Absorptive Removal of Palm Oil Free Fatty Acids Onto Silica/smectite Composite: A Statistical Study using Box-Behnken Design in Response Surface Methodology

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**Abstract**

Response Surface Methodology was used to evaluate the main and interactions effects of contact time (20–60 min), temperature (60–90°C) and adsorbent dosage (1–2%) of the palm oil free fatty acids (FFAs) adsorption onto a silica/smectite composite. The regression model was found to be able to predict more than 99% of the targeted response variation in the studied range ($R^2 = 99.31\%$). An ANOVA was used to evaluate the accuracy of the regression model and it was found to predict more than 99% of the response variation. The Pareto Charts of Standardized Effects showed that almost all the explanatory factors were influential. The factorial plots evidenced that time/temperature interaction was most effective and the corresponding contour and surface plots were drawn. The second-order kinetic model was better followed with the highest value of the determination coefficient ($R^2 = 0.996$) and the lowest value of Root Mean Square Deviation of 0.555. Response Optimizer Function showed an optimum for FFAs removal of more than 90% (27.18 mg of KOH/g) at the adsorbent dosage of 2%, contact time of 60 min, and temperature of 90°C. Moreover, a good correlation between the predicted and experimental values was observed within reasonable limits.

**Introduction**

Palm oil is mainly made up of triglycerides of fatty acids and glycerol. Some of those fatty acids which have escaped to be “imprisoned” in glycerides are called free fatty acids (FFAs). The so-called FFAs can be produced by many means such as hydrolysis of triglycerides during palm oil processing, natural release in crude palm oil, and action of enzymes in the palm fruits by microbial lipases. The reaction of oil with water during storage, lengthy storage of products and contamination of fungi in palm oil also produce FFAs (Che Man et al. 1999; Atinafu and Bedemo 2011). Frying oils have high FFAs contents due to the repeated heating that favours various chemical reactions including oxidation, hydrolysis, cyclization, polymerization and degradation. Such reactions give rise to many degrading products like monoglycerides, diglycerides, volatile compounds, lipid peroxides, hydrocarbons, oxygenated products and FFAs (Kheang et al. 2006; Sukiran et al. 2011; Guo et al. 2016) which deteriorate the quality of the oil. Despite the important role of FFAs in a wide range of industrial fields (anticorrosive agent, antimicrobial protection...) (Foucaud et al. 2021), their content in some products like cooking oil should be 5% at the highest (Azeman et al. 2015) in order to assure a good quality for human health.. In fact, an abnormal increase in FFAs concentration due to one or more of the aforementioned means limits the quality of oil and makes it unhealthy for human consumption. On one hand, it may lead to various health issues such as risk of high blood pressure, cardiovascular disease and atherosclerosis and limit its conservation as well as environmental issues (Ebgouge et al. 2008; Azeman et al. 2015; Gadiraju et al. 2015; Sarkar and Mohan 2017). On the other hand, low FFAs contents produce good physicochemical properties for the palm oil products and make it valuable for food applications, industrial applications such as production of cosmetics and biodiesels. Oils containing more than 1% of FFAs will form a difficult emulsion of soap during the separation of biodiesel and provoke the clogging of the engine (Ismaila et al. 2017; Japir et al. 2017; Tan et al. 2018; Susilowati et al. 2019a). Due to the high demand in palm oil industry market
nowadays and the fact that palm oil quality and price is indeed dependent on the FFAs content in palm oil, it is thus imperative to match the standards of palm oil quality. That reduction during refinery will provide the consumers with attractive products having a long shelf life and fulfilling the standards of the production of some products. Therefore, many adsorbent types ranging from natural biosources to synthetic materials have been already used. Extensive results so far put emphasis on the effect of some experimental parameters such as dosage of the adsorbent, temperature, contact time and on the kinetic study of the adsorption process (Sukiran et al. 2011; Pohndorf et al. 2016; Ismaila et al. 2017; Baptiste et al. 2020; Kurtulbaş et al. 2021). Response Surface Methodology (RSM) is a collection of tools developed in the 1950s for the purpose of determining optimum operating conditions in applications in the chemical industry (Myers et al. 1989). The response of interest is influenced by several variables and the objective of the study is to optimize this response by minimizing the total number of experimental runs (Arenas et al. 2007; Turan et al. 2011; Ranganath and Vipin 2015; Zolgharnein et al. 2015). The so-called technique uses quantitative data from appropriate experiments to determine and simultaneously solve multi-variable equations correlating a response with independent parameters (input variables) (Annadurai and Sheeja 1998; Resende et al. 2020). The graphical representations of these equations are called response surface and they can be used to describe the individual and cumulative effect of the input variables on the response. To date, the mathematically evaluation of the effects of some fundamental processing parameters such as time, temperature and adsorbent dosage as well as their interactions on the removal of FFAs has not been investigated enough (Ayu Putranti et al. 2018; Susilowati et al. 2019b). On this line, the novelty of the present study focuses on the palm oil FFAs adsorption onto a new silica/smectite clay based composite previously synthesized by an eco-friendly pathway using low cost natural resources, clay and rice husks (Kepdieu et al. 2023). Also, emphasis was put on the optimization of the fundamental parameters affecting the FFAs adsorption using RSM as well as the non-linear kinetic modelling and mechanism of the process.

