bio-fuel production in various sludge pretreatment..

Thermal Pretreatments : Noike et al (1992)., showed that optimum temperature in terms of 33% volatile suspended solids degradation and 100% bio-fuel production was achieved in 170ºC at 60 min. No further improvement for longer contact times. This is in line with the findings of Gary et al. (2007), who concluded that temperature and duration of the optimum pretreatment depend on the nature of the sludge: the greater the proportion of difficult hydrolyzing biological sludge substrates, higher the intensity of pretreatments needed

Wang Wei et al., (2003), found that water could absorb microwave and increase temperature rapidly within short time. Municipal wastewater treatment plant sewage sludge was used to be heated by microwave digestion reactor. A sludge total solid (TS) was 2%, 4% and 5%. Microwave heating temperature was 150°C, 170°C and 190°C, reaction time was 5 minutes. Results show that, temperature rising trend from ambient to three specified temperature was similar. Colloid structure was destroyed to release soluble organic components. Dewater ability and settling performance were improved. TS and suspended solid content (SS) were reduced. High temperature resulted high SS dissolving ratio. For TS 2% sludge, at 190°C, 40.0% of SS dissolved. An innovative thermal sludge pretreatment option is Microwave(MW) irradiation. MW technology is capable of rapid and more uniform heating of polar molecules (such as water) while using less energy than conventional heating.

Bougrier et al., (2006) compared the thermal pretreatments (130ºC, pH=10, 150ºC and 170ºC during 30min) performance of waste activated sludge collected from urban wastewater plants with untreated sludge samples. The results indicated that there was positive effect on solubilization rates and mechanization when thermal pretreatment was added. Particularly, the 170ºC treatment led to comparable results in anaerobic digestion performance increase: about 80% improvement in removal of matter and in biogas yield.

Climent et al., (2007) investigated the thermal pretreatment at low temperatures between 70ºC to 134ºC prior to thermophilic digestion and revealed an increase of 50% in biogas production at 70ºC with 9h. No effect for high-temperature treatment.

Chemical Pretreatment:

Saktaywinet al., (2005) found that around 60% of soluble COD generated due to ozonation was biodegradable at the early stage of ozonation, while the remaining soluble organic matter was refractory. Yeom et al.,(2002), showed that when the ozone dose was 0.1 g O3/g TSS, the biodegradation was about 2-3 times greater compared with raw sludge in both aerobic and anaerobic conditions for 5 days.

Thermochemical Pretreatment:

Kim et al., (2003), compared the four pretreatment methods, they selected optimum conditions for thermal (121ºC for 30 min), chemical (7 g/l NaOH addition), ultrasonic (42 kHz for 120min) and thermochemical (121ºC for 30min, 7g/l NaOH addition) pretreatments. Other thermochemical experiments have been studied with hydrogen peroxide and Fenton‘s reagent (Valo et al., 2004), but the result showed no evident improvement in COD solubilization and was lower than the level obtained after the thermal treatment at 130ºC.

Mechanical Pretreatment :

Poornima Devi et al., (2014) proposed, excess sludge disintegration by energy intensive processes like mechanical pretreatment is considered to be high in cost. In this study, an attempt has been made to disintegrate excess sludge by disperser in a cost effective manner by deflocculating the sludge using sodium dodecyl sulphate (SDS) at a concentration of 0.04 g/g SS. The disperser pretreatment was effective at a specific energy input of 5013 kJ/kg TS where deflocculated sludge showed higher chemical oxygen demand solubilisation and suspended solids reduction of 26% and 22.9% than flocculated sludge and was found to be 18.8% and 18.6% for former and latter respectively .

