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Photocatalytic Treatment of Oily Wastewater

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Abstract: Oily wastewater is among the most difficult to treat in conventional treatment plants. It is produced in increasing quantities in recent years, which can lead to serious environmental and population health problems if not treated properly. Recently, it was found that treating oily water through the photocatalytic process is a safe and highly efficient method. The present study is concerned with the treatment of the effluents of edible oils plants through the photocatalytic process, using corn oil, sunflower oil, and using titanium dioxide as a catalyst. The most important elements affecting the photocatalytic process were studied, such as the initial concentration of the oil, the concentration of the catalyst, and the number of revolutions per minute of the pump used. The two types of oils were also mixed in different proportions, and the effect of the aforementioned elements was studied. The most important conclusions obtained were as follows. When studying single oil emulsion (corn oil/water emulsion), it was found that increasing the initial concentration reduces the degradation rate. Three initial concentrations of the oil were studied 1000, 2000, and 3000 mg/L. The percentage degradation for these initial concentrations was 92.7, 92.6, and 79.41, respectively. The trend for the number of revolutions per minute (r.p.m) are opposite to this, i.e., increasing rpm leads to an increase in the degradation rate. When mixing oils at a ratio of 50/50, it is found that increasing the number of (r.p.m) leads to a decrease in the degradation rate, while mixing the two oils at a ratio of 75/25, corn oil/sunflower oil, the results are reversed and the oil mix behaves the same way as a single corn oil/water mix. In contrast, it is found that by increasing the initial concentration or the catalyst in the oil mixture, the degradation rate increases. Thus, it is concluded that mixing the effluents of oil wastes has a retardation effect on its degradation.

***Keywords*:** Corn oil, Oily water, Photo-catalysis, Treatment, Wastewater

I. INTRODUCTION

Environmental pollution, particularly water contamination, has emerged as a major problem of global environmental challenges as a result of rapid development of industry and business [1]. The growing amount of organic wastewater discharged into the environment could result in unanticipated environmental issues such as photosynthesis inhibition [2], toxicity, limited biodegradability, and a possible harm to the ecosystem and human health [3, 4].

A variety of technologies has been developed to remove organic pollutants from wastewater, including biodegradation, adsorption, and membrane processes. However, conventional waste water treatment processes are regarded ecologically unfriendly and inefficient for several persistent organic contaminants, making wastewater treatment difficult [5]. As a result, a highly effective and environmentally acceptable technique for removing organic contaminants is critical. Because of its efficient use of solar energy and high degradation efficiency, photo catalytic degradation has sparked scientific and technical interest as a green technology for treatment of polluted streams [6, 7].

Photocatalysis is defined as "acceleration of the photo-reactions rates by exploiting of the photocatalysts". Photocatalysis has been involved in various application fields including agriculture (in removal of residual pesticides), air purification, water splitting, and wastewater treatment. Photo catalysts can oxidize organic pollutants into harmless molecules (such as CO_2 and water) and sterilize bacteria when they are activated by

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photons. In secondary wastewater treatment, this method is highly successful at eliminating harmful organic compounds and killing a range of bacteria and viruses [8].

Because of its photostability, low energy consumption, excellent flat band potential, low cost, and lack of toxicity [9] titanium dioxide (TiO_2) is considered one of the most promising photo catalysts for waste water treatment among the numerous photocatalysts now being explored [10]. Unfortunately, due to its large band gap, TiO_2 can only absorb UV radiation from the sun, which accounts for less than 5% of the overall solar spectrum. The rapid recombination of photo generated electrons and holes in TiO_2 also restricts the usage of photo-generated carriers [11]. A popular and successful method for preventing photoelectrons and holes from recombination is to utilize a photo catalyst in conjunction with a highly conductive material [12, 13].

Vegetable oils and fats are important constituents of foods and are essential components of our daily diet [14]. Vegetable oils are obtained by mechanical expelling or solvent extraction of oleaginous seeds (soybeans, rapeseed, sunflower, etc.) or oleaginous fruit like palm and olive [15].

Huge amounts of oily effluents have emerged due to the increasing demands of edible oils and the expansion in oil plants. Thus, efficient means of oily wastewater should be used for treating such oily effluents and the photocatalytic oxidation process is a prime candidate for that purpose.

Corn oil is a popular vegetable oil in many countries. Because of its pleasant nutty flavor, its good stability, and its popularity for making margarines, corn oil has long been considered a premium vegetable oil. Among all of the vegetable oils, corn oil ranks tenth in terms of annual production, and it represents about 2% of the vegetable oil produced worldwide. The chemical composition of corn oil is distinguished by its high levels of polyunsaturated fatty acids (an average value of 60–75% linoleic acid), and among the commodity vegetable oils corn oil has the highest levels of unsaponifiables (>2%), the highest levels of phytosterols (>1%), and the highest levels of γ-tocopherol (about 0.10%) [16].

Sunflower oil is the second most important virgin oil in Europe but, from the nutritional point of view, the assessment of this oil has become increasingly poorer over the last few years because of the high amount of linoleic acid in traditional sunflower seeds. Today sunflower oil with a high oleic acid content is coming more into the focus of interest since the fatty acid composition is more comparable to rapeseed and olive oil [17].

For their importance, the present study has focused on the use of photo catalytic process to treat oily water polluted by edible oils such as corn oil and sunflower oil using TiO_2 as a photocatalyst. In one set of experiments, corn oily water is treated as an example of a single pollutant oily water. Besides, a dual components oily water is treated under the same operating conditions. The results of the two treatment processes are compared. This will help in making the decision whether to treat streams of single pollutants separately in an oil plant or treat the mixed streams containing more than one pollutant in a single treatment step. Sunflower oil is used as the secondary pollutant with corn oil.

II. MATERIALS AND METHOD

II.1. Materials*:*

The materials used are:
Corn oil and sunflower oil (for preparation of oil/water emulsion).

TiO_2: Anatase type, is used as a photocatalyst (packed and produced by El-Gomhouria Co.)
Sodium lauryl sulphate ($NaC_{12}H_2$) is used as a stabilizer to get a stable emulsion, produced by Al-Nasr pharmaceutical Chemicals Co.

II.2. Method*:*

II.2.1. **Preparation of oil/water emulsion***:*

Using distilled water and edible-grade corn oil, oil/water emulsions are prepared with oil concentrations of 1000, 2000 and 3000 mg of oil/L. First, 500 ml of distilled water was mixed with the required weight of corn oil and 0.5 g of the sodium lauryl sulfate, which serves as an emulsifier, is added. The solution was then diluted in

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a volumetric flask to 1000 ml. The mixture was agitated through a magnetic stirrer for 30 min at maximum speed until a milky white oily water is formed [18].

II.2.2. Establishing the calibration curve*:*

By logging the absorbance data for a variety of emulsions with known concentrations at the wavelength for maximum absorbance (λmax), the calibration curve for oil/water emulsion is created. The value of λmax, was determined using a double beam UV- visible Spectrophotometer (Shimadzu model 1601), Japan, and this value was (930nm) and it was used in all subsequent investigations using the assigned Spectrophotometer. A calibration curve is established, for oil/water emulsions with different concentrations, as shown in Fig. 1 and the values of absorbance, and hence, the oil concentrations (mg/L) of the tested samples are determined.

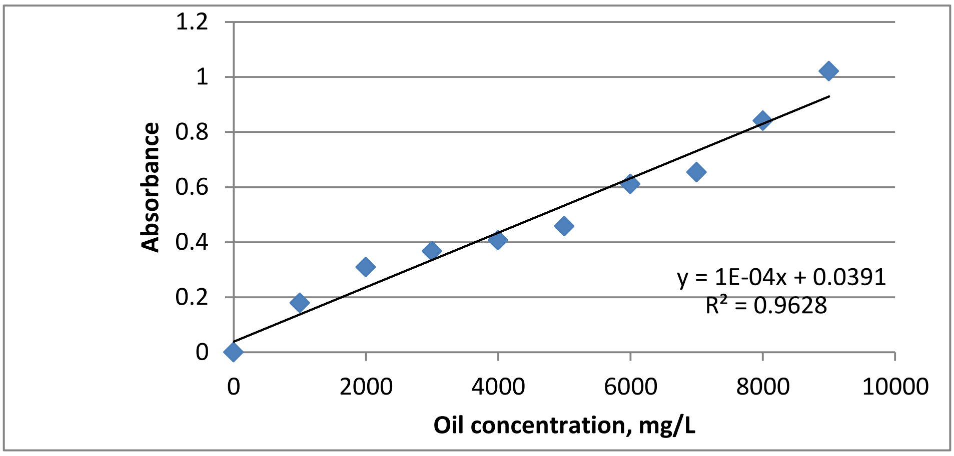

Figure 1: Determination of the correlation coefficient

II.2.3. Experimental Procedure and Operational Conditions*:*

Initially, the emulsion is prepared by adding 1gm of sodium lauryl sulfate to oil/water mix of the required concentration (1000, 2000 or 3000 mg/L) and mixing it using a magnetic stirrer for 30 min until the emulsion becomes homogenous. The emulsion is transferred to the feed- discharge tank, catalyst is added at concentrations 0.5, 1.0 or 1.5 g/L and the plastic pipes are connected to form a closed cycle including the UV lamp, the tubular reactor and the pump is operated at 20 or 60 rpm. Samples are withdrawn periodically every 10 minutes and its concentration is measured on the Spectrophotomer and the results are recorded.

III. RESULTS AND DISCUSSION

The residual oil concentration is measured periodically every 10 minutes and is used as a measure for tracking the photocatalytic degradation of oil in the emulsion. Tests are run on single oil emulsion (corn oil/water emulsion) and on mixed oils emulsion (corn oil/sunflower oil/water emulsion) and results are compared.

III.1. Experimentation on corn oil:

Tests are run on oil/water emulsion to study the effect of circulation rate, initial oil concentration and catalyst concentration on the rate of degradation of oil. A constant concentration of emulsifier, 1g/L is used throughout all the tests.

III.1.1. The effect of rate of circulation (rpm) on oil degradation:
(Using catalyst concentration 1.0 g/L)

Tests are run on oil/water emulsion of oil concentrations 1000, 2000 and 3000 mg/L, using catalyst concentration 1 g/L at two different speeds of rotation; 20 and 60 rpm. The results of this test are presented in Fig. 2 for initial oil concentration 1000 g/L and Figs. 3-5 for the three concentrations used.

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Examination of Fig. 2 shows that oil concentration decreased to 106.01 and 73.21 mg/L when rate of circulation 20 and 60 rpm are used, respectively. This corresponds to a percentage oil degradation of 89.40 and 92.68%, respectively.

