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# Synthetic Biochar Activated by Potassium and Zinc for Glyphosate Removal: Optimization with Design Experiment, Kinetics, and Isotherms Studies

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## ABSTRACT

In this study, glyphosate removal from aqueous solution was compared using activated carbon prepared from rice husk and activated with KCl or $ZnCl_2$. The Min Run Res IV design was used to select the main effect factors of adsorption, and the 3D response surface design was applied to evaluate the interactive effects of the three most important variables. Two adsorption isotherms (Langmuir and Freundlich) and two models of kinetics (pseudo first and second order reaction) were used. The Min Run Res IV design considered five variables, including pH, temperature, time, dose of adsorbents, and type of metals. The three significant factors were further examined using 3D response surface plots, and the optimal conditions were found to be pH 5.8, dose 265 mg, and KAC more effective than ZnAC. The results showed that the adsorption data fitted the Langmuir isotherm model better than the Freundlich model. The rate of glyphosate adsorption followed a pseudo-second-order model.

***Keywords:*** Adsorption, Glyphosate, Surface response, Experimental Design, Kinetics

## 1. Introduction

Pesticides are a group of chemical compounds widely used worldwide to protect crops from damage caused by insects, diseases, weeds, and other pests. widespread use has led to undesirable side effects such as acute and chronic toxicity, including teratogenic, carcinogenic, and mutagenic effects (Kouras *et al.,* 1998). Pesticide residues can be found in various environmental compartments, including soil, air, and water (Roby *et al.,* 2015, Yigit and Velioglu 2020).

The contamination of surface and groundwater by pesticides is a significant issue that scientists have been addressing for many years in order to prevent accumulation and contamination. The presence of pesticides in water can cause serious problems for both the environment and human health (Rani *et al.,* 2021). Necessitating their removal from aqueous solutions. Various water treatment methods have been utilized to remove pesticides from water, including precipitation, coagulation/flotation, sedimentation, filtration, membrane processes, advanced oxidation process (AOPs), electrochemical techniques, ion exchange, biological processes, and chemical processes (Ahmed *et al.,* 2017, Salimi *et al.,* 2017, Saleh *et al.,* 2020). Each method has its own advantages and limitations in practical applications. Among the chemical treatments, the sorption of pesticides onto activated carbon has gained attention from researchers due to its effectiveness in removing pesticides and heavy metal ions at trace levels (Derylo-Marczewska *et al.,* 2019, Wang *et al.,* 2021). Adsorption has emerged as the most effective method and offers several advantages, including economic, ecological, and technological benefits, as well as high removal efficiency. The lower cost, easy availability, and absence of complex regeneration processes have further emphasized the potential of these materials as sorbents (Mondol and Jhung 2021, Ponnuchamy *et al.,* 2021).However, the high cost of this process limits its large-scale usage. To overcome this issue, there has been a focus on exploring newer, cheaper, and locally available waste materials for the removal of pesticides and other organic and inorganic contaminants from water.

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Researchers have investigated materials such as rice bran, orange peel, bagasse fly ash, rice husk ash, and other cellulosic materials like sunflower stem and palm seed coat, as well as olive stones (Durán *et al.,* 2019, Ponnuchamy *et al.,* 2021, Rana *et al.,* 2021).

Traditional adsorption studies often involve a trial-and-error approach, where one factor is varied at a time while keeping others constant. This method can be time-consuming and may not provide a comprehensive understanding of the complex interactions between variables. Experimental design offers a systematic approach to efficiently explore multiple factors simultaneously, reducing the number of experiments required and optimizing resources. The design of experiments (DOE) is a powerful tool that can significantly enhance the efficiency and insight gained from adsorption studies.

