Advance Treatment of Wastewater Generated During Biodiesel Production

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Abstract— Biodiesel is having a great importance recently due to lack of available conventional energy resources. To complete the demand of energy it is required to find alternative energy source that serve the energy need and emit lower pollutants. This work involves production of biodiesel by alkali catalysed transesterification process and generation of wastewater by wet washing and treatment of wastewater. The wastewater involves various components like soaps, salts, catalyst, methanol, glycerol etc. By applying Advance treatment technique, we can reduce biological oxygen demand (BOD), chemical oxygen demand (COD), oil and grease, total dissolve solids (TDS), total suspended solids (TSS), chloride, ammoniacal nitrogen, total solids (TS) etc. In this work, UV/H_2O_2, Fenton reaction and Photo-Fenton method are applied for wastewater treatment and the results are compared.

Keywords: Biodiesel, Alkali Catalysed Transesterification, Wet Washing, Primary Treatments, Secondary Treatments, Advance Treatments, Photo-Fenton

I. INTRODUCTION

Biodiesel is a mixture of fatty acid alkyl esters, which is made from a vegetable oil and animal fats.Petrochemicals sources supplies Majority of the energy that is needed by world. The amount ofthese sources is finite and it will be consumed shortly. Due to high energy demand in the world and the pollution problem caused, it is necessary to develop a new renewable energy source. Biodiesel is biodegradable, non-toxic and has low emission of pollutants as compared to petroleum fuels. Biodiesel is carbon-neutral. Waste cooking oil is considered a good alternative because it is inexpensive. E.U. state occupies 89% of biodiesel from which 1.9 billion (51%) biodiesel is produced by Germany. Due to increase in population, usage of waste cooking oil generated in homes and restaurants is increasing rapidly.

Biodiesel production process is based on alkali transesterification of oily feedstock. The main process steps are as follows: transesterification reaction, the separation of the ester phase from the methanol/glycerol phase, wet washing, the separation of biodiesel from wastewater. It also involves the processing of the crude from glycerol phase through acidification and the separation of glycerol from alcohol. Thus, purification of crude biodiesel and the recovery of the excess alcohol and glycerol are required to improve the biodiesel quality and to reduce the biodiesel production costs. Crude biodiesel can cause problems and there is a limitation of it .In the operation of adiesel engine such as plugging of filters, coking on injectors, engine knocking is often occurs. A number of technologies for the purification of biodiesel are commercially available.

For purifying crude biodiesel two methods are generally applied: wet washing and dry washing. Relatively expensive membrane separation technologies are used for biodiesel purification, but yet, it's a less convenient method than wet washing. Wet washing is widely used for removing excess contaminants and left chemicals from biodiesel. Dry washing uses an ion exchange resin or a magnesium silicate powder to remove impurities. Both wet and dry washing methods were used at commercial scale, but only wet washing fulfilled the requirements of Specific Standard. The washing with hot water and distilled water result in the biodiesel purity of 99%.

The wet washing method yields wastewater called biodiesel wastewater, containing the unreacted oilor fat, catalyst, salts, soaps, organic impurities, etc. Biodiesel wastewaters can be hazardous to the environment and must not be disposed into sewage systems, rivers or lakes without a prior appropriate treatment. So by applying the advance treatment to biodiesel wastewater hazardous content can be reduce to some level at which it will not affect the crops and living organism.

II. MATERIALS AND METHODS

A. Transesterification Process:

In this process, 200ml of soyabean oil taken into a beaker & heated it up to 60 °C. If temp goes above 60 °C, then it is not feasible for the reaction with methanol. So, the range between 50-60 ℃ is allowable for the reaction. Then 2 gm NaOH added into the 50 ml methanol & stirred it to dissolve all the NaOH. Then added the mixture of methanol & NaOH into the heated cooking oil & heated the mixer for 1 hour with continuous stirring. Fed the mixer into the separated funnel for approximately 24 hours, two layers (Biodiesel & Glycerol) areseparated as the upper layer consist of Biodiesel & bottom layer consist of Glycerol.

B. Wet washing of Biodiesel:

Distilled water has been poured into the biodiesel that was separated from transesterification process. The process was quick, after pouring water intothat bio diesel, after some time it turned out into thetwo layers, the upper was the pure biodiesel and thelower was the wastewater containing the impurities.

