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Process Optimization Photo-Esterification of Free Fatty Acids in Waste Cooking Oils under UV Irradiation *via* **the RSM Method**

Zahra Abbasi 10, Mehdi Ahmadi^{1, 2, 3} * 0

¹ Faculty of Science, Ilam University, P.O. Box 69315516, Ilam, Iran

² Environmental Technologies Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran ³ Department of Environmental Health Engineering, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

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In this research study, UV irradiation was employed to decrease the free fatty acids (FFAs) of waste cooking oil (WCO). In the first step, under the UV irradiation, the photocatalytic reaction of Cr-TiO2 with methanol and free fatty acids in WCO was studied. Optimization was performed with Design Expert Software and using the Box- Behnken method. We investigated the effects of the main parameters, including the molar ratio of methanol to WCO, irradiation time, and type of photocatalyst. By using UV radiation, 0.9661% of the response changes were justified with a Quadratic model. The methanol-to-WCO ratio parameter showed a positive effect with a greater slope. The transesterification reaction of triglycerides with methanol was performed in the second step using the Verma method. Solid catalysts were found to be highly active for the photo-esterification of FFAs with methanol in the UV irradiation. While performing the esterification step in the presence of the UV irradiation in the presence of Cr-TiO₂ photocatalysts, the efficiency was 76.3%-89.5%. The order of photocatalytic esterification reaction by Cr-TiO₂ was approximately equal to one. The kinetics of the transesterification stage was investigated. The first-order kinetic model showed a correlation coefficient of $R^2 = 0.997$. The amount of activation energy was 7.103 kJ/mol, indicating the warming nature of the reaction. Concerning the production of H+, CH₃O and R-COOH on the photocatalyst surface, a possible reaction mechanism for the esterification process is proposed. For the mechanism of the transesterification reaction, OH or OR were considered active species.



GRAPHICAL ABSTRACT

Introduction

Long-chain mono alkyls of fatty acids resulting from the reaction of alcohol with oil are called biodiesel. Biodiesel is made from oils, in which suction uses edible oils as raw materials. The oils used include edible oils such as sunflower oil [1], soybean [2], palm oil [3], etc. Biodiesel produced from edible vegetable oils is called the firstgeneration biofuel. In addition, there are many concerns about using a potential food source as a biofuel. To solve this problem, non-edible oils have also been studied. Among the non-edible oils for biodiesel production, Jatropha oil, rubber seed oil, and so on, have been studied. Biodiesel produced from non-edible vegetable oils is referred to as the second-generation biofuel [4]. Biodiesel produced mostly from vegetable oils, is a mixture of mono-alkyl esters and is thought to replace diesel as a fuel. Edible and non-edible vegetable oils can be used as raw materials in biodiesel production. Biodiesel is produced from various vegetable oil sources such as soybean, sunflower, cottonseed, etc. [5-9]. However, the future of these edible oils is uncertain due to the increasing global food demand. In addition, the use of edible oils for biodiesel significantly

increases its production costs. The higher the oil's acidity, the lower the conversion and efficiency of transesterification. If FFA is present in large amounts in the primary oil, a play catalyst is needed first to neutralize the FFA. The reaction between the catalyst and the FFA leads to the consumption of catalysts and the formation of soap and water, called soaping. So far, various studies have been performed on alkaline and acid catalysts to produce biodiesel, but few studies have reported photocatalysts and irradiation in biodiesel production [10-13].

A heterogeneous catalyst's morphology is one factor affecting its activity [14-16]. Due to the different morphology of a heterogeneous, the amount of its optical, electronic, and catalytic properties varies. Many efforts have been made to improve the performance of titanium dioxide nanowires and nanostructures by making controlled size or shape at the nanoscale to improve photocatalytic, photovoltaic, electrochemical and dielectric properties [17-20]. Chai et al. (2012) used Pt nanoparticles and g-C₃N₄ nanoparticles to investigate the photocatalytic activity of TiO₂ in the visible region. In this study, urea precursor was used to synthesize g-C₃N₄, and

the thickness of the synthesized g-C₃N₄ sheets was 10 nm. If $g-C_3N_4$ and $Pt-TiO_2$ are used in a ratio of respectively, 70 to 30, the maximum photocatalytic activity to produce H₂ will be obtained [22]. Wang et al. (2017) used a singlestep method to synthesize sulfur-doped TiO₂ nanosheets photocatalyst on reduced graphene oxide (TiO_2 -S/rGO). The results showed that doping with sulfur on TiO₂ would decrease the TiO₂ gap. They concluded that the effect of rGO presence in the structure of this photocatalyst increased electron transfer and electron-hole separation, resulting in increased photocatalyst efficiency [23]. In a study to optimize the sulfonate-glucose acid catalyst (SGAC) for the palm oil esterification reaction using the RSM method with the CCD model, Lockman et al. performed a one-step reaction in a reflux system at 65 °C. The RSM method has shown the relationship between three variables that significantly affect the conversion of FFA, including the molar ratio of alcohol to oil, the concentration of the loaded catalyst, and the reaction time. The results revealed that the catalyst concentration parameter had the greatest effect on the conversion rate and production efficiency. Optimal conditions were obtained using the RSM method as 94.5% FFA conversion and 92.4% biodiesel efficiency [24]. The production of biodiesel from the waste of edible oils has not been widely used, and it is still too early to use this method to remove oily pollutants and turning it into a useful fuel in the industry. In the present work, we assessed the factors affecting the efficiency of biodiesel production by synthesizing two-dimensional photocatalysts and using the response surface method (RSM). The response surface method is a widely used statistical technique for optimizing process variables and a comprehensive understanding of the complex inter-parameter interactions of any experiment [25].

