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OPTIMIZATION AND KINETICS STUDIES OF THE DISSOLUTION OF DOLOMITE IN SULPHURIC ACID (H_2SO_4) VIA BOX-BEHNKEN EXPERIMENTAL DESIGN

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ABSTRACT

Background: The recovery of any valuable component from dolomite as a double carbonate mineral depends on its dissolution efficiency. **Aim:** This study aimed to optimize and provide a simplified novel approach to the kinetics of dolomite dissolution in sulphuric acid solution using the Box-Behnken experimental design. **Methods:** The dolomite sample was dissolved in a sulphuric acid solution at seventeen different experimental conditions. The residue containing impurities was removed via filtration, while precipitation was carried out at the optimum conditions. **Results and Discussion**: The relationship between the independent and dependent variables best fits into the two-factor interaction model with a coefficient of determination of 0.9492**,** adjusted R^2 of 0.9187, and predicted R^2 of 0.7514. The total residual sum of 3×10^{-13} and adequate precision of 18.769 show that the predicted dissolution efficiency is much closer to the experimental values. The analysis of variance revealed that the individual effect of acid concentration, temperature, and dissolution time all positively contribute to the dissolution. The interactive effect of acid concentration with temperature and the interactive effect of temperature with dissolution time also positively influences the dissolution efficiency. Following the dissolution of dolomite in sulphuric acid, a white precipitate was formed at room temperature, which dissolved back at a temperature of 70 ^{o}C, agitation speed of 900 revolutions per minute, and within 10 minutes. A predictive approach using a two-factor interactive model was applied to generate the kinetic data. **Conclusions:** The established model equation is suitable for predicting dolomite dissolution in sulphuric acid. The application of the shrinking core model to the generated data shows that the reaction between dolomite and sulphuric acid is film diffusion control with a first-order reaction (0.6587) and activation energy of 27.5 $KJmol^{-1}k^{-1}$.

Keywords: *Concentration, Temperature, Time, Dissolution Efficiency, Kinetics*.

1. INTRODUCTION:

Dolomite is a naturally occurring double carbonate mineral of magnesium and calcium with the chemical formula $MgCa(CO_3)_2$ (Baba *et al.,* 2014; Pultar *et al.,* 2019; Ajala *et al.,* 2019). Dolomite ore can be used directly as an accelerating agent for cement hydration in concrete and a neutralizing agent in acidic soil (Mubaroka and Kurniawanb, 2015; Sivrikaya, 2018; Ajala *et al.,* 2019). In addition, dolomite is rich in magnesium. Hence it can be used for the production of magnesium-based compounds such as magnesite ($MgCO_3$), magnesium oxide (MgO), magnesium sulfate, as well as calcium sulfate, commonly known as gypsum ($CaSO_4$), (Yildirim *et al.,* 2010; Sivrikaya, 2018). The abundant dolomite of Nigeria is spread across Abuja and the following states: Kogi, Oyo, Yobe, Kwara, Edo, and Nasarawa (Mookah and Abolarin, 2005).

Optimization of process variables helps to determine the best process conditions at which the process response can be determined (Abali *et al.,* 2011; Umar *et al.,* 2016). Earlier studies usually employed one factor at a time for optimization studies, which is a challenge, and the interactive effects between the process variables are usually not accounted for (Baba *et al.,* 2014; Umar *et al.,* 2016). The Box-Behnken method under the response surface methodology in Design-Expert 11.0 software requires a minimal number of experimental runs to carry out regression and graphical analysis of experimental outcomes. Dolomite, as an alkaline ore, is usually soluble in mineral acid. Different studies have investigated the dissolution of dolomite in different acid systems such as hydrochloric acid (Abali *et al.,* 2011; Baba *et al.,* 2014; Pultar *et al.,* 2019; Solihin *et al.,* 2018), nitric acid (Pultar *et al.,* 2019; Are *et al.,* 2020). However, the optimization study of dolomite dissolution in sulphuric acid is yet to be reported. Therefore, this study is put forth to establish the optimum conditions for dolomite dissolution in sulphuric acid solution. The optimization study of process parameters using Design-Expert software is limited as it does not give information on the kinetics of a chemical reaction.

Kinetics study is a useful investigative tool that helps understand how a chemical reaction proceeds (Faraji *et al.,* 2020). Reaction kinetics can be used for reactor design, determination of the volume and size of a reactor, process scale-up, and determination of process variables that affect the rate of a chemical reaction (Fogler, 2016; Faraji *et al.,* 2020). As useful as kinetics is, it is very difficult to achieve due to the complex experimental work and data collection involved (Zhang, 2008; Zhao *et al.,* 2017; Zhou *et al.,* 2018; Faraji *et al.,* 2020). A simplified alternative method was investigated to overcome this difficulty, hence the novelty of this study.

Therefore, this study aimed to investigate the use of a two-factor interactive model developed from the Box-Behnken Experimental method under surface response methodology to study the kinetics of the dissolution of dolomite in H_2SO_4.

2. MATERIALS AND METHODS

2.1 Materials

A representative sample of the dolomite used in this study was collected from *Oreke* village, Ifelodun Local Government, Kwara State, Nigeria. Sulfuric acid is of analytical grade (98%) from Guangdany Guanghua Chemical Factory Co. Ltd. Shanfau, Guandang, China.

2.2 Method

2.2.1 Dissolution Study

The dissolution study was carried out in a 500 ml conical flask reactor. The 300 ml of the specified sulphuric acid concentration was measured in the reactor and heated to the reaction temperature. After this, 1.5 g of the dolomite was weighed into the reactor. The dissolution was allowed to continue until the specified reaction time was completed. The agitation speed was constant at 900 revolutions per minute (RPM). After the dissolution, the content of the reactor was filtered using Whatman filter paper, and the dissolution efficiency was calculated using Equation 1.

$$\text{Dissolution Efficiency (\%)} = \frac{Mass\ of\ disolved\ dolomite\ X\ 100\ \%}{Initial\ Mass\ of\ dolomite} \qquad \text{(Eq. 1)}$$

2.2.2 Precipitation Study

Following the dissolution study, 3 g of dolomite was dissolved in 300 mL of H_2SO_4 at 78°C, 2 M acid concentration, 10 minutes dissolution time, and 900 RPM. The solution was quickly filtered when hot to separate the impurities present in the dolomite. The filtrate was then cooled down to room temperature to enhance precipitation. To know if the precipitate could redissolve, the mixture was heated, and at a temperature of 70 °C and an agitation speed of 900 RPM, a white precipitate was formed. The mixture was filtered using Whatman filter paper, and the residue was oven dry at 70 °C.