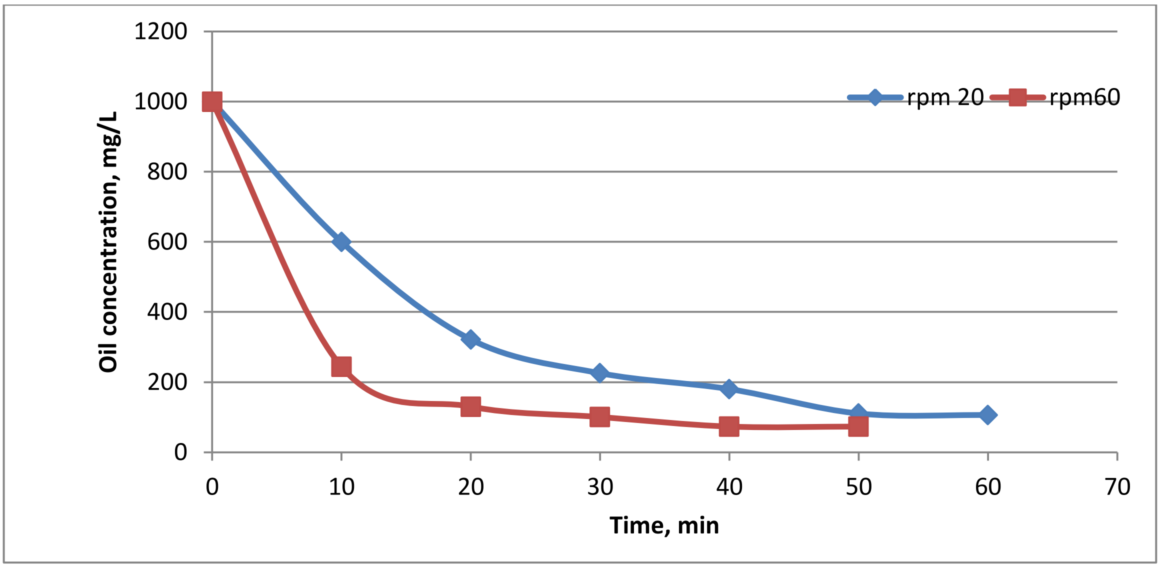

Figure 2: Effect of circulation rate on oil degradation (Initial oil concentration 1000 mg/L)

Tests are repeated under the same conditions except that an oil/water emulsion of oil concentration 2000 mg/L is used. Oil concentration at the end of the test was 253.8 and 146.0 when using circulation rates of 20 and 60 rpm, respectively. Thus increasing the rate of circulation increases the rate of oil degradation. A percentage oil degradation of 87.31 and 92.7 are obtained for rpm 20 and 60 (after 60 min.), respectively. Comparing the results with the previous test shows that percentage oil degradation is slightly lower when oil concentration is increased from 1000 to 2000 mg/L.

The corresponding results for initial oil concentration 3000 mg/L showed that oil concentration at the end of experiments was 461.00 and 276 mg/L for circulation rates 20 and 60 rpm, respectively. The corresponding percentage oil degradation achieved was 84.63 and 90.80, respectively. Comparing the results of these tests indicates that percentage oil degradation is higher for higher values of rpm. This result agrees with the work of Mahmoud, M.A. et al. and Wang, QE, et al. [19, 20] . This is explained as follows: as the rate of circulation increases the number of exposures to UV light per unit time increases thus enhancing the photocatalytic degradation of the oil.

Figure 3 is a cumulative figure for the results given by oil emulsions of three different initial concentration; 1000, 2000 and 3000 mg/L at low circulation rate of 20 rpm. It is clear that: at circulation rate 20 rpm, lower residual oil concentration associated with higher percentage degradation are achieved when using lower oil concentrations (106, 253.8 and 463.76 mg/L for initial oil concentrations 1000, 2000 and 3000 mg/L, respectively.

The corresponding results for higher circulation rate; 60 rpm, are given in Figure 4. It is clear that the same trend is followed as when using circulation rate of 20 rpm; i.e. higher percentage degradation for lower oil concentrations. However, better results are obtained when using higher circulation rate (residual oil concentration of 73.21, 146 and 276.02 mg/L as compared to 106, 253.8 and 84.54 mg/L when using circulation rate 20 rpm). The percentage oil degradation was 92.67, 92.60 and 84.54% for 1000, 2000 and 3000 mg/L oil emulsion. Thus, the highest percentage oil degradation is obtained from an oil emulsion of 1000 mg/L; using a circulation rate of 60 rpm.

The results of the present test are summarized in Fig. 5 for different initial oil concentrations (1000, 2000 and 3000 mg/L and different circulation rates; 20 and 60 rpm. This figure shows that the highest percentage degradation of 92.7% is obtained for emulsion with initial oil concentration 2000 mg/L, using catalyst concentration 1 g/L at 60 rpm. While the least percentage oil degradation is obtained from an emulsion with initial oil concentration 3000 mg/L using catalyst concentration 1.0 g/L at 20 rpm.

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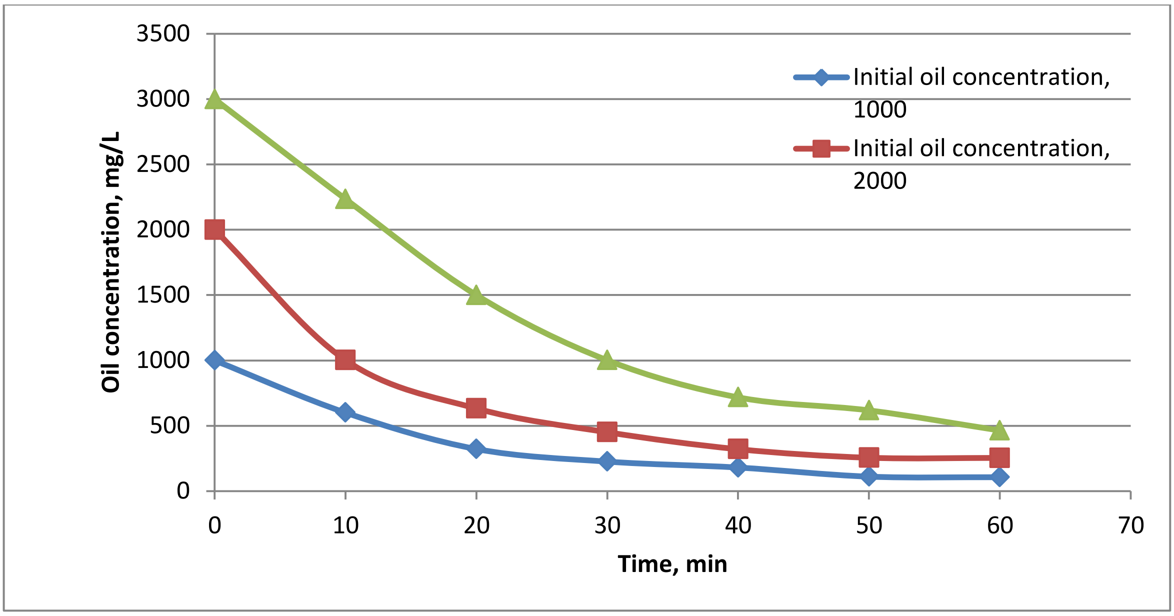

Figure 3: Degradation rate of oil emulsions with different concentrations at circulation rate 20 rpm

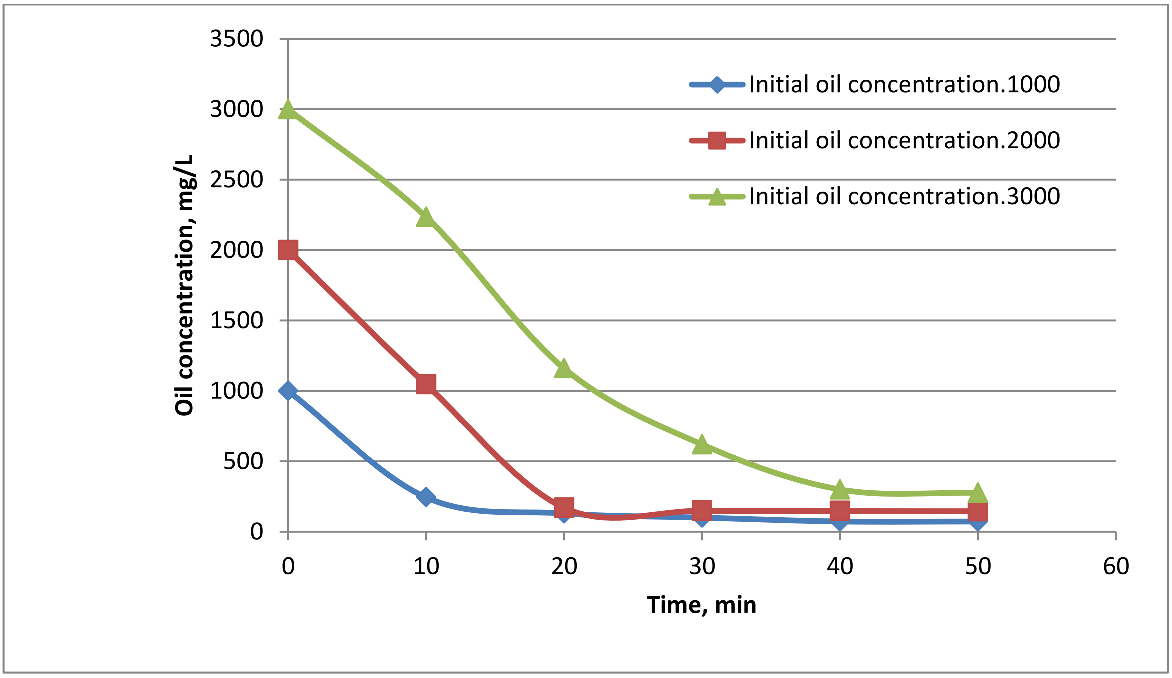

Figure 4: Degradation rate of oil emulsions with different concentrations at circulation rate 60 rpm