**Experimental**

**Adsorbent**

The adsorbent used in this study was synthesized from a 20 µm mesh enriched smectite clay fraction and silica from rice husk ash as starting materials. It led to a product which structure was largely described in previous work (Kepdieu et al. 2023) as a delaminated/exfoliated porous material with a specific surface area of 300 m²/g.

**Palm oil**

The palm oil used in this study is locally purchased from Master Foods Co., Cameroon. It was kept in the dark chamber at a low temperature (~20°C) to avoid any degradation by oxidizing and photocatalytic reaction (Woumfo et al. 2007; Syamila et al. 2019).
Batch adsorption

For RSM studies, preliminary experiments help to choose the factor's domains as time (from 20 to 60 min), temperature (from 60 to 90°C) and adsorbent dosage (from 1 to 2%) for design of experiment. The batch tests were performed in a thermostatically controlled reflux reactor following a method described in some previous works (Ayu Putranti et al. 2018; Baptiste et al. 2020). 5 g of oil was introduced in the reactor and when the indicated temperature value (60, 75 or 90°C) was reached. A known amount of adsorbent was added and the mixture was stirred at 250 rpm for a fixed time following the runs provided by the matrix of experiences. The mixture was filtered under vacuum using Whatman paper N°1. The oil was allowed to settle for 20 min and 1000 mg of the supernatant was then used to determine the FFA left in the treated oil.

For kinetics, the study was conducted in a larger range of time (from 0 to 90 min) and the data were compared to three models. On the same line, the influence of temperature and adsorbent dosage on the removal of FFAs was also evaluated. For 5 g of oil, the adsorbent dosage varied as 1, 1.5, 2, 2.5 and 3% at t = 90 min and the temperature values were 60, 75 and 90°C.

Assessment of FFAs content of treated oil supernatant

The oil was tested for acidity using the American Oil Chemists’ Society (AOCS) method Ca 5a–40 (1989) adapted by Japir et al. (Japir et al. 2017). First of all, 1000 mg of the treated oil sample were placed in a dried conical flask. Approximately 10 mL of pre-neutralized ethanol were then added to the sample. Afterward, 4 drops of 1% phenolphthalein indicator was then added to the mixture. The flask was subsequently placed on a hot plate and heated until a temperature of around 40°C was attained. The mixture was then titrated with alcoholic potassium hydroxide solution (0.05 N) until a pink color emerged for at least 30 s. Indeed, if molecules of FFAs are labeled with the formula RCOOH, the acid-base reaction which occurs between them and alcoholic KOH is total and the balance equation of the reaction is Eq. (1).

\[
RCOOH + (K^+ + OH^-) \rightarrow RCOO^- + K^+ + H_2O
\]

1

For treated sample, the FFA content expressed as Current Acid Value was determined using Eq. (2) (Akinola et al. 2010; Medeiros Vicentini-Polette et al. 2021).

\[
Current\text{acid}\text{Value} = \frac{C_{KOH} V_{eq} M_{KOH}}{m_0}
\]

2

Where \(C_{KOH}\) is the molar concentration of the alcoholic KOH solution (0.05 mol/L), \(V_{eq}\) the equivalent Volume of the pre-neutralized ethanol (mL), \(M_{KOH}\) molar mass of KOH (56.1 g/mol) and \(m_o\) the weight
of the treated oil sample (1000 mg). The FFA content was determined in oil by titration of the supernatant after treatment and the quantity adsorbed (response) was calculated and expressed as Acid value drop (AV drop) in Eq. (3)

$$AV\ drop = \text{Initial Acid value} - \text{Current Acid value}$$ (3)

Box-Behnken Design/Response Surface Methodology

In this study, RSM was applied to evaluate the effects of three independent variables contact time ($X_1$), temperature ($X_2$), and adsorbent dosage ($X_3$), on the FFAS removal efficiency expressed as AV drop. Experimental adsorption design was established using Box-Behnken Design (BBD) implemented in Minitab 21. It is a three-factors and levels (−1, 0, 1) system consisting of 15 experimental runs. They were designed to optimize Acid Value (AV) drop in palm oil. The ranges of the considered variables as well as the corresponding levels in coded and uncoded values are summarized in Table 1.