2.3 The Kinetic Study of Dissolution of Dolomite in Sulphuric Acid Using Box-Behnken Design

The different experimental conditions were imputed into the developed model equation to determine the fraction of dolomite dissolved at those conditions. At a constant temperature of 77.56 °C, the effect of acid concentration on the dissolution of dolomite was varied between 0.5 M to 3 M, and the dissolution time was also varied between 10 to 60 minutes. The effect of temperature was studied between 30 to 80 °C, while dissolution time was varied from 10 to 60 minutes at a constant acid concentration of 2 M.

3. RESULTS AND DISCUSSION:

3.1 Regression model and Statistical Analysis

In this study, three factors (temperature, time, and acid concentration) were chosen based on literature; preliminary experiments were carried out before the selections of the lower and upper limits of each of the independent variables, the codes, ranges, levels, and the type of factor studied is shown in Table1. Table 2 shows the seventeen experimental runs generated by Box-Behnken

Design. Laboratory experiments were carried out under each of the experimental conditions. The experimental responses (dissolution efficiency) were supplied into the software for regression and graphical analysis. To determine the model that can best establish the relationship between the dependent and independent variables, four different models, linear, two-factor interaction (2FI), quadratic, and cubic, were tested for R^2, adjusted R^2, and predicted R^2. The model with R^2 values close to 1 is most preferred. In Table 3, 2FI was chosen due to the highest value of predicted R^2 (0.7514) and the adjusted R^2 of 0.9187. The 2FI model was then used for the regression and statistical analysis. The predicted dissolution efficiency of the dolomite in sulphuric acid obtained from the model is much closer to the actual experimental values, with a total residual sum of $3\text{x}10^{-13}$ (Table 2). The plot of the predicted against the actual in Figure 1 shows that most dissolution efficiencies are above 95% while only a few are below the mark.

Table 3. Model Summary Statistics

Source	Std. Dev.	R²	Adjusted R²	Predicted R²	
Linear	3.85	0.6077	0.5172	0.1819	
2FI	1.58	0.9492	0.9187	0.7514	Suggested
Quadratic	1.58	0.9647	0.9192	0.4354	
Cubic	0.0894	0.9999	0.9997		Aliased

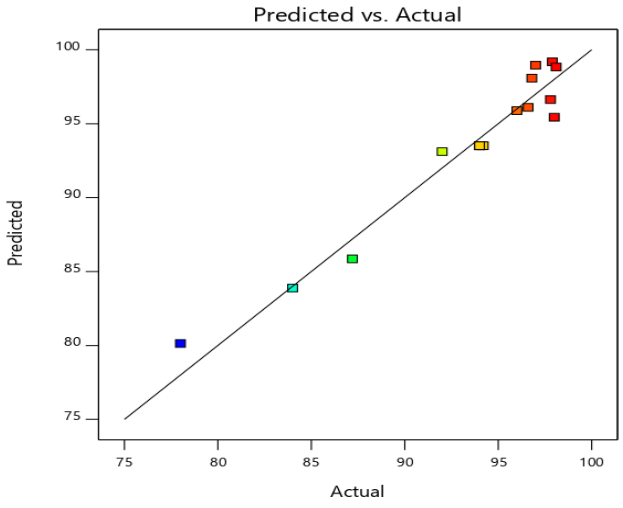

Figure 1. The plot of Predicted against the actual Dissolution Efficiency of Dolomite in Sulphuric Acid

For any given level of each element, Equation 2 in terms of coded factors and Equation 3 can be used to make predictions about the response.

Final Equation in Terms of Coded Factors

$$\text{Dissolution Efficiency (\%)} = +93.51 +2.53A +4.03B +3.85C -1.10AB -3.25AC -5.50BC \qquad \text{(Eq. 2)}$$

Final Equation in Terms of Actual Factors

$$\text{Dissolution Efficiency (\%)} = + 49.03376 + 7.59600\ \text{acid Concentration} + 0.530600\text{Temperature} +0.820000\text{Reaction Time} - 0.035200\ \text{acid Concentration} * \text{Temperature} - 0.104000\ \text{acid Concentration} * \text{Reaction Time} - 0.008800\ \text{Temperature} * \text{Reaction Time} \qquad \text{(Eq. 3)}$$

The Model F-value of 31.13 implies that the model is significant. There is only a 0.01% chance that a large F-value could occur due to noise**.** P-values less than 0.0500 indicate model terms are significant. In this case, acid concentration (A), temperature (B), reaction time (C), acid concentration and reaction time (AC), and temperature and acid concentration (BC) are significant model terms. This implies that they have measures of influence over the dissolution of dolomite sulphuric acid. Since there are not too many insignificant model terms, the model reduction was unnecessary. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 18.769 indicates an adequate signal. This model can be used to navigate the design space.

3.1.1 Individual Effect of Acid Concentration, Temperature, and Reaction Time on the Dissolution Efficiency of Dolomite in Sulphuric Acid

The single effect of acid concentration, temperature, and reaction time on the dissolution efficiency of dolomite in sulphuric acid is presented in Figure 2. As the acid concentration increases from 0.5 to 3 M, the dissolution efficiency rises from 90.9 to 96%. This implies that as the acid concentration increases, the strength of the dissolution agent that can effectively react with the molecules of the dolomite also increases, thereby resulting in the increased dissolution of the dolomite (Faraji *et al.,* 2020). Hence, acid concentration has a positive influence on dissolution efficiency. Furthermore, as the temperature rises from 30 to 80 °C, the dissolution efficiency increases from 87.9 to 97.5%, implying that temperature positively affects dolomite dissolution in sulphuric acid. This is because the temperature helps the reactant molecules gain sufficient kinetic energy for an effective collision to occur. Finally, the single effect of time shows that as the reaction time increases from 10 to 60 minutes, the dissolution efficiency increases from 89.7 to 97.3%, implying that reaction time has a positive influence on dissolution efficiency and that increasing the reaction time also enhances longer periods of contact between the ions from sulphuric acid and the molecules of dolomite.

3.1.2 Interactive Effect of the independent variables on the dissolution of dolomite in sulphuric acid

The interactive effect of the contour plot between reaction temperature and the acid concentration on the dissolution efficiency is presented in Figure 3a, while the three-dimensional plot is shown in Figure 3b. It is clear that increasing the dissolution temperature from 30 to 80°C and the acid concentration from 0.5 to 3 M increases dolomite dissolution in sulphuric acid from 90 to 97.2%. This implies that an increase in acid concentration brings about an increase in the dissolution agent, while an increase in temperature helps to increase the kinetic energy of the dissolution agent, thereby increasing its activity in dissolving the dolomite. The interactive effect between temperature and acid concentration positively influences dissolution (Faraji *et al.,* 2020; Are et al., 2021).