Among these methods, mechanical pretreatment of sludge like homogenization has been considered effective for cell disruption. Mechanical homogenization is the dissolution and diffusion of a solid, liquid or gaseous phase in a continuum that is not consulate with that phase. Of late, this has been reported as a sludge pretreatment method, which changes both the rate and extent of sewage sludge degradation in the 9 lipids extraction process. It was mainly developed for stabilization of food and dairy emulsions, and has opened up more and more new application areas (Rai and Rao, 2009). It has several advantages in comparison to other sludge disintegration methods, i.e. no chemical changes or denaturing during cell lysis, easy operation, and high lysis efficiency. The high-energy requirement in this treatment can be reduced by combining with other treatment methods based on different mechanism of action that could allow obtaining higher disintegration (Uma Rani et al.,2012).Extracellular polymeric substances (EPS) are secreted by microorganisms, play an important role in bio flocculation process by interacting with the solids (Kavitha et al., 2013). Hence it is essential to remove the EPS before pretreatment to reduce the organic solids

Bio-Fuel From Sludge:

Eric Williams et al.,(2015) carried out that the sun-to-wheels pathway for bio fuel production is currently inefficient compared to PV. An idealized crop based bio fuel with maximum photosynthetic efficiency and 100% utilization of co-products can only achieve a system efficiency of around 0.35%. In comparison, current PV sun-to wheels efficiency is about 5.4%. The current net efficiency to produce motive power from silicon photovoltaic modules is estimated at 5.4%, much higher than 0.03% efficiency for corn based bio-ethanol.

Olkiewicz et al.,(2014) proposed the effects of pretreatment on the lipid extraction and biodiesel production from municipal wastewater treatment plant sludge. All types of sludge used in this tests have a significant amount of Palmitic acid (C16:0), stearic acid (C18:0) and oleic acid (C18:1), which are essential for the production of biodiesel. Among the four sledges tested, the primary sludge achieved the greatest lipid (27%) and biodiesel (19%).

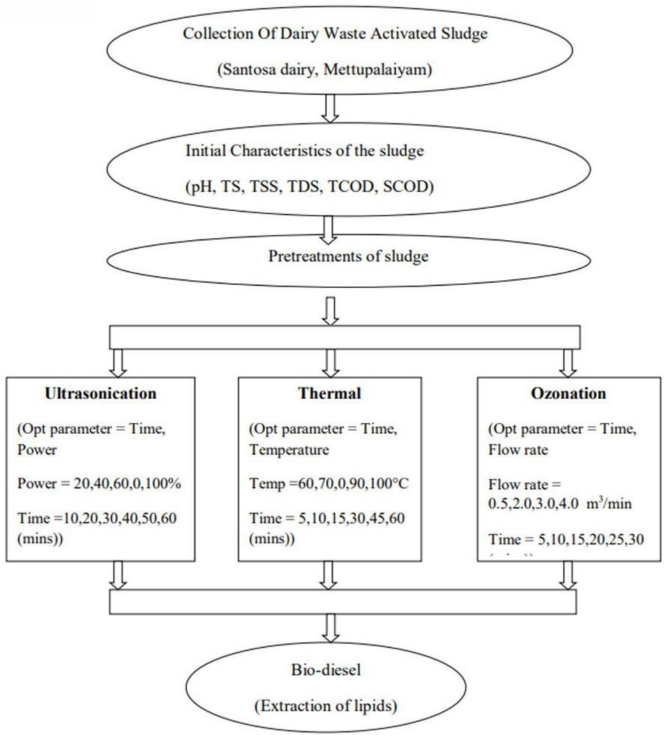
III METHODOLOGY

The lab study has been carried out to analyze the effect of disintegration and the effect of homogenization pretreatment of dairy waste activated sludge and biofuel production was analyzed. The optimum conditions for sludge disintegration have been studied before going to extraction process.

The secondary sludge, produced by an activated sludge process was collected after thickening by floatation in Santosa Dairy industry, Mettupalaiyam. The sample was immediately stored in the laboratory prior to the analysis.

Always wash glass lab ware immediately after use. If a thorough cleaning is not immediately possible, always allow the glassware to soak. If not cleaned immediately some residues may be impossible to remove. Most new glass is slightly alkaline and should be washed and soaked in a 1% HCL or HNO3 solution before wash and rinsed. Never soak for long periods in strong alkaline solutions as it will damage the glass wares. Do not use wire brushes or brushes with a wire core as it can abrade the glass .

The schematic representation of methodology of the work is shown in



CHARACTERISATION OF SLUDGE

The initial characteristics of sludge includes Total Solids (TS), Total Suspended Solids (TSS), Total COD (TCOD), Soluble COD (SCOD), pH has determined using standard methods (APHA, 2005).