In the present study, a 2D TiO_2 photocatalyst with different percentages of Cr was synthesized. TiO_2 photocatalysts in sheet form provides a special surface suitable for increasing the process

efficiency. These types of structures have a higher level and a large number of hydroxyl groups against oxide precursors (TiO₂). One promising application of a heterogeneous photocatalyst is the esterification of free fatty acids to methyl esters for biodiesel production. The optimal conditions for the effect of photocatalysts on oilfree fatty acid conversion have been investigated, followed by scrutinizing, and then transesterification for biodiesel production. What follows reflects the investigation of the kinetic and thermodynamic parameters of the two steps and the proposed mechanism.

Materials and Methods

Titanium n-butoxide, hydrofluoric acid (HF), sodium hydroxide (NaOH, 10%), potassium hydroxide (KOH), chromium (III) acetylacetone (Cr (acac)₃), hydrochloric acid (HCl, 37%), ethanol (EtOH, 98%), methanol (CH₃OH, 99.8%), toluene (C₆H₅CH₃, 99.8%), 2-propanol ((CH₃)₂CHOH, 99.9%), deionized water and waste oil collected from of Ahvaz city were used. Also, we applied ultrasonic device model UP-200H, incubator shaker model 1SH 554D made by Fanavaran Sahand Azar Tabriz-Iran, X-ray diffraction spectroscopy device (XRD model BW1840, field emission microscope device (FESEM) model MIRA3TESCAN-XMU, Sco made by DRS South Korea, Transmission Electronics (TEM) Model LEO 906 E Made in Germany, GBC Cintra 101 Dual UV-Vis Spectrophotometer, Beam Fourier Transformer Spectrometer (FT-IR), Shimadzu FTIR-8300, Tuttlingen D Centrifuge -78532, A&D model digital scale with measuring accuracy of 000 0.0001 g made in Japan, Clarus-580 PerkinElmer gas chromatography device made in the USA, Shimaz model oven made in Iran.

Synthesis of Photocatalysts

Cr-doped-TiO₂ nanoparticles should be prepared using the hydrothermal method [26]. The 4.65 ml of titanium n-butoxide was dissolved in 45 ml of ethanol under stirring, and then 1.9 ml of hydrochloric acid was slowly added to the above solution.



Figure 1: The used waste oil

Overnight under stirring, the uniform solution was transferred to an autoclave and heated at 150 °C for 9 h. After cooling at room temperature, the precipitates were separated by centrifugation and washed with ethanol. Two-dimensional pure TiO_2 nanomaterials, doped with Cr, were calcined at 400 °C for 1 h.

Preparation of Waste Cooking Oil

Since waste oil collected from restaurants contains water and solid particles, it was first separated using an impurity filter and fine solid particles. To remove the water in the waste oil, it was heated at 100 °C for 3 h using continuous stirring to evaporate the water in the waste oil. Figure 1 displays the used waste oil.

The acidity of the oil is determined by the acid number. The amount of FFAs in the oil was determined by titration (ASTM standard D974-08). To determine the amount of acid, 2 g of oil was dissolved in 100 ml of solution with specified ratios of toluene: 2 - propanol: water (100: 99: 1 v: v: v). The solution was titrated at room temperature using a standard 0.1 M solution of KOH in 2-propanol and titrated with the pnaphthol benzein detector. The color change from orange to green indicates the endpoint of the titration. The amount of oil acid can then be calculated using Equation (1).

$$A = \frac{[56.1 \times M \times (a-b)]}{W} \tag{1}$$

Using the Equation (2) of free fatty acids and Equation (3), the concentration of free fatty acids in the oil was calculated.

FFAs wt% =
$$\frac{[28.2 \times M \times (a-b)]}{W}$$
 (2)

FFAs concentration, mol.
$$m^{-3} = \frac{\rho}{1000} \times \frac{[M \times (a-b)]}{W}$$
 (3)

M denotes the molar concentration of the alkali standard solution, an indicates the volume of the alkali standard solution, b symbolizes the volume of control, W denotes the sample weight, and shows the density. Pearson (1981) method was used to calculate the soap index [27]. The soaping index was obtained from Equation (4).

$$S = \frac{N \times 56.1 \times (A-B)}{W}$$
(4)

A denotes Hydrochloric acid used for control titration (ml), B is Hydrochloric acid used for

sample titration (ml), W symbolizes Oil weight in grams, and N is Normality. The molecular weight of the oil (M) was obtained from Equation (5).

$$M = \frac{56100 \times 3}{S - A}$$
(5)

Photo-esterification of free fatty acid with photocatalyst

The WCO obtained from the restaurant was used after removing the solids using a strainer and removing the water in the oil during the esterification step. A reactor equipped with a UV lamp (with 4 UV-C lamps (15 W)- Philips, Netherlands, λ =254 nm) was used. The cabin was placed inside the incubator shaker to precisely control the temperature and stirring settings during the tests. The incubator temperature was set at 25 °C, and the stirring speed was 180 rpm. Figure 2 presents a schematic of the photoreactor used in the study.

Using Design-Expert software and Box- Behnken method was used to optimize reaction conditions and calculate esterification under different reaction conditions. The FFA% conversion rate was determined according to the acid content ratio using the Equation (6).

$$\% C_{FFA} = \frac{A_i - A_t}{A_i} \times 100\% \tag{6}$$

 A_i is the initial acidic index of the waste oil, and A_t is the acidic index after the photo-esterification reaction.

Photocatalyst Recovery and reuse in the photoesterification process

Reusing catalysts is an important factor in evaluating the performance of a heterogeneous catalyst. To evaluate the stability of the photocatalyst in the optimal conditions obtained with the software, there were five photoesterification reactions with $Cr-TiO_2$ catalysts with three percent different from Cr, and then biodiesel production with alkali catalyst was performed to confirm the recyclability of the photocatalyst. After each experiment, twodimensional pure TiO_2 nanosheets were doped with Cr by centrifugation and filtration. It was then washed several times with ethanol, dried at $100 \,^{\circ}C$ for 2 h, and calcined for one hour at 400 $^{\circ}C$ for a repeatability test.