The interactive effect of the contour plot between reaction time and the acid concentration on the dissolution efficiency is presented in Figure 4a, while the three-dimensional plot is shown in Figure 4b. It is clear that increasing the dissolution time from 10 to 60 °C and the acid concentration from 0.5 to 3 M results in an increase in dolomite dissolution in sulphuric acid from 85 to 97.2%. This implies that an increase in acid concentration brings about an increase in dissolution agents. At the same time, sufficient time is provided for the reactant molecules of the dolomite to dissolve in the sulphuric acid. Hence, an increase in the interactive effect between acid concentration and reaction time positively influences the dissolution of dolomite in sulphuric acid.

The interactive effect of the contour plot between reaction time and the temperature on the dissolution efficiency is presented in Figure 5a, while the 3D plot is shown in Figure 5b. Increasing the dissolution temperature from 10 to 60 minutes and from 30 to 80 °C leads to an increase in the dissolution of dolomite in sulphuric acid from 85 to 97.2%. This implies that as the temperature increases, the kinetic energy of the reactant molecules also increases, and sufficient time is required to attain a high dissolution efficiency of the dolomite in sulphuric acid. Therefore, it can also be inferred that the interactive effect between dissolution time and the temperature positively influences the dissolution efficiency.

3.1.3 Optimization Constraints for the Dissolution of Dolomite in Sulphuric Acid

The point prediction of the optimum point was arrived at via the numerical optimization method. The optimization constraints (Table 5) were chosen based on economic cost, safety, and environmental considerations. For example, high acid concentration values can potentially harm humans and the environment. In addition, prolonged dissolution time can lead to overstretching of equipment and increase operational costs in an industrial setting.

Table 5. Optimization Constraints on Dissolution of Dolomite in Sulphuric Acid

Name	Goal	Lower Limit	Upper Limit
A:acid Concentration	is target = 2	0.5	3
B: Temperature	is in range	30	80
C:Reaction Time	Minimize	10	60
Dissolution Efficiency	Maximize	78	98.1

The predicted optimum point of dissolution of dolomite in sulphuric acid is presented in Figure 6. At an acid concentration of 2 M, the temperature of 78 °C, the reaction time of 10 min, and a constant agitation speed of 900 RPM, 99.2% dissolution efficiency were predicted. This is close to the 96.7% dissolution efficiency validated at the same predicted independent optimum points. Therefore, the desirability of 1 in this study is most preferred. The outcome of the dissolution in this study agrees with the report by Baba *et al.* (2014) who achieved 99.3% dissolution efficiency of dolomite in hydrochloric acid at 80 °C, 2 M acid concentration. However, the 60-minute reaction time is higher than the 10-minute dissolution time in H_2SO_4 in this study. In a similar study, are et al. (2021) reported 99.5% dolomite dissolution in nitric acid at 2.5 M acid concentration, 50-minute dissolution time, 55 °C, and 250 RPM.

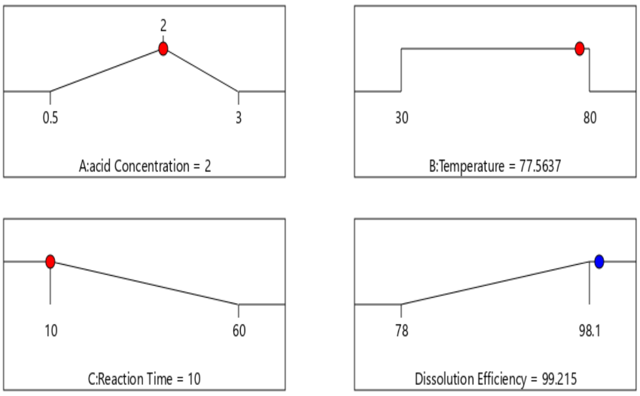

Figure 6. Predicted Optimum Point of Dissolution of Dolomite in Sulphuric Acid

3.2 Precipitation Study

Information on the dissolution of dolomite in sulphuric acid and the precipitation of any substance has not been properly documented. However, it was discovered in this study that the filtrate recovered from dolomite dissolution at the optimum point formed a white precipitate suspected to be magnesium oxide. Further precipitation attempts from the filtrate using calcium oxide and sodium hydrogen carbonate as precipitants did not result. This implies that there was complete precipitation.

3.3 Application of Box-Behnken Experimental Design in the Kinetic Study of Dissolution of Dolomite in Sulphuric Acid

The developed model equation 3 in this study was used to predict the fractions of dolomite that reacted at different experimental conditions

3.3.1 The effect of H_2SO_4 concentration on the reaction of dolomite

The results of the variation in the acid concentration from 0.5 to 3 M on the fraction of dolomite that reacted are presented in Figure 7. It can be observed that the fractions of dolomite that dissolved increase with increased acid concentration from 0.5 to 2 M and increase in dissolution time from 10 to 60 Minutes. This implies that the increase in acid concentration positively influenced the dissolution of the dolomite particles as sufficient dissolution time favors the dissolution process (Baba *et al.,* 2014; Pultar *et al.,* 2019, Are *et al.,* 2021). However, a further increase in the acid concentration from 2.5 to 3 M and an increase in the dissolution time from 10 to 60 minutes shows an inverse relationship with the dissolved dolomite fraction. This implies that the dissolution of dolomite in H_2SO_4 is not favored by an increase in the acid concentration beyond 2 M. The heights dissolution fraction of 1 is predicted at 2.5 M acid concentration, the temperature of 77.56 °C and 10 minutes. This is similar to the 0.993 fractions of dissolved dolomite in hydrochloric acid at 2 M, 80 °C, and 60 minutes of dissolution time.

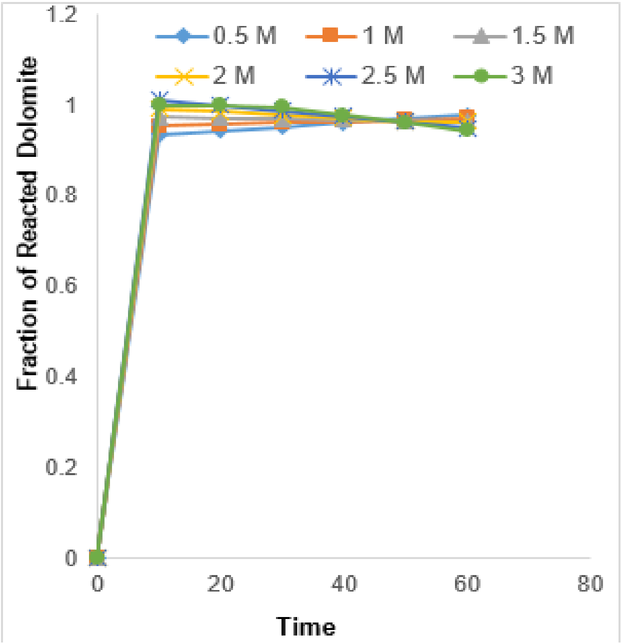

Figure 7. Effect of H_2SO_4 concentration on the kinetic study of dolomite at a temperature of 77.56 °C