C. Advance Wastewater Treatment

1) Hydrogen Peroxide and Ultraviolet Radiation (H_2O_2/UV)

In this process, the biodiesel wastewater is fed into the reactor which consists of UV lamp, circulating water pump and magnetic stirrer. Then gradually added the hydrogen peroxide. Initially, the concentration of hydrogen peroxide fixed and vary the time. From which the optimum time is obtained. Then, for this optimum time, vary the concentration of hydrogen peroxide. From which the effective concentration of hydrogen peroxide was obtained.

2) Fenton Reaction

In this process, initially the wastewater's pH is adjusted by the dilute sulphuric acid(H_2SO_4). The range of pH was between 3-4. Then wastewater is fed into the beaker and the solution of $FeSO_4$*$7H_2O$ (0.2mM) was added and the mixer allow to be stirred for 30 min. From this the optimum Fenton reagent's concentration obtained.

3) Photo-Fenton Oxidation

In this process the optimum concentration from Fenton reaction is used and vary with time. Initiallythe wastewater fed into the photocatalytic reactor then the solution of $FeSO_4$*$7H_2O$ is added into it and stirred it for 1 min and slowly added the hydrogen peroxide. The sample was taken out at aninterval of 5minutes.

Fig. 1: Photo-Fenton oxidation

III. RESULT AND DISCUSSION

A. Hydrogen Peroxide and Ultraviolet Radiation(H_2O_2/UV)

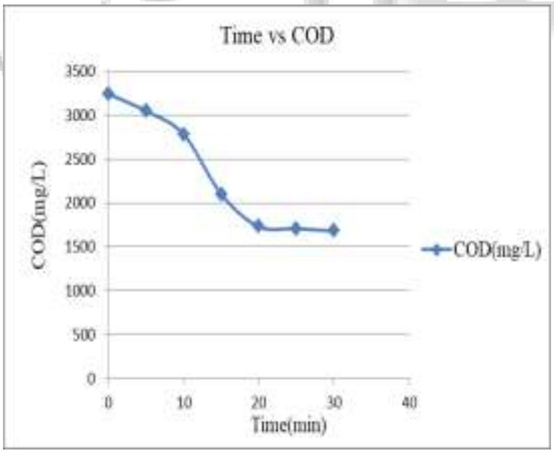

Fig. 2: COD removal profile at a concentration of H_2O_2 = 50mM

Time(min)	COD(mg/L)	% Removal
0	3240	0
5	3047	6
10	2780	14.9
15	2100	35
20	1731	46
25	1708	47
30	1681	48.11

Table 1: Experimental data of COD removal atdifferent time

This table and figure shows the removal of COD. In 20 minutes the COD level decreased rapidly after that the reduction rate is slow down as the amount of H_2O_2 decreased in water. After 20 minutes the degradation may be due to the effect ofUV irradiation.

B. For fix time (30 minutes) and varying concentration of H_2O_2

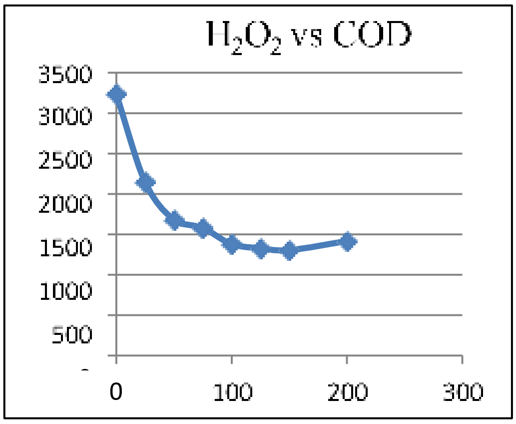

Fig. 3: COD removal profile at differentconcentration of H_2O_2

H_2O_2 (mM)	COD(mg/L)	% Removal
0	3240	0
25	2150	34
50	1681	48
75	1580	51
100	1379	57
125	1328	59
150	1305	59.72
200	1416	56.29

Table 2: Experimental data of COD removal atdifferent concentration of H_2O_2

From the above result take the 30 minutes as the optimum time and for that changing the concentration of H_2O_2 and got the optimum concentration of H_2O_2 = 150mM. After that if the concentration is increased the percentage removal decreased. The excess amount of H_2O_2 reacts with the hydroxyl ions and decreased the overall efficiency.