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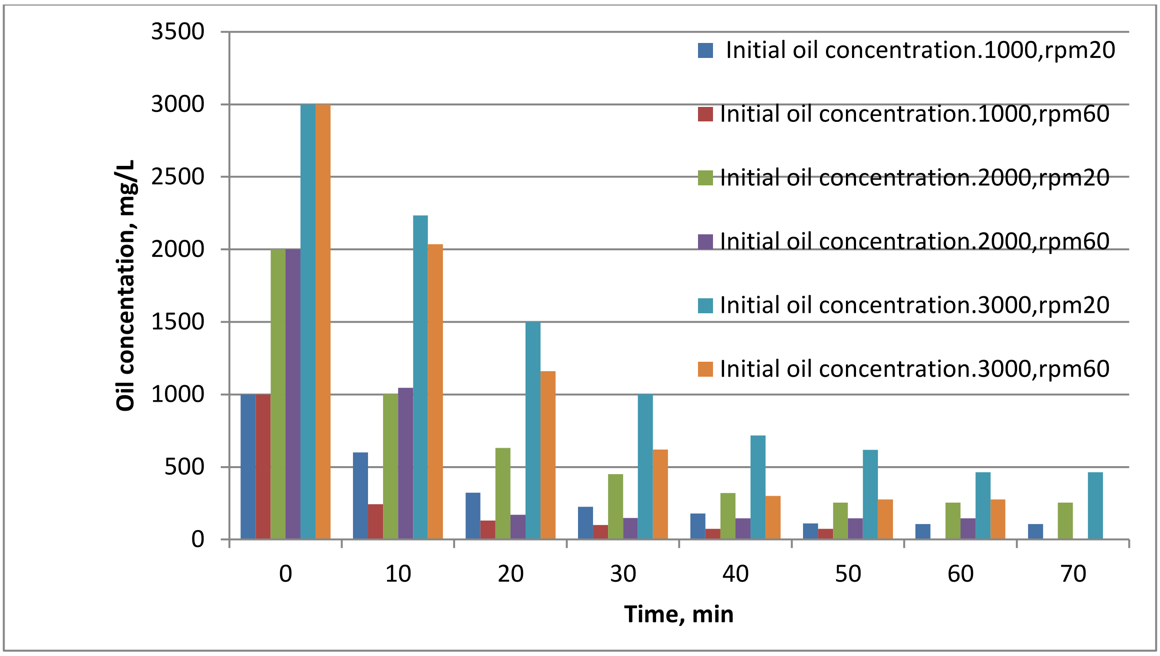

Figure 5: Results of the effect of circulation rate on different oil concentrations

III.1.2. Effect of initial concentration of oil (corn oil):

The photocatalytic degradation test is run on emulsions with initial oil concentrations 1000, 2000 and 3000 mg/L at 2 different catalyst concentrations; 0.5 and 1 g/L.

III.1.2.1. Results for 0.5 g/L catalyst concentration:

The results of corn oil degradation, using 0.5 g/L catalyst at 60 rpm, is represented in Table 1 for different oil concentrations.

Table 1: Effect of initial oil concentration on rate of degradation of corn oil (Catalyst concentration 0.5 g/L, 60 rpm)

Time, (min)	Oil concentration, (mg/L)	Degradation, %	Oil concentration (mg/L)	Degradation %	Oil concentration (mg/L)	Degradation %
0	1000.00		2000		3000.00	
10	550.25	44.97	826.42	58.67	1530.85	48.97
20	280.76	71.92	374.42	81.27	717.25	76.09
30	110.33	88.96	289.65	85.51	550.85	81.63
40	78.81	92.12	235.94	88.20	437.03	85.43
50	78.80	92.12	231.00	88.45	438.00	85.40

Examination of the figures in Table 1 indicates that using catalyst concentration 0.5 g/L, the residual oil concentration in effluent was 78.8, 231 and 438 mg/L when using initial oil concentrations 1000, 2000 and 3000 mg/L, respectively. This corresponds to percentage degradation of 92.12, 88.45 and 85.4%, respectively. Thus, lower residual oil concentration and higher percentage oil degradation are accomplished when treating emulsions with relatively low initial oil concentration. This result agrees with the work of Mahmoud, M.A. et al. and Wang, QE, et al. [19, 20]. This is because the higher the oil concentration in the solution, the more contact time is required to achieve the same degradation rate as at a low oil concentration; which means lower values for percentage degradation.

III.1.2.2. Results for 1g/L catalyst concentration:

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Another set of experiments was run under the same operating conditions except that the catalyst concentration is increased to 1g/L; at rpm 60. The results are presented in Table 2. The results of this set of experiments show that residual oil concentration in effluent was 71.21, 146 and 276.02 for initial oil concentrations 1000, 2000 and 3000 mg/L, respectively. The corresponding percentage degradation was 92.67, 92.7 and 79.41%, respectively. Thus, an increase of initial oil concentration reduces the percentage degradation of oil and the residual concentration of oil. This result agrees with the work given in reference [19].
The same trend of the results is noticed when using catalyst concentration 1.0 mg/L; with slightly better performance expressed as lower values of residual oil and higher values of percentage degradation. Thus, it could be concluded that the photocatalytic degradation of oil is more efficient at lower values of initial oil concentration. This is true for both concentrations of catalyst tested.

Table 2: Effect of initial oil concentration on rate of degradation of corn oil (Catalyst concentration 1 g/L, 60 rpm)

Time (min)	Oil concentration1 (mg/L)	Degradation %	Oil concentration2 (mg/L)	Degradation %	Oil concentration3 (mg/L)	Degradation %
0	1000.00		2000.00		3000.00	
10	244.19	75.58	1046.41	47.67	2236.03	25.49
20	130.16	86.98	170.75	91.46	1160.65	49.99
30	100.54	89.94	149.00	93.04	620.32	66.62
40	73.21	92.97	146.84	92.67	300.36	76.09
50	73.00	92.70	146.60	92.67	276.02	79.41

III.1.3. Effect of catalyst concentration:

This test was run on oil/water emulsions with oil concentration 1000, 2000 and 3000 mg/L; using catalyst concentrations 0.5, 1.0 and 1.5 g/L at circulation rate of 60 rpm.
The results of the test run on emulsion with 1000 mg/L oil concentration are presented in Figure 6. Examination of the results shows that increasing catalyst dose results in lowering the value of residual oil concentration and increasing the percentage oil degradation. A pronounced increase in percentage oil degradation is noticed for higher initial oil concentration of 3000 mg/L (79.41% for catalyst concentration 1.0 g/L as compared to 92.73% for catalyst concentration 1.5 g/L). Thus an increase of catalyst concentration enhances oil degradation and this agrees with the work of Zare, E.N., et al. [21]. This is because reactive species are formed at the surface reaction centers of the catalyst. Hence, a positive correlation is observed between the rate and the catalyst dosage until reaching an optimum catalytic dosage. However, above the optimum limit, a negative impact is observed, and this limit varies with the system under consideration. The presence of excessive catalysts dose may lead to increased turbidity and blocking effect; which results in a reduced luminous transmission through the bulk solution.

A similar test is run on emulsion with initial oil concentration2000 mg/L. Results showed that the residual oil concentration was 231, 146 and 148.8 mg/L for catalyst concentrations 0.5, 1.0 and 1.5 mg/L, respectively. This corresponds to percentage oil degradation of 88.45, 92.67 and 92.7% for catalyst concentration 0.5, 1.0 and 1.5 mg/L, respectively. Thus increasing catalyst concentration increases percentage oil degradation.

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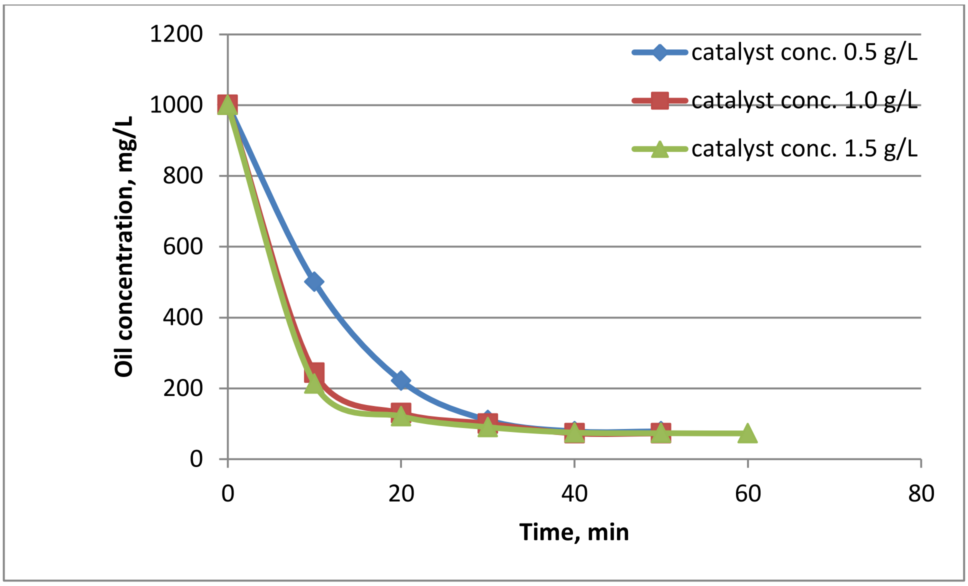

Figure 6: Effect of catalyst concentration on oil degradation (for initial oil concentration 1000 mg/L, 60 rpm)

Tests run on emulsion with initial oil concentration 3000 mg/L showed that residual oil concentrations 438, 276 and 255.5 mg/L were obtained for catalyst concentrations 0.5, 1.0 and 1.5 g/L, respectively. Thus, increasing catalyst concentration results in lowering the residual oil concentration. This agrees with the work of Hsiao, M. C., et al. and Tetteh, EK et al. [22, 23]. The enhancing effect of increasing catalyst concentration is more pronounced for higher initial oil concentration; where increasing catalyst dosage secures the presence of enough active sites on catalyst surface for performing the degradation of all oil present.

Table 3 and Figure 7 collect the results of the effect of catalyst concentration on the photocatalytic degradation of oil; for the three initial oil concentrations tested; 1000, 2000 and 3000 mg/L. It is clear that the lowest residual oil concentration was 73 mg/L and it is satisfied by an oil/water emulsion of 1000 mg/L, using catalyst concentration 1.5 g/L; at circulation rate 60 rpm. The highest percentage degradation was satisfied by an emulsion of initial oil concentration 1000; using catalyst concentration 1.5 g/L.