Total solids :

Take a clean china dish, wash it and dry it in the oven at 105oC for one hour. Measure the dry weight of china dish and note it as W1. Now take 10ml of dairy sludge in the china dish. Place the china dish containing dairy sludge in the oven at 105oC for one to two hours. Now take out the china dish from oven and cool it in the desiccator. Measure the weight of the china dish with residue as W2.

Total Solids = (W2 – W1) / V

Where,

W1 = Initial dry weight of china dish

W2 = Weight of china dish + residue

V = volume of the sample (ml)

Total Suspended Solids :

Take a clean china dish, wash it and dry it in the oven at 105oC for one hour. Measure the dry weight of china dish with filter paper (0.45µm) and note it as W1. Now take 10ml of dairy sludge and filter using filter paper. Note it as W2 and place the china dish containing filtered dairy sludge in the oven at 105oC for one to two hours. Now take out the china dish from oven and cool it in the desiccator. Measure the weight of the china dish with filter paper as W3.

Total Suspended Solids (%) = (W3 -W2) /V

Where,

W1 = Initial dry weight of china dish + filter paper

W2 = Weight of china dish + residue along with filter paper before drying

W3 = Weight of china dish + residue along with filter paper after drying V = volume of the sample(ml)

Total Dissolved Solids :

Take a clean china dish, wash it and dry it in the oven at 105oC for one hour. Measure the dry weight of the china dish and note it as W1. Filter 10ml of dairy sludge through a clean dry filter paper. Now pour 10ml of filtered sample in to the china dish. Place the china dish containing dairy sludge in the water bath for evaporation. Measure the weight of china dish with residue as W2

Total Dissolved Solids = (W2 – W1) /V

Where,

W1 = Initial dry weight of filter paper

W2 = Weight of filter paper + residue

V = volume of the sample (ml)

Total Chemical Oxgen Demand (TCOC)

10 ml of sample has been taken in a 250 ml reflux flask along with a pinch of mercuric sulphate. 15 ml of sulphuric acid is to be added slowly, followed by 7 ml of 0.25N potassium dichromate solution. The mixture has been refluxed for 2 hours. After cooling, the mixture is diluted twice its volume with distilled water and titrated against 0.25N ferrous ammonium sulphate using ferroin indicator. The endpoint is the appearance of reddish brown color. Calculation were done as follows

Total Chemical Oxygen Demand (mg/L) = (A−B)×N×8000 /V

Where,

A = Volume of ferrous ammonium sulphate used up for blank solution

B = Volume of ferrous ammonium sulphate used up for sample titration

N = Normality of ferrous ammonium sulphate

Soluble Chemical Oxgen Demand (SCOC)

1.5 ml sludge sample was taken in a eppendorf tube and centrifuged at 17000 rpm for 15 minutes.The 1 ml supernatant of centrifuged sample was taken and made up to 10 ml in reflux flask. A pinch of mercuric sulphate and a few glass beads. 15 ml of sulphuric acid is added slowly, followed by 7 ml of 0.25N potassium dichromate solution.

The mixture was refluxed for 2 hours. After cooling, the mixture was diluted to twice its volume with distilled water and titrated against 0.25N ferrous ammonium sulphate using ferroin indicator. The endpoint is the appearance of reddish brown color.

Calculation are done follows,

Soluble Chemical Oxygen Demand (mg/L) = (A−B)×N×8000 /V

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B = Volume of ferrous ammonium sulphate used up for sample titration

N = Normality of ferrous ammonium sulphate

COD Solubilization :

COD solubilization will be calculated using the following formula.

COD Solubilization (%) = SCOD / TCOD * 100

pH :

Initially the electrode is washed with distilled water and wiped off using soft tissue. Now take some amount of buffer solution of pH 9 in a beaker. Immerse the electrode without touching the sides and bottom of the beaker. Ensure whether it shows the pH 9 or not. Again wash the electrode using sludge and wiped off.

PRETREATMENTS OF DAIRY SLUDGE

Before the extraction of lipids, the sludge has been pretreated using pretreatments such as ultra-sonication, thermal and ozonation. The combination of ultra sonication, thermal and ozonation pretreatments also been carried out for effective solubilization of sludge.