<table>
<thead>
<tr>
<th>Temps</th>
<th>Temperature</th>
<th>Adsorbent dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_1$</td>
<td>t/min</td>
<td>$X_2$ T/°C</td>
</tr>
<tr>
<td>-1</td>
<td>20</td>
<td>-1</td>
</tr>
<tr>
<td>0</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>1</td>
</tr>
</tbody>
</table>

If the natural variables (uncoded units) are labeled as $U_1$, $U_2$ and $U_3$ corresponding to dimensionless coded variables $X_1$, $X_2$, $X_2$ respectively, the conversion of natural variables ($U_{ij}$) into coded ones ($X_{ij}$) is done following Eq. (4) (Merabet et al. 2009; Zolgharnein et al. 2015).

$$X_{ij} = (U_{ij} - U_{j}^0)/\Delta U_j$$

Where $X_{ij}$, $U_{ij}$ and $U_{j}^0$ are the values of the coded variable, the natural variable and the natural value at the center of the domain of factor $j$ at the $i$th experiment respectively. $\Delta U_j$ is the half variation step of the factor domain of the natural variable.

The effect of the processing parameters as well as their interactions were investigated on the adsorption of FFAs by calculating the coefficients of the linear terms $b_i$ and the coefficient of interactions $b_{ij}$ ($i \neq j$) between factors $i$ and $j$ using Equations (5) and (6).
where \( X_{in} \) and \( X_{jn} \) are the values of the coded variables of factor \( i \) and \( j \) respectively.

The polynomial regression model used to describe the effects of the processing parameters is based on Taylor series and given in Eq. (6) (Khuri and Mukhopadhyay 2010; Turan et al. 2011; Zulfiqar et al. 2016; Kumar and Das 2017; Jawad et al. 2020; Dbik et al. 2022).

\[
Y = b_0 + \sum_i b_i X_i + \sum_i \sum_j b_{ij} X_i X_j + \sum_i \sum_j \sum_l b_{ijl} X_i X_j X_l + \ldots
\]

Where \( Y \) and \( b_0 \) represent the theoretical response of a test and that at the center of the experimental domain respectively, with \( 1 \leq n \leq k \), \( 1 \leq i \leq j \leq k \), and \( 1 \leq i \leq j \leq l \leq k \).

In the present study, a simple second order form of Eq. (6) for three factors is considered and given in Eq. (7).

\[
Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3
\]

Regression and graphical analysis were done using Minitab21 Software. Analysis of variance (ANOVA) was done on the regression model and on the model coefficients to test their significance, and adequacy. Thus, parameters such as the correlation coefficient \( R^2 \), \( R^2 \) (Adjusted), F-value, and P-value (probability) were generated to determine the relevance and suitability of the predicted model.

**Kinetic studies**

For kinetics studies, a non-linear approach was done considering Equations (8) and (9) where \( Q_e \) and \( Q_t \) represented the quantities of FFAs adsorbed at equilibrium and at a time \( t \) respectively. \( AV_e \), the acid value of the oil at equilibrium, \( AV_t \), the acid value of the oil after treatment for time \( t \) (min) and \( m \), the mass of oil.

\[
Q_e = \frac{AV_0 - AV_e}{m}
\]

\[
Q_t = \frac{AV_0 - AV_t}{m}
\]
Using the classical equations of the pseudo-first order, pseudo-second order and intra-particle diffusion models as reported by many authors (Ahmad et al. 2009; Pohndorf et al. 2016; Baptiste et al. 2020; Kurtulbaş et al. 2021) and introducing in the acid value parameter, the kinetics equations in their non-linear form have been re-written and presented in Equations (10)-(12).

\[
(AV_0 - AV_t) = (AV_0 - AV_e)[1 - \exp(-K_1 t)] \quad (Pseudo-1st order) \quad (10)
\]

\[
(AV_0 - AV_t) = \frac{K_2 (AV_0 - AV_e)^2 t}{1 + K_2 (AV_0 - AV_e)t} \quad (Pseudo-2nd order) \quad (11)
\]

\[
(AV_0 - AV_t) = K_{id} * t^{\frac{1}{2}} + \gamma \quad (Intraparticle diffusion)
\]

Where \(K_1 \) (min\(^{-1}\)), \(K_2 \) (mg\(^{-1}\).g.min) and \(K_{id} \) (in mg/min\(^{0.5}\)) are the kinetic constants of the pseudo-1st order, pseudo-2nd order and intraparticle diffusion respectively; \(\gamma\) (mg/g) is associated to the boundary layer thickness.

In order to validate the best fitting to the model with more accuracy, the determination coefficient and the root mean square deviation designated by \(R^2\) and RMSD have been calculated using Equations (13) and (14).

\[
R^2 = 1 - \frac{\sum_{k=1}^{n} (v_{exp,k} - v_{mod,k})^2}{\sum_{k=1}^{n} (v_{mod,k} - \hat{v}_{exp,k})^2}
\]

\[
RMSD = \sqrt{\frac{\sum_{k=1}^{n} (v_{exp,k} - v_{mod,k})^2}{n}}
\]

Where: \(v_{exp,k}\) and \(v_{mod,k}\) are the experiment and the expected values of the \(k^{th}\) test. \(\hat{v}_{exp}\) is the average experimental value. \(n\) is the total number of tests.