Table 3: Effect of catalyst concentration on oil degradation (For initial oil concentration 1000, 2000 and 3000 mg/L, 60 rpm)

	1000 mg/L			2000 mg/L			3000 mg/L		
Time (min)	0.5 (g/L)	1.0 (g/L)	1.5 (g/L)	0.5 (g/L)	1.0 (g/L)	1.5 (g/L)	0.5 (g/L)	1.0 (g/L)	1.5 (g/L)
0	1000.00	1000.00	1000.00	2000.00	2000.00	2000.00	3000.00	3000.00	3000.00
10	500.25	244.19	213.14	826.42	930.41	1130.36	1530.85	2036.03	1951.54
20	221.75	130.16	128.32	374.42	350.753	500.61	717.25	1160.65	961.39
30	110.32	100.54	95.56	269.65	201.007	240.91	550.85	620.32	532.98
40	78.81	73.215	80.32	238.94	156.546	151.35	439.03	300.36	361.25
50	78.80	73.00	74.61	231.00	146.21	148.80	438.00	276.02	257.54
60			**73.00**	231.00	146.00	148.80	**438.00**	276.00	255.50

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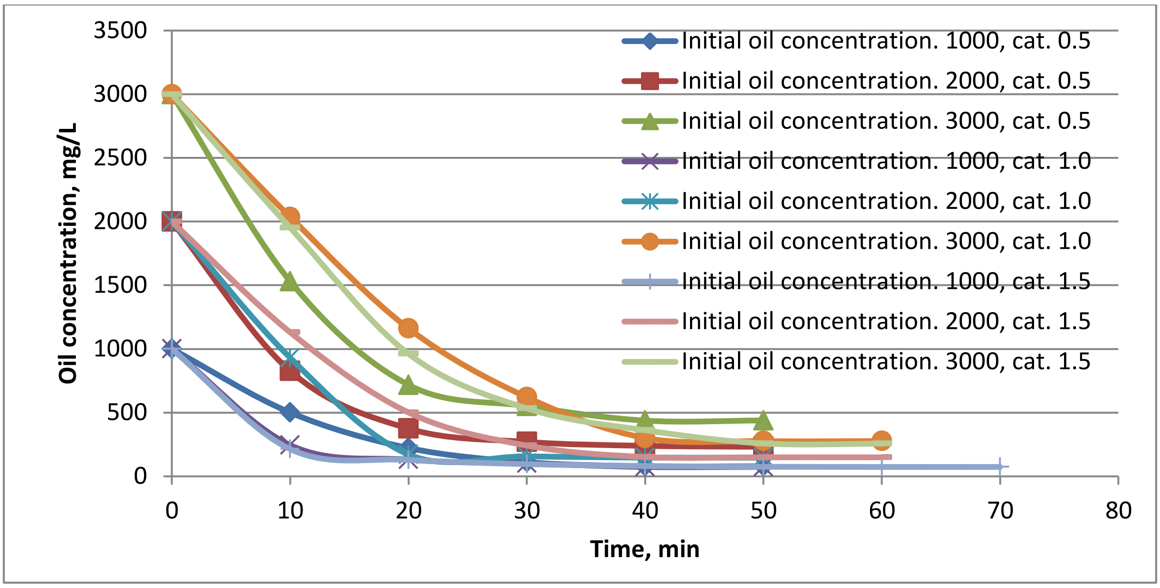

Figure 7: Effect of catalyst concentration on oil degradation
(For initial oil concentration 1000, 2000 and 3000 mg/L, 60 rpm)

III.2. Experimentation on plant oil mix (corn oil and sunflower oil):

In this part experiments are run on emulsions of oil mix/water. The oils used are corn oil and sunflower oil in different mixing ratios; 50/50 and 75/25 corn oil/sunflower oil. This helps in taking the decision whether to dispose and treat the effluents produced from each oil plant separately or mixing it in a single treatment step. The same parameters are studied, as given before for corn oil.

III.2.1. Effect of circulation rate on oil mix degradation:

III.2.1.1. Oil mix 50/50 corn oil/sunflower oil:

The results of this test are represented graphically in Figures 8-10 for oil concentrations 1000, 2000 and 3000 mg/L, respectively at circulation rates 20 and 60 rpm, using catalyst concentration 1g/L.

The results of this test show that: the residual oil concentration from an oil mix with initial oil concentration 1000 mg/L was 289 and 393 mg/L; for 20 and 60 rpm, respectively. Thus, the residual oil concentration increases with increasing circulation rate. The percentage oil degradation corresponding to these values are 71.1 and 60.75% for 20 and 60 rpm, respectively.

The results for a 50/50 corn oil/sunflower oil mix with initial concentration 2000 mg/L are represented in Figure 9. The residual oil concentration was 464 and 795 mg/L for 20 and 60 rpm, respectively. These values correspond to percentage oil degradation of 76.8 and 60.25%, respectively. The results had the same trend as those for initial oil concentration 1000 mg/L, i.e., higher concentration for residual oil is obtained as rpm is increased.

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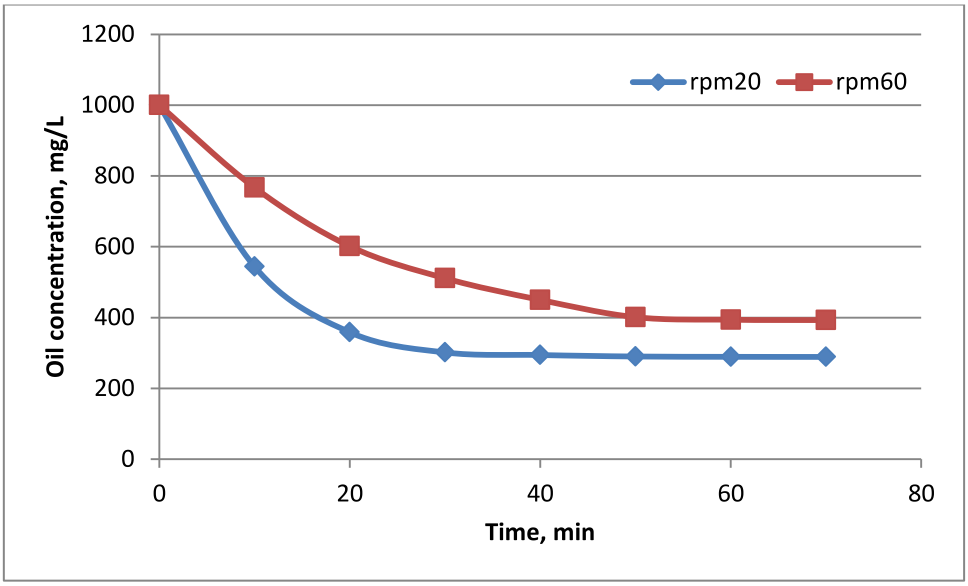

Figure 8: Effect of circulation rate on photocatalytic degradation of oil mix (Initial oil concentration 1000 mg/L, oil mix 50/50 corn oil/sunflower oil)

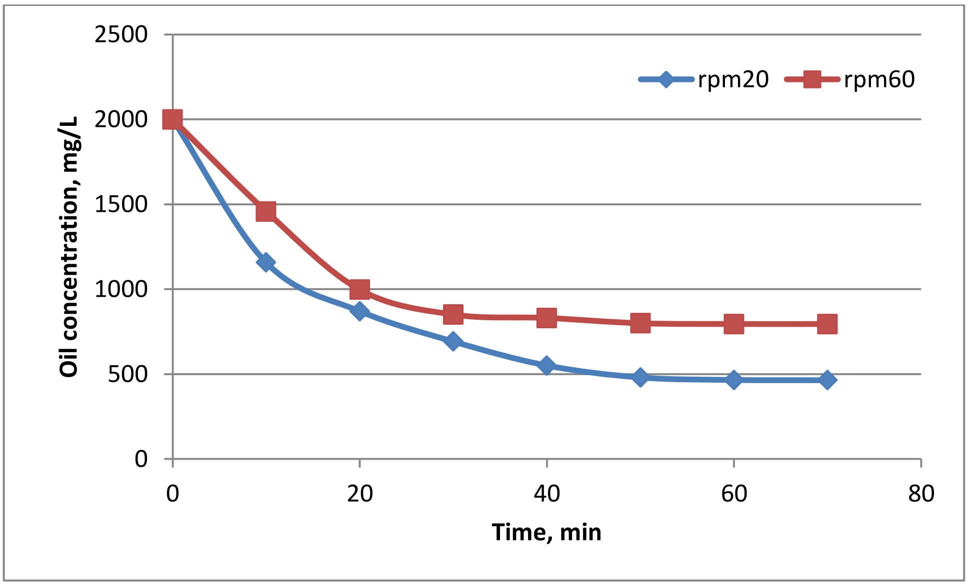

Figure 9: Effect of circulation rate on photocatalytic degradation of oil mix (Initial oil concentration 2000 mg/L, oil mix 50/50 corn oil/sunflower oil)

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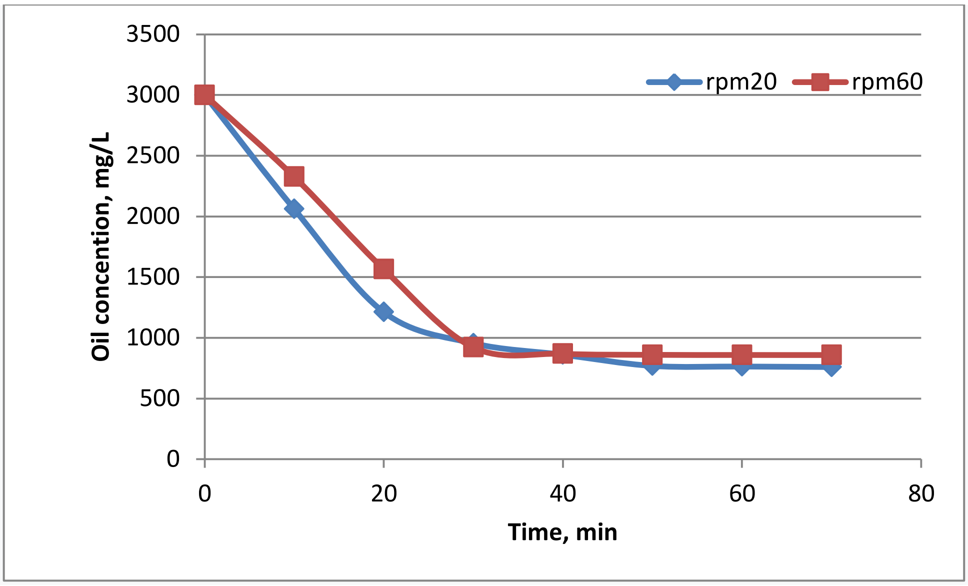

Figure 10: Effect of circulation rate on photocatalytic degradation of oil mix (Initial oil concentration 3000 mg/L, oil mix 50/50 corn oil/sunflower oil)

Table 4: Effect of rpm of oil mix 50/50 corn oil/sun flower oil on oil degradation (For initial oil concentration 1000, 2000 and 3000 mg/L, 20, 60 rpm)

Oil conc.	1000		2000		3000	
Time (min)	rpm =20	rpm =60	rpm=20	rpm=60	rpm=20	rpm=60
0	1000.00	1000.00	2000.00	2000.00	3000.00	3000.00
10	543.98	767.07	1156.74	1457.62	2060.65	2326.12
20	358.74	601.50	870.32	996.90	1211.74	1565.06
30	301.65	511.11	691.89	850.54	955.18	920.98
40	294.39	450.00	550.29	830.65	860.87	868.72
50	290.21	401.20	480.01	799.32	769.03	860.08
60	289.32	393.98	465.65	795.01	763.90	858.94
70	289.00	393.00	464.00	795.00	760.00	858.50
Degradation, %	71.10	60.70	76.80	60.25	74.67	71.38

The addition of sunflower oil to corn oil decreases the poly unsaturated fatty acids; an action which enhances the oxidative stability of the oil mix thus the values of residual oil concentration are higher compared to those obtained from pure corn oil. Higher rpm values enhance the reduction of poly unsaturated fatty acids thus increasing the residual oil concentration.