Figure 2: Schematic representation of the photoreactor



Figure 3: XRD patterns of prepared nanocomposites

Results

Photocatalyst Characterization

The XRD pattern for pure samples of titanium dioxide nanoparticles and titanium dioxide nanoparticles with three different percentages of chromium is shown in Figure 3. As seen from Figure 3, all of the samples show the same trend and confirmed the pure anatase crystal structure (JCPDS file No. 21-1272).The peaks in the areas of 48.9 °, 37.8 °, and 25.1 ° are corresponding to (200), (004), and (101) anatase crystal planes, respectively.

This is consistent with the structure of the titanium dioxide layers reported by Wang *et al.* In the final composite pattern, all samples were synthesized in the anatase phase [28].

The surface morphology of the synthesized samples was studied using FESEM and TEM methods. Figures 4a, 4b, 4c, 4d, 4e, 4f, 4g, and 4h show that the FESEM and TEM of the sample are square and rectangular cubic titanium dioxide and have relatively identical dimensions.

The images show the layered structure of titanium dioxide with chromium particles scattered in the sheets, which causes the accumulation of layers of titanium dioxide and the formation of uneven surfaces of titanium dioxide. The FT-IR spectrum for TiO₂, 2% Cr -TiO₂, 8.5% Cr - TiO₂, and 15% Cr - TiO₂ are shown in Figure 5. In all synthesized samples, broadband adsorption is seen in 1300-3300 cm⁻¹, related to the O-H bond's tensile vibration. The peaks in the 1740 cm⁻¹ and 1300 cm⁻¹ regions are characterized by different states to the tensile vibrations of the Ti-O bond [29].



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Figure 4: FESEM and TEM images; (a) 2D TiO₂, (b) 2D TiO₂ with 2% chromium, (c) 2D TiO₂ with 8.5% chromium, (d) 2D TiO₂ with 15% chromium



Figure 5: FT-IR spectrum

Table 1: Specifications of waste oil

Characteristic	Amount
Acidic index	8.14 mg/g KOH
Soap Index	180.01mg/g KOH
Molecular Weight	978.7 g/mol
Density	930 kg/m ³
FFAs	4.09 %

Physico-chemical properties of waste oil

The characteristics of the acid index, saponification index, average molecular weight, density and free fatty acid are calculated according to Equations 1, 2, 3, 4, and 5 and are shown in Table 1.

Free fatty acids result from the breakdown of triglycerides in the oil, which is higher in this type of oil due to the repeated use of waste oils. With higher the amount of free fatty acids, the level of oil damage is increased. In the transesterification process for biodiesel production, free fatty acids must be less than 0.5% to prevent saponification and reduce biodiesel efficiency [30]. Thus, the sterilization process takes place first in waste oils with high levels of free fatty acids.

Analysis of Results of Photo-Esterification by UV Irradiation

Response Surface Method (RSM) from Design Expert 10.0.7 software is a powerful tool for statistical modeling that shows the best relationship between parameters using the least experimental experiments. Studies were performed by designing experiments from Design Expert software using the BBD method. In the present study, three independent parameters considered, including the type were of photocatalyst (2% Cr-TiO₂, 8.5% Cr-TiO₂, and 15% $Cr-TiO_2$), the molar ratio of methanol to WCO (6:1, 9:1 and 12:1) and irradiation time (1 to 3 hours), and for each of the three independent parameters, the upper and lower levels were determined. Table independent 3 represents design parameters and levels of values and related codes. The results obtained in experiments designed by

the BBD method can be calculated to investigate the interaction effects of the parameters and their statistical analysis. The response surface method is applicable to find the optimal state of the interaction of parameters and to estimate the best optimal process conditions with the least number of experiments [31]. Biodiesel was prepared using the first stage of photo-esterification by ultraviolet irradiation using the response surface method using the BBD model. The relationship between three parameters was investigated, namely type of photocatalyst, irradiation time, and the molar ratio of methanol to oil with the percentage of conversion of FFAs. The percentage of FFAs conversion into methyl ester in the photoesterification step was calculated by Equation (6). The determined experiments with the obtained efficiencies are shown in Table 2.

To determine the main effects and statistically important interactions and the effect on the percentage of FFAs, analysis of variance (ANOVA) was used. The same statistical operation was applied to determine the main effects and important interactions in terms of statistics and in terms of effectiveness in fatty acid conversion efficiency in the photo-esterification stage and analysis of variance. The results of the analysis of variance of the effect of different variables on the percentage of free fatty acid conversion are given in Table 4, in which 2FI which deals with the interactions of two factors, Quadratic and cubic, are examined by the software. Table 3 indicates that the Quadratic model is the proposed software model.

responses					
Run	Factor 1	Factor 2	Factor 3	Response	
	A: %Cr-TiO ₂	B: Time h	C: Alcohol to Oil	CFFAs %	
1	15	3	9	63.5	
2	8.5	2	9	54.1	
3	15	1	9	39.2	
4	2	2	6	42.5	
5	8.5	1	12	49.3	
6	8.5	1	6	38.1	
7	15	2	6	46.8	
8	8.5	2	9	53.9	
9	15	2	12	65.9	
10	8.5	2	9	54.2	
11	2	1	9	43.8	
12	2	2	12	59.4	
13	8.5	2	9	53.9	
14	8.5	3	12	75.2	
15	8.5	2	9	53.8	
16	2	3	9	46.9	
17	8.5	3	6	52.7	

Table 2: Box-Behnken design for three factors in three levels: Design matrix, and the measured and predicted

Table 3: Data analysis of FFA conversion percentage data using UV irradiation

Model Summary Statistics						
Sourco	Std Dov	D Squarad	Adjusted	Predicted	DDECC	
Source	Stu. Dev.	K-Squareu	R-Squared	R-Squared	F KE35	
Linear	4.47	0.8276	0.7879	0.6459	534.20	
2FI	3.38	0.9241	0.8785	0.6377	546.48	
<u>Quadratic</u>	<u>1.79</u>	<u>0.9852</u>	<u>0.9661</u>	<u>0.7635</u>	<u>356.85</u>	Suggested
Cubic	0.16	0.9999	0.9997		+	Aliased