**Results and discussion**

**Response Surface Methodology**

**Experimental Design matrix and response**
15 experimental runs proposed by the system occurred in repetitious way to optimize the level of chosen variables. The three variables (coded and uncoded), the experimental conditions determined with Eq. (4) as well as the corresponding experimental response values are summarized in Table 2.

<table>
<thead>
<tr>
<th>Run order</th>
<th>T/min</th>
<th>t/°C</th>
<th>d (%)</th>
<th>X₁</th>
<th>X₂</th>
<th>X₃</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>40</td>
<td>60</td>
<td>2.0</td>
<td>20.67</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>60</td>
<td>75</td>
<td>1.0</td>
<td>21.81</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>40</td>
<td>75</td>
<td>1.5</td>
<td>22.44</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>20</td>
<td>75</td>
<td>2.0</td>
<td>15.13</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>60</td>
<td>90</td>
<td>1.5</td>
<td>26.08</td>
</tr>
<tr>
<td>6</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>60</td>
<td>75</td>
<td>2.0</td>
<td>24.39</td>
</tr>
<tr>
<td>7</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>40</td>
<td>60</td>
<td>1.0</td>
<td>18.22</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>40</td>
<td>90</td>
<td>2.0</td>
<td>19.23</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>60</td>
<td>1.5</td>
<td>12.69</td>
</tr>
<tr>
<td>10</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>40</td>
<td>90</td>
<td>1.0</td>
<td>19.87</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
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<td>-1</td>
<td>20</td>
<td>75</td>
<td>1.0</td>
<td>12.56</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>40</td>
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<td>1.5</td>
<td>19.23</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>40</td>
<td>75</td>
<td>1.5</td>
<td>19.23</td>
</tr>
<tr>
<td>14</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>60</td>
<td>60</td>
<td>1.5</td>
<td>21.58</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>20</td>
<td>90</td>
<td>1.5</td>
<td>14.62</td>
</tr>
</tbody>
</table>

**Table 2**
Coded and uncoded values from Box-Behnken's matrix and experimental data of AVdrop

Mathematical modeling and Pareto charts of standardized effects

Using Minitab 21 software, an updated resource for RSM; the main coefficients bᵢ and the interaction coefficients bᵢⱼ were calculated from the experimental responses. The regression model of the study in coded values is then given by Eq. (15).

\[
AV\ drop\ (mg\ of\ KOH/g) = 19.230 + 4.858 X_1 + 1.23 X_2 + 1.271 X_3 - 1.158 X_1 X_1 + 0.678 X_2 X_2 + 0.400 X_3 X_3 + 0.642 X_1 X_2 + 0.003 X_1 X_3 + 0.030 X_2 X_3 \quad (15)
\]
The (+) positive sign of the main and interaction coefficients shows the synergetic behaviour of the processing parameters towards the adsorption process (Kumar and Das 2017). Figure 1 shows the Pareto chart of the Standardized Effects, which gives the relative importance of the individual and interaction effects. The vertical line in the chart indicates the minimum statistically significant effect magnitude at the 95% confidence level (Turan et al. 2011).

Concerning the main effects, temperature, dosage, and time of respective coefficients of 1.231, 1.271 and 4.858 given by the model's equation are in the order of their increasing influence on the process of adsorption of FFAs on the composite. The overall positive values of the coefficients confirm that when the level of a factor increases independently; it is favorable for the adsorption process. It also emerges from the Pareto diagram that the significance level is 2.57 and therefore, the factors time, temperature and adsorbent dosage are all significant and more for the first. Moreover, in the studied range of parameters, time/temperature interaction is more influential for the process compared to the time-dosage interaction and temperature-dosage interaction which are very weak with 0.03 and 0.003 as coefficients respectively.

