Enhancing the Catalytic Performance of NiO during the Transesterification of Waste Cooking Oil Using a Diatomite Carrier and an Integrated Ni\textsuperscript{0} Metal: Response Surface Studies

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ABSTRACT: Two types of NiO-based composites (NiO@diatomite and Ni/NiO@diatomite) were synthesized as modified products of enhanced catalytic performances during the transesterification reactions of waste cooking oil. The influence of the diatomite substrate and the integration of metallic Ni\textsuperscript{0} in inducing the catalytic activity were evaluated in a series of transesterification reactions. The experimental conditions were adjusted according to the response surface methodology and the central composite statistical design. Experimentally, the diatomite substrate and the Ni\textsuperscript{0} metal induced the efficiency of the reaction to achieve a yield of 73.4\% (NiO@diatomite) and 91\% (Ni/NiO@diatomite), respectively, as compared to 66\% for the pure phase (NiO). This was obtained under experimental conditions of 80 °C temperature, 100 min time, 12:1 methanol/oil molar ratio, and 3.75 wt \% loading. The theoretical optimization functions of the designs suggested enhancement to the experimental conditions to achieve a yield of 76.3\% by NiO@diatomite and 93.2\% by Ni/NiO@diatomite. This reflected the role of the diatomite substrate in enhancing the surface area, the adsorption of fatty acids, and the exposure of the catalytic sites in addition to the effect of the Ni\textsuperscript{0} metal in enhancing the catalytic reactivity of the final product. Finally, the biodiesel produced over Ni/NiO@diatomite as the best product was of acceptable properties according to the international standards.

1. INTRODUCTION

Nowadays, global efforts have been devoted to replacing the unsustainable sources of energy that are internationally exploited as the main source of energy. Conventional sources of energy such as petroleum and coal are non-renewable and cannot be regenerated.\textsuperscript{1} Thus, the world encountered a critical problem to meet the global needs of energy with the onset of the industrial revolution and with the economic development due to extreme consumption of energy.\textsuperscript{2} On the other hand, the ignition of fossil fuels releases highly toxic compounds that are classified under the carcinogenic category and increase greenhouse gas emissions. As a result, fossil fuels have crucial effects on human health and on the surrounding environment.\textsuperscript{3} Biodiesel is one of the various renewable sources that were proposed as proficient alternatives for fossil fuels. Chemically, biodiesel is formulated as a fatty acid methyl ester (FAME) and is characterized by non-toxic, biodegradable, and eco-friendly properties. Furthermore, biodiesel exhibits brilliant technical properties including high flash point, high cetane number, excellent lubricity, and good viscosity, which qualify it to act efficiently inside engines.\textsuperscript{4,5}

Mainly, biodiesel is produced by transesterification reaction in the presence of a suitable catalyst to accelerate the rate of the reaction. The used catalysts in the transesterification process can be divided into two types: homogeneous and heterogeneous catalysts.\textsuperscript{6} Although homogeneous catalysts exhibit high catalytic activity within the reaction medium, they have significant disadvantages such as separation difficulty, corrosion property, and toxic byproducts.\textsuperscript{7} Heterogeneous catalysts show effective advantages that overcome the drawbacks of the homogeneous forms as they are distinguished by reusability, thermal stability, low economic cost, eco-friendly properties, and non-corrosion properties.\textsuperscript{8} The efficiency of heterogeneous catalysts is a function of surface area, chemical stability, surface reactivity, recovering method, and the concentration of catalytic sites.\textsuperscript{9,10}

Previous studies have declared that the applications of NiO as a catalyst were recognized to suffer from some drawbacks such as the low surface area, difficult separation, and low stability.\textsuperscript{11} Additionally, as a heterogeneous catalyst in biodiesel production, it is of limited efficiency and it achieved low biodiesel yields.\textsuperscript{12} Thus, researchers have directed their

Received: March 10, 2021
Accepted: April 14, 2021
Published: April 26, 2021
attention to tackling these drawbacks and inducing its reactivity by doping its structure with other metals, integrating it in composites, and by supporting it in a significant carrier or substrate that provides promising properties as an effective catalyst of thermo-chemical stability.\textsuperscript{11,13} The doping process of NiO with Ni in its metallic form was recommended as an effective method to enhance the chemical and physical properties of the structure as well as its catalytic performance.\textsuperscript{14}

Diatomite is a natural material of high reserves and it is composed of a siliceous skeleton that is characterized by a highly regular porous structure, a high surface area, and thermo-chemical stability.\textsuperscript{14,15} Using the diatomite structure as a carrier for the different types of metal oxide-based catalysts was reported as an effective technique that preserves the loading particles free from each other without agglomeration.\textsuperscript{16} This was credited to its structural ability to create chemical bonds between the metal oxides and the structural silicone hydroxyl.\textsuperscript{17} Therefore, the formation of the composite with diatomite or using it as a substrate was investigated as an effective method that induces the catalytic activity as well as the textural properties of the loaded metal oxide.

The present study focuses on the catalytic activity of synthetic NiO as a heterogeneous catalyst during transesterification reactions of waste cooking oil (WCO). The study involves a systematic investigation of the role of the diatomite frustules as catalyst carriers as well as the integration of metallic Ni\textsuperscript{0} in enhancing the catalytic activity of NiO. The catalytic performances were evaluated considering the obtained biodiesel yields based on different experimental factors (temperature, time, loading, and methanol content). The influence of the factors and their values were studied using Expert-Design software (Version 6.0.5) based on the response surface methodology (RSM) and the central composite rotatable design (CCD).