3.3.2 Effect of temperature on the reaction between dolomite and H_2SO_4

There must be an effective collision between reactant molecules for a chemical reaction by the collision theory. For an effective collision to occur, there must be enough kinetic energy to drive the reactant molecules to collide with each other. The kinetic energy of a chemical reaction is a function of the reaction temperature (Are *et al.,* 2021). To understand how the reaction temperature affects the reaction between dolomite and H_2SO_4, the effect of temperature was varied between 303 K and 352 K at reaction time variation of 10 to 60 Minutes while the acid concentration was kept constant at 2 M (Figure 8). There is a proportional increase relationship between the fraction of dolomite that reacted and the increase in the reaction temperature from 303k to 333 k. The reaction time also increased from 10 to 60 minutes. Therefore, it can be inferred that as temperature increases, the reactant monocles of dolomite and H_2SO_4 gain enough kinetic energy to overcome the energy barrier and go into reaction, resulting in a higher fraction of dissolved dolomite. However, there is a decline in the fraction of dolomite that dissolved as the temperature increases from 343 K to 353 K. This could be attributed to higher kinetic energy gained by the liquid phase (H_2SO_4), which leads to molecular loss due to evaporation as a result of prolonging heating time.

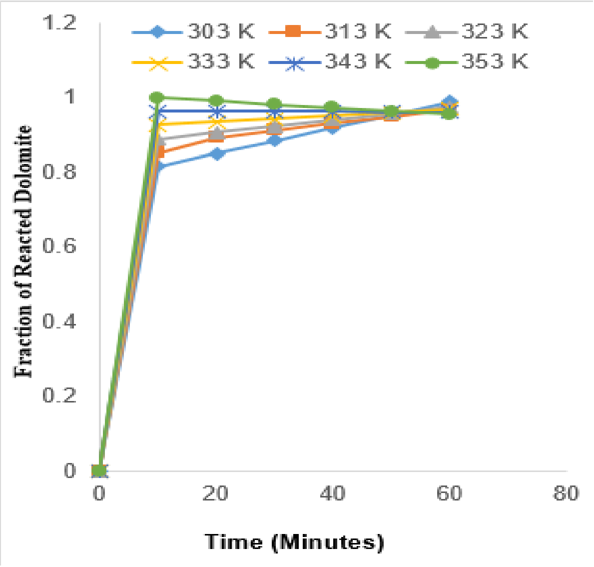

Figure 8. Effect of Temperature on the kinetic study of dolomite at 2 M and 10 minutes reaction time

3.3.3 Dissolution Kinetics of Dolomite in H_2SO_4

The dissolution of dolomite in H_2SO_4 is an exothermic reaction (equation 2) that involves the effervescence of carbon dioxide (CO_2), the formation of water, and calcium and magnesium sulfate. The magnesium ion (Mg^{2+}) and calcium ion (Ca^{2+}) from dolomite individually displace the hydrogen ion (H^+) in sulphuric acid. This agrees with the rule that cation above H^+ in the electrochemical series will displace H^+ during the chemical reaction. The amount of the sulfate ions (SO_4^{2-}) available for both Mg^{2+} and Ca^{2+} to bond with increases as the acid concentration increases. The binding of Mg^{2+} and Ca^{2+} with the SO_4^{2-} results in the breakdown of the crystal structure of the dolomite, this process is known as dissolution. The amount of the SO42- present in the solution must be increased to increase the extent of dolomite dissolution. This can be achieved by increasing the concentration of the H_2SO_4. The reaction mechanism developed in this study is presented in equations 4 to 11.

$$CaMg(CO_3)_2 + 2H_2SO_4 \rightarrow CaSO_4 + MgSO_4 + 2CO_2 + 2H_2O \quad \text{(Eq. 4)}$$

$$2H_2SO_4 \rightleftharpoons 4H^+ + 2SO_4^{2-} \quad \text{(Eq.5)}$$
$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgCO_2 \quad \text{(Eq.6)}$$
$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \quad \text{(Eq. 7)}$$
$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4 \quad \text{(Eq. 8)}$$
$$MgCO_3 \rightarrow Mg^{2+} + CO_3^{2-} \quad \text{(Eq. 9)}$$
$$Mg^{2+} + SO_4^{2-} \rightarrow MgSO_4 \quad \text{(Eq. 10)}$$
$$4H^+ + 2CO_3^{2-} \rightarrow 2CO_2 + 2H_2O \quad \text{(Eq.11)}$$

The rate-determining step in any reaction mechanism is considered to be the slowest step (Fogler, 2016; Faraji *et al.,* 2020). Theoretically, equation 4 could be assumed to be the slowest step since higher bonding energy is involved. The chemical structure of dolomite [$CaMg(CO_3)_2$] shown in Figure 9 has four strong ionic bonds at the point of cleavage compared to the chemical structure of magnesium carbonate (Figure 10) and calcium carbonate (Figure 11), which has two ionic bonds each at the point of cleavage. Equations 6, 7, and 8 have only one ionic bond each at the point of cleavage, while equation 1 and 9 has only weaker covalent bonds at the cleavage point. Since higher ionic bonds are present in $CaMg(CO_3)_2$, it will require higher dissociation energy to break $CaMg(CO_3)_2$ into its component. Therefore, equation 4 will require more time to go to completion, and it is therefore considered to be the slowest step.

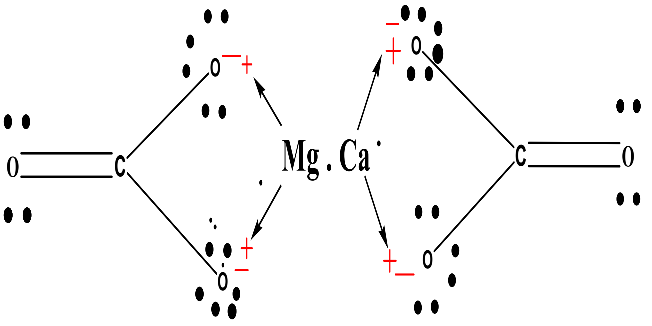

Figure 9. Chemical Structure of $CaMg(CO_3)_2$

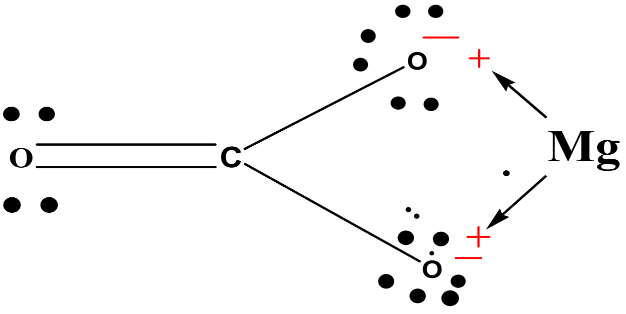

Figure 10. Chemical Structure of $MgCO_3$

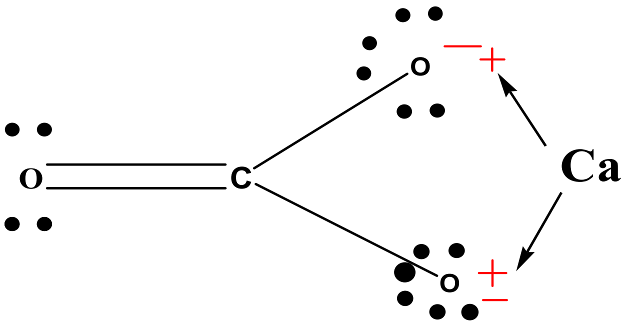

Figure 11. Chemical Structure of $CaCO_3$

Since equation 4 is considered to be the rate-determining step, their rate equation can then be written thus:
Rate of disappearance = $K[CaMg(CO_3)_2]$ (Eq.12)
From the rate law in Equation 12, the reaction is first order.