Ultrasonication pretreatment

The ultrasonic mechanical disintegration of sludge has been carried out using mechanical Homogenizer having input as power. 200 ml of sludge has to be taken for this pretreatment. The optimizing parameters used in this pretreatment methods are time(0,10,20,30,40,50,60 mins) and power (20,40,60,80,100%) for disintegration of sludge. The total COD and soluble COD for the corresponding time and power has been known in the laboratory and calculated. The graph should be plotted between time and TCOD, time and SCOD respectively. Then from the graph, the optimum power and time has been identified.

Thermal pretreatment

The thermal treatment has been carried out by heating the sludge at increasing temperatures for the particular time. The optimizing parameters used in this pretreatment methods are time (0,5,10,15,30,45,60 mins) and temperature (60,70,80,90,100°C) for solubilization of sludge. The total COD and soluble COD for the corresponding time and temperature has been known in the laboratory and calculated. The graphs were plotted between time and TCOD, time and SCOD respectively and then optimum temperature is identified.

Ozonation pretreatment

The ozonation pretreatment of sludge has been carried out using ozone generator for different flow rate. The generators convert oxygen into ozone by using ultraviolet radiation or by an electric discharge field. The optimizing parameters used in this pretreatment methods are time (0,5,10,15,20,25,30 mins) and flow rate (0.5, 2.0,3.0,4.0 m3 /min) for disintegration of sludge. Ozonation has been shown to prevent mold growth on chees and inactive airborne molds in cheese ripening and storage facilities. Ozone treatment has also been found to be a promising method for reducing the concentration of pollutants in dairy wastewaters. The total COD and soluble COD for the corresponding time and flow rate has been known in the laboratory and calculated. The graphs were plotted between time and TCOD, time and SCOD respectively. Then from the graph, the optimum flow rate and time has been identified

Combination of pretreatments

The combination of pretreatments of sludge has been carried out by optimizing the time and power for the optimum values of ultra-sonication, followed by thermal and ozonation treatments for effective results and influence of biodiesel production

Extraction of lipids

The lipids from the optimized sludge have been extracted by using ethanol as solvent using Folch method where the optimized sludge is filtered (funnel with a folded filter paper). 8ml of a 2:1 chloroform-ethanol mixture was added in the optimized sludge. The sludge was manually suspended by vigorously shaking the tube for a few seconds and 2 ml of 0.73% of NaCl water solution was added. By the phase separation method, the biodiesel and the centrifuged sludge were separated.

IV RESULTS AND DISCUSSION

INITIAL CHARACTERISTICS OF SLUDGE

The initial characteristics of waste activated sludge from Dairy industry were determined using standard methods (APHA 2005) and the results are as shown in table 1.

Table 1 :

S.NO	PARAMETERS	UNIT	VALUE
1	Total solids	(mg/L)	16,000
2	Total Suspended solids	(mg/L)	10600
3	Dissolved solids	(mg/L)	5400
4	TCOD	(mg/L)	13200
5	SCOD	(mg/L)	200
6	Ph	-	7.84

PRETREATMENTS OF SLUDGE

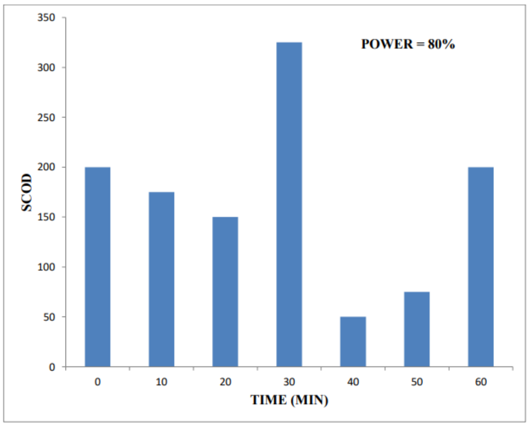
The ultrasonication pretreatment was carried out by sonicator by giving power as input. The TCOD and SCOD values for different power (20,40,60,80,100%) and time (10,20,30,40,50,60 mins) have been tabulated in table 2 and 3 . The optimum time and power has been identified as 30 mins and 80% . which were shown graphically in figure 1 and 2 respectively