2. RESULTS AND DISCUSSION

2.1. Characterization. 2.1.1. X-ray Diffraction. X-ray diffraction (XRD) analysis was performed to detect the structural modifications between the diatomite precursor and the modified composites (Figure 1A). The distinctive broad peak of amorphous silica, which characterizes the opaline structure of diatomite, was observed at 2\(\theta\) angles of 22.\textsuperscript{16} After the loading process, the obtained diffraction pattern demonstrates their observable peaks related to the NiO catalyst in addition to the broad peaks of siliceous diatomite (Figure 1B). The observed deviating for the broad peak of diatomite related mainly to the interaction effect of the loaded NiO and its complexes with the silanol groups. The identification peaks were observed at 37.4\(^\circ\) (111), 43.41\(^\circ\) (200), and 62.7\(^\circ\) (220), which demonstrates its crystallization in the cubic system with a crystalline size of 22 nm (ICDD file. no. 089-7130; JCPDS no. 47-1049). Figure 1C confirms the effective incorporation of Ni\textsuperscript{2+} in the composite with the structure of NiO considering the presence of the diatomite skeletons as substrates. The two characteristic peaks of NiO were identified at 37.42\(^\circ\) (111) and (200) 43.38\(^\circ\) (ICDD file#089-7130; JCPDS, no. 47-1049) (Figure 1C). The peaks of metallic Ni\textsuperscript{0} were observed at 2\(\theta\) angles of 44.58 and 51.9\(^\circ\) (Figure 1C).

2.1.2. Morphological Studies. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) images were demonstrated to study the morphological changes of the diatomite precursor, NiO@D, and Ni/NiO@D (Figure 2). The refined diatomite exhibits its remarkable pennate structure of numerous pores, which were arranged in a regular pattern and display sizes ranging from 250 nm to nearly 500 nm (Figure 2A). Figure 2B,C shows the homogeneous incorporation of the loaded nanoparticles successfully throughout the diatomite structure without over-coating of its surface. Basically, the magnifcent changes in the diatomite structure, which can be credited to the homogeneous decoration of the frustules with the NiO and Ni/NiO particles, are the partial blocking of its pores (Figure 2B). There are no significant differences between the morphological features of the loaded NiO and Ni/NiO particles. Both forms were detected as nano-globular or spherical grains on the surface of diatomite (Figure 2C).

Figure 2D–F shows the HRTEM images, which reflect the internal difference between the purified diatomite, NiO@D, and Ni/NiO@D. The diatomite precursor displays its remarkable structure of diatom skeleton with amazing nanopores arranged in a regular fashion (Figure 2D). The NiO and Ni/NiO nanoparticles were detected within the size range from 5 nm up to 150 nm as decorated spherical grains for the skeleton of diatomite and distributed uniformly on its surface as well as within its pores (Figure 2E,F).

2.1.3. Fourier-Transform Infrared Spectroscopy Analysis. Figure 3A indicates the chemical changes between the raw diatomite, NiO@D, and Ni/NiO@D. The purified diatomite displayed two significant bands at 3437 cm\(^{-1}\) and about 1638 cm\(^{-1}\), which were attributed to the presence of silanol groups (Si–O–H) of opaline silica within the diatomite structure and the vibration of water molecules (H–O–H)\textsuperscript{17} (Figure 3A(A)). Additionally, two considerable bands for the symmetric and asymmetric stretching of siloxane groups (Si–O–Si) were reported at 1092 and 799 cm\(^{-1}\), respectively\textsuperscript{19} (Figure 3A(A)). The changes in the intensities and positions of the distinctive bands of diatomite after the modification supported the successful loading of the NiO particles on the diatomite structure (NiO@D), which emphasizes the chemical interactions between them\textsuperscript{20} (Figure 3A(B)). Moreover, Ni–O stretching was detected by new bands from 500 to 700 cm\(^{-1}\), which confirm the loading of
The recognized Fourier-transform infrared spectroscopy (FT-IR) spectrum of the Ni/NiO@D made no observable changes in the main bands, which were detected for the composite before the reduction process (Figure 3A(C)). The main differences were related only to the slight deviation of the bands from their position, which gives an indication about slight changes in the chemical structure after the incorporation of the Ni\textsuperscript{0} metal.

The elemental composition was evaluated based on the EDX analysis to give more information about the loading process. Figure 3B. A shows the EDX analysis of the NiO@D and assures the presence of Ni, Si, and O elements at 12.6, 41.2, and 46.2% as elemental percentages, respectively. The determined percentages of Ni, Si, and O elements for Ni/NiO@D are 18.7, 40.3, and 40.98%, respectively (Figure 3B(B)). The noticed depletion in the oxygen content reflected the role of the reduction processes in converting Ni(OH)\textsubscript{2} into Ni\textsuperscript{0} metal.

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2.1.4. Textural Properties. The recognized textural properties including the surface area, the pore volume, and the pore diameter of the three products are presented in Table S2. There is an observable enhancement in the pore volume and the surface area after the loading processes. The obtained pore volumes of diatomite, NiO@D, and Ni/NiO@D are 0.032, 0.116, and 0.117 cm\textsuperscript{3}/g, respectively. The measured pore diameters are 5.41, 5.86, and 5.84 nm for diatomite, NiO@D, and Ni/NiO@D, respectively. Also, the measured surface area of diatomite (117.7 m\textsuperscript{2}/g), NiO@D (406.3 m\textsuperscript{2}/g), and Ni/NiO@D (400.5 m\textsuperscript{2}/g) reflected strong enhancement after the loading processes. This demonstrates the homogenous distribution of the loaded NiO oxide with partial blocking of the pores of the diatomite frustules. Moreover, the expected dissolution effect for the used NaOH on the siliceous structure of diatomite during the loading reactions increases the diameter of the present pores as weak zones for the reactions.\textsuperscript{22–24} Additionally, the detection of the loaded particles as homogeneously distributed globules of nano-size has an effective role in improving the total surface area.

