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Production and characterization of biodiesel from microalgae cultivated in municipal wastewater treatment plant.

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ABSTRACT

The combination of microalgae – based biofuel with municipal wastewater treatment has major advantages. The study aims to figure out the ability of producing biodiesel from High Rate Algal Pond (HRAP) constructed to treat municipal wastewater. Facultative algal pond followed by (HRAP) were designed and constructed in sewage wastewater treatment plant Zinin, Giza. The removal efficiency of COD and BOD of facultative pond was 57% and 59.6% respectively. The COD & BOD removal percentage decreased to -50% after HRAP this could be explained by the algal production. The results showed that oil content of biomass collected from HARP was 5% and the biodiesel yield was 70.9%. The fractions of biodiesel produced contained variety of fatty acids such as Palmitic, Oleic and linolenic acids.
Keywords: Algae, biofuel, biodiesel properties, lipid, High Rate Algal Pond

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INTRODUCTION

Petroleum sourced fuels generate pollutants and global warming effects, and are also considered to be unsustainable sources of energy due to their depleting supply. Therefore, it is essential to develop sustainable and eco-friend (clean) energy sources. One of the promising energy sources is biodiesel produced from microalgae, which has several advantages comparing with petroleum diesel origin; it is principally a renewable, biodegradable, less-toxic energy, and essentially a sulfur- and aromatics-free energy [1]. Unlike other biofuel feed stocks (i.e., corn and soy), algae do not compete with existing food commodities, also, The growth of microalgae is extremely fast, microalgae can generally double their biomass within 24 hours. The oil contents in several microalgae exceed over 30–80% by weight of dry biomass [2]. One of the most important merits of this fuel is that it can directly be used in existing diesel engines without any further modifications and can also be blended in a suitable ratio with petro diesel [3]. These facts have been a driving force in the development of bioenergy for commercialization. To cover the increasing of global need of energy, bioenergy production based on photosynthetic organism such as microalgae, will require tremendous amount of water for cultivation [4].It is known that microalgae can be cultivated on various sources of water such as wastewater, sea-water, and fresh-water [5]. Moreover, algae can grow in nutrient rich wastewaters, and may perform nitrogen (N) and phosphorus (P) removal, thus reducing nutrient loads to receiving water bodies [6].Therefore, wastewater has already been used for cultivation microalgae, but the main purpose was focused on nutrient removal [7,8,9]. Recently, cultivation of microalgae in wastewater is being extended to a process for nutrient removal as well as a solution of water and nutrients demanded in mass-cultivation of microalgae as a feedstock of biodiesel [10, 11]. Compared to the activated sludge wastewater treatment process, which introduces, a biological floc, to degrade carbon organic materials to CO_2, algae can assimilate organic pollutants into cellular constituents such as lipids and carbohydrates, this will achieve high pollutant reduction in a more environment-friendly way [12].Algal production has been estimated to yield from 3200 to 14,600 gallons of oil/acre/year [13,2]. 130 fold increase over soybean, the leading feedstock for biodiesel production.

The present study was a part of ongoing research to evaluate a High rate algal pond (HRAP) in cultivation of microalgae on municipal wastewater for biodiesel production as renewable clean energy as well as, its treatment efficiency of municipal wastewater.

MATERIALS AND METHODS

Design and construction of High Rate Algal Pond

As this study part of ongoing project; HRAP is the same design mentioned in article [14]. HRAP made of a closed loop recirculation channel that is typically about 0.3 m deep and 1.5 m^3 volume mixing and circulation are produced by a paddle wheel; also, the HRAP received wastewater from secondary facultative pond 1.0 m deep and 5 days retention time(Figure1).Two hydraulic retention times (HRT) were applied to the HRAP namely 6 and 4 days, operating conditions during the two loads are recorded in Table (1).The surface loading rate didn't vary significantly as the HRT change (Table 1& Figure 2) it only increased by 6g COD/m^2.day by decreasing HRT.