ANOVA for Response Surface Quadratic Model					
Source	Sum of Squares	df	Mean Square	F Value	P-value
Model	1486.16	9	165.13	51.60	< 0.0001
A-Cr-TiO ₂	64.98	1	64.98	20.31	0.0028
B-Time	576.30	1	576.30	180.09	< 0.0001
C-Alcohol to Oil	607.26	1	607.26	189.76	< 0.0001
AB	112.36	1	112.36	35.11	0.0006
AC	1.21	1	1.21	0.38	0.5581
BC	31.92	1	31.92	9.98	0.0160
A ²	35.47	1	35.47	11.08	0.0126
B ²	31.32	1	31.32	9.79	0.0166
C ²	27.86	1	27.86	8.71	0.0214
Residual	22.40	7	3.20		
Lack of Fit	22.29	3	7.43	275.22	< 0.0001
Pure Error	0.11	4	0.027		
Cor Total	1508.56	16			

Table 4: ANOVA of FFA conversion in the presence of UV irradiation

As seen in Table 3, the Quadratic model is proposed as the best relationship between the independent variables. In this model, the coefficient of explanation: 0.9852, adapted: 0.9661, shows that the Quadratic model justifies approximately 0.9661% of the response changes. The standard deviation of this model is equal to 1.79, and the PRESS value is 356.85.

The effect of each of the desired parameters on the percentage of conversion of fatty acids in the photo-esterification stage by ultraviolet radiation is measured by their coefficients. Parameters with a positive coefficient have a positive effect on increasing conversion efficiency, and parameters with a negative coefficient hurt efficiency. According to Table 5, the first-degree statements of the molar ratio of methanol to WCO and the irradiation time to the type of photocatalyst are of great importance, and the second-degree statements of all three parameters of the photocatalyst type, irradiation time, and the ratio of methanol to residual oils are important, including the interaction of photocatalyst type parameters at irradiation time and irradiation time in the molar ratio of methanol to WCO.

Tuble of Summary of Sumstan results for quantum equation				
Std. Dev.	1.79	R-Squared	0.9852	
Mean	52.54	Adj R-Squared	0.9661	
C.V. %	3.40	Pred R-Squared	0.7635	
PRESS	356.85	Adeq Precision	26.558	
-2 Log Likelihood	52.93	BIC	81.27	
		AICc	109.60	

Table 5: Summary of statistical results for quadratic equation

After evaluating the fitting defects and statistical analysis related to different models, considering the proposed parameters, a mathematical model for the percentage of fatty acid conversion in Equation (7) was presented.

```
C_{\text{\%FFAs}} = +47.38886 - 0.27828 \text{ Cr-TiO}_2 + 3.99173 \text{ Time-} 4.36391 \text{ Alcohol to Oil+} 0.81538 \text{ * Cr-TiO}_2 \text{ *}
Time+ 0.028205 \text{ Cr-TiO}_2 \text{ Alcohol to Oil+} 0.94167 \text{ *Time * Alcohol to Oil-} 0.068698 \text{ (Cr-TiO}_2)^2 \text{ } 2.72750 \text{ (Time)}^2 + 0.28583 \text{ (Alcohol to WCO)}^2 (7)
```

As we can see in the proposed model, the $C_{\% FFAs}$ in the photo-esterification stage in the presence of ultraviolet radiation with certain coefficients

depends on independent parameters. Figure 6 demonstrates the actual values versus the predicted values using the software model. When the data is normally distributed and the test errors are normal, the dots are around the straight line. It is clear that there is not much difference between the actual values and the predicted values.

As seen in Figure 6, this diagram does not show a specific trend, indicating the increase or decrease of residues, and the assumption that the residues are independent is acceptable. Figure 6 shows the perturbation diagram. In this diagram, it is possible to compare the effect of all parameters at a specific point in the design space, which shows the effect of each parameter on the FFAs conversion and ignores the effect of the interaction of the parameters on each other. As can be seen from Figure 6, all three parameters affect the C_{%FFAs}. A parameter's steep slope or curvature indicates the sensitivity of reaction efficiency to the desired parameter. If the line is relatively smooth, it indicates the insensitivity of the response to the desired parameter. The effect of parameter A, a type of photocatalyst with a different percentage of chromium, is initially incremental and has an almost constant effect on efficiency. Parameter C shows a positive effect with a greater slope. To study the interaction effects between independent parameters on the desired response, three-dimensional diagrams can be used that can show the interaction effects of the two parameters on the response. Figure 7 depicts the contour line diagram and the threedimensional diagram of the percentage conversion of FFAs according to the interaction of the parameters in the quadratic model.

The diagrams in Figure 7 depicts the threedimensional diagram and contour of the response surface for the percentage conversion of free fatty acids per change of photocatalyst type and irradiation time at the photo-esterification step, as can be seen in Figure 7, the reaction efficiency increases with increasing irradiation time. Thus, in 3 h of irradiation has shown a higher conversion percentage. On the other hand, by increasing the UV irradiation time from one hour to three hours, the duration of light irradiation to the photocatalyst increases and sufficient time is provided to separate the electron from the photocatalyst capacity strip, and the probability of electron-hole formation is higher and increases. Reaction efficiency has a positive effect with a direct effect on increasing reaction efficiency [31]. The effect of ultraviolet radiation on electron-hole separation of photocatalysts is not significantly different and is almost the same for all three types of photocatalysts with different chromium percentages. In photocatalyst, it shows a higher efficiency with 8.5% than the other two types, but this increase is not significant in relation to the effect of irradiation time on the reaction efficiency.