2.2. Transesterification Results Based on the Response Surface Studies. 2.2.1. Analyses of the Validation and the Variances of the Approaches. The validation of the studied designs, as well as the second-order quadratic polynomial model as the representative model, was evaluated based on the regression inspection of the variance function (ANOVA). The built design includes 26 suggested tests for the three catalysts (NiO, NiO@diatomite (NiO@D), and Ni/NiO@diatomite (NiNiO@D)) for the interaction between the different experimental factors [(A) temperature, (B) transesterification interval, (C) catalyst loading, and (D) methanol/oil ratio] (Table 1).

The linear regressions between the predicted response (biodiesel yields) and the experimentally measured results for NiO, NiO@D, and Ni/Ni@D are of excellent fitting degrees ($R^2 > 0.97$). Therefore, performing the suggested experiments according to the polynomial model has a strong significance and can represent the influence of the parameters as well as
their interactions with each other (Figure 4A). This was supported by the obtained prediction deviation curves for the conducted tests using the three catalysts (NiO, NiO@D, and Ni/NiO@D). The curves show the regular distribution for the deviated values of the responses on both the negative and positive sides of the reference line within the obtained range from $-0.79$ to $0.51$ for NiO, $-1.49$ to $1.64$ for NiO@D, and $1.19$ to $1.17$ for Ni/NiO@D (Figure 4B). Moreover, the obtained regression relations for the studentized residuals demonstrate the normality of the model during the description and the prediction processes of the responses as a function of the selected parameters (Figure 5). This reflects significant accuracy during the predictions of the responses (biodiesel yields) according to the suggestions of the polynomial model.

The main ANOVA parameters of the model-F, model-prob $> F$, lack of fit, and the sum of squares were addressed also to evaluate the validation and the significance of the selected model (Table 2). The recognized model-F values of NiO (240.8), NiO@D (267.3), and Ni/NiO@D (148.5) were related to significant models with a noise effect of less than 0.01% for the three models (Table 2). The obtained model-Prob-F values of NiO, NiO@D, and Ni/Ni@D for the addressed parameters are less than 0.05%. These values reflect the significance of the inspected parameters and give indications about the nonlinear regression between the responses (biodiesel yields) and the influence of these parameters (Table 2). There are observable agreements between the values of pred $R$-squared (NiO (0.98), NiO@D (0.98), and Ni/NiO@D (0.96)), adj $R$-squared (NiO (0.99), NiO@D (0.99), and Ni/NiO@D (0.98)), and adeq precision (NiO (0.89), NiO@D (0.93), and Ni/NiO@D (0.88)) confirm adequate signals for three catalysts and strong

| std run | temperature ($^\circ$C) (A) | time (min) (B) | methanol/oil ratio (C) | loading (wt %) (D) | biodiesel yield (%) (NiO) (Y) | biodiesel yield (%) (NiO@D) (Y) | biodiesel yield (%) (Ni/NiO@D) (Y) |
|---------|-----------------------------|-----------------|------------------------|-------------------|-------------------------------|---------------------------------|-----------------------------------|
| 6       | 80.00                       | 20.00           | 12.00                  | 2.50              | 50.6                          | 59.3                            | 74.3                              |
| 17      | 30.00                       | 100.00          | 8.00                   | 3.75              | 54                            | 61.3                            | 78.3                              |
| 11      | 30.00                       | 180.00          | 4.00                   | 5.00              | 41.3                          | 47.8                            | 66.9                              |
| 22      | 55.00                       | 100.00          | 12.00                  | 3.75              | 66.2                          | 73.4                            | 91                                |
| 10      | 80.00                       | 20.00           | 4.00                   | 5.00              | 41.2                          | 49.7                            | 64.9                              |
| 7       | 30.00                       | 180.00          | 12.00                  | 2.50              | 50.7                          | 59.3                            | 73.8                              |
| 8       | 80.00                       | 180.00          | 4.00                   | 5.00              | 50.8                          | 58.6                            | 74.9                              |
| 23      | 55.00                       | 100.00          | 8.00                   | 5.00              | 53.8                          | 61.2                            | 78.7                              |
| 24      | 55.00                       | 100.00          | 8.00                   | 3.75              | 57.6                          | 64.9                            | 82.7                              |
| 25      | 55.00                       | 100.00          | 8.00                   | 3.75              | 60.2                          | 67.5                            | 85.3                              |
| 4       | 80.00                       | 180.00          | 4.00                   | 5.00              | 47                            | 54.4                            | 70.6                              |
| 15      | 30.00                       | 180.00          | 12.00                  | 5.00              | 54.7                          | 61.4                            | 78.5                              |
| 20      | 55.00                       | 180.00          | 8.00                   | 3.75              | 57                            | 64.3                            | 82.3                              |
| 16      | 80.00                       | 180.00          | 12.00                  | 5.00              | 64.3                          | 70.9                            | 88.2                              |
| 5       | 30.00                       | 20.00           | 12.00                  | 5.00              | 41.3                          | 49.7                            | 66.3                              |
| 3       | 30.00                       | 20.00           | 12.00                  | 5.00              | 38.4                          | 45.6                            | 61.2                              |
| 13      | 30.00                       | 20.00           | 12.00                  | 5.00              | 42.9                          | 52                              | 70.2                              |
| 1       | 30.00                       | 20.00           | 4.00                   | 2.50              | 27                            | 35.3                            | 49.6                              |
| 26      | 55.00                       | 100.00          | 8.00                   | 3.75              | 60.3                          | 67.5                            | 85.3                              |
| 21      | 55.00                       | 100.00          | 4.00                   | 3.75              | 52.9                          | 60.3                            | 78.5                              |
| 18      | 80.00                       | 100.00          | 8.00                   | 3.75              | 63.4                          | 70.5                            | 86.9                              |
| 9       | 30.00                       | 20.00           | 4.00                   | 5.00              | 30.8                          | 39.3                            | 53.3                              |
| 2      | 80.00                       | 20.00           | 4.00                   | 2.50              | 37.3                          | 45.5                            | 60.8                              |
| 19      | 55.00                       | 20.00           | 8.00                   | 3.75              | 50.6                          | 58.8                            | 76.3                              |
| 14      | 80.00                       | 20.00           | 12.00                  | 5.00              | 54.4                          | 63.7                            | 79.3                              |

Figure 4. The correlation between the expected biodiesel yields and the determined yields (A) and the standard deviation of the expected biodiesel yields for the suggested 26 tests (B).
significances for the studied quadratic polynomial models to navigate the designs spaces (Table 2).