Figure 1: Flow diagram of Facultative and HRAP

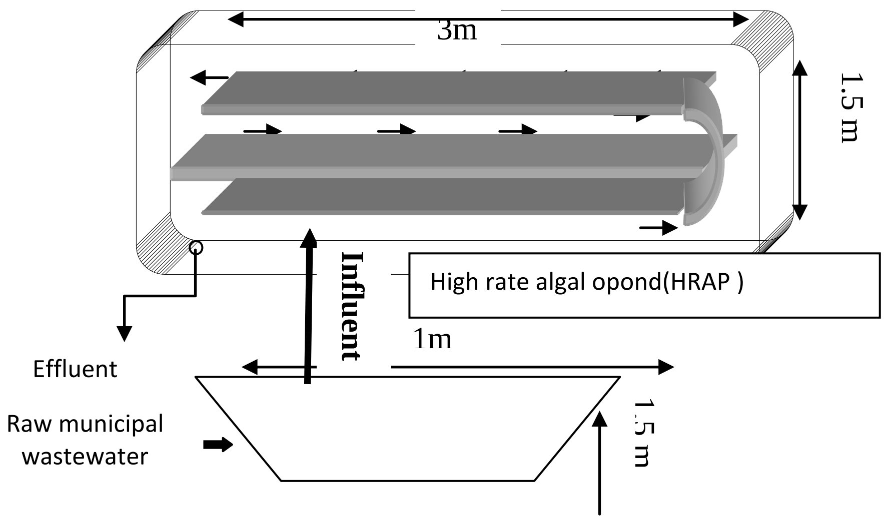
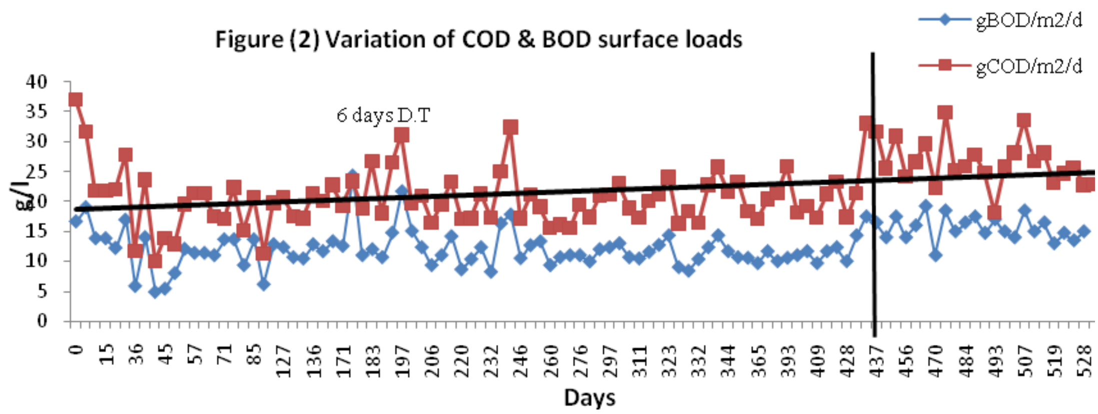


Table 1: Operating conditions of the HRAP

HRT (day)	6	4
Surface OLR (g COD/m^2/day) *	20.3	26.7
Surface OLR (g BOD/m^2/day)*	11.9	15.6

*Average load



Physicochemical Characteristics of raw treated Wastewater

The performance of the integrated system was monitored twice a week for more than one year. The raw wastewater, the facultative pond effluents (effluent 1) and the effluent of HRAP (effluent 2) were analyzed. The physico-chemical analysis covered: Total chemical oxygen demand (COD_{tot}) , soluble chemical oxygen demand (COD_{sol})), Biochemical oxygen demand (BOD_{tot}) , soluble biological oxygen demand (BOD_{sol}), total Kjeldahl nitrogen (TKN), nitrite-nitrogen (NO_2-N), nitrate-nitrogen (NO_3-N), Total suspended solids (TSS), oil and grease and total phosphorus (TP).

Algal community structure

It is well known that it is hard to control HRAP community structure. The most dominant algal species were green group, *Scenedesmus obliquus, Micractinium pusillum, Dictyosphaerium pulchellum* and *Coelastrum sp*. After about three month's operation, the pond began to be dominant with *Scenedesmus quadricauda* [14]. Dry weight was collected on maximum growth and dried at 60Cº.

Determination of total lipid content

The oil extraction was carried out according to Bligh and Dyer modified method [15]

The fatty acid profile of the extracted oil The fatty acid composition of the extracted oil was determined using a Gas-Chromatography (GC) with a split automatic injector and silica capillary column DB-5 (length: 60 m; ID: 0.32mm. Helium was used as carrier gas at a flow rate of 1ml/min. The column was held at 150ºC for 1 min and ramped to 240 ºC, at rate 30 ºC/min, and it was then held at 240ºC, for 30min. Standards were used to give rise to well-individualized peaks that allow the identification of the fatty acids composition.

Biodiesel production

The method for biodiesel production was carried according to [16] The purity of methyl esters in the biodiesel layer obtained by GC analysis according to the method SRPS EN 14103. The conditions of GC analysis were as mentioned above using an internal stander for quantitative analysis [17].