III.2.1.2. Oil mix 75/25 corn oil/sunflower oil:

Experiments are run on 75/25 corn oil/sunflower oil mixes using three initial oil concentrations 1000, 2000 and 3000 mg/L at circulation rates 20 and 60 rpm and catalyst concentration 1 g/L. The results of this test are represented graphically in Figure 11 for initial oil concentrations 1000. The results indicates that: for oil mix of 1000 mg/L initial oil concentration the residual oil concentration was 289 and 160 mg/L for 20 and 60 rpm, respectively (Figure 11). Thus, the results takes the same trend of pure corn oil emulsion, i.e., increasing

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circulation rate enhances oil degradation. Percentage oil degradation was 71.1 and 84.0% for rpm 20 and 60, respectively.

For initial oil concentration 2000 mg/L, the residual oil concentration was 456 and 464 mg/L for 20 and 60 rpm, respectively. This gives percentage oil degradation of 76.8 and 77.2 %, respectively. For initial oil concentration 3000 mg/L the residual oil concentration was 584.5 and 585 mg/L for 20 and 60 rpm, respectively. The percentage oil degradation was 80.55 and 80.50 for the same order.

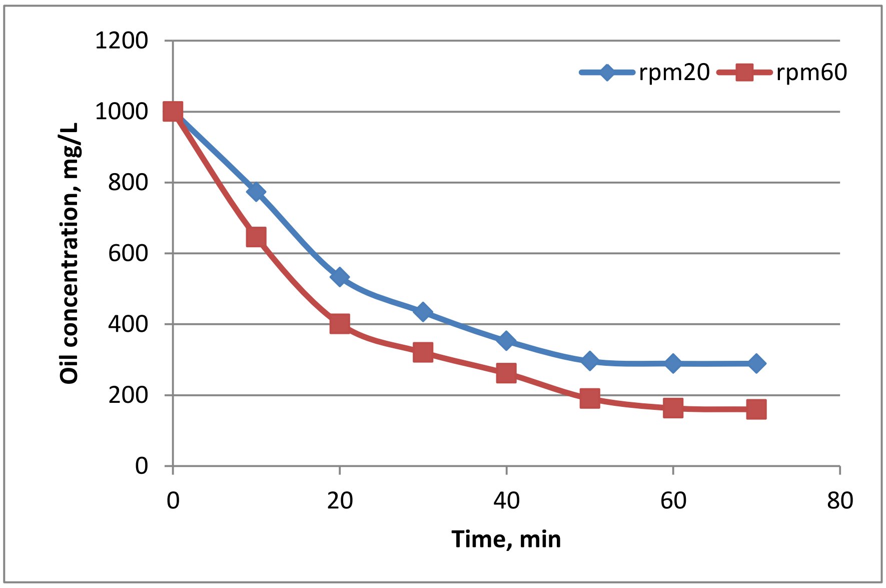

Figure 11: Effect of circulation rate on photocatalytic degradation of oil mix (Initial oil concentration 1000 mg/L, oil mix 75/25 corn oil/sunflower oil)

Table 5 and Fig. 12 collect the data for the effect of rpm on 75/25 corn oil/sunflower oil mix for the 3 initial oil concentrations tested; 1000, 2000 and 3000 mg/L. Examination of the figures in the table indicates that increasing rpm increases percentage oil degradation for the three initial oil concentrations tested.

Table 5: Effect of rpm of oil mix 75/25 corn oil/sun flower oil on oil degradation (For initial oil concentration 1000, 2000 and 3000 mg/L, 20, 60 rpm)

Oil concentration (mg/L)						
	1000 mg/L		2000 mg/L		3000mg/L	
Time (min)	rpm=20	rpm=60	rpm=20	rpm=60	rpm=20	rpm=60
0	1000	1000	2000	2000	3000	3000
10	773.39	645.32	1111.66	933.55	1690.32	1691
20	532.90	400.87	720.32	700.21	1003.44	1030.09
30	434.28	320.25	630.98	645.95	828.30	828.40
40	352.71	261.33	530	560.66	721.08	720.31
50	295.59	190.11	463.94	480	598.06	601
60	288.91	163	457.91	465.12	584.52	585
70	289	160	456	464	584.50	585
Degradation, %	71.10	84	77.20	76.80	80.55	80.50

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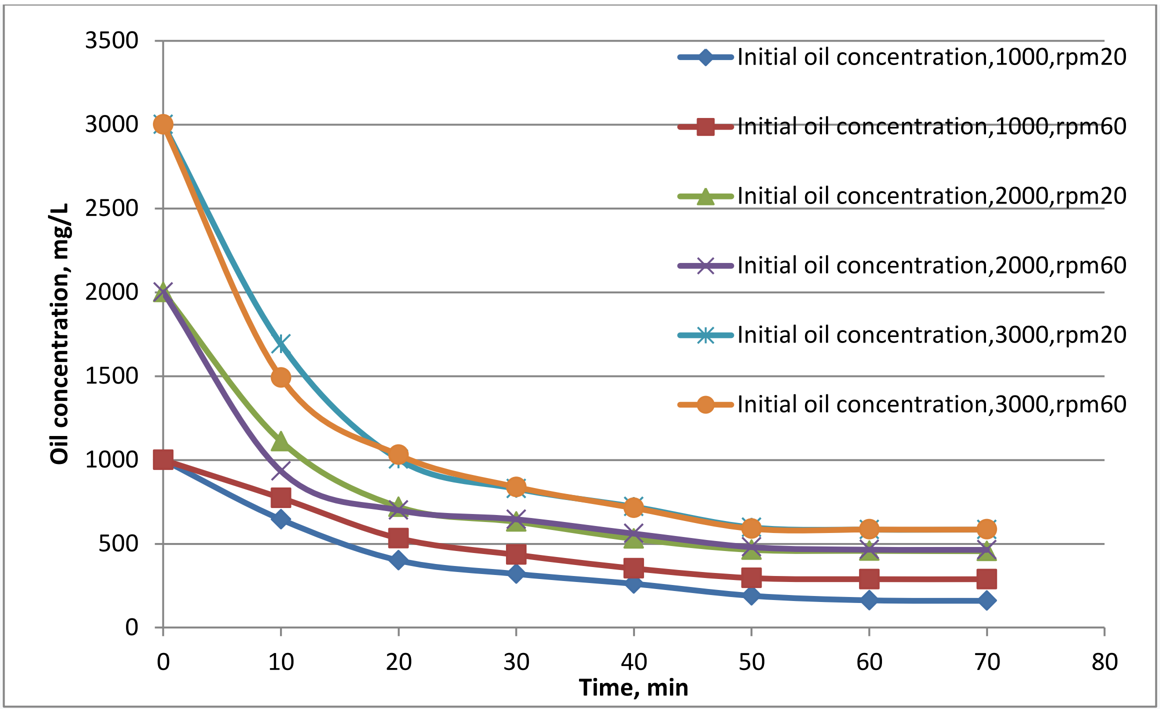

Figure 12: Effect of circulation rate on photocatalytic degradation of oil mix (Initial oil concentration1000, 2000, 3000 mg/L, oil mix 75/25 corn oil/sunflower oil)

III.2.2. Effect of initial oil mix concentration on its degradation:

Tests are run on oil mixes 50/50 and 75/25 corn oil/sunflower oil with initial oil concentrations 1000, 2000 and 3000 mg/L, at circulation rate 60 rpm and catalyst concentration 1 g/L.

III.2.2.1. Oil mix 50/50 corn oil/sunflower oil:

The results of this test are represented as in Figure 13 for the three initial oil concentrations tested; 1000, 2000 and 3000 mg/L.

Examination of the results show that lower residual oil concentration is achieved from an oil mix/water emulsion with low initial oil concentration. The values recorded for residual oil concentration were 393, 795 and 858.5 mg/L for initial oil mix concentrations 1000, 2000 and 3000 mg/L, respectively. These values correspond to percentage oil degradation 60.7, 60.25 and 71.38% for the same sequence. These values of percentage degradation are much lower than their corresponding values obtained when treating corn oil separately (60.7% compared to 92.68 for corn oil individually; 60.25 compared to92.7 for corn oil individually and 71.38% compared to 90.8% for corn oil individually; under the same other operating conditions. Thus, mixing the effluents of oil wastes has a retardation effect on its degradation. This agrees with the work of Frankel, E. and X. Huang [24, 25] .

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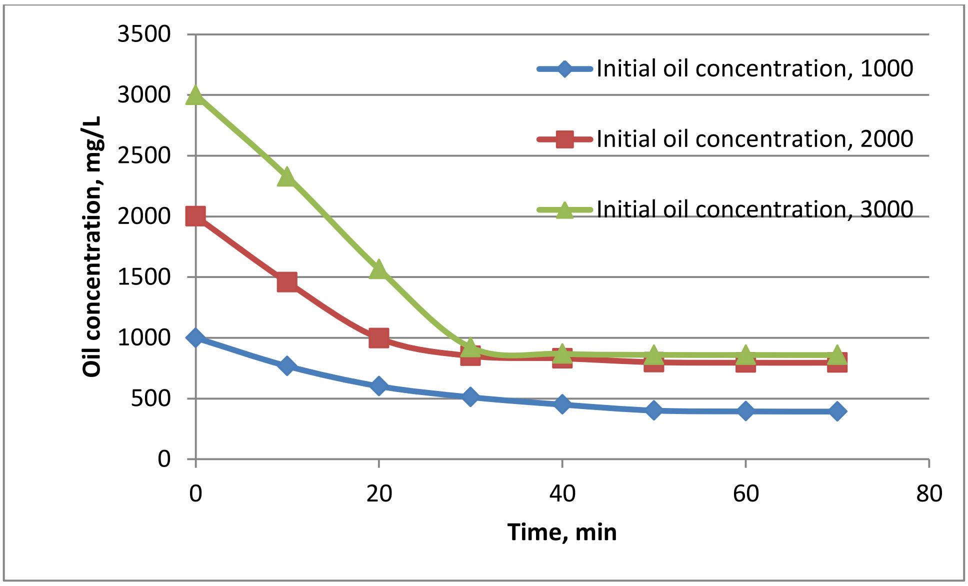

Figure 13: Effect of initial oil concentration of 50/50 corn oil/sunflower oil mix on its degradation

III.2.2.2. Oil mix 75/25 corn oil/sunflower oil:

This test is run on oil mixes with initial oil concentrations 1000, 2000 and 3000 mg/L using 1.0 g/L catalyst at 60 rpm. The results of this test are shown in Figure 14. Residual oil concentrations of 289, 464 and 585 mg/L are obtained from oil mixes with 1000, 2000 and 3000 mg/L initial oil concentration. This corresponds to percentage oil degradation of 71.1, 76.8 and 80.5%, respectively. Thus lower levels of residual oil concentration are satisfied with oil mixes with lower values of initial oil concentration. However, higher percentage oil degradation is noticed with oil mixes with higher initial oil concentrations (71.1, 76.8 and 80.5% for initial oil concentrations 1000, 2000 and 3000 mg/L, respectively.