**ANOVA and Henry Normal plot**

Further analysis has been carried out to evaluate the accuracy of the mathematical model of the current study (Merabet et al. 2009). In order to minimize error, all the experimental results were duplicated and the average was taken. The significance of the model is mainly calculated by regression coefficient ($R^2$) value (Burton et al. 1988; Gato et al. 2007; Piñeiro et al. 2008; Kumar and Das 2017). The significance was examined based on the magnitude of the F-values, while the P-value less than 0.05 is considered to be statistically significant with a 95% confidence level (Abdulsalam et al. 2020). Therefore ANOVA for the AV drop of palm oil was done and the details are presented in Table 3.
Table 3
Analysis Of Variance (ANOVA) for the Surface response for the full quadratic model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Degree of freedom</th>
<th>Adjusted Square Sum</th>
<th>Adjusted Mean Sum</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>9</td>
<td>223.267</td>
<td>24.807</td>
<td>79.62</td>
<td>0.000</td>
</tr>
<tr>
<td>Linear</td>
<td>3</td>
<td>213.819</td>
<td>71.273</td>
<td>228.76</td>
<td>0.000</td>
</tr>
<tr>
<td>t/min</td>
<td>1</td>
<td>188.762</td>
<td>188.762</td>
<td>605.85</td>
<td>0.000</td>
</tr>
<tr>
<td>T/°C</td>
<td>1</td>
<td>12.128</td>
<td>12.128</td>
<td>38.93</td>
<td>0.002</td>
</tr>
<tr>
<td>d (%)</td>
<td>1</td>
<td>12.929</td>
<td>12.929</td>
<td>41.50</td>
<td>0.001</td>
</tr>
<tr>
<td>Square</td>
<td>3</td>
<td>7.793</td>
<td>2.598</td>
<td>8.34</td>
<td>0.022</td>
</tr>
<tr>
<td>t/min*t/min</td>
<td>1</td>
<td>4.947</td>
<td>4.947</td>
<td>15.88</td>
<td>0.010</td>
</tr>
<tr>
<td>t/°C*T/°C</td>
<td>1</td>
<td>1.657</td>
<td>1.657</td>
<td>5.32</td>
<td>0.069</td>
</tr>
<tr>
<td>d (%)*d (%)</td>
<td>1</td>
<td>0.591</td>
<td>0.591</td>
<td>1.90</td>
<td>0.227</td>
</tr>
<tr>
<td>2-Way Interaction</td>
<td>3</td>
<td>1.655</td>
<td>0.552</td>
<td>1.77</td>
<td>0.269</td>
</tr>
<tr>
<td>t/min*T/°C</td>
<td>1</td>
<td>1.651</td>
<td>1.651</td>
<td>5.30</td>
<td>0.070</td>
</tr>
<tr>
<td>t/min*d (%)</td>
<td>1</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
<td>0.993</td>
</tr>
<tr>
<td>t/°C*d (%)</td>
<td>1</td>
<td>0.004</td>
<td>0.004</td>
<td>0.01</td>
<td>0.919</td>
</tr>
<tr>
<td>Error</td>
<td>5</td>
<td>1.558</td>
<td>0.312</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack-of-Fit</td>
<td>3</td>
<td>1.558</td>
<td>0.519</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Pure Error</td>
<td>2</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>224.824</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$R^2 = 99.31\%$, ANOVA shows that $R^2 = 99.31\%$, meaning that more than 99% of the variation in adsorption can be explained by its relationship with the factors considered and displaying an agreement between experimental and predicted values (Merabet et al. 2009). It is also noticed that the mathematical models for all responses are validated from the statistical test results since the F-value is 79.62 >>> 1 and p-value < 0.001% for the model and such results have been proved by other authors (Zhang and Zheng 2009; Bilici Baskan and Pala 2010; Ojewumi et al. 2021; Dbik et al. 2022). Furthermore, in the Normal Probability plot (Henry normal plot) shown in Fig. 2 all the points are around the straight line, meaning that the residuals follow a normal distribution. This confirms that the model accurately describes the variations in responses and also proves that the values obtained are regular, symmetrical, and have no abnormal or aberrant values (Dbik et al. 2022).
Factorial plots

The previous data showed that the mathematical model developed is appropriate for the study of the FFAs on the silica/smectite composite. The factorial plots given by main effect, interactions’ effects, contours, and surface plots of the process are given in Figs. 3 and 4.

The main effects and the interaction plots for the adsorption of FFAs onto the composite are in accordance with the predictions of the regression model and the Pareto charts of standardized effects. Concerning Figure (3), it comes out that all the factors seem to affect the FFAs uptake because the lines are not horizontal. Substantially, the relationship between time, temperature, adsorbent dosage, and the response (AV drop) is synergically since the mean value of the response increases as those factors’ levels increase.

Figure 4(i) shows non-parallel curves indicating that time/temperature interaction is observable and almost significant as shown by Pareto charts (Fig. 1). Moreover, Fig. 4(ii) shows that when the temperature is fixed at its lowest value (60°C), the AV drop increases from 12.69 to 14.62 mg of KOH/g when the contact time varies from 10 to 60 min respectively. This corresponds to a half-variation of 0.97. For the highest value of the temperature (90°C), the AV drop increases from 21.68 to 26.08 mg of KOH/g for the same gap of time corresponding to a half-variation of 2.2. The two half-variations are different and graphically, it is also materialized by two parallel lines on top of the charts of Fig. 5(ii). These remarks confirm the existence of interactions between time and temperature.

Figure 4(iii) shows almost parallel curves indicating minor or no interactions between time and dosage. According to Fig. 4(iv), when the dosage is fixed at its lowest value (1%), the AV drop increases from 12.56 to 15.13 mg of KOH/g when the time varies from 10 to 20 min respectively. This corresponding half-variation is 1.29. For the highest value of the dosage (2%), the calculated half-variation corresponding to an increase in mean AV drop from 21.81 to 24.39 is the same. Furthermore, these results are graphically proved by the two parallel lines on top of the charts of Fig. 4(iv).