Physical and Chemical Characterization of the Biodiesel

Various analysis was done for characterization of biodiesel produced from HRAP such as Cetane number rand Acid value.

Cetane number

Cetane number (CN) is widely used as diesel fuel quality parameter related to the ignition delay time and combustion quality. Some equations correlate cetane number with the composition of biodiesel. In this search, the correlation formulated by Clements [19] was used:

$$CN = \sum X_{ME} \text{ (wt. \%)}. CN_{ME.} \quad \text{............. ....} (1)$$

Where
CN, is the cetane number of the biodiesel.
X_{ME}, is the weight percentage of each methyl ester.
CN_{ME}, is cetane number of individual methyl ester.

Acid value

The acid value (AV), also called neutralization number or acid number, is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize the acidic constituents in one gram of sample.

Determination of Acid Value/Free Fatty Acid (FFA)

Acid value was determined according to [20]. 2 g of the oil was measured and poured in a beaker. A neutral solvent (a mixture of Petroleum ether and ethanol) was prepared and 50ml of it was taken and poured into the beaker containing the oil sample. The mixture was stirred vigorously for 30minutes. 0.56g of potassium hydroxide (KOH) pellet was measured and placed in a separate beaker and 0.1M KOH was prepared, 3drops of phenolphthalein indicator was added to the sample and was titrated against 0.1M KOH till the color change observed turned pink and persisted for 15minutes.

$$AV = V.xNx56.1/W \text{ oil}$$

Where; V= volume of standard alkali used;
N= normality of standard alkali used;
Woil = weight of oil used
FFA =AV/2.

Wastewater

The wastewater used in this study was derived from Zin in sewage treatment plant in Giza Governorate. The pre-settled sewage which used in this study was under continuous monitoring program under normal operating conditions to put a specific characterization of wastewater.

RESULTS AND DISCUSSION

The chemical characteristics of the domestic wastewater are recorded in Table 2.The average ratio of COD:BOD was 2.1:1. These values are consistent with Metcalf and Eddy's values (2005) [21], who stated that for domestic sewage which can be treated using a variety of biological treatment methods, which vary from 2 to 1.5.The ratio of inorganic N/P ratio in wastewater is 12; this value is close to the optimal inorganic N/P ratio for freshwater algae growth which was suggested to be in the range of 6.8–10 [22, 23].

The results recorded in Table 2 showed that the HRAP removal efficiency of carbon, presented by COD and BOD didn't change significantly during the two different loads. The removal efficiency of COD and BOD of facultative pond was 57% and 59.6%, respectively during the first load and almost the same during the second load (Figures 3&4).

Table 2: Characteristics of Raw wastewater and Ponds effluents

Parameter	Units	Influent	Effluent 1*	Effluent 2**	
				6hrs D.T	4hr D.T
pH		7.5±0.3	7.7±0.3	8.8±0.6	8.2±0.4
COD tot	mg/l	354±78	148±47.8	216.2±64.8	241±55
COD sol	mg/l	168±51	72.9±23.8	100±26	141.1±39
BOD tot	mg/l	207±53	80.3±28.3	115.6±44.7	124.7±38.9
TSS	mg/l	185±44	71.5±26.1	110.7±71.6	117±38.6
TKN	mg/l	48±9.5	40.5±10	31.5±13	39.1±3.8
Ammonia	mg/l	24±4.2	19.8±4	14.3±5.8	16.6±2.9
Nitrite	mg/l	0.09±0.2	0.15±0.3	0.4±0.5	0.05±0.02
Nitrate	mg/l	0.22±0.3	0.5±0.5	0.6±0.6	0.6±0.3
Phosphorous	mg/l	1.9±0.7	1.1±0.5	1.4±0.6	1.6±0.4