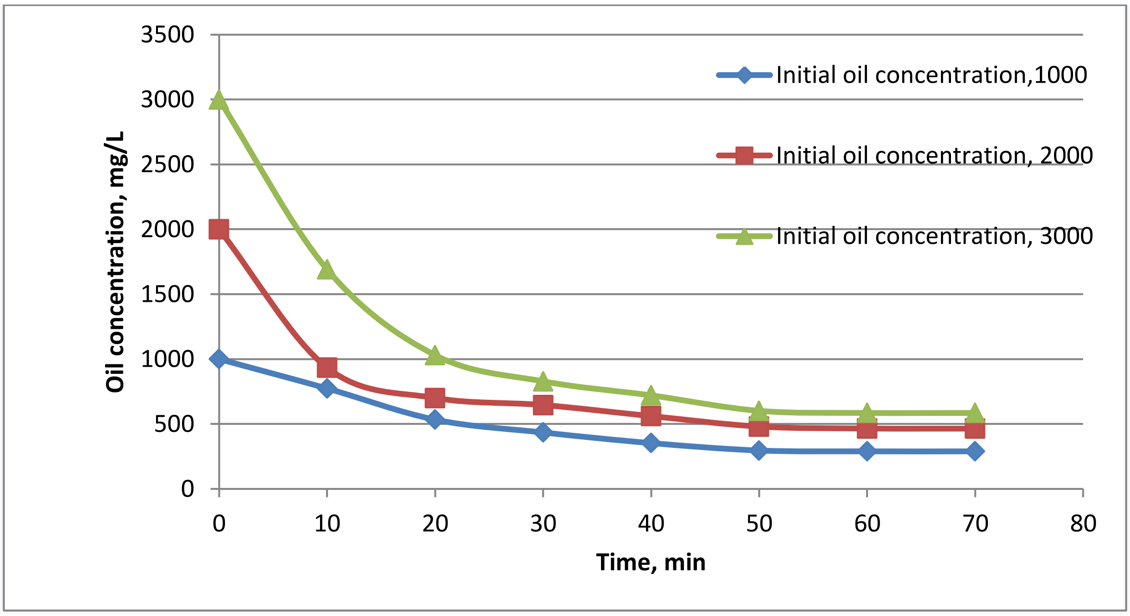

Figure 14: Effect of initial oil mix concentration on its degradation (75/25 corn oil/sunflower oil, rpm = 60)

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Table 6 collects the results of this test for oil mixes 50/50 and 75/25 corn oil/sunflower oil. It is clear that the lowest residual oil concentration is 289 mg/L and it is obtained from an oil mix 75/25 corn oil/sunflower oil of initial oil concentration 1000 mg/L and the highest value (858.5 mg/L) is obtained from an oil mix 50/50 corn oil/sunflower oil with initial oil concentration 3000 mg/L. The highest percentage reduction of oil (80.5%) is obtained from an oil mix 75/25 corn oil/sunflower oil with initial oil concentration 3000 mg/L, and the lowest value is obtained from an oil mix 50/50 corn oil/sunflower oil with initial oil concentration 2000 mg/L.

Table 6: Effect of initial oil concentration of oil mixes 50/50 and 75/25 on its degradation

Oils ratio	50/50			75/25		
Time (min)	Initial oil conc. 1000 mg/L	Initial oil conc. 2000 mg/L	Initial oil conc, 3000 mg/L	Initial oil conc. 1000 mg/L	Initial oil conc. 2000 mg/L	Initial oil conc. 3000 mg/L
0	1000	2000	3000	1000	2000	3000
10	767.07	1457.62	2326.12	773.39	933.55	1491
20	601.5	996.9	1565.06	532.9	700.21	1030.09
30	511.11	850.54	920.98	434.28	645.95	838.4
40	450	830.65	868.72	352.71	560.66	713.31
50	401.2	799.32	860.08	295.59	480	590
60	393.98	795.01	858.94	288.91	465.12	585
70	393	795	**858.5**	**289**	464	585
Degradation%	60.7	**60.25**	71.38	71.1	76.8	**80.5**

III.2.3. Effect of catalyst concentration on oil mix degradation:

This test is run on oil mix 50/50 corn oil/sunflower oil, using catalyst concentrations 1.0 and 1.5 g/L at 60 rpm for three values of initial oil concentrations 1000, 2000 and 3000 mg/L. The results are given in Figures 15-17 for initial oil concentrations 1000, 2000 and 3000 mg/L, respectively. Examination of the results shows that: for initial oil concentration 1000 mg/L the residual oil concentration is 393 and 133 mg/L for catalyst concentrations 1.0 and 1.5 g/L, respectively and the percentage degradation was 60.7 and 86.7% for the same sequence. Thus increasing catalyst concentration increases percentage oil degradation and reduces the remaining oil concentration of an emulsion with initial oil concentration 1000 mg/L

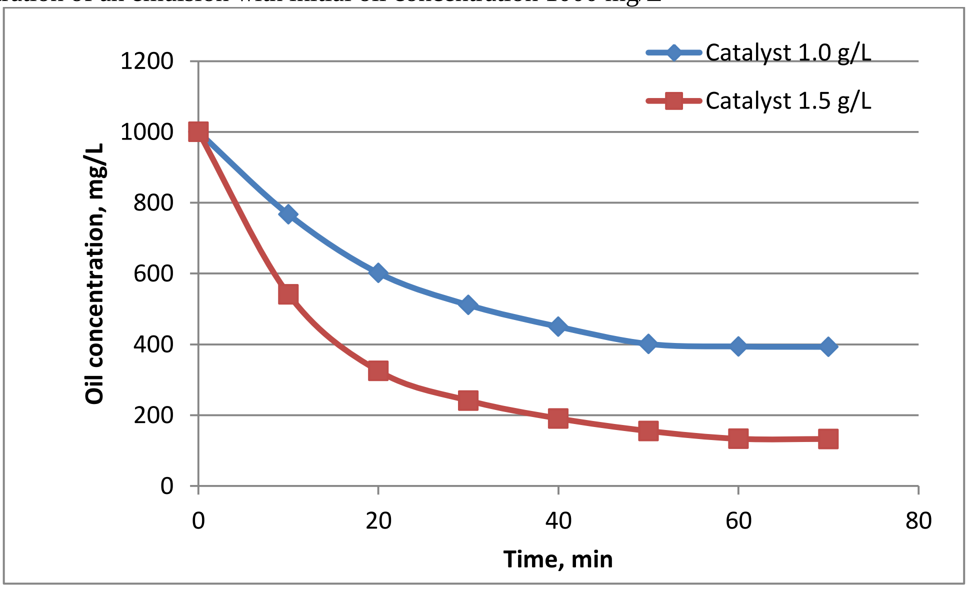

Figure 15: Effect of catalyst concentration on oil degradation (Initial oil concentration 1000 mg/L, oil mix 50/50 corn oil/sunflower oil)

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Experiments run on emulsion with 2000 mg/L initial oil concentration showed a residual oil concentration of 795 and 245 mg/L for catalyst concentrations 1.0 and 1.5 g/L, respectively. The corresponding percentage reduction in oil concentration was 60.25 and 87.45% for the same sequence.

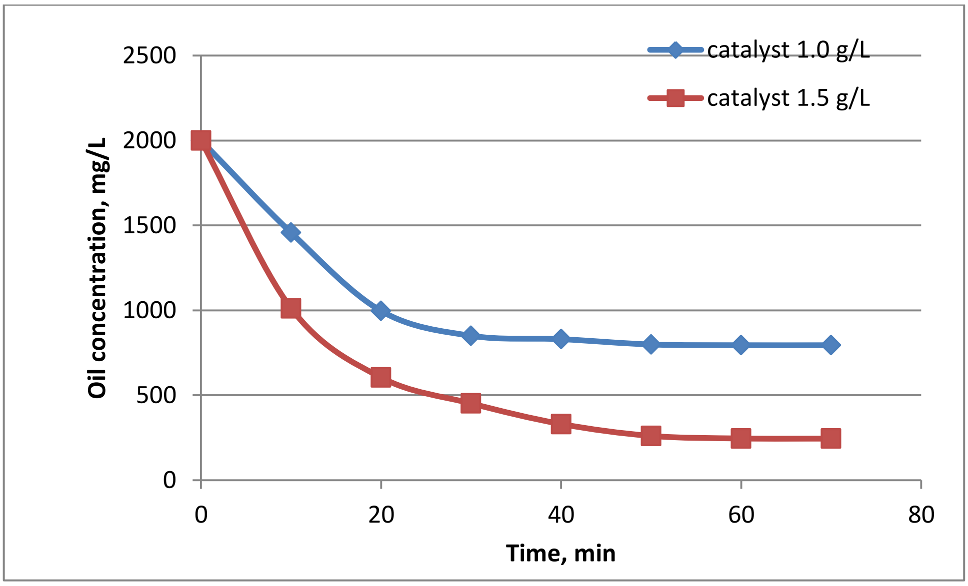

Figure 16: Effect of catalyst concentration on oil degradation
(Initial oil concentration 2000 mg/L, oil mix 50/50 corn oil/sunflower oil)

The results of this test for emulsion with initial oil concentration 3000 mg/L are represented in Fig. 17. It is clear that the enhancing effect of increasing catalyst concentration is more pronounced in the early stages of photocatalytic degradation of oil.