Figure 6: Real values versus predicted values and different parameters



Figure 7: Three-dimensional diagram and contour Simultaneous effect of photocatalyst type and irradiation time on the percentage of conversion of fatty acids after photo-esterification with the UV irradiation



Figure 8: Three-dimensional diagram and contour of the effect of irradiation time to alcohol to oil ratio on the percentage of conversion of fatty acids after photo-esterification

Figures 8a and 8b show the irradiation time to alcohol to oil ratio on reaction efficiency. As can be seen, irradiation time and methanol to oil ratio significantly affect increasing efficiency. With increasing irradiation time, the probability of electron-hole formation in the photocatalyst increases. and with increasing collision probability, the probability of surface adsorption on the catalyst and collision with the formed radicals increases. The esterification reaction is an equilibrium reaction and according to the Le Chatelier's principle, the reaction efficiency increases by increasing the molar ratio of alcohol to oil to a greater extent than the stoichiometry of the reaction [33]. In this study, by increasing the molar ratio of methanol to WCO, an increase in the conversion efficiency of free fatty acids was observed.

Figure 9 depicts the interaction of photocatalyst type and alcohol-to-oil ratio on the percentage of fatty acids. Yield is affected by the amount of methanol present in the reaction. The interaction of methanol content with the reaction with photocatalyst type shows a small effect of photocatalyst type with methanol content. In addition to the effects of electron-hole formation and preventing its recombination, another factor could be due to the layered surface of these photocatalysts. With more loading of chrome, the roughness on the layered surface is greater. This factor can affect the first photocatalytic process, i.e. the adsorption of molecules on the photocatalyst surface, which is a characteristic of heterogeneous catalyst processes. Increasing the amount of chromium on the photocatalyst TiO_2 increases the contact surface, and the probability of the reactants on the photocatalyst surface increases. Simultaneous effects of surface and prevention of electron-hole recombination are effective in reaction efficiency [33].

Optimization

Response level optimization aims to find the optimal point in the experimental design space

where the response can be maximum, minimum, or within the test range. This study considered the maximum effect on the conversion of free fatty acids as the target. To obtain the optimal point, we considered the parameters of irradiation time and methanol to oil ratio in the desired range and the type of photocatalyst in 8.5% of chromium. The maximum utility under the considered conditions was 0.964. To prepare oil with less free fatty acid for transesterification reaction and also to investigate the recovery of spot catalyst with optimal conditions, we had %8.5 $Cr-TiO_2$ photocatalyst, the molar ratio of methanol to WCO 12 to 1 and irradiation time of 3 h with efficiency. The reaction was 73.85%.



Figure 9: Three-dimensional diagram and contour of the simultaneous effect of the type of photocatalyst and the molar ratio of methanol to oil on the percentage of fatty acids after photo-esterification





Concerning the %15 Cr-TiO₂ photocatalyst, the optimal conditions: the molar ratio of methanol to oil was 11.7 to 1, and the irradiation time was 2 h and 54 min, with a free fatty acids conversion percentage of 76.84%. The maximum utility under the considered conditions was 1. Considering the %2 Cr-TiO₂ photocatalyst, the optimal conditions: the molar ratio of methanol to oil was 12 to 1 and the irradiation time was 3 hours with a conversion percentage of free fatty acids of 62.24%. The maximum utility under the given conditions was 0.651.

Biodiesel Efficiency

Experiments were performed to evaluate the efficiency of biodiesel to evaluate the photoesterification stage. Thus, four samples of waste oil with four photocatalysts (pure TiO₂, %2 Cr-TiO₂, %8.5 Cr-TiO₂ and %15 Cr-TiO₂) in the photoesterification step under optimal conditions were obtained with the software (For pure TiO₂, %2 Cr-TiO₂ and %8.5 Cr-TiO₂ molar ratio of methanol to WCO 12 to 1, the UV irradiation time 3 hours and for %15 Cr-TiO₂ molar ratio of alcohol to oil 11.7 to 1 and time irradiation (2 h and 54 min) was evaluated to reduce free acids.

To prepare these samples for the transesterification step, water and methanol were removed by the Verma method. A sample was examined as control without photo-esterification step. The results are demonstrated in Figure 10.

According to the results obtained in the previous sections, it was observed that due to the free fatty acid in the waste oil, the esterification step is necessary. In the sample formed without the esterification step, due to the effect of the high FFA content of the soap and difficulty of the separation of the product, which reduced the yield, the biodiesel production efficiency came by 52.9%. While performing the sterilization step in the presence of ultraviolet radiation in the presence of Cr-TiO₂ photocatalysts, an efficiency of 76.3% -89.5% was observed. Due to the fact that the photo-esterification step is performed in the presence of ultraviolet radiation and sufficient energy is provided to separate electrons and create electron-holes on the surface of pure TiO₂ structure with a gap of 3.15 eV energy, high efficiency was not realized compared with loading percentages of chromium on TiO₂ surface. This can be analyzed due to the high recombination in the TiO₂ structure and the effect of chromium on the structure as electron storage at the same time as the pure TiO_2 state has resulted in higher efficiency.

Reuse of Photocatalysts

Photocatalyst stability is one of the important factors in photocatalytic processes. To investigate this factor, the recycling rate of photocatalysts was tested in up to five steps. The results are revealed in Figure 11.