Considering the obtained results for the validation and the variances of the approaches, the relations between the experimental factors [(A) temperature, (B) transesterification interval, (C) catalyst loading, and (D) methanol/oil ratio] and the biodiesel yields (Y) as responses can be represented by the following polynomial regression equations for NiO (eq 1), NiO@D (eq 2), and Ni/NiO@D (eq 3).

\[
Y(\text{NiO}) = +60.52 + 4.89 \times A + 4.91 \times B + 6.59 \times C + 1.76 \times D - 1.91 \times A^2 - 6.81 \times B^2 - 1.06C^2 - 4.91D^2 - 0.27\times
\]
\[
A \times B + 0.069 \times A \times C + 0.21 \times A \times D - 0.031 \times B \times C + 0.11 \times B \times D - 0.056 \times C \times D
\]

\[
Y(\text{NiO@D}) = +67.73 + 4.98 \times A + 4.32 \times B + 6.77 \times C + 1.63 \times D - 1.91 \times A^2 - 6.26 \times B^2 - 0.96 \times C^2 - 4.76\times
\]
\[
D^2 - 0.21 \times A \times B + 0.000 \times A \times C + 0.28 \times A \times D - 0.062 \times B \times C - 0.26 \times B \times D - 0.22 \times C \times D
\]

\[
Y(\text{Ni/NiO@D}) = +85.67 + 4.78 \times A + 4.76 \times B + 6.96 \times C + 2.18 \times D - 3.20 \times A^2 - 6.50 \times B^2 - 1.05 \times C^2 - 5.10\times
\]
\[
D^2 - 0.14 \times A \times B - 0.18 \times A \times C - 0.044 \times A \times D - 0.64 \times B \times C + 0.12 \times B \times D - 0.019 \times C \times D
\]

2.2.2. Influence of the Controlling Factors and the Interaction Effect. 2.2.2.1. Interaction Effect between the Reaction Temperature and Time. The interaction effect

Figure 5. Normal probability plot for studentized residuals for the suggested experimental conditions over NiO (A), NiO@D (B), and Ni/NiO@D (C).
Table 2. ANOVA for the Studied CCD

| source | sum of squares NiO | sum of squares NiO@D | sum of squares Ni/NiO@D | DF NiO | DF NiO@D | DF Ni/NiO@D | mean square NiO | mean square NiO@D | mean square Ni/NiO@D | F-value NiO | F-value NiO@D | F-value Ni/NiO@D | prob > F NiO | prob > F NiO@D | prob > F Ni/NiO@D | significance |
|--------|-------------------|---------------------|------------------------|--------|----------|------------|----------------|------------------|-------------------|------------------|------------|----------------|----------------|-------------|----------------|-----------------|--------------|
| model  | 2619.70           | 2475.1              | 2830.95                | 14     | 14       | 14         | 187.12         | 176.80           | 202.21           | 240.82      | 267.28         | 148.55        | <0.0001     | <0.0001        | <0.0001        | significant  |
| A      | 431.20            | 446.0               | 411.84                 | 1      | 1        | 1          | 431.20         | 446.01           | 411.84           | 554.94      | 674.29         | 302.56        | <0.0001     | <0.0001        | <0.0001        |
| B      | 433.16            | 335.4               | 408.03                 | 1      | 1        | 1          | 433.16         | 335.40           | 408.03           | 557.46      | 507.08         | 299.75        | <0.0001     | <0.0001        | <0.0001        |
| C      | 781.44            | 825.5               | 870.84                 | 1      | 1        | 1          | 781.44         | 825.53           | 870.84           | 1005.69     | 1248.07        | 639.75        | <0.0001     | <0.0001        | <0.0001        |
| D      | 55.83             | 47.69               | 85.80                  | 1      | 1        | 1          | 55.83          | 47.69            | 85.80            | 71.85       | 72.11          | 63.04         | <0.0001     | <0.0001        | <0.0001        |
| A²     | 9.38              | 9.37                | 26.18                  | 1      | 1        | 1          | 9.38           | 9.37             | 26.18            | 12.07       | 14.16          | 19.23         | <0.0001     | 0.0031         | 0.0011         |
| B²     | 118.90            | 100.4               | 108.11                 | 1      | 1        | 1          | 118.90         | 100.43           | 108.11           | 153.02      | 151.84         | 79.42         | <0.0001     | <0.0001        | <0.0001        |
| C²     | 2.90              | 2.37                | 2.81                   | 1      | 1        | 1          | 2.90           | 2.37             | 2.81             | 3.73        | 3.59           | 2.06          | <0.0001     | 0.0296         | 0.01787        |
| D²     | 61.84             | 58.08               | 66.54                  | 1      | 1        | 1          | 61.84          | 58.08            | 66.54            | 79.58       | 87.81          | 48.88         | <0.0001     | <0.0001        | <0.0001        |
| A×B    | 1.16              | 0.72                | 0.33                   | 1      | 1        | 1          | 1.16           | 0.72             | 0.33             | 1.49        | 1.09           | 0.24          | 0.0481      | 0.03184        | 0.0318         |
| A×C    | 0.076             | 0.000               | 0.53                   | 1      | 1        | 1          | 0.076          | 0.000            | 0.53             | 0.097       | 0.000          | 0.39          | 0.0409      | 0.0341         | 0.0470         |
| A×D    | 0.68              | 0.121               | 0.031                  | 1      | 1        | 1          | 0.68           | 0.121            | 0.031            | 0.88        | 1.83           | 0.022         | 0.0369      | 0.02034        | 0.0283         |
| B×C    | 0.016             | 0.063               | 6.63                   | 1      | 1        | 1          | 0.016          | 0.063            | 6.63             | 0.020       | 0.094          | 4.87          | 0.02898     | 0.04643        | 0.0495         |
| B×D    | 0.18              | 1.10                | 0.23                   | 1      | 1        | 1          | 0.18           | 1.10             | 0.23             | 0.23        | 1.67           | 0.17          | 0.0392      | 0.02232        | 0.0291         |
| C×D    | 0.051             | 0.81                | 5.6 × 10⁻³              | 1      | 1        | 1          | 0.051          | 0.81             | 5.6 × 10⁻³       | 0.02032     | 0.02921        | 0.0499        | <0.0001     | 0.0031         | 0.0011         |
| residual | 8.55              | 7.28               | 14.97                  | 11     | 11       | 11         | 0.78           | 0.66             | 1.36             |            |               |              |            |                |                |
| lack of fit | 8.54          | 7.28               | 14.97                  | 10     | 10       | 10         | 0.85           | 0.73             | 1.50             |            |               |              |            |                |                |
| pure error | 5 × 10⁻³          | 0.000              | 0.000                  | 1      | 1        | 1          |                |                 |                 |            |               |              |            |                |                |
| cor total | 2628.24          | 2482.4             | 2845.92                | 25     | 25       | 25         |                |                 |                 |            |               |              |            |                |                |