The shrinking model (SCM) is one of the mathematical relations used to study the kinetics behavior of reaction spherical particles in a liquid medium. The dolomite particle is assumed to be spherical, while the H_2SO_4 is in a liquid phase. Hence the use of SCM is considered suitable for this study. For kinetic model determination, the data obtained in Figures 7 and 8 are further subjected to the three model division of the SCM shown in Equations 13 to 15.
Film diffusion control:

$$X = \frac{6\mathrm{bD}C_A}{\mathrm{PoRo}^2\mathrm{t}} = K_1 t \qquad (13)$$

$$1 - (1 - x)^{1/3} = \frac{6\mathrm{bD}C_A}{\mathrm{PoRo}^2 t} = K_2 t \qquad (14)$$

$$1 + 2(1 - \mathrm{x}) - 3(1 - \mathrm{x})^{\frac{2}{3}} = K_3 t \qquad (15)$$

Were ρ_o is the molar density of solid reactant (mol/m^3), Ro is the radius of a sphere (m), *b* is the stoichiometric coefficient of the solid, *D* is the effective diffusion coefficient (m^2/s), and C_A is the concentration of *A* in the bulk solution (mol/m^3), K_1, K_2, K_3 are rate constant for diffusion control, surface chemical reaction control and Product layer diffusion control respectively (Gerald *et al.*, 2012; Ajemba *et al.*, 2013; Are *et al.*, 2021). Therefore, model consideration is based on the highest coefficient of determination (R^2) value.

Table 6 shows the apparent rate constants and correlation coefficient (R^2) at various temperatures and concentrations for the three models. Model consideration is based on the highest coefficient of determination (R^2) value. Judging from the values of R^2, it can be inferred that the mechanism of the reaction follows the order of film diffusion control > ash layer diffusion control > chemical reaction control with average R^2 values (0.9953 > 0.98175> 0.94755) from effect of concentration and average R^2 (0.99494 > 0.98454 > 0.97186) from effect of concentration. This agrees with the report by Baba *et al.* (2014) that the reaction between dolomite and hydrochloric acid is film diffusion control. However, Are *et al.* (2021) reported that the reaction between dolomite and nitric acid is ash layer diffusion control. Figure 12 presents the film diffusion control plot with the individual R^2 value at different concentrations.

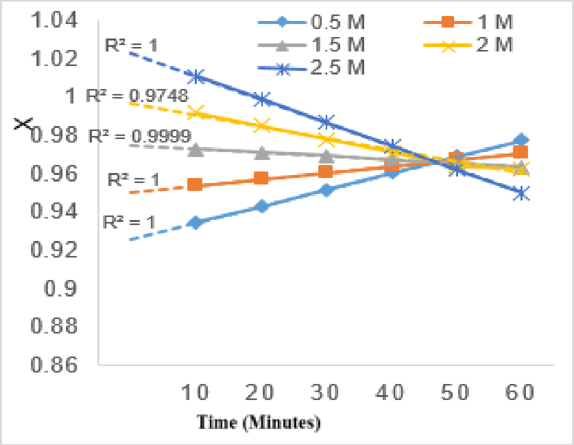

Figure 12. Plot of Film Diffusion Control for Effect of Acid Concentration

3.3.4 Order of reaction between dolomite and H_2SO_4

The speed at which a chemical reaction proceeds is judged by order of the reaction. This is determined by plot the apparent rate constant (slope of Figure 12) against the natural logarithm of the corresponding acid concentration shown in Figure 13. From the slop of 0.6587, the reaction order is first ordered with the H^+ concentration, and it agrees with the reaction order determined by the rate law. It is also close to the 0.77 reaction order Pultar *et al.* (2019) reported for dolomite dissolution in nitric acid. However, it is below 0. 0.9152 reaction order reported by Are *et al.* (2021).

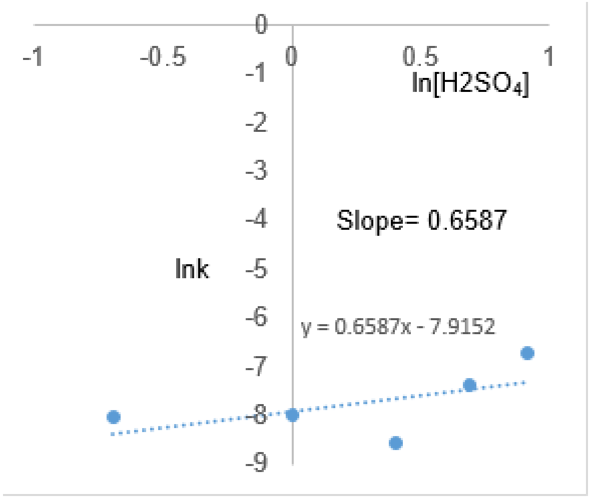

Figure 13: Plot of lnk Vs ln[H_2SO_4]

3.3.5 Activation Energy of the reaction between dolomite and H_2SO_4

The Arrhenius equation (equation 16) is a mathematical expression used to evaluate the amount of energy (activation energy) needed for a chemical reaction to occur.

$$k = Aexp\left(-\frac{Ea}{RT}\right) \qquad (Eq.16)$$

Where K is the rate constant, Ea depicts the activation energy, 'A' stand for the frequency factor, R is the universal gas constant, and T is the temperature of the reaction
Linearizing equation 16 by taking the natural logarithm gives rise to $\ln K = \ln A - \frac{Ea}{RT}$ (17) which is similar to the equation of straight-line $Y = mx + C$. A plot of the lnK against T^{-1} in Figure 14 gives rise to a slope equal to $-\frac{Ea}{R}$

Therefore, $Ea = -slope\ x\ R$, where R = 8.3145 $Jmol^{-1}k^{-1}$ and the slope is -3340.26
$Ea = -(-3308.11)K\ x\ 8.3145\ J/molK$ =27505.28 $Jmol^{-1}k^{-1}$ = 27.5 $KJmol^{-1}k^{-1}$

The activation energy of 27.5 $KJmol^{-1}k^{-1}$ is the amount of energy needed for the reaction between dolomite and H_2SO_4 to occur, and it can also be referred to as the amount of energy required to dissolve dolomite in H_2SO_4. The activation energy of 27.5 $KJmol^{-1}k^{-1}$ is close to the 26.605 $KJmol^{-1}$ reported by Are et al. (2021), but it is below the 30 to 57 $KJmol^{-1}k^{-1}$ reported by Pultar *et al.* (2019) for dissolution of dolomite in nitric acid. However, Baba *et al.* (2014) reported lower activation energy of 20.77 $KJmol^{-1}$ for dolomite dissolution in hydrochloric acid.