Cycls CFFA %

Figure 11: FFA conversion rate in five stages of photocatalyst reuse

Figure 11 reveals the FFA conversion rate in the five steps of photocatalyst recovery. In the first cycle, in the presence of photocatalysts for 2% -Cr-TiO₂, 8.5% -Cr-TiO₂ and 15% -Cr-TiO₂, the FFA conversion rates are 64.8%, 75.2% and 72.4%, respectively. After five experiments, the conversion rate is still 54.5%, 66.3%, and 58.9% for the catalysts by the UV irradiation for 3 hours, respectively. The reason for the slight decrease in conversion rate is that the glycerin produced inside the photocatalyst or by-products is adsorbed on the photocatalyst and as a result, the active sites are reduced. This is also acceptable by looking at the results for a 2% by weight of chromium catalyst that did not have a large dropin conversion rate. With increasing the percentage of chromium on the structure of titanium dioxide, the structural surface is more uneven, and with the recovery of photocatalysts, the probability of sediment 813 enetrateon to active centers is higher, and the efficiency naturally decreases in the later stages of catalyst use [34-36]. The results show that the photocatalyst has strong chemical stability and operational stability, i.e. the photocatalyst is recyclable. The unchanged catalytic activity of photocatalysts, even after five FFA esterifications, shows no reduction in catalyst mass due to decomposition and mass loss of chromium species due to elution in the reaction mixture.

Kinetics of the photo-esterification step

The optimal conditions were obtained from the optimization of independent parameters using Design Expert software in the previous topic. Using these optimal points, the kinetics of the photo-esterification process was investigated. The method of Guo et al. was used for kinetic study [35]. To study the kinetics of the Cr-TiO₂ photocatalytic sterilization reaction. an experimental study was performed under conditions of %15 Cr-TiO₂ photocatalyst, the molar ratio of alcohol to oil 10.7:1, and under the UV irradiation. The kinetic equation of esterification can be expressed as:

The conversion rate equation of FFA and methanol is expressed as follows:

$$-\frac{dC_A}{dt} = k C_A^a C_B^b$$

$$C_A = C_{A_0} (1 - X_A) \text{ and } C_B = C_{B_0} (1 - X_B)$$
(8)

Where, C_A and C_B are the concentrations of FFAs and methanol at time t, respectively. C_{B0} and C_{A0} are the initial concentrations of FFAs and methanol, a and b are the reaction stages of fatty acids and methanol. K represents the reaction rate constant. X is the conversion of FFAs in the esterification reaction. Given the high concentration of methanol used, we consider the changes in methanol concentration to be constant; therefore, k C_B^a can be considered as a constant. If we consider that:

$$k' = k C_B^b$$

The equation is rewritten as follows:

$$-\frac{dc_A}{dt} = \mathbf{k}' \ c_A^a = -\frac{d[c_{A_0}(1-x)]}{dt} = \frac{dx}{dt}$$
(9)

$$\frac{dx}{dt} = \frac{k' \left[c_{A_0}(1-x) \right]^{a}}{c_{A_0}}$$
(10)

If we have fixed values together with the characteristic sign that:

$$k'' = \frac{k'}{c_{A_0}}$$
$$\frac{dx}{dt} = k'' [c_{A_0}(1-x)]^a$$
(11)

From the two sides that take ln, we have:

$$ln\frac{dx}{dt} = lnk'' + aln[c_{A_0}(1-x)]$$
(12)

Using this linear equation, the reaction order and the rate constant can be calculated [Figure 12]. A is the slope of the line, which indicates the order of the reaction, and lnk'' is the width of the origin, which is used to calculate the rate constant.

In Figure 13, the ln dx/dt diagram is plotted in terms of $ln[c_{A_0}(1-x)]$. This curve can be fitted and the reaction rate constant and reaction order can be obtained by linear fitting.



Figure 12: A conversion rate of FFAs at different temperatures









According to the obtained data, photocatalytic esterification by $Cr-TiO_2$ has been photoesterification with a reaction order of 1.008, which is approximately equal to one. According to the velocity and temperature constants, the activation energy is calculated by Arrhenius equation [37]:

$$lnK = -\frac{E_a}{RT} + lnA \tag{13}$$

From the lnK diagram in 1/T, E_a is the activation energy in J.mol⁻¹ (Figure 14).

Given the linear regression coefficient, $R^2 = 0.99079$, the proposed reaction kinetics model is reasonable; the activation energy required by the Cr-TiO₂ photocatalyst for WCO photoesterification is 31.36 kJ/mol. The results of kinetic parameters showed that the Cr-TiO₂ photocatalyst requires less energy for WCO esterification and can be performed under mild conditions.

Mechanism of Photo-Esterification Step

The basic mechanism of the photocatalytic reaction relies on the production of electron-hole pairs and their function in the reaction as follows: The impact of light with sufficient energy leads to the transfer of electrons from the TiO₂ capacitance band to the TiO_2 conduction band and the formation of holes in the TiO₂ capacitance band. The electrons transferred to the conduction band and the holes formed in the capacitance band can react with the adsorbed species on the photocatalyst surface. According to the DRS curve, the energy gap for pure titanium dioxide is 3.15eV and for titanium dioxide with 2% chromium 2.79eV, titanium dioxide with %8.5 chromium 2.5eV and titanium dioxide with %15 chromium 2.7eV. Obviously, doped Cr can significantly improve the absorption of TiO_2 in the visible light region. After irradiation, electrons are excited

from the TiO₂ capacitance band and transferred to their conduction band, forming a hole in the capacitance band [27]. The overall reaction uses the pore oxidation energy directly and reacts with the adsorbed H₂O and OH on the surface to form a hydroxyl radical with strong oxidation properties. The reaction in the adsorption step follows the following steps: Photon absorption by the Cr/TiO_2 photocatalyst, mainly by the TiO₂ sites, and the electrons production by the photon e and the hole and Cr surface electrons. Methanol (CH₃OH) and FFA (R-COOH) are located on the surface of the Cr-TiO₂ photocatalyst. Due to the large number of active sites, methanol and FFA are adsorbed to the photocatalyst surface. Due to the high oxidation potential of the holes created, the adsorbed CH₃OH on the photocatalyst surface reacts with the hole (h⁺) to produce H⁺ ions and CH_3O · radicals. At the same time, the RCOOH adsorbed on the photocatalyst surface is reduced by accepting the electrons produced (e⁻) on the surface to form the free radical RCOOH. Then, a reaction is performed between RCOO·, H⁺, CH₃O· produced to form methyl ester and water. Finally, the reaction products are separated from the photocatalyst surface. The mechanism of photocatalyst performance in the photo-esterification step is shown below.