C. Fenton Reaction

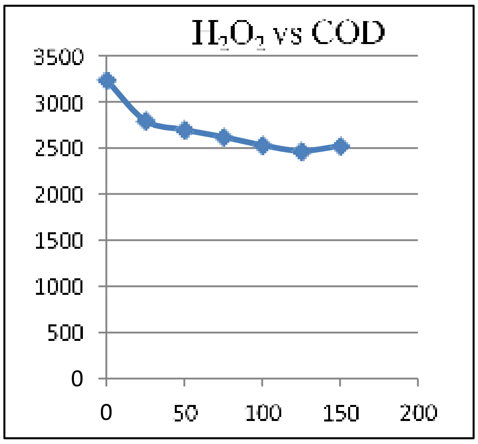

Fig. 4: Effect of concentration of H_2O_2 in Fentonreaction with concentration of Fe2+ = 0.2Mm

H_2O_2 (mM)	COD(mg/L)	% Removal
0	3240	0
25	2796.77	13
50	2699.8	16.67
75	2621	19
100	2531.74	21.86
125	2470	23.76
150	2524	22

Table 3: Experimental data of COD removal byFenton reaction

From this result, the concentration of H_2O_2 is obtained in the presence of iron (Fe^{2+}) salts whichis known as the Fenton-reagent. The maximum removal is obtained at the concentration of Fe^{2+} = 0.2mM and H_2O_2 = 125mM. The excess amount of H_2O_2 reduced the removal efficiency. The optimum pH is in the range of 3-5.

D. Photo-Fenton Oxidation

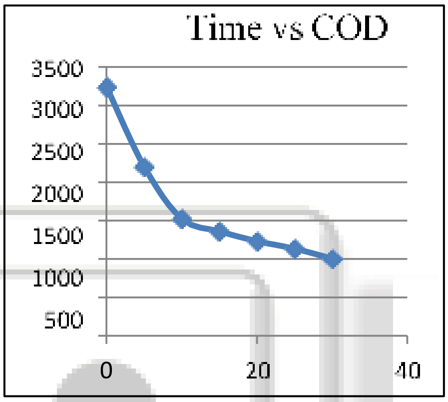

Fig. 5: COD removal profile by photo-Fentonoxidation process

Time(min)	COD(mg/L)	% Removal
0	3240	0
5	2203.2	32
10	1522.8	44
15	1360	58
20	1231.12	62
25	1134	65
30	1004.4	69

Table 4: Experimental data of the photo-Fenton oxidation process at a concentration of Fe^{2+}/ H_2O_2 = 0.2/125 mM

From the Fenton process, the concentration of Fenton reagent is obtained. Using that in photo Fenton process which is the combination of Fenton reagent and UV irradiation and collected the 6 sample at interval of 5 minutes. The percentageremoval of COD is high by photo Fenton process compared to rest of two i.e., 69%. So, by using photo Fenton method up to 69% of COD removed at lab scale, the efficiency may be increased at the industry level.

IV. CONCLUSION

The application of Photo-Fenton process for thetreatment of wastewater generated during biodiesel production resulted in conversion of up to 69%, in terms of removal of the COD content. By comparison, UV/H_2O_2 and Fenton reaction resulted in degradation of only 59.72% and 23.76%, respectively. But, significantly irradiation time in UV/H_2O_2 process increases the power consumption; in other words, a high cost. Thesefact shows the importance of the combined actionof H_2O_2, ferrous ions and UV radiation in the Photo-Fenton process for the removal of COD in wastewater. The optimum concentrations of the Photo-Fenton reagents for 69% removal, determined in this work, were: [H_2O_2] = 125mM and [Fe^{2+}] = 0.2 mM. Also the iron content is within the local environmental legislation limit for disposal of iron ions (0.27mM). From aneconomical point of view, in this condition, it is not necessary to apply another process to remove the iron residual, fact that is very attractive.

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