| NiO | NiO@D | Ni/NiO@D | std. dev. | mean | C.V. | PRESS | adeq precision |
|-----|-------|----------|-----------|------|------|-------|----------------|
|     |       |          | 0.88      | 50.3 | 1.75 | 46.5  | 0.89           |
|     |       |          | 0.81      | 58.1 | 1.4  | 38.4  | 0.93           |
|     |       |          | 0.94      | 64.7 | 1.56 | 52.99 | 0.87           |
| R²  |       |          |           |      |      |       |                |
| adj R² |     |          |           |      |      |       |                |
| pred R² |     |          |           |      |      |       |                |
| adeq precision | |          |           |      |      |       |                |
between the reaction temperature and time was inspected considering the intermediate values of the catalyst load (3.75 g) and the methanol to oil ratio (8:1). Considering the 3D regression curves, the interaction between the temperature and the transesterification intervals has a vital effect on inducing the catalytic activities of the three catalysts (NiO, NiO@D, and Ni/Ni@D) (Figure 6A–C). Based on the obtained trends, the activities of NiO, NiO@D, and Ni/Ni@D were enhanced at all the studied temperatures from 20 min up to 100 min and then declined again with the expanding interval up to 180 min (Figure 6A–C). The remarkable declination activities of the three catalysts as a function of the determined biodiesel yields are related to the reversible properties of these types of transesterification reactions. After certain intervals, the formed fatty acid esters can be affected by hydrolysis processes and converted again to their parent-free fatty acids. Therefore, transesterification of WCO over NiO, NiO@D, and Ni/Ni@D is preferred to be conducted for 100 min considering the experimental inputs.

For the interaction influence of temperature at its lower level (30 °C), the recognized yields by NiO, NiO@D, and Ni/Ni@D after 100 min are 54, 61.3, and 78.3%, respectively (Figure 6A–C). At 55 °C, the achieved yields are 60.2% (NiO), 67.5% (NiO@D), and 85.3% (Ni/Ni@D) (Figure 6A–C). At the upper values of temperature (80 °C), the determined yields increased to 63.4, 70.5, and 86.9% for NiO, NiO@D, and Ni/Ni@D, respectively (Figure 6A–C). These results demonstrate the strong positive influence on the

Figure 6. 3D curves or the interaction between the transesterification intervals and the temperature (A–C), the interaction between the transesterification intervals and the methanol content (D–F), and the interaction between the transesterification intervals and the lodgings of the catalysts (G–I).
temperature in the catalytic activities of the three catalysts at certain time intervals. This is related to the endothermic behaviors of these reactions, which make the high temperature values favorable to enhance the kinetic energy and prompt the transformation rates.\textsuperscript{14,26} Moreover, such conditions are valuable in reducing the viscosity, immiscibility, and mass transfer resistance, which enhance the homogeneity of the mixture and the interaction chances between the reacted components.\textsuperscript{27,28} Based on the previous findings, a reaction temperature of 80°C and a reaction interval of 100 min are the best conditions for the transesterification of WCO over NiO, NiO@D, and Ni/NiO@D.