Kinetics of the Transesterification Step

Although the importance of biodiesel as an alternative fuel has increased over the past twenty years, the chemical kinetics of transesterification, as the most common method of biodiesel production, is still debated. Friedman *et al.* [38] have studied the kinetics of biodiesel. In Friedman's model, the general reaction is as follows:

Triglycerides + 3 ROH
$$\xrightarrow{Catalyst}$$
 3 FAME + Glycerol

In this study, first and second-order rate equations are investigated using Friedmann's proposed reaction. In addition, five assumptions are considered to simplify the conditions for examining the equation:

1. Due to the hydroxyl groups present in the oil structure, high dissolution of methanol in the oil

can be expected. For this reason, the reaction mixture can be considered as a homogeneous system where there are no restrictions on mass transfer.

2. This step has followed the photo-esterification step and according to the results obtained, the percentage of free fatty acid has decreased in the previous sections. Therefore, the soaping reaction is ignored.

3. According to the results obtained in the previous sections, the percentage of free fatty acids with high efficiency has decreased. The amount of free fatty acids in the reaction is ignored.

4. The concentrations of monoglycerides and diglycerides are ignored, which are insignificant compared with triglycerides in the oil sample.

5. Due to the large amount of methanol and the low concentration of the product, one can expect that the feedback reactions are negligible.

Taking into account the above assumptions, the kinetics of the transesterification reaction has been investigated. The relevant formulas are reviewed below. The transesterification reaction proceeds in three stages of successive and reversible reactions [39]. Transesterification begins with the reaction of triglyceride (TG) and methanol to produce diglyceride (DG) and one mole of methyl ester. Diglycerides react with methanol to form monoglycerides (MG) and another mole of methyl ester. The monoglycerides eventually react with methanol to form one mole of methyl ester.

 $\begin{aligned} Triglycerides + CH_3OH &\stackrel{k}{\Leftrightarrow} FAME + Diglycerides\\ Diglycerides + CH_3OH &\stackrel{k'}{\Leftrightarrow} FAME + Monoglycerides\\ Monoglycerides + CH_3OH &\stackrel{k''}{\Leftrightarrow} FAME + Glycerol\\ Where \ k = \frac{k_a}{k_b} \cdot k' = \frac{k'_a}{k'_b} \text{ and } k'' = \frac{k''_a}{k''_b}. \end{aligned}$

According to Friedmann's proposed equation, the general equation was considered as follows:

Triglycerides + 3
$$CH_3OH \xrightarrow{NaOH} 3 FAME + Glycerol$$

To investigate the kinetics of the second stage of biodiesel production from the esterified sample, %15 Cr-TiO₂ photocatalyst and a molar ratio of alcohol to oil of 10.7 to 1 were investigated, and then the obtained sample with reduced fatty acid was used as a raw material in the second stage. To investigate this step, the Verma method has been used [40]. Esterified oil is used as a prototype and the molar ratio of methanol is 6 times that of oil. The amount of NaOH as a catalyst is 1% by weight. The samples were studied at three temperatures of 30, 45, and 60 °C at times of 30, 60, 90, and 120 min.

First-order kinetics

The FAME and TG conversion rate equation is expressed as follows:

$$-\frac{d[TG]}{dt} = K \ [TG] \tag{14}$$

$$-\frac{d[TG]}{[TG]} = K dt \tag{15}$$

$$\ln\left(\frac{[TG]}{[TG]_0}\right) = -K t \tag{16}$$

Given $[TG] = [TG]_0(1 - X_{TG})$, X_{TG} is the rate of conversion of triglycerides at any time.

The triglyceride conversion rate equation is rewritten as follows:

$$\ln(1 - X_{TG}) = -K t \tag{17}$$

The relationship between the rates of the two reciprocating reactions is as follows:

$$-r_{TG} = \frac{1}{3}r_{FAME}$$

The triglyceride conversion rate is equivalent to one third of the FAME conversion.

$$X_{TG} = \frac{1}{3} X_{FEME}$$

By substituting in Equation (17), we have:

$$\ln(3 - X_{FEME}) = -K t + \ln(3)$$
(18)

From the curve $ln(3 - X_{FEME})$ in terms of t, we will have a first-degree equation with slope k, which is the reaction rate constant (Figure 15).



Figure 15: Curve $\ln(3 - X_{FEME})$ in terms of t

Second Order Kinetics

In the equation [TG] triglyceride concentration, $[TG]_0$ is the triglyceride concentration at zero and K is the reaction rate constant.

$$-r_{TG} = -\frac{d[TG]}{dt} = K [TG]^2$$
(19)

Given that the $[TG] = [TG]_0(1 - X_{TG})$, X is the percentage of triglyceride conversion at any time.

$$-\frac{dX_{TG}}{dt} = K \left[[TG]_0 (1 - X_{TG}) \right]^2$$
(20)

$$\frac{dX_{TG}}{[(1-X_{TG})]^2} = -K[TG]_0^2 dt$$
(21)

Consider constant values: $K[TG]_0^2 = k'$

$$\frac{X_{TG}}{1-X_{TG}} = \mathbf{k}'t \tag{22}$$

The triglyceride conversion rate is equivalent to one third of the FAME conversion.

$$X_{TG} = \frac{1}{3} X_{FEME}$$

By substituting in Equation (22) we have:

$$\frac{X_{FAME}}{3 - X_{FAME}} = \mathbf{k}' t \tag{22}$$

From the curve $\frac{X_{FAME}}{3-X_{FAME}}$ in terms of t, we will have a quadratic equation with slope k' (Figure 16).

The mean correlation coefficient and rate constant in both reaction times are shown in Table 6.