The temperature-dosage interaction effects presented in Figs. 4(v) and 4(vi) show similar results with Figs. 4(iii) and 4(iv). Indeed, when the temperature is fixed at its lowest value (60°C), the AV drop increases from 18.22 to 19.87 mg of KOH/g when the dosage varies from 1 to 2% respectively. This corresponds to a half-variation of 0.8. For the highest value of the temperature (90°C), the corresponding calculated half-variation is almost the same (0.89) but with a slight difference proving that the interaction is a little bit more significant than the time//dosage interaction. This result is also evidenced in Pareto charts where the time/dosage's coefficient is 10 times greater than the temperature/dosage's coefficient. Furthermore, these results are graphically proved by the two parallel lines on top of the charts in Fig. 4(iv).

Response surfaces plots in 2D or 3D provide a simple method for optimizing the process and identifying interactions between variables (Ojewumi et al. 2021; Dbik et al. 2022). Since the three independent factors studied are all significant, two of them, time and temperature have been chosen to produce surface plots of AV drop and presented on Fig. 5. On the 3D plot (Fig. 5(a)), the horizontal plane of the figure
materializes the domain of variation of time and temperature, and the vertical axis the variation of the mean values of AV drop. The 3D plot is in accordance with the previous results since it can be evidenced that the mean AV drop values rises when time or temperature increase.

For better understanding, a projection along the z-axis (Acid drop’s axis) at different values of AV drop has been done and the results obtained are presented in Fig. 5(b) as contours plots.

The so-called contour plots represent an infinity of combinations between time and temperature levels with adsorbent dosage held at a constant level of 1.5% corresponding to 0 in coded value (Merabet et al. 2009). Considering that the recommended acid value should be equal to or less than 10 mg of KOH/g in palm oil and that one of the untreated oils is around 30 mg of KOH/g, it can be noticed in Fig. 5(b) that the hatched area is satisfactory (AV drop ≥ 20 mg of KOH/g). That area covered 45 to 60 min for time and 60 to 90°C temperature. On the other hand, the plot demonstrates that a contact time of less than 45 min is not interesting at any level of temperature.

**Optimization of the AV drop**

Using the Response Optimizer Function, further evaluation has been carried out in order to determine the optimal conditions of the process with respect to the acid value reference. Those conditions are then reported in Table 4 and plotted in Fig. 6.

For the aforementioned reasons, 26.08 mg of KOH/g was taken as the targeted response and 20 mg of KOH/g as the minimum value. The system has generated a double response prediction with an ideal desirability value of 1.000 with 95% of confidence.

<table>
<thead>
<tr>
<th>Solution</th>
<th>t/min</th>
<th>T/°C</th>
<th>d (%)</th>
<th>AV drop</th>
<th>Standard Error fit</th>
<th>Confidence Index</th>
<th>Desirability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>90</td>
<td>2</td>
<td>27.18</td>
<td>0.659</td>
<td>95%</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>53.8</td>
<td>90</td>
<td>2</td>
<td>26.08</td>
<td></td>
<td>95%</td>
<td>1</td>
</tr>
</tbody>
</table>

**Verification and validation of the model**

For a model to be validated, the predicted responses must be close to the experimental ones. A scatterplot has been drawn to verify the relationship between AV drop (experimental) and AV drop (Predicted) values. The results are shown in Fig. 7. The comparison between these results shows that we have an excellent estimate of the model since almost all the points are along the first bisector line. It can therefore be adapted for the interpretation of tests.
Studies of some parameters on the adsorption of FFA onto the Silica/smectite Composite

In order to extend the study on the adsorption of FFAs from palm oil, a detailed evaluation of the influence of the parameters contact time, temperature and dosage of the adsorbent has been carried out on palm oil with 30 mg/KOH as initial acid value.

Effect of temperature and adsorbent dosage on the removal of FFAs

The plots of the FFAs removal as a function of temperature on one hand and as a function of adsorbent dosage on the other hand are presented in Fig. 8.

Figure 8(a) presents the influence of the temperature on the FFA adsorption assessed from the treated palm oil. It shows that the rate of adsorption of FFAs increases with the treatment temperature. Indeed, the higher the temperature from 60–90 min, the lower is the viscosity of the palm oil, thus promoting greater mobility of the molecules of FFA. Simultaneously, there would also be activation of an increasing number of adsorption sites when the temperature rises (Ahmad et al. 2009; Baptiste et al. 2013, 2020). The process would be endothermic because it is favored by the increase in temperature (Yuney et al. 2020). Figure 8(b) indicates a perceptible increase in the adsorbed quantity of FFAs with the dosage from 1 to 2% after which the variation is almost stable. That initial rapidly increasing tendency in the rate of absorption of FFA when the adsorbent dose increases would be the result of an abundance of the active sites available to act with the molecules of FFA. This behaviour is no longer significant above 2% and can be explained by the fact that, beyond this dose, practically all the FFAs are already retained. Some authors share the idea of the formation of a bulk which on the one hand would obstruct the other active sites of the composite and on the other hand, would limit the mobility of FFA in the oil/adsorbent mixture (Baptiste et al. 2020). It, therefore, seems judicious for economic purposes to consider 2% for yields around 90%.