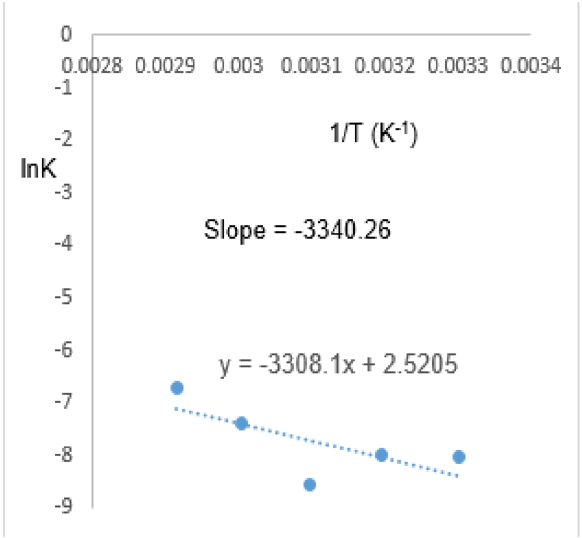

Figure. 14: Plot of lnk Vs 1/T (K^{-1})

4. CONCLUSION:

Dolomite dissolution in sulphuric acid solution was optimized using Box-Behnken Experimental Design. The ANOVA shows that the single effects of temperature, acid concentration, and time all have positive, significant effects on the dissolution efficiency. Furthermore, the interactive effect between acid concentration and temperature and the interactive effect between temperature and dissolution time have significant positive effects on dissolution efficiency. At an acid concentration of 2 M, the temperature of 78 °C, the reaction time of 10 minutes, and a constant agitation speed of 900 RPM, an optimal point prediction of 99.2% dissolution efficiency were established, while 96.7% dissolution efficiency was validated with the formation of white precipitate at room temperature. In the kinetic study, under the influence of acid concentration, the highest dissolution fraction of 1 was predicted at 2.5 M acid concentration, the temperature of 77.56 °C, and 10 minutes. Under the influence of dissolution temperature, a heights dissolution fraction of 1 was predicted at 2 M acid concentration, the temperature of 80 °C, and 10 minutes. From the rate-determining step, the reaction order between dolomite and H2SO4 is first order. The kinetic study also confirmed this with the value of 0.6587, signifying a first-order reaction. The activation energy of the reaction between dolomite and H_2SO_4 is 27.5 $KJmol^{-1}k^{-1}$and is film Diffusion Control. Hence, using two-factor interaction under the Box-Behnken Experimental Design method is a suitable novel approach to studying the kinetics of dolomite dissolution in H_2SO_4.

5. DECLARATIONS

5.1. Study Limitations

No limitations were known at the time of the study.

5.2. Funding source

The authors funded this research.

5.3. Competing Interests

No competing interest

5.4. Open Access

6. REFERENCES:

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Table 1. Factors and boundary conditions for the dissolution of dolomite in sulphuric acid

Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	acid Concentration	M	Numeric	0.5000	3.00	-1 ↔ 0.50	+1 ↔ 3.00	1.75	0.8839
B	Temperature	oC	Numeric	30.00	80.00	-1 ↔ 30.00	+1 ↔ 80.00	55.00	17.68
C	Reaction Time	Min	Numeric	10.00	60.00	-1 ↔ 10.00	+1 ↔ 60.00	35.00	17.68

Table 2. Experimental and predicted dissolution efficiency from Box-Behnken experimental design

Run	A: acid Concentration M	B: Temperature oC	C: Reaction Time Min	Dissolution Efficiency (%)		Residual
				Actual	Predicted	
1	1.75	55	35	94	93.51176	0.488235
2	1.75	55	35	94.1	93.51176	0.588235
3	1.75	55	35	94	93.51176	0.488235
4	0.5	55	10	84	83.88676	0.113235
5	3	80	35	97	98.96176	-1.96176
6	0.5	55	60	96.8	98.08676	-1.28676
7	1.75	80	60	96	95.88676	0.113235
8	1.75	80	10	97.9	99.18676	-1.28676
9	1.75	30	60	98.1	98.83676	-0.73676
10	0.5	80	35	96.6	96.11176	0.488235
11	0.5	30	35	87.2	85.86176	1.338235
12	3	30	35	92	93.11176	-1.11176
13	3	55	60	97.8	96.63676	1.163235
14	1.75	55	35	94.2	93.51176	0.688235
15	1.75	30	10	78	80.13676	-2.13676
16	3	55	10	98	95.43676	2.563235
17	1.75	55	35	94	93.51176	0.488235
Sum Total						**3E-13**

Table 4: ANOVA for 2FI model **dissolution efficiency of** dolomite in sulphuric acid

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	467.28	6	77.88	31.13	< 0.0001	Significant
A-acid Concentration	51.01	1	51.01	20.39	0.0011	Significant
B-Temperature	129.61	1	129.61	51.81	< 0.0001	Significant
C-Reaction Time	118.58	1	118.58	47.40	< 0.0001	Significant
AB	4.84	1	4.84	1.93	0.1944	Insignificant
AC	42.25	1	42.25	16.89	0.0021	Significant
BC	121.00	1	121.00	48.37	< 0.0001	Significant
Residual	25.02	10	2.50			
Lack of Fit	24.99	6	4.16	520.53	< 0.0001	significant
Pure Error	0.0320	4	0.0080			
Cor Total	492.30	16				

Adequate precision: 18.769

Table 6: Apparent rate constants and correlation coefficient, $R^{2,}$ and at various temperatures and concentrations for SCM