The first-order kinetic model showed the highest correlation coefficient, $R^2 = 0.997$. The reaction kinetics is of the first-order type.

Thermodynamic parameters are one of the criteria that are of special importance in describing the reaction process. By examining the velocity constant in terms of temperature, one can comment on the nature of the reaction (endothermic or exothermic). The activation energy was calculated to evaluate the thermodynamic feasibility and spontaneous nature of the process. According to the rate and temperature constants (Figure 17), the activation energy is calculated by Equation (12).

According to the linear regression coefficient, i.e. R^2 = 0.9977, the proposed reaction kinetics model is reasonable. From the slope of the diagram, the activation energy value was 7.103 kJ/mol. Positive

values of activation energy indicate the warming nature of the reaction process.



Figure 16: The curve $\frac{X_{FAME}}{3-X_{FAME}}$ in terms of t

Kinetic model	k	R^2
first time	0.0018	0.997
second time	0.0021	0.994



Figure 17: Arrhenius equation curve

Mechanism of Transesterification Step

-OH or -OR species are active in the transesterification reaction with the base catalyst. Mechanistic pathways for homogeneous and heterogeneous that play as catalysts essentially follow one principle. Homogeneous base catalysis is mostly used in commercial biodiesel production processes because in this process high efficiency is achieved in a short time (10 minutes to 2 h) with a mild reaction temperature (25-70 °C). The reaction mechanism consists of 3 steps, which are shown below. The first step produces the basic reaction of the methoxide ion, which is so strong

that by attacking the methoxide ion (methanol as the reacting alcohol) on the carbon of the carbonyl group, the triglyceride molecule forms a quadrilateral mediator. In the second step, the quadrilateral mediator reacts with alcohol to regenerate the methoxide ions. The last step involves the rearrangement of quadrilateral intermediates to form methyl esters and diglycerides. This mechanism is available for the reaction of methoxide with diglyceride, and then methoxide with monoglyceride in the same way. This process is repeated twice, producing three FAME molecules and one glycerol molecule [34].





Conclusion

Biodiesel is a renewable alternative fuel that emits less harmful gases than fossil fuels. Oil esterification is one of the most advanced methods of oil technology that changes the main structure of glycerides without chemical changes in the fatty acid making up the structure of triglycerides. Sources of biodiesel are vegetable oils and animal fats. The primary purpose of this study was to develop suitable processes for producing biodiesel from oils with a high percentage of FFAs. Another goal is to understand the relationship between the FFAs percentages in the oil source and reduce its use of light sources and photocatalysts and biodiesel production efficiency. Biodiesel production from frying oil residues was investigated by a two-step process. In the first step, the free fatty acids in the oil were esterified with methanol by a photocatalytic process using a Cr/TiO₂ semiconductor composite and ultraviolet radiation as the light source. The catalytic performance of Cr/TiO₂ under different conditions in the waste oil esterification process was investigated. The characterization results confirmed the photocatalysts synthesis with twodimensional structure. Characterization has shown that chromium nanoparticles are located on the surface of TiO₂ nanosheets, and also DRS ensures the reduction of the TiO₂ energy gap with different percentages of chromium doped on its surface. To achieve the optimal effective parameters, the response level method has been used. The waste oil reacted with methanol in the presence of a photocatalyst and was converted to methyl ester. After re-esterification, the oil was titrated, and its free fatty acids were reduced. Under these conditions, the oil was used in the transesterification reaction. In the sample formed without the esterification step, due to the effect of the soap's high free fatty acid content and the difficulty in separating the product, which reduced the yield, the biodiesel production efficiency was 52.9%. While performing the sterilization step in the presence of Cr-TiO₂ photocatalysts with ultraviolet radiation, the efficiency was 76.3% -89.5%. Photocatalytic recovery was investigated in five steps. After five experimental steps, the conversion rate by ultraviolet irradiation for 3 hours was the percentage of FFA conversion in the presence of photocatalysts for %2 Cr-TiO₂, %8.5 Cr-TiO₂, and %15 Cr-TiO₂; 66.3%, 58.9% and 54.5% were obtained, respectively. With increasing the percentage of chromium on the structure of titanium dioxide, the structure's surface was more uneven. With the recovery of photocatalysts, the probability of sediment penetration to active centers was higher, and the efficiency naturally decreased in the later stages of the catalyst used. The photocatalytic reaction mechanism was investigated based on the production of electron-hole pairs. Exposure of light to sufficient energy led to the electrons transfer from the TiO₂ capacitance band to the TiO₂ conduction band and the formation of holes in the TiO_2 capacitance band. The electrons transferred to the conduction band, and the holes formed in the capacitance band can react with the adsorbed species on the photocatalyst surface. Given the DRS curve and the reduction of energy gap for pure titanium dioxide relative to Cr-TiO₂, it is obvious that doped Cr has significantly

improved the absorption in the visible light region of TiO₂. The proposed mechanism of photon absorption was investigated by the Cr/TiO₂ photocatalyst, mainly by TiO₂ sites, and the production of electrons induced by the photon eand the hole h⁺. Cr surface electrons were also considered. -OH or -OR transesterification reaction was considered as an active species in the current study. The first step was formed by the attack of methoxide ions on the carbon of the carbonyl group of quadrilateral-mediated triglyceride molecules. In the second step, the quadrilateral mediator reacts with methanol to regenerate the methoxide ions. The last step involves the rearrangement of quadrilateral intermediates to form methyl esters and diglycerides. This mechanism was proposed for the reaction of methoxide with diglyceride and then methoxide with monoglyceride in the same way. The predominant methyl esters in biodiesel are methyl palmitic, methyl stearic, methyl oleic, methyl linoleic, methyl linolenic, and methyl myristic.

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ORCID

Zahra Abbasi <u>https://orcid.org/0000-0001-9580-5423</u> Mehdi Ahmadi <u>https://orcid.org/0000-0002-9227-7562</u>

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