*Facultative pond effluent' ** HRAP pond effluent

Figure (3) COD removal effeciency

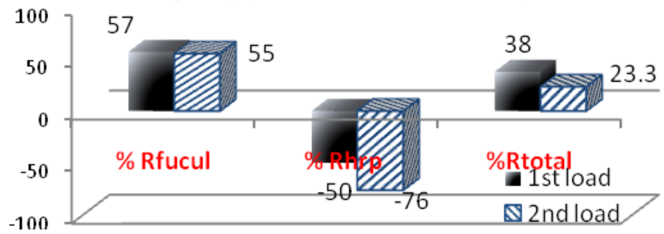
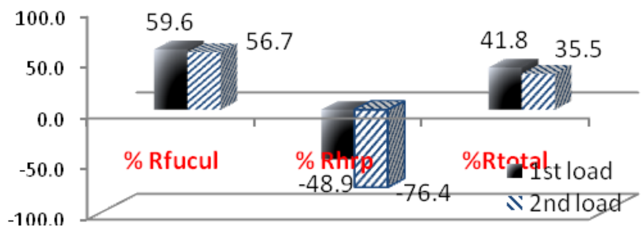
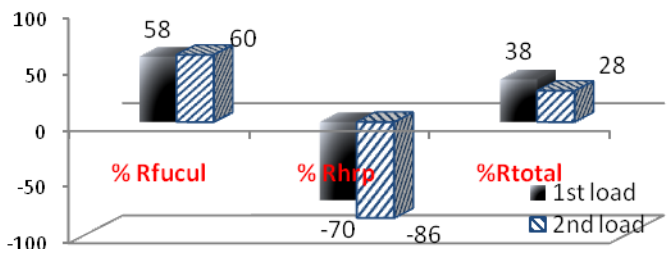


Figure (4) BOD removal effeciency



Figure(5) TSS removal effeciency



The COD & BOD removal percentage decreased to -50% after HRAP this could be explained by the algal production, also, TSS decreased to -70% in the first load and -86% in the second load, thus we can conclude that the algal biomass production increased in the second load (Figure 5). Performance of the integrated system (Figures 3-5) showed that COD, BOD & TSS average removal percentage was 38, 42 &38% during first load and slightly decreased to 23, 35 &28 %, respectively.

Total lipid and its composition:

The total lipid percentage of HRAP community was 5% ±2.4 which is the average reading. The GC analysis for the fatty acid composition of total lipid showed the presence of Palmitic acid (C16:0), Oleic acid and Linolenic acid in high percentage, 34%, 10.3% and 13.8% respectively. Such oil is promising for biodiesel production.

Biodiesel production and characterization:

The yield percentage of biodiesel produced from HRAP community oil through conventional acid transesterification method was 70.6%.with purity percentage 85% according to GC-analysis. The color of obtained biodiesel was brownish yellow.

The GC analysis of the biodiesel as shown in table (3) revealed that its major compositions of saturated and mono-unsaturated fatty acids. The high percentage of Palmitic acid methyl ester (C16:0, 28.7%) prove the high stability of such biodiesel [25, 26]. Low percentage of fatty acids with carbon chain more than 18, means low viscosity of produced biodiesel [27].

Table 3: Fatty Acids Profile of Biodiesel from algal biomass oil.

Fatty acids	Common name	Mass Fraction (%)
C:10:0	Capric acid	1.33
C:12:0	Lauric	2.74
C:14:0	Myristic	3.1
C:16:0	Palmitic	28.7
C:18:0	Stearic acid	5.6
C:16:1	Palmetolic	1.3
C:16:2	Hexadecadienoic	2.2
C:18:1	Oleic	15.1
C:18:2	Linoleic	5.4
C:18:3	Linolenic	13.5
C:20:1	Eicosenoic	3.2
C:22:0	Behenic	1.3
C:24:0	Tetracosanoic	1.7
Total fatty acids (%)		85.17
Saturated fatty acids (%)		44.5
Unsaturated fatty acids (%)		40.67

Table 4: Certain characteristics of oil and biodiesel

Selected properties	Oil	Biodiesel	Biodiesel ASTM
Acid value (mg KOH)	22	0.5	≤ 0.5
Free fatty acid %	11%	0.25%	-
Cetane number	-	44	40-55

The calculated Cetane number (CN) of biodiesel obtained by using equation 1 was equal to 44 table 4.

Higher the cetane number means the fuel has better ignition quality. Higher cetane number indicates shorter time between the initiation of fuel injection and the ignition. This results in higher combustion efficiency and smoother combustion [28].

The determination of acid value of HRAP community oil and that of biodiesel revealed high decreasing from 22 of oil to 0.5 of biodiesel obtained by acid transesterification reaction. This result agree with the acid value of biodiesel according to ASTM due to a good quality of biodiesel produced from the oil of HRAP community biomass.

CONCLUSION

Biodiesel produced from HRAP community biomass has high percentage of palmitic acid methyl and high cetane number, means the fuel is not liable to degradation with high combustion efficiency. The low value of acid value and low viscosity increase the advantages of obtained biodiesel for blending with petroleum diesel to reduce the consuming of diesel.

Recommendations

-The biodiesel produced from HRAP could be blended in a suitable ratio with petro diesel.
-Investigation on the characterizations of the blended samples.

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