Table 2:

Time(mins)/ Power(%)	0	10	20	30	40	50	60
20	13200	4000	3600	400	2800	2400	2000
40	13200	1600	8400	6800	3600	6000	8000
60	13200	1600	800	1600	5600	5200	4800
80	13200	8000	8000	3200	400	4400	7600
100	13200	8000	7600	6400	11600	11200	16800

Ultrasonication pretreatment of sludge (TCOD in mg/l)

Figure 1 :



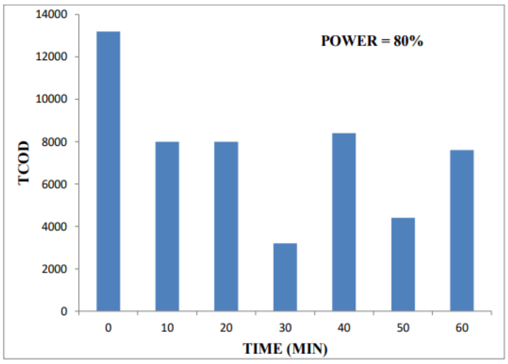
Optimum power and time from Ultrasonication (TCOD in mg/l)

Table 3:

Time(mins)/ Power(%)	0	10	20	30	40	50	60
20	200	100	75	200	75	75	150
40	200	200	25	125	150	125	125
60	200	25	225	225	450	25	250
80	200	175	150	325	50	75	200
100	200	75	400	525	325	225	325

Ultrasonication pretreatment of sludge (SCOD in mg/l)

Figure 2:



Optimum power and time from Ultrasonication (SCOD in mg/l)

Thermal pretreatment

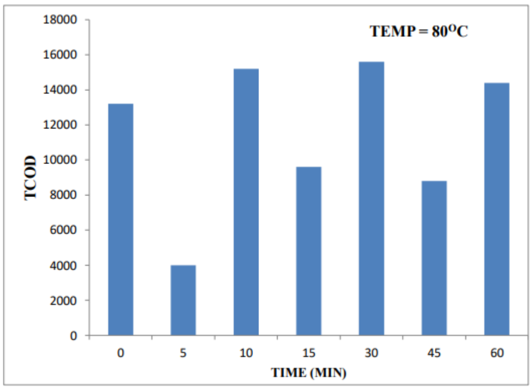
The thermal pretreatment was carried out by heating with higher temperatures. The TCOD and SCOD values for different temperature (60,70,80,90,100°C) and time (5,10,15,30,45,60 mins) have been tabulated in table 4 and 5. The optimum time and temperature has been identified as 5 mins and 80°C. which were shown graphically in figure 3 and 4 respectively.

Table 4:

Time(mins)/ Temp(°C)	0	5	10	15	30	45	60
60	13200	3600	11600	6800	12400	3200	9600
70	13200	4000	15200	9600	15600	8800	14400
80	13200	4400	11200	11600	12400	9600	15200
90	13200	1600	400	3200	7600	10800	6800
100	13200	8400	5600	7200	11600	6800	10800

Thermal pretreatment of sludge (TCOD in mg/l)

Figure 3:



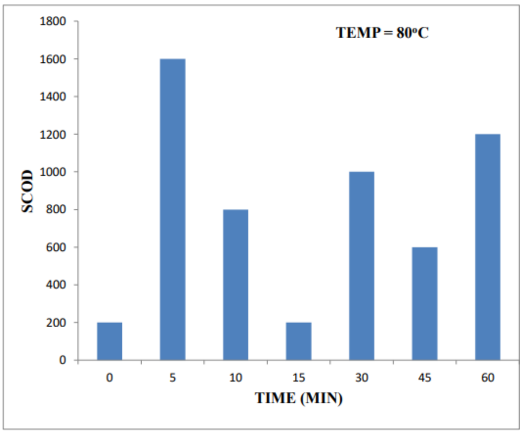
Optimum temperature and time from thermal (TCOD in mg/l)

Table 5:

Time(mins)/ Temp(°C)	0	5	10	15	30	45	60
60	200	200	200	400	800	200	600
70	200	400	200	1000	3200	600	1400
80	200	1600	800	200	1000	600	1200
90	200	400	200	800	1600	1000	1400
100	200	800	5000	1000	1800	200	1200

Thermal pretreatment of sludge (SCOD in mg/l)

Figure 4:



Optimum temperature and time from thermal (SCOD in mg/l)

Ozonation pretreatment

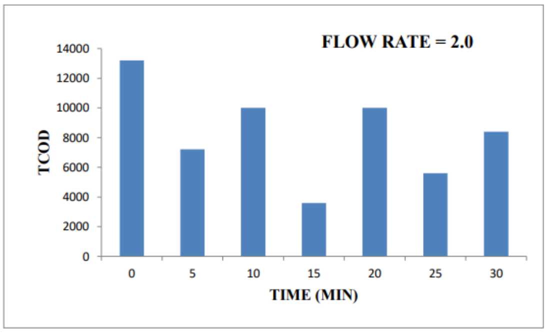
The ozonation pretreatment was carried out by using ozone generator. The TCOD and SCOD values for different flow rates (0.5,2.0,3.0,4.0 m3 /min) and time (5,10,15,20,25,30 mins) have been tabulated in table 6 and 7. The optimum time and flow rate has been identified as 15 mins and 2.0 m3 /min which were shown graphically in figure 5 and 6 respectively.

Table 6:

Time(mins)/ Flow rate(m^3/min)	0	5	10	15	30	45	60
0.5	13200	8400	2400	6800	9200	6400	8800
2.0	13200	7200	10000	3600	10000	5600	8400
3.0	13200	6800	10000	15200	16800	15200	16800
4.0	13200	7200	7600	10800	5200	10400	4400

Ozonation pretreatment of sludge (TCOD in mg/l)

Figure 5:



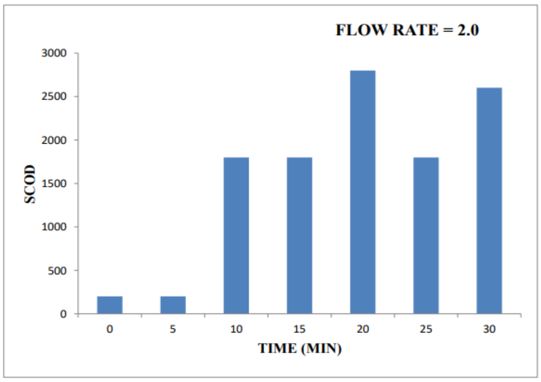
Optimum flow rate and time from ozonation (TCOD in mg/l)

Table 7 :

Time(mins)/ Flow rate(m^3/min)	0	5	10	15	30	45	60
0.5	200	200	200	1000	600	600	800
2.0	200	200	1800	1800	2800	1800	2600
3.0	200	0	200	200	1200	600	1800
4.0	200	1200	600	1200	1400	200	1800

Ozonation pretreatment of sludge (SCOD in mg/l)

Figure 6:



Optimum flow rate and time from ozonation (SCOD in mg/l)

EXTRACTION OF LIPIDS

The lipid from the sludge was extracted by Folch method of extraction of lipids in laboratory. The optimized sludge was added with chloroform-ethanol (2:1) and is filtered by funnel in the apparatus. The biodiesel was extracted by phase separation process in the bottom phase as shown in figure 7.

V. CONCLUSION

There are currently considerable concerns in developing efficient and environmental friendly ways to convert waste activated sludge to bio-diesel, as clean, renewable fuel for multiple utilizations. The initial characteristic of the dairy waste activated sludge has been found out (pH, TS, TSS, TDS, TCOD, and SCOD). The pretreatment of the sludge such as ultra-sonication, thermal and ozonation and combination of pretreatments has been carried out for effective disintegration of flock. The pretreatments from the sludge showed some improving extraction efficiency in the sludge. The optimized values of time, power, temperature, flow rate were found out graphically. After optimizing those parameters, the lipids from the sludge were extracted by using Folch method successfully. The production of biodiesel by this method is comparatively efficient for the use of fuels in vehicles

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