Process Variable	X = k_1t (Film Diffusion Control)		Kinetic Equation 1 – (1 – X)1/3 = k_2t (Chemical Reaction Control)		1 + 2(1 – X) – 3(1 – X) 2/3 = k_3t (Ash Layer Diffusion Control)	
Temp (°C)	K_1 x 10^{-3}	R^2	K_2 x 10^{-3}	R^2	K_2 x 10^{-3}	R^2
30	3.48	1	6.618	0.9395	9.25	0.9591
40	2.192	0.9722	3.935	0.9495	5.814	0.9927
50	1.72	1	3.725	0.9798	5.257	0.9867
60	0.84	1	2.058	0.9932	2.861	0.9958
70	-0.04	1	-0.12	0.9989	-0.16	0.9997
80	-0.9	0.9995	-6.29	0.8244	-5.54	0.9565
Average		0.995283		0.94755		0.98175
Conc (M)						
0.5	0.858	1	2.391	0.9895	3.221	0.9939
1	0.335	1	0.998	0.9982	1.332	0.9989
1.5	0.19	0.9999	0.62	0.9991	0.81	0.9996
2	0.62	0.9748	2.72	0.9388	3.22	0.9543
2.5	1.22	1	7.45	0.9339	6.59	0.976
Average		0.99494		0.97186		0.98454

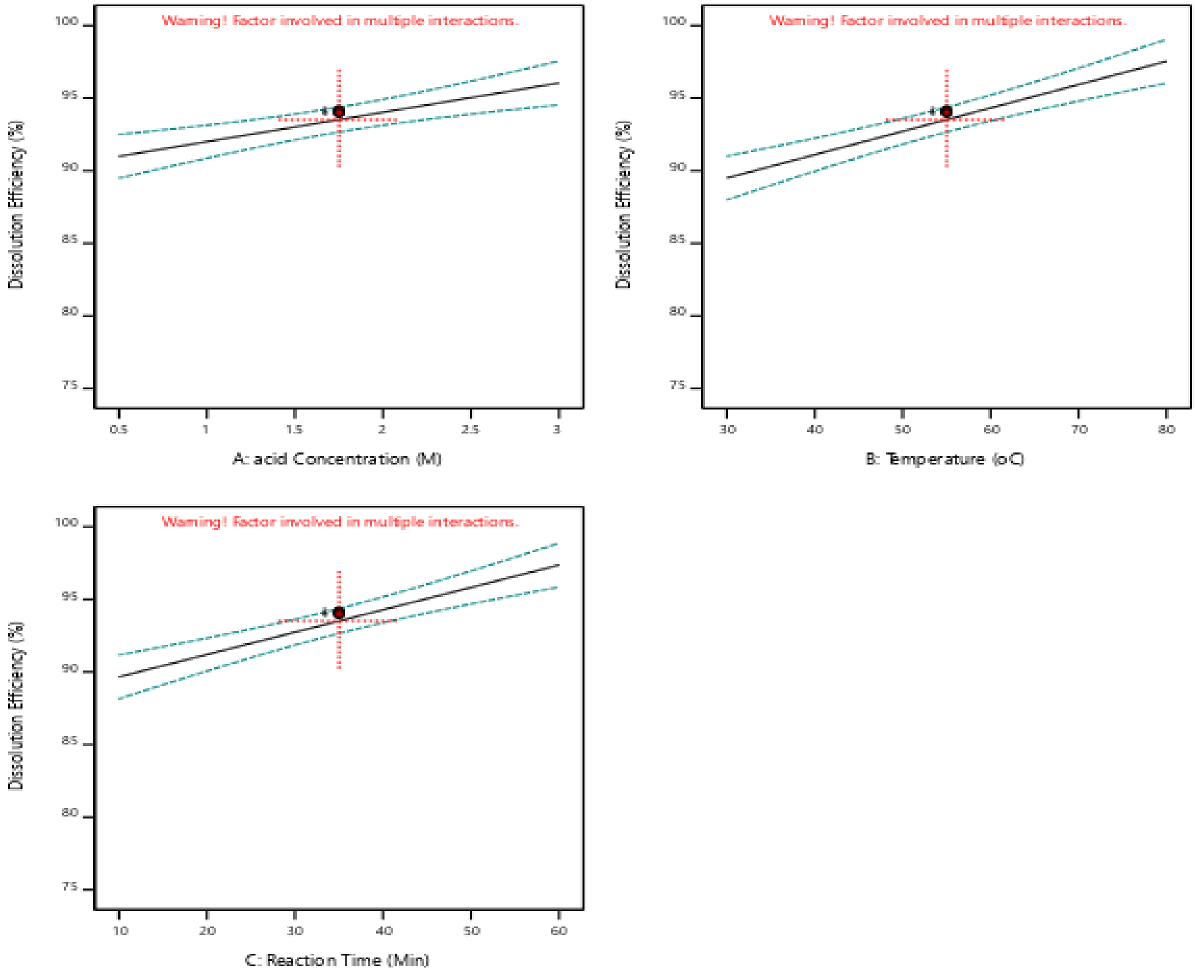

Figure 2: *Single Effect of Acid Concentration, Temperature, and Reaction Time on the Dissolution Efficiency of Dolomite in Sulphuric Acid*

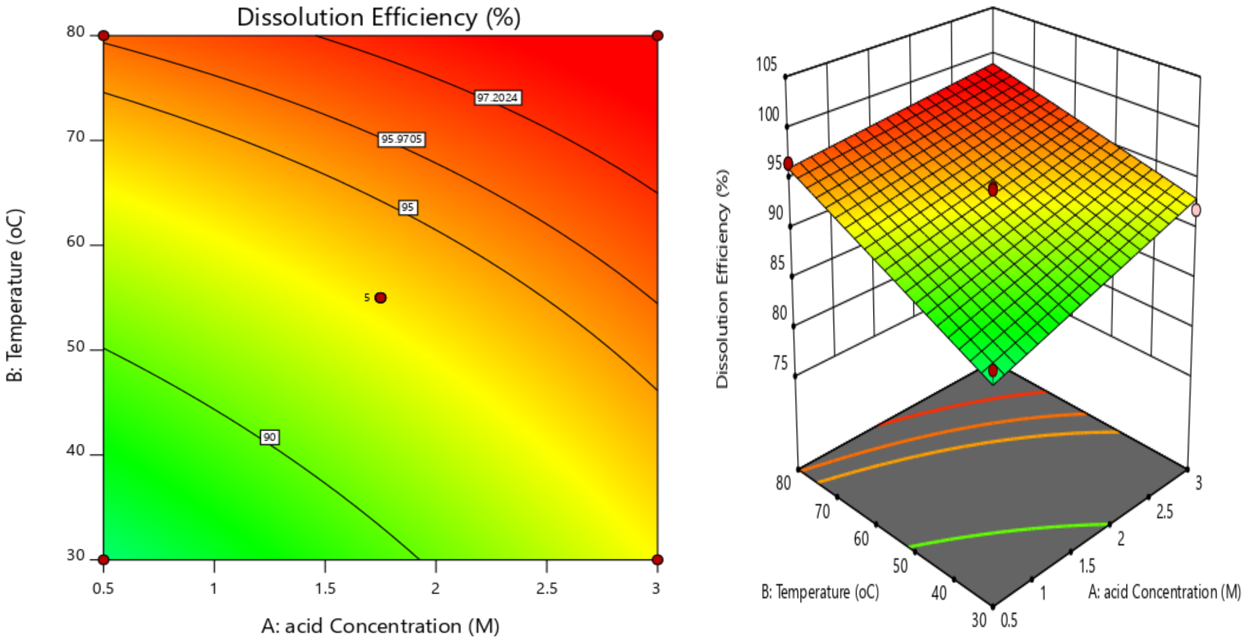

Figure 3: *(a) Contour Plot; (b) Three Dimensional (3D) plot; of the interactive effect of temperature and acid concentration on the dissolution of dolomite in sulphuric acid*