Kinetics studies

• Effect of contact time

In order to further understand the mechanism of the adsorption of FFAs onto the silica/smectite based composite. Kinetic studies involving pseudo-first-order, pseudo-second-order and intraparticle diffusion model in non-linear regression have been done and the results are given in Fig. 9.

Figure 9 shows that the amount of adsorbed FFAs increases with contact time until it reaches a steady state. Indeed, from 0 to 60 min of oil/adsorbent contact, a rapid increase in the quantity adsorbed is noted due to the high concentration of active sites at the surface of the adsorbent used. After 60 min, the rate becomes slower and tends towards equilibrium, which corresponds to about 27 mg of KOH/g (about 90% of FFAs adsorbed). The steady-state trend is explained by the reduction of sites and the potential
diffusion of adsorbate molecules into the pores of the adsorbent, and therefore this rate ceases to develop when almost all the active sites are occupied. Similar results were obtained by Susemo et al. in the adsorption of FFAs from sardine oil by attapulgite and bentonite (Suseno et al. 2013). The effectiveness of the composite is mostly explained by the presence of pores and mesopores in its exfoliated structure. A similar explanation has been reported in the literature for the adsorption of free fatty acids from rice husk on magnesium silicate (Clowutimon et al. 2011). The kinetics constants are given in Table 5.

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Equations</th>
<th>Constants notations</th>
<th>Constant values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-1st order</td>
<td>$Q_t = Q_e (1 - e^{-k_1 t})$</td>
<td>$R^2$</td>
<td>0.867</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RMSD</td>
<td>3.188</td>
</tr>
<tr>
<td>Pseudo-2nd order</td>
<td>$Q_t = Q_e t^{2/3} Q_e + k_2 Q_e t$</td>
<td>$R^2$</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RMSD</td>
<td>0.555</td>
</tr>
<tr>
<td>Intraparticle Diffusion</td>
<td>$Q_t = K_{id} t^{1/2} + \gamma$</td>
<td>$\gamma$</td>
<td>0.0023</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.9643</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RMSD</td>
<td>1.650</td>
</tr>
</tbody>
</table>

$K_1$ (min$^{-1}$), $K_2$ (mg$^{-1}$ g.min), and $k_{id}$ (mg/g min$^{0.5}$) are the kinetic constant of the 1st order, 2nd order, and intra-particle diffusion kinetic constant respectively. $\gamma$ (mg/g) is associated with the boundary layer thickness, $t$ (min) is the time; $Q_e$ and $Q_t$ (mg/g) represent the amounts of FFAs adsorbed at equilibrium and at time $t$ respectively.

The most fitted model is the pseudo-2nd order which exhibited the highest determination constant $R^2$ (0.9958) and the lowest Root Mean Square Deviation (RMSD) of 0.556 compared to other models. This model suggests an adsorption mechanism with two steps including mostly hydrogen bonds and
electrostatic interactions. The proposed mechanism is given in Fig. 8. It starts with a speedy step corresponding to the external diffusion of FFAs from the oil to the surface of the adsorbent due to the gradient of concentrations between the oil and adsorbent surface. The following step is a steady one that can be ascribed to the interaction between the adsorbate and the adsorbent particles (Nwabanne et al. 2018; Baptiste et al. 2020). However, the determination constant corresponding to intraparticle diffusion is $R^2 = 0.9643$. That value is bigger enough to involve that some molecules can also perfectly fit the intraparticle diffusion model as the porous structure of the composite is also favorable for that (Mbah et al. 2005; Sabah et al. 2007).

**Proposed mechanism of the adsorption of FFA onto Silica/smectite composite**

Based on the FTIR analysis of the composite which previously evidenced the presence of residual silanol (Si-OH) groups on the adsorbent surface (Kepdieu et al. 2023). The adsorption mechanism is weak interactions such as hydrogen bonding between the hydroxyl groups both found on the FFA molecules (RCOOH) and the silanols groups (Si-OH) on the composite surface. Moreover, palm oil is an acid substance (Afane ZE et al. 1997; Domonhédo et al. 2018), it therefore gives to protonate the oxygen atoms of Si-O-Si and Si-OH groups found on the composite surface before the formation of electrostatic interactions. The protonated groups (Si-OH$^+$-Si and Si-OH$_2$$^+$) and other FFAs molecules interact following the illustrative scheme given in Fig. 10. Another mechanism tendency may involve the ionic interaction between the polar carbonyl groups of FFA and the hydrophilic silanol (≡ Si-OH) and siloxane (≡ Si-O-Si≡) groups which may drop the surface tension at the interface of FFA and silica. This will then higher affinity and an increased adsorptive potential of adsorbent to FFA. (Kheang et al. 2006; Parida et al. 2006; Siwińska-Stefańska et al. 2008).