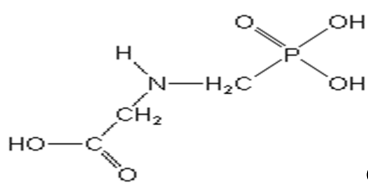
This study aimed to investigate the ability of low-cost adsorbents, specifically activated carbon prepared from Rice husk and chemically activated with KCl and $ZnCl_2$, to remove the herbicide glyphosate from water under different experimental conditions. The conventional approach of altering one variable while maintaining the others constant can be a lengthy process and fails to consider the interaction between variables (Herath *et al.,* 2019). Using min-run screening methodology for statistical optimization may offer an improved approach for constructing the model, designing the experimental plan, and evaluating and optimizing the experimental data. The selection of this herbicide was based on its wide usage in controlling pests and weeds in various crops. The objective was to assess the removal efficiency of these adsorbents under different conditions, including contact time, temperature, activated carbon dosage, initial solution pH, and pesticide concentration.

## 2. Materials and Methods

### 2.1 Materials

All chemicals used are of analytical grade and were purchased from NATCO. All solutions were prepared in deionized water (DI). Activated carbons were derived from rice husk. The process involved washing, crushing, and grinding the products in a laboratory mill to achieve a size range of 0.5 - 3.0 mm. Solid matter was then dried in an air oven. To impregnate the carbons, appropriate amounts of KCl and $ZnCl_2$ (0.10 g/g carbon) were used. The impregnating solution was left overnight, followed by drying at 383 K and carbonization at 773 K for two hours. The activated carbon derived from rice husk that activated with KCl (referred to as KAC) and $ZnCl_2$ (referred to as ZnAC).

Glyphosate (2-[(phosphonomethyl) amino] acetic acid) whose trade name Roundup, has been used to study the removal capacity of the prepared activated carbon and kinetics property.




Glyphosate

### 2.2. Characterization

Specific surface area and porosity were determined by methylene blue adsorption method (MB) (Ruiz-Hitzky 2001, Gürses *et al.,* 2004, Qadeer and Akhtar 2005). Methylene Blue, also known as Basic Blue 9, was selected for its well-established strong adsorption properties onto solids and its recognized utility in characterizing adsorptive materials. The methylene blue trihydrate compound, with a molecular weight of 373.9 g/mol, was used in this study and the specific surface area was calculated using Eq. 1 (El-Geundi *et al.,* 2014).

$$S_{MB} = 1.72 x q_{\max} \quad (1)$$

Bulk density (Db) and particle density (Dp) were measured from Eqs. 2 and 3.

$$D_p = \frac{m_S}{V_S} \quad (2)$$

$$P_S = 1 - \frac{D_b}{D_p} \quad \text{......(3)}$$

where: $m_S$ = oven dry mass of the sample (g), Vs = Volume of the solids only, $cm^3$, and $P_S$ is the pore space.

### 2.3. Experimental design

The use of Minimum Run Resolution IV design in this study with experimental design offers efficiency, cost-effectiveness, the identification of significant factors, understanding of interaction effects, and statistical analysis capabilities. These benefits contribute to the overall improvement and optimization of adsorption processes. Minimum Run Resolution IV design, one of the types of factorial design, is a standard two-level factorial design that enables the estimation of main effects. It is highly regarded for its ability to minimize the number of runs while still producing reliable results. Min Run Res IV design was applied within 12 runs with two-level (high and low) and five independent factors including pH (from 4 to 8), temperature (25-45 °C), time (20-120 min), dose of adsorbent (100 – 500 mg), and metal activator (KCl or $ZnCl_2$). This study will use the software of Design Expert, version 13.0.5.0. For each run, the samples used in the adsorption tests were prepared to match the specific conditions at each run. The final concentration of glyphosate remaining in the solution after adsorption was measured and recorded. Table 1 provides the 12 runs, levels of independent variables, and their coded and un-coded values for glyphosate adsorption. The significance of each factor on the overall adsorption process was determined by ranking the operation parameters using Perturbation analysis. To assess the accuracy of the model, Pareto analysis and analysis of variance (ANOVA) tests were conducted.