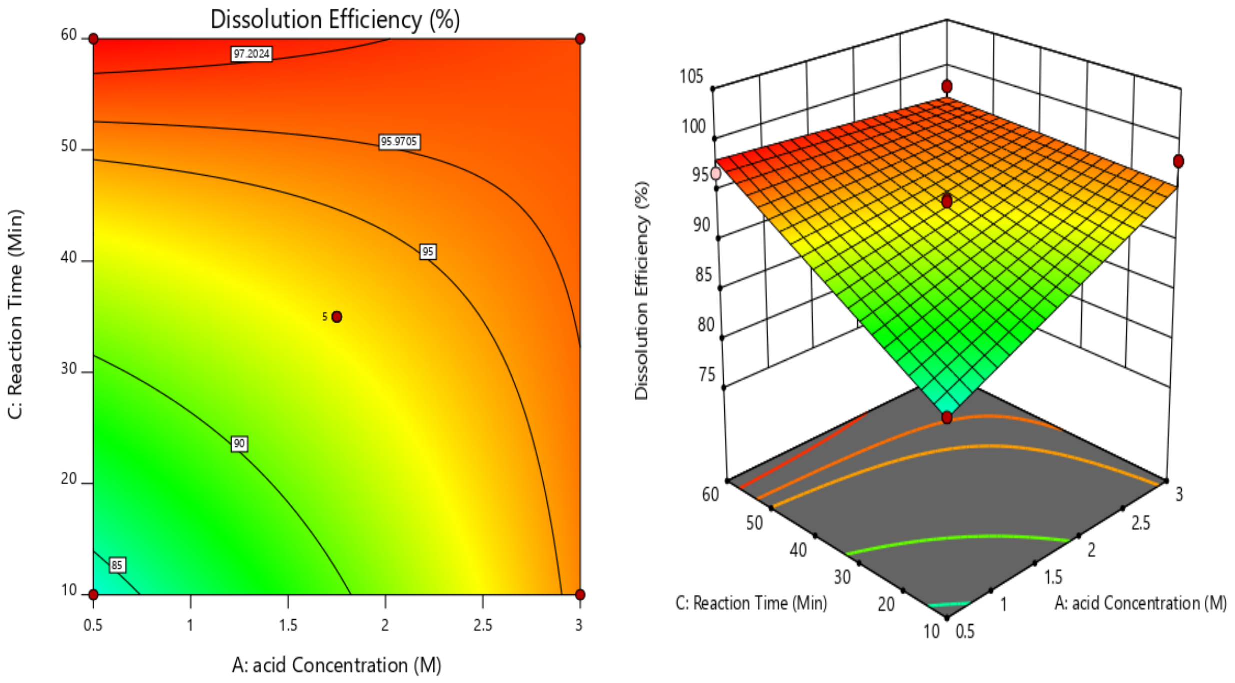

Figure 4: *(a) Contour Plot; (b) 3D Plot; of the interactive effect of reaction time and acid concentration on the dissolution of dolomite in sulphuric acid***.**

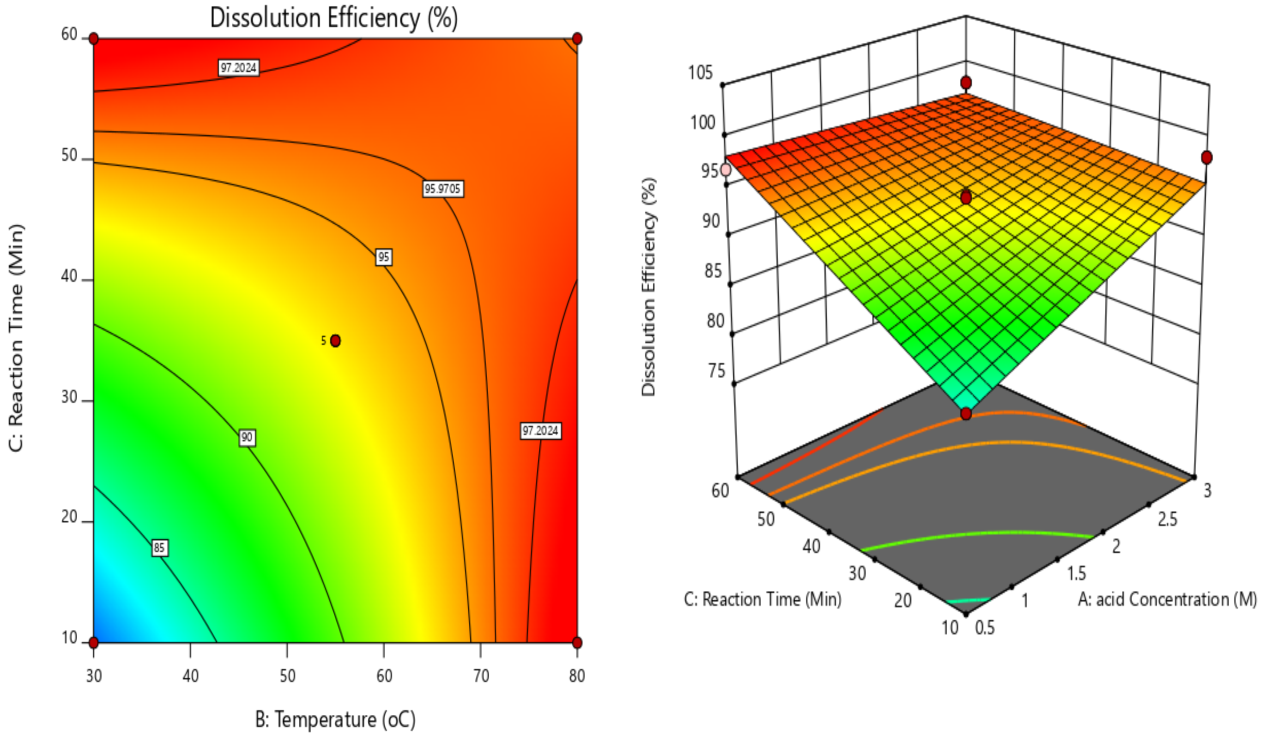

Figure 5: *(a) Contour Plot; (b) 3D plot; of the interactive effect of reaction time and temperature on the dissolution of dolomite in sulphuric acid***.**