### 2.2.2. Interaction Effect between the Methanol to Oil Ratio and the Reaction Time.

The interaction effect between the reaction time and the methanol content was evaluated based on the 3D regression curves considering the intermediate values of catalyst loading (3.75 wt %) and temperature (55°C) (Figure 6D–F). The methanol content has a remarkable influence on enhancing the catalytic performance and intensifying the effect of the reaction time within the experimental range from 4 (methanol):1 (oil) up to 12 (methanol):1 (oil) (Figure 6D–F). Generally, the incorporation of methanol as an essential reactant for the conversion of WCO into FAME, which makes the adjusted ratio, has a vital effect on preserving the reaction balance in addition to its role in reducing the viscosity, the immiscibility, and the mass transfer resistance.\textsuperscript{17,29}

For the interaction influence of methanol content at its lower ratio (4:1), the recognized yields by NiO, NiO@D, and Ni/NiO@D after 100 min as the best interval are 52.9, 60.3, and 78.5%, respectively (Figure 6D–F). With the existence of the methanol content at a ratio of 8:1, the achieved yields are

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**Figure 7.** 3D curves or the interaction between the temperature and the catalyst loadings (A–C), the interaction between the temperature and the methanol content (D–F), and the interaction between the methanol content and the loadings of the catalysts (G–I).
60.2% (NiO), 67.5% (NiO@D), and 85.3% (Ni/Ni@D) (Figure 6D–F). At the upper values of methanol content (12 (methanol):1 (oil)), the determined yields increased to 66.2, 73.4, and 91% for NiO, NiO@D, and Ni/Ni@D, respectively (Figure 6D–F). Therefore, the incorporation of methanol content at a ratio of 12 (methanol):1 (oil) is the favorable value for the effective transesterification of WCO over NiO, NiO@D, and Ni/Ni@D considering the reaction interval at certain values.

2.2.2.3. Interaction Effect between the Catalyst Loading and Reaction Time. The interaction effect between the time intervals and the used loading of the catalysts was evaluated based on the 3D regression curves considering the intermediate values of methanol to oil ratio (8:1) and the temperature (55 °C) (Figure 6G–I). The inspected trends from the curves demonstrate the strong positive influence of the used catalyst loading on intensifying the catalytic performances of NiO, NiO@D, and Ni/Ni@D within the range from 2.5 to 3.75 wt % at all the studied time intervals (Figure 6G–I). This can be explained as a result of the predicted enhancement in the surface area as well as the exposure of the active sites and this has a strong impact on inducing the reaction rates. 29,30 Beyond dosages of 3.75 wt % up to 5 wt %, the catalytic performances show adverse effects during the transesterification reactions (Figure 6G–I). This was discussed in the literature as a result of the influence of the suspended solid particles on increasing the viscosity and the mass transfer resistance, which in turn affect negatively the efficiency of the reactions. 31

For the interaction influence of the catalyst loading at its lower level (2.5 wt %), the recognized yields by NiO, NiO@D, and Ni/Ni@D after 100 min as the best interval are 53.8, 61.2, and 78.7%, respectively (Figure 6G–I). With the existence of 3.75 wt % of the catalysts, the achieved yields are 60.2% (NiO), 67.5% (NiO@D), and 85.3% (Ni/Ni@D) (Figure 6G–I). At the upper values of the catalyst loading (80 °C), the determined yields declined to 57.6, 64.9, and 82.7% for NiO, NiO@D, and Ni/Ni@D, respectively (Figure 6G–I). Therefore, the incorporation of NiO, NiO@D, and Ni/Ni@D at a 3.75 wt % catalyst loading is the favorable value for the effective transesterification of WCO over them considering the reaction interval at certain values.

2.2.2.4. Temperature and Catalyst Loading. The interaction properties between the studied temperature and catalyst loading were studied based on the 3D curves considering the intermediate values of methanol content (8:1) and the transesterification interval (100 min) (Figure 7A–C). It can be observed from the studies that the increase in the temperature has a strong positive influence on enhancing the effect of the used loadings of NiO, NiO@D, and Ni/Ni@D (Figure 7A–C). Based on the previously detected best loading (3.75 wt %), adjusting the temperature at 30 °C resulted in yields of 54, 61.3, and 78.3% for NiO, NiO@D, and Ni/Ni@D, respectively (Figure 7A–C). At 55 °C, the achieved yields are 60.2% (NiO), 67.5% (NiO@D), and 85.3% (Ni/Ni@D) (Figure 7A–C). At the upper values of temperature (80 °C), the determined yields increased to 63.4, 70.5, and 86.9% for NiO, NiO@D, and Ni/Ni@D, respectively (Figure 7A–C). Moreover, the observed results reflect the strong positive interaction of the loading values on the effect of temperature as the best yields were recognized as a function of the temperature was detected at loading values of 3.75 wt % for the three catalysts.

2.2.2.5. Temperature and Methanol/Oil Ratio. The interaction properties between the studied temperature and the methanol content were studied based on the 3D curves considering the intermediate values of catalyst loadings (3.75 wt %) and the transesterification interval (100 min) (Figure 7D–F). It can be observed from the studies that the increment in the temperature has a strong positive influence on enhancing the effect of methanol. Based on the previously detected best temperature (80 °C), adjusting the ratio at 4:1 resulted in yields of 55.7, 63.06, and 79.4% for NiO, NiO@D, and Ni/Ni@D, respectively (Figure 7D–F). At 8:1, the achieved yields are 63.5% (NiO), 70.5% (NiO@D), and 86.9% (Ni/Ni@D) (Figure 7D–F). At the upper values of methanol ratio (12:1), the determined yields increased to 69.1, 76.6, and 89.3% for NiO, NiO@D, and Ni/Ni@D, respectively (Figure 7D–F). Moreover, the observed results reflect a significant interaction role for the methanol content in the effect of temperature as the best yields were recognized as a function of the temperature at a methanol/oil ratio of 12:1 for the three catalysts.

2.2.2.6. Methanol/Oil Ratio and Catalyst Loading. The interaction properties between the methanol content and the loading of the catalysts were studied based on the 3D curves considering the intermediate values of temperature (55 °C) and the transesterification interval (100 min) (Figure 7G–I).
It can be observed from the studies that the increment in the methanol content has a strong positive influence on inducing the influence of the used catalyst loading during the transesterification reactions (Figure 7G–I). Based on the previously detected best loading value (3.75 wt %), adjusting the ratio at 4:1 resulted in yields of 52.9, 60.3, and 78.5% for NiO, NiO@D, and Ni/Ni@D, respectively (Figure 7G–I). At 8:1, the achieved yields are 60.2% (NiO), 67.5% (NiO@D), and 85.3% (Ni/Ni@D) (Figure 7G–I). At the upper values of methanol ratio (12:1), the determined yields increased to 66.2, 73.4, and 91% for NiO, NiO@D, and Ni/Ni@D, respectively.