**Table 1:** Matrix of Min Run Res IV Design and responses

| Independent variables | | | | | | Removal % |
|---|---|---|---|---|---|---|
| **Run** | **pH** | **Temperature $^0$C** | **Time (min)** | **Dose(mg)** | **Metal** | |
| **1** | 4 | 25 | 20 | 500 | ZnAC | 73.2 |
| **2** | 8 | 25 | 120 | 500 | KAC | 93.7 |
| **3** | 8 | 45 | 20 | 500 | ZnAC | 90.1 |
| **4** | 4 | 45 | 20 | 500 | KAC | 80.8 |
| **5** | 8 | 25 | 120 | 100 | ZnAC | 84.8 |
| **6** | 4 | 25 | 120 | 100 | KAC | 79 |
| **7** | 4 | 45 | 120 | 500 | ZnAC | 76 |
| **8** | 4 | 45 | 20 | 100 | ZnAC | 72.2 |
| **9** | 8 | 45 | 120 | 100 | KAC | 92.3 |
| **10** | 4 | 25 | 120 | 500 | KAC | 82.2 |
| **11** | 8 | 45 | 20 | 100 | ZnAC | 78.2 |
| **12** | 8 | 25 | 20 | 100 | KAC | 88.2 |

### 2.4 Batch adsorption study

To study the adsorption isotherms of the herbicide onto prepared activated carbons, the Bottle-point procedure (Ho and McKay 2003) has been applied. 0.1 g of adsorbent (KAC or ZnAC) was weighted and then placed inside glass bottles containing 50 ml of the adsorbate (glyphosate) with different concentrations (mg. $L^{-1}$). The bottles containing adsorbent, and adsorbate were held in shaken water bath for 3 hours at desired temperature. The suspension was centrifuged, if necessary, after equilibrium time and the absorbance of each sample was monitored using Du 800 spectrophotometer, Beckman Coulter (three replicates should be taken for the determination of the concentrations). The amount of herbicide adsorbed ($q_e$, mg $L^{-1}$) was calculated according to Eq. 4.

$$q_e = \frac{(C_o - C_e)V(L)}{M(g)} \quad \text{......(4)}$$

The removal percentage of herbicide (R%) was calculated using the following equation, Eq. 5:

$$R\,\% = \frac{C_o - C_t}{C_o} \times 100 \quad \text{......(5)}$$

The maximum adsorption capacity of the activated carbon can be calculated according to Eq. (6):

$$q_t = \frac{(C_o - C_t)V}{M} \quad \text{......(6)}$$

where $C_o$, $C_e$, $C_t$ are the initial, equilibrium concentration, and concentration at time intervals (mg $L^{-1}$) of herbicides, V is the solution volume (L), M is the mass of adsorbent (g).

Two models of isotherm were applied, Langmuir and Freundlich adsorption isotherms, to study the adsorption mechanism of herbicide (Khalaf, 2014) using Eqs. 7 and 8, respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad \text{......(7)}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{......(8)}$$

where $K_F$ is the Freundlich constant, n is the Freundlich exponent, $a_L$ and $K_L$ are the Langmuir isotherm constants.

In the context of adsorption studies, the kinetics of both herbicides uptake by the adsorbent is an important aspect. Two commonly employed kinetic models in adsorption research are the pseudo-first order and pseudo-second-order adsorption kinetics (Ojedokun and Bello 2017). These two models for the present study can be calculated using equations (9) and (10), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 . t}{2.303} \quad \text{......(9)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 . q_e^2} + \frac{t}{q_e} \quad \text{......(10)}$$

where qe and qt are the amounts of herbicide adsorbed (mg $g^{-1}$) at equilibrium and at time t(min), respectively, k1 the rate constant adsorption ($min^{-1}$) according to pseudo first order and k2 is the pseudo second order rate constant ($g.mg^{-1}min^{-1}$).

## 3. Results and Discussion

### 3.1 KAC and ZnAC Characterization

Data of Table 2 showed that the carbon activated with zinc salt (ZnAC) has higher surface area (622 $m^2gm^{-1}$) than that prepared from potassium salt (598 $m^2gm^{-1}$). Also, ZnAC has the highest value of $q_{max}$, bulk density, particle density and pore space (361 $mg/g^{-1}$, 0.76 $gm/cm^3$, 0.98 $gm/cm^3$ and 22) respectively. Evans *et al.,* studied the relationship between particle size and bulk density for crab-shell chitosan particles and found that the change of particle size influences bulk density, but it is not only the controlling parameter (Evans *et al.,* 2002).