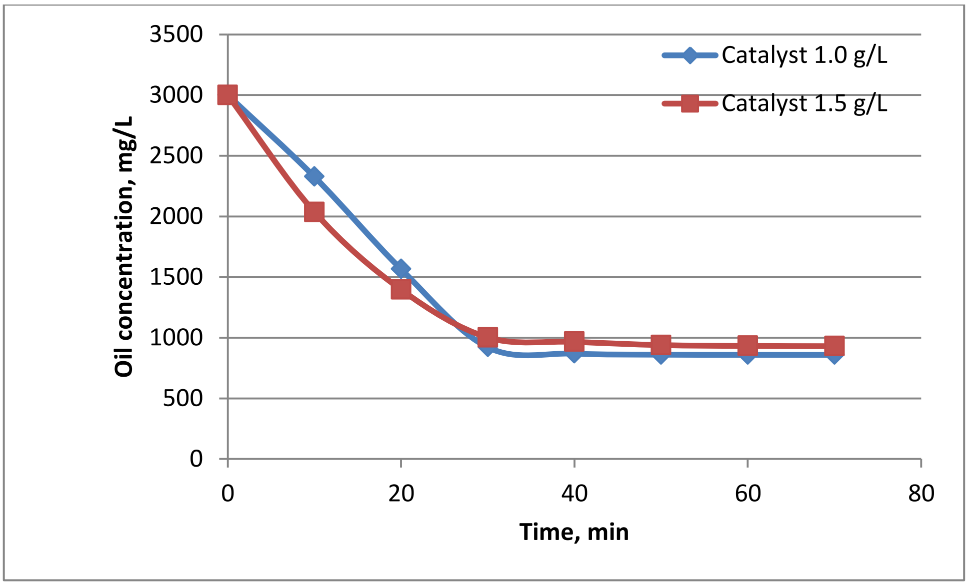

Figure 17: Effect of catalyst concentration on oil degradation
(Initial oil concentration 3000 mg/L, oil mix 50/50 corn oil/sunflower oil)

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Examination of the results of this test indicates that the enhancing effect of increasing catalyst dose is more pronounced for oil mixes with relatively higher initial oil concentrations. This is more clear when increasing initial oil concentration from 1000 to 2000 mg/L.
Comparison of the results of effect of catalyst concentration for single oil emulsion and mixed oil emulsions is given in Tables 7, 8 and Figure 18, 19. For catalyst concentrations 1.0 and 1.0 g/L, respectively. Results for single oilemulsion are include as well. Examination of the figures in Tables 7 and 8 shows that: for single oil emulsion, the highest percentage reduction in oil concentration was 92.70% and it is obtained for an oil emulsion of initial oil concentration 2000 mg/L, using catalyst concentration 1 g/L. and circulation rate 60 rpm. The lowest percentage oil reduction was 79.41% and it is obtained for an oil emulsion of initial concentration 3000 mg/L using catalyst concentration 1g/L and circulation rate 60 rpm.

For oil mix emulsions, the highest percentage reduction in oil concentration was 87.45% and it is obtained for 50/50 corn oil/ sun- flower oil emulsion of initial oil concentration 2000 mg/L, using catalyst concentration 1.5 g/L and circulation rate 60 rpm. The lowest percentage oil reduction was 60.25 % and it is obtained for 50/50 corn oil/sunflower oil emulsion of initial concentration 2000 mg/L using catalyst concentration 1g/L and circulation rate 60 rpm.

Table 7: Effect of catalyst concentration on oil degradation of single corn oil, oil mix 50/50 and 75/25 corn oil and sunflower oil (For initial oil concentration1000, 2000 and 3000 mg/L, 60 rpm, 1 g of catalyst)

1(g) of catalyst/L									
	Single corn oil			50/50 mix oil			75/25 mix oil		
Time(min)	Oil concentration(mg/L)								
0	1000	2000	3000	1000	2000	3000	1000	2000	3000
10	244.19	1046.41	2236.03	767.07	1457.62	2326.12	645.32	933.55	1691.00
20	130.16	170.75	1160.65	601.50	996.90	1565.06	400.87	700.21	1030.09
30	100.54	149.00	620.32	511.11	850.54	920.98	320.25	645.95	828.40
40	73.21	146.54	300.36	450.00	830.65	868.72	261.33	560.66	720.31
50	73.21	146.00	276.02	401.20	799.32	860.08	190.11	480.00	601.00
60				393.98	795.01	858.94	163.00	465.12	585.00
70				393.00	795.00	858.50	160.00	464.00	585.00
Degradation%	92.67	92.70	79.41	60.70	60.25	71.38	84.00	76.80	80.50

Table 8: Effect of catalyst concentration oil degradation of single corn oil, oil mix 50/50 (For initial oil concentration 1000, 2000 and 3000 mg/L, 60 rpm, 1.5 g of catalyst)

1.5 (g) of catalyst						
	Single corn oil			50/50 mix oil		
Time(min)	Oil concentration(mg/L)					
0	1000	2000	3000	1000	2000	3000
10	213.14	1130.36	1951.54	541.65	1012.80	2035.85
20	128.32	500.61	961.39	325.09	605.11	1396.01
30	95.56	240.91	532.98	241.33	452.30	1001.91
40	80.32	151.35	361.25	190.91	330.98	965.87
50	74.61	148.80	257.54	155.60	261.00	939.04
60	73.00	148.80	255.50	133.50	246.00	931.95
70	73.00			133.00	245.00	930.00
Degradation%	92.70	92.56	91.48	86.70	87.45	69.00

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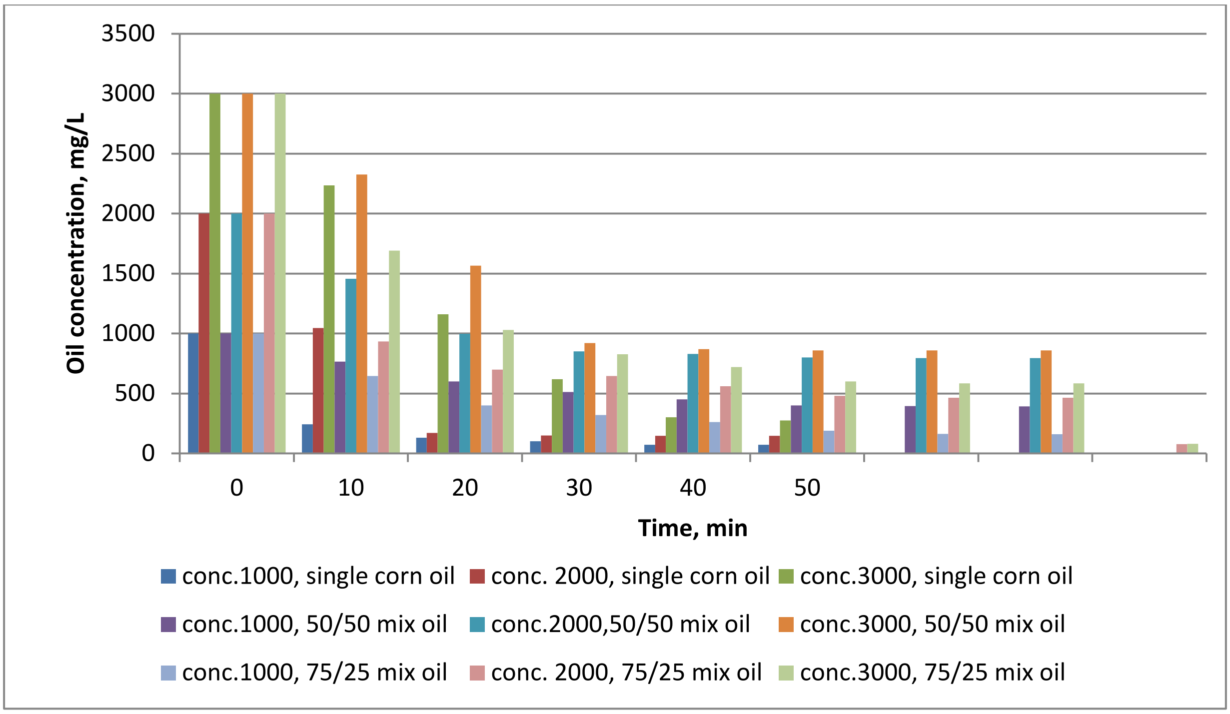

Figure 18: Effect of catalyst concentration single corn oil and mix oil 50/50 and 75/25 corn oil and sun flower oil on oil degradation (For initial oil concentration 1000, 2000 and 3000 mg/L, 60 rpm, 1 g/L of catalyst)

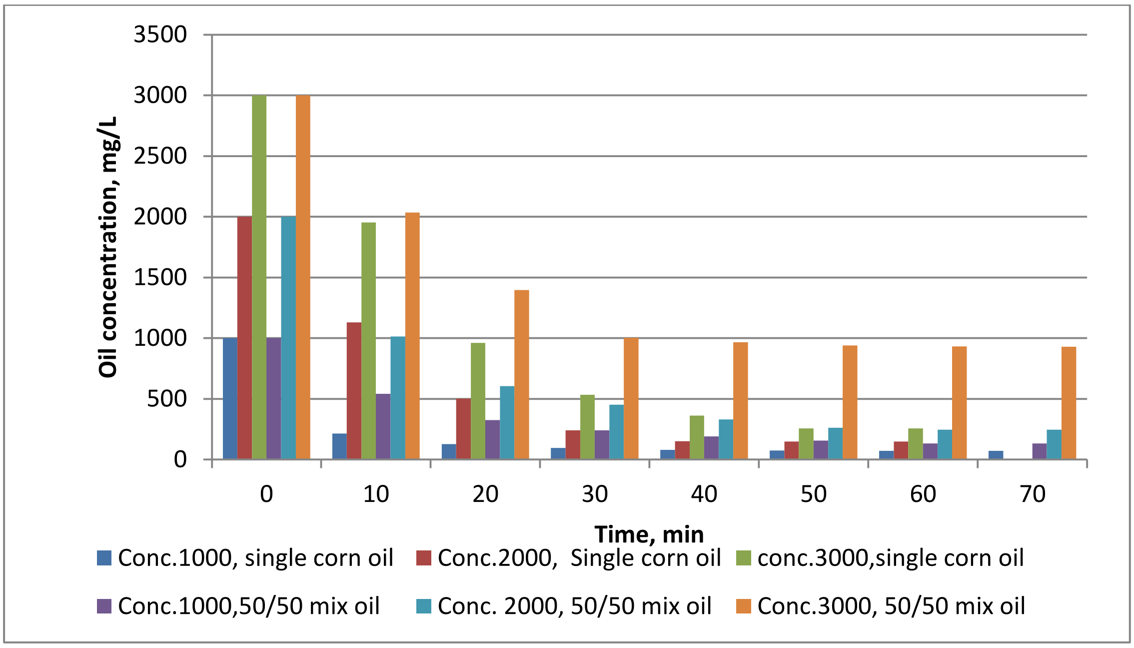

Figure 19: Effect of catalyst concentration single corn oil and mix oil 50/50 on oil degradation (For initial oil concentration 1000, 2000 and 3000 mg/L, 60 rpm, 1.5 g of catalyst)

IV. CONCLUSION

The most important conclusions obtained from the present study are:

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- **For single oil emulsion (corn oil/water emulsion),** at 20 (r.p.m), lower residual oil concentration associated with higher percentage degradation are achieved when using lower oil concentrations (106, 253.8 and 463.76 mg/L for initial oil concentrations 1000, 2000 and 3000 mg/L, respectively.