2.2.3. Statistical Optimization. Based on the advantages of the optimization function in the Design-Expert software and the prediction options of the quadratic programming, the suggested solutions to optimize the transesterification of WCO into biodiesel over NiO, NiO@D, and Ni/Ni@D were obtained and are presented in Table 3. The suggested optimum solutions were investigated considering the lower and the higher levels of the studied parameters and the adjusted scheme constraints (Table S3). The suggested conditions can induce the catalytic performance of NiO to achieve a biodiesel yield of 68.5% by adjusting the factors at a temperature of 72.2 °C, the time at 149.4 min, the methanol ratio at 11.7:1, and the NiO loading at 3.76 wt % (Table 3). Also, the suggested solution can enhance the obtained yield with the existence of the NiO@D catalyst to 76.3% by adjusting the factors at a temperature of 76 °C, the time at 108.4 min, the methanol ratio at 11.5:1, and the NiO@D loading at 3.9 wt % (Table 3). This was reported also from the suggested solution for the Ni/NiO@D catalyst; the obtained yield can be improved to 93.2% by adjusting the factors at a temperature of 63.7 °C, the time at 117.4 min, the methanol ratio at 11.6:1, and the NiO@D loading at 3.97 wt % (Table 3).

The obtained results reflected the advantages of the design in suggesting more suitable conditions to induce the activities of NiO, NiO@D, and Ni/Ni@D catalysts during the transesterification reactions of WCO. Additionally, the theoretical suggestion and the experimental results demonstrate significant enhancement in the catalytic performance of NiO after loading, supporting it over the diatomite frustules as a carrier or a substrate. Moreover, the integration of NiO in the composite with the Ni0 metal resulted in a significant enhancement in the activity of the final product, achieving the best transesterification efficiency. This can be explained based on several factors including (1) the role of the diatomite substrate in enhancing the surface area and the exposure of the NiO catalyst, (2) the hydroxyl bridges of diatomite induced the adsorption process of the free fatty acids, which is an essential step in the transesterification process, (3) the reported higher catalytic activity of the metallic nickel (Ni0) than NiO induced the activity of the final product as a catalyst in the transesterification reaction of WCO.

2.3. Technical and Safety Properties. The technical properties of the resulted biodiesel over Ni/NiO@D catalyst as the best product were evaluated considering the suggested limitations by the international standards of biofuels (ASTM D-6751 and EN 14214 standards) (Table 4). The determined values of density and viscosity match the requirements of the qualified biodiesel according to the suggested levels by both the ASTM D-6751 standard and the EN 14214 standard (Table 4). Recognizing the cetane index at a value beyond 45 recommends the product as a safe fuel of low emission if it was applied in the engines. Moreover, the determined flashpoint of the biodiesel product is within the suggested limitations for the safe fuels to be transported and handled in a safe manner (Table 4).

2.4. Comparison Study. The achieved yields over the synthetic NiO and its modified forms were compared with other studied catalysts in literature considering the reaction conditions (Table 5). As can be concluded from the table, the modified forms of NiO, especially the Ni/NiO@D composite, achieved higher yields than most of the presented catalysts, including CaO/SiO2, zeolite Na-X, cesium-modified silica, and coconut coir husk considering its economic value as it can achieve that after a short interval in the presence of low methanol content and at low temperatures as compared to the other catalysts.

3. CONCLUSIONS

NiO@diatomite and Ni/NiO@diatomite nanocomposites were characterized as novel composites of enhanced catalytic properties during the transesterification reactions as compared to pure NiO. They achieved higher biodiesel yield from WCO (73.4% for NiO@diatomite and 91% for Ni/NiO@diatomite) considering the best condition suggested by the statistical Central composite rotatable design (80 °C temperature, 100 min time, a 12:1 methanol/oil molar ratio, and 3.75 wt % loading). The optimization function of the Design Expert software and the used polynomial model suggested enhanced conditions that can achieve yields of 76.3% (NiO@diatomite) and 93.2% (Ni/NiO@diatomite). Such an enhancement is related to the role of the diatomite substrate in promoting surface area, the adsorption of the fatty acids, and the exposure of the catalytic. Additionally, the integrated Ni0 metal has an effective role in enhancing the catalytic reactivity of the final product.

4. METHODOLOGY

4.1. Materials. A refined diatomite sample (SiO2 (97.87%), Al2O3 (1.79%), and L.O.I (0.34%)) were used as starting substrates for the loaded metal oxides. Sodium hydroxide (NaOH, 97%), hydrazine solution (35 wt %), nickel nitrate hexahydrated form (Ni(NO3)6H2O) (99%), and hydrochloric acid (HCl) (37%) of analytical grade were obtained from El-Nasr Company, Egypt. Commercial WCO
and methanol (98% purity) from Cornel Lab Company were used in the transesterification processes.

### 4.2. Decorating the Diatomite Frustules by NiO and Ni/NiO

#### 4.2.1. Refining of Diatomite

The raw diatomite was refined from the associated impurities by a gentle leaching process where 5 g of the sample was treated with HCl (10%) for 4 h and the temperature of the reaction was adjusted to 100 °C. The treated sample was filtrated and washed with hydrogen peroxide for 5 h to remove the organic matter and the previous step was repeated for three cycles. Finally, the sample was washed with distilled water and dried for further synthesis steps.