**Comparison of the results obtained in this study with other published works.**

Table 6 displays a comparative value of the bleaching capacity of adsorbents used in this work with respect to those of other materials available in the literature.
Table 6
Comparison with other results on FFA adsorption

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Optimum parameters</th>
<th>FFA adsorbed (mg /g of adsorbent)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffee Husk Ash</td>
<td>30°C/1%w/5.5 h</td>
<td>1966</td>
<td>(Vanida Chaigulprasert 2018)</td>
</tr>
<tr>
<td>Silica/smectite composite</td>
<td>95°C/1h/2% W</td>
<td>617</td>
<td>Current work</td>
</tr>
<tr>
<td>Strong base anion exchange resin</td>
<td>Ambient/8 h 0.4%</td>
<td>589.5</td>
<td>(Mhadmhan et al. 2023)</td>
</tr>
<tr>
<td>Magnesium silicate-derived rice husk</td>
<td>50°C/1h/2% w</td>
<td>185</td>
<td>(Clowutimon et al. 2011)</td>
</tr>
<tr>
<td>Mesoporous silica functionalized (mSiO$_2$-NH$_2$)</td>
<td>70°C/1.5h/5%</td>
<td>147 (528 µmol/g)</td>
<td>(Ahn and Kwak 2020)</td>
</tr>
<tr>
<td>Commercial Magnesium silicate</td>
<td>50°C/1h/4%w</td>
<td>70</td>
<td>(Clowutimon et al. 2011)</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>25°C/1h/x%w</td>
<td>46.20</td>
<td>(Bayrak 2006)</td>
</tr>
<tr>
<td>Mesoporous silica functionalized (mSiO$_2$-OH)</td>
<td>70°C/1.5h/5%</td>
<td>28 (101µmol/g )</td>
<td>(Ahn and Kwak 2020)</td>
</tr>
</tbody>
</table>

Conclusions

The adsorption of Free Fatty Acids (FFAs) onto a silica/smectite based composite can be well understood by Response Surface Methodology. The main parameters affecting the process such as time, temperature, and adsorbent dosage were determined by Pareto Charts of Standardized effects. It showed that time is the more influential and significant parameter in the process, followed by adsorbent dosage and then temperature with respective coefficients of 4.158, 1.271, and 1.231. The temperature was effective in the process with corresponding contour and surface plots allowed us to know the sets of factors’ levels that lead to good results (remaining Acid value ≤ 10 mg of KOH/g). The optimization of the model confirms that more than 27 mg of KOH/g, i.e. around 90% of the FFA were adsorbed. The adsorption process well fitted with second order with a determination coefficient of 0.996 and a value of RMSD (0.555). It, therefore, displayed a two steps mechanism with the transfer of FFA molecules from the oil to the surface of the composite followed by the interaction between these molecules and the surface of the composite surface. The Box-Behnken Design in Response Surface Methodology is therefore convenient and suitable.
to explain the influence of the studied factors. The mechanism of elimination of FFAs in oil by a low cost and environmentally friendly adsorbent silica/smectite based composites was also detailed.

**Declarations**

**Ethics Approval**

Not applicable: Authors declare no research involving human participants and/or animals was conducted.

**Consent to Participate**

All the authors are voluntarily participating for the submission of this research work.

**Consent to publication**

The authors confirm that this manuscript has not been submitted or published previously to any other journal and give full consent for publication of the research work.

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**Conflicts of Interest**

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter discussed in this manuscript.

**Data Availability**

The [xls] data used to support the findings of this study are available from the corresponding author upon request.

**Authors Contributions**

Jean Marie Kepdieu: Investigation, Roles/Writing - original draft, Data curation. Njiomou Djangang Chantale: Conceptualization, Methodology; Writing - review & editing, Visualization: Validation; Supervision. Gustave Tchanang: Writing - review & editing. Jacques Romain Njimou: Investigation, Writing - review & editing. Sanda Andrade Maicaneanu and Chedly Tizaoui: Methodology, Writing - review & editing.

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References


Figures
Figure 1

Pareto Chart of the standardized effects on AV drop by adsorption onto silica/smectite clay
Figure 2

Henry normal plot for the adsorption of FFAs onto the silica/smectite composite

Figure 3

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Figure 6

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Figure 7

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Figure 8

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Figure 9

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Figure 10

Suggested mechanism of the adsorption of FFA onto silica/smectite composite