- At 60 (r.p.m) the same trend is followed as when using circulation rate of 20 rpm; i.e. higher percentage degradation for lower oil concentrations. However, better results are obtained when using higher circulation rate (residual oil concentration of 73.21, 146 and 276.02 mg/L as compared to 106, 253.8 and 84.54 mg/L when using circulation rate 20 rpm)

- The percentage oil degradation was 92.67, 92.60 and 84.54% for 1000, 2000 and 3000 mg/L oil emulsion. Thus, the highest percentage oil degradation is obtained from an oil emulsion of 1000 mg/L; using a circulation rate of 60 rpm, while the least percentage oil degradation is obtained from an emulsion with initial oil concentration 3000 mg/L using catalyst concentration 1.0 g/L at 20 rpm.

- The higher the oil concentration in the emulsion, the more contact time is required to achieve the same degradation rate as at a low oil concentration; which means lower values for percentage degradation.

- The photocatalytic degradation of oil is more efficient at lower values of initial oil concentration. This is true for both concentrations of catalyst tested.

- Increasing catalyst dose results in lowering the value of residual oil concentration and increasing the percentage oil degradation. A pronounced increase in percentage oil degradation is noticed for higher initial oil concentration of 3000 mg/L (79.41% for catalyst concentration 1.0 g/L as compared to 92.73% for catalyst concentration 1.5 g/L). Thus an increase of catalyst concentration enhances oil degradation.

- The lowest residual oil concentration was 73 mg/L and it is satisfied by an oil/water emulsion of 1000 mg/L, using catalyst concentration 1.5 g/L; at circulation rate 60 rpm. The highest percentage degradation was satisfied by an emulsion of initial oil concentration 1000; using catalyst concentration 1.5 g/L.

- **For oil mix emulsion**, results showed that increasing catalyst concentration increases percentage oil degradation and reduces the remaining oil concentration of an emulsion with initial oil concentration 1000 mg/L.

  - **T**he enhancing effect of increasing catalyst dose is more pronounced for oil mixes with relatively higher initial oil concentrations. This is more clear when increasing initial oil concentration from 1000 to 2000 mg/L**.**
  - **For 50/50 oil mix emulsion**, the residual oil concentration increases with increasing circulation rate. The percentage oil degradation corresponding to these values are 71.1 and 60.75% for 20 and 60 rpm, respectively.
  - Higher residual oil concentration and lower percentage oil degradation are satisfied when increasing circulation rate from 20 to 60 rpm.
  - **For 75/25 corn oil/sunflower oil mix emulsion**, increasing rpm increases percentage oil degradation for the three initial oil concentrations tested.
  - The lowest residual oil concentration is 289 mg/L and it is obtained from an oil mix 75/25 corn oil/sunflower oil of initial oil concentration 1000 mg/L and the highest value (858.5 mg/L) is obtained from an oil mix 50/50 corn oil/sunflower oil with initial oil concentration 3000 mg/L.
  - The highest percentage reduction of oil (80.5%) is obtained from an oil mix 75/25 corn oil/sunflower oil with initial oil concentration 3000 mg/L, and the lowest value is obtained from an oil mix 50/50 corn oil/sunflower oil with initial oil concentration 2000 mg/L.
  - Oil mix 75/25 corn oil /sunflower oil shows the same trend as single oil emulsion (corn oil/water emulsion); i.e., increasing circulation rate results in increasing percentage degradation of oil and reducing residual oil concentration .However, the situation is different with 50/50 oil mix/water emulsion; where it is noticed that increasing rate of circulation decreases percentage oil degradation.
  - When testing oil mixes, the percentage degradation of oil (84%) is higher for oil mix 75/25 corn oil/sunflower oil at rate of circulation 20 rpm and it is accomplished by oil emulsion of initial oil concentration 1000 mg/L.
  - Residual oil concentrations are highly increased and percentage oil degradation is highly decreased when corn oil is mixed with sunflower oil.

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- For the 3 initial oil concentrations tested, single oil emulsion has higher percentage oil degradation than mixed oil emulsion. This is followed by 75/25 corn oil/sunflower oil emulsion and next by 50/50 oil mix emulsion.
- The percentage oil degradation is higher for lower initial oil concentration in case of single oil emulsion. However, this situation is reversed with oil mixes, i.e. lower percentage degradation with lower initial oil concentration.

REFERENCES:

[1] Mishra, R.K., *Fresh water availability and its global challenge.* British Journal of Multidisciplinary and Advanced Studies, 2023. **4**(3): p. 1-78.

[2] Xiong, J.-Q., et al., *A comprehensive review on the effects of engineered nanoparticles on microalgal treatment of pollutants from wastewater.* Journal of Cleaner Production, 2022. **344**: p. 131121.

[3] Nguyen, M.-K., et al., *Occurrence and fate of pharmaceutical pollutants in wastewater: Insights on ecotoxicity, health risk, and state–of–the-art removal.* Chemosphere, 2024: p. 141678.

[4] Vijayanand, M., et al., *Polyaromatic hydrocarbons (PAHs) in the water environment: A review on toxicity, microbial biodegradation, systematic biological advancements, and environmental fate.* Environmental research, 2023. **227**: p.١١٥٧١٦ .

[5] Chan, S.S., et al., *Recent advances biodegradation and biosorption of organic compounds from wastewater: Microalgae-bacteria consortium-A review.* Bioresource Technology, 2022. **344**: p. 126159.

[6] Casagli, F., et al., *Balancing microalgae and nitrifiers for wastewater treatment: can inorganic carbon limitation cause an environmental threat?* Environmental science & technology, 2021. **55**(6): p. 3940-3955.

[7] Al-Nuaim, M.A., A.A. Alwasiti, and Z.Y. Shnain, *The photocatalytic process in the treatment of polluted water.* Chemical papers, 2023. **77**(2): p. 677-701.

[8] Sathya, R., et al., *Towards sustainable wastewater treatment by biological methods–A challenges and advantages of recent technologies.* Urban Climate, 2023. **47**: p. 101378.

[9] Yadav, S., et al., *Food-waste-derived hydrochar to a low-cost p-type semiconducting photocatalyst (Zn–Al@ HC): multifunctional role in real wastewater treatment and environmental sustainability.* Journal of Materials Chemistry A, 2024.

[10] Ebanezar John, A., et al., *Factors that enhance the efficiency of TiO2 based heterogeneous photocatalyst for its application in waste water treatment containing organic dye.* Sustainable Water Resources Management, 2024. **10**(3): p. 1-15.

[11] Iqbal, M.A., et al., *Advanced Photocatalysis as a Viable and Sustainable Wastewater Treatment Process: A Comprehensive Review.* Environmental Research, 2024: p. 118947.

[12] Nabgan, W., et al., *A review on the design of nanostructure-based materials for photoelectrochemical hydrogen generation from wastewater: Bibliometric analysis, mechanisms, prospective, and challenges.* International Journal of Hydrogen Energy, 2024. **52**: p. 622-663.

[13] Ahmed, S.F., et al., *Carbon-based nanomaterials: characteristics, dimensions, advances and challenges in enhancing photocatalytic hydrogen production.* International journal of hydrogen energy, 2024. **52**: p. 424-442.

[14] Ganduglia-Pirovano, M.V., A. Hofmann, and J. Sauer, *Oxygen vacancies in transition metal and rare earth oxides: Current state of understanding and remaining challenges.* Surface science reports, 2007. **62**(6): p. 219-270.

[15] Verma, M., et al., *Efficient photocatalytic degradation of Malachite green dye using facilely synthesized cobalt oxide nanomaterials using citric acid and oleic acid.* Journal of Physics and Chemistry of Solids, 2021. **155**: p. 110125.

[16] Ma, Y., et al., *Titanium dioxide-based nanomaterials for photocatalytic fuel generations.* Chemical reviews, 2014. **114**(19): p. 9987-10043.

[17] Schneider, J., et al., *Understanding TiO2 photocatalysis: mechanisms and materials.* Chemical reviews, 2014. **114**(19): p. 9919-9986.

[18] Mohammed, R.M. and K.M.M. Al-zobai, *Photocatalytic degradation of organic pollutants in petroleum refinery using TiO2/UV and ZnO/UV by batch and continuous process.* Solid State Technology, 2020. **63**(3 :(p. 5390-5404.

[19] Mahmoud, M.A., et al., *Degradation of oily effluents using immobilized photocatalyst: Laboratory experimentation and plant design.* Alexandria Engineering Journal, 2023. **65**: p. 295-305.

Print ISSN 2682-3993

Online ISSN 2682-4000

[20] Wang QE, Zheng K, Yu H, Zhao L, Zhu X, Zhang J. Laboratory experiment on the nano-TiO2 photocatalytic degradation effect of road surface oil pollution. Nanotechnology Reviews. 2020 Sep 23;9(1):922-33.

[21] Zare, E.N., et al., *An overview on non-spherical semiconductors for heterogeneous photocatalytic degradation of organic water contaminants.* Chemosphere :٢٨٠ .٢٠٢١ ،p. 130907.

[22] Hsiao, M. C., et al., *Optimized conversion of waste cooking oil to biodiesel using modified calcium oxide as catalyst via a microwave heating system.* Fuel, 2020. **266**: p. 117114.

[23] Tetteh EK, Rathilal S, Naidoo DB. Photocatalytic degradation of oily waste and phenol from a local South Africa oil refinery wastewater using response methodology. Scientific reports. 2020 Jun 1;10(1):8850.

[24] Frankel, E. and S. Huang, *Improving the oxidative stability of polyunsaturated vegetable oils by blending with high‐ oleic sunflower oil.* Journal of the American Oil Chemists' Society, 1994. **71**(3): p. 255-259.

[25] Bi J, Huang X, Wang J, Wang T, Wu H, Yang J, Lu H, Hao H. Oil-phase cyclic magnetic adsorption to synthesize Fe3O4@ C@ TiO2-nanotube composites for simultaneous removal of Pb (II) and Rhodamine B. Chemical Engineering Journal. 2019 Jun 15;366:50-61.