#### 4.2.2. Decorating of Diatomite with NiO and Ni/NiO

First, 1.5 g of the purified diatomite was incorporated within 50 mL of an aqueous solution of nickel nitrate for 30 min at a constant stirring speed (500 rpm). Then, 50 mL of sodium hydroxide (2 M) was poured gently into the reaction mixture fixed under the effect of a sonication field (150 W, 20 kHz) for 2 h at a reaction temperature of about 150 °C to distribute the synthetic particles uniformly throughout the porous skeletons of diatomite. Finally, the prepared material was filtrated, washed, and dried at 100 °C overnight, and then calcined at 400 °C for 2 h to confirm the formation of the nickel oxide. The product was labeled as NiO/diatomite (NiO@D).

A portion of the prepared nickel nitrate/sodium hydroxide mixture was separated for the partial reduction of Ni (OH)$_2$. 25 mL of hydrazine was incorporated slowly in the reaction as a reducing agent under a high stirring speed to confirm strong homogeneity between the reactants. After that, the preparation steps were completed according to the previous procedures involving the calcination step at the same temperature. The product was labeled as Ni/NiO@diatomite (Ni/NiO@D).

### 4.3. Characterization

The crystalline structure of the prepared catalyst was characterized by an X-ray diffractometer, PANalytical (Empyrean). The morphological modifications of the final product were studied considering the SEM images obtained by a scanning electron microscope (Gemini-Zeiss, Ultra 55S). The internal changes within the formation of the catalyst were examined based on the HRTEM images taken by a transmission electron microscope (JEOL-JEM2100). The chemical changes in the surficial functional groups were detected by an FT-IR Raman spectrometer (Vertex 70). Both BET and BJH methods were conducted to clarify the significant surface area and the pore size, respectively.

### 4.4. Transesterification System

The system of the transesterification process is composed of three main parts: a three-necked glass flask that acts as the conversion system attached with a digital heater to control the reaction temperature and provided with a condenser to prevent the release of the used methanol. The reaction parameters which affect the biodiesel yield were investigated for three products in a comparison study (NiO, NiO@D, and Ni/NiO@D) according to statistical models which were built using Expert-Design software (Version 6.0.5) based on the RSM and the CCD. The design was built considering the suggested lower and higher levels of the essential experimental factors (temperature (°C), time (min), dosage (wt %), and methanol/oil ratio), which were selected based on series of primary tests and presented in their actual and coded values (Table S1).

The experiments were conducted according to fixed procedures that involved first filtration of the oil samples (40 g), which were then heated at 70 °C for 10 min to confirm the removal of the solid suspensions and the humidity. After that, the used oil samples were mixed with the catalysts at the adjusted dosages for certain intervals according to the suggested conditions of the design. Then, the converted oil samples were transferred into a separating funnel with Whitman filter paper to remove the glycerol layers away from the biodiesel yield. Finally, the biodiesel yields were heated at 80 °C for 1 h to evaporate the excess amounts of methanol. The concentrations of FAME were measured by a gas chromatography device (Agilent 7890A). The used internal standard during the analysis is methyl heptadecanoate after diluting the oil samples with n-hexane. The percentages of the produced biodiesel can be calculated according to the following formula (eq 4).

$$\text{biodiesel yield (\%)} = \frac{\text{(weight of biodiesel} \times \% \text{ FAME)}}{\text{weight of oil}} \times 100$$

The influence of the parameters and the interaction between these parameters in the achieved biodiesel yields were evaluated based on the second-order polynomial equation (eq 5).

$$Y = \beta_0 + k \sum_{i=1}^{k} \beta_i X_i + k \sum_{i=1}^{k} \beta_i X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j$$

$Y$ is the obtained biodiesel as a response, $X_i$ and $X_j$ are the input experimental factors, $\beta_0$ is the constant, $\beta_i$ is the linear coefficient term, $\beta_i$ is the quadratic coefficient term, $\beta_{ij}$ is the cross-product coefficient term, and $K$ is the number of studied experimental factors.

| catalyst               | time (h) | temperature (°C) | methanol to oil | dosage (wt %) | yield (%) | references |
|------------------------|----------|------------------|-----------------|---------------|-----------|------------|
| CaO/SiO$_2$            | 3        | 65               | 21:1           | 11            | 90.2      | 33         |
| CaO                    | 3        | 65               | 20:1           | 5             | 95        | 34         |
| zeolite Na-X           | 8        | 65               | 6.1            | 3             | 83.5      | 35         |
| cesium-modified silica | 3        | 65               | 20:1           | 3             | 90        | 36         |
| coconut coir husk      | 3        | 130              | 12:1           | 10            | 89.8      | 37         |
| NiO                    | 149 min  | 72               | 11.7:1         | 3.7           | 68.5      | this study |
| NiO@D                  | 108 min  | 76               | 11.5:1         | 3.9           | 76.8      | this study |
| Ni/NiO@D               | 117 min  | 63.7             | 11.6:1         | 4             | 93.2      | this study |

Obtained Yields: Table 5. Comparison Study between the NiO-Based Catalyst and Other Synthetic Catalysts in the Literature Considering the Obtained Yields.
Values of the inserted variables in the statistical design; the textural characterization of raw diatomite and NiO@D, and Ni/ NiO@D catalysts; and the optimization test scheme constraints for the optimizing solutions of the transesterification tests over NiO, NiO@D, and Ni/NiO@D catalysts (PDF)

ACKNOWLEDGMENTS

This research was funded by the Deanship of Scientific Research at Princess Nourah bint Abdulrahman University through the Fast-track Research Funding Program to support publication in the top journal (grant no. 42-FTTJ-07).

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**NOTE ADDED AFTER ISSUE PUBLICATION**

One of the institution names featured in this article was corrected to address incorrect formatting in the affiliations and acknowledgements. The revised version was published on the Web on May 18, 2021.