**Table 2**: Textural data for the adsorbents according to adsorption of methylene blue.

| Tested Activated Carbon | $q_{max}$ ($mg.g^{-1}$) | $S_{MB}$ ($m^2.g^{-1}$) | Bulk Density $D_b$ ($g.cm^{-3}$) | Particle density, $D_P$ ($g.cm^{-3}$) | Pore Space ($P_S$) |
|---|---|---|---|---|---|
| **KAC** | 347 | 598 | 0.43 | 0.52 | 0.17 |
| **ZnAC** | 361 | 622 | 0.76 | 0.98 | 0.22 |

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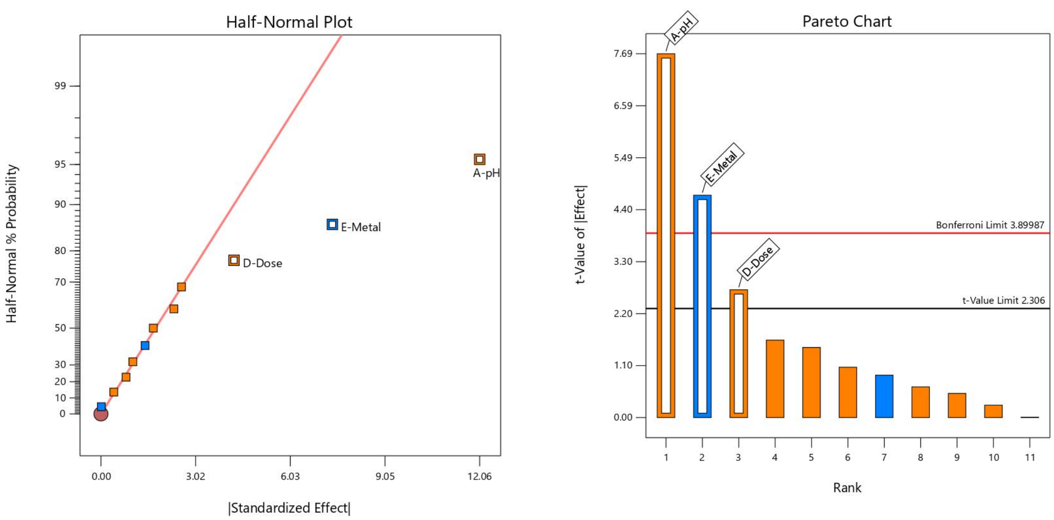
**3.2 Results of experimental design**

Table 3 expose the results of Min Run Res IV Design. The wide range of the removal (%) from 72.2 to 93.7 suggests that the glyphosate removal % varied significantly under different conditions. ANOVA was conducted to assess the suitability of the Min. Run Res IV Design, and the results are presented in Table 3. The "Prob>F" values, which were found to be less than 0.05, indicate that the model terms were statistically significant. The "Pred $R^2$ " value of 0.7974 reasonably agrees with the "Adj $R^2$" value of 0.8820, the difference is less than 0.2. The "Adeq Precision" metric, which evaluates the signal-to-noise ratio, found to be 14.37 (higher than 4) signifies a satisfactory signal level. This model can be utilized to explore the design space. The removal of the glyphosate can be given by Eq. (11).

$$R\,\% = +69.08125 + 2.34531\,pH - 0.00281\,Dose + 0.002234\,pH.Dose \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(11)$$

Figure 1 exposes the half-normal plot of standardized effects and Pareto chart, which are a commonly used graphical tool for identifying the main effects of the independent variables. The results indicate that the pH, dose of adsorbents and the type of metal activation significantly affect the removal of glyphosate.

To study the interaction of the three factors, 3D response surface plots were created based on the quadratic model. These plots show the relationship between two independent variables within their experimental ranges while keeping other variables constant. They provide insights into the main and interactional effects of these variables. The quadratic model used in this study had three factors, resulting in 3D response plots where one variable was set constant at its center level. In Figure 2, the response surface plot illustrates the relationship between pH values and the dose of adsorbents. The experiments were conducted at doses from 100 to 500mg and pH from 4 to 8. The plot reveals that the glyphosate removal % increased with high dose up to 500mg/L and at high pH up to 8. Thus, the highest removal is observed at high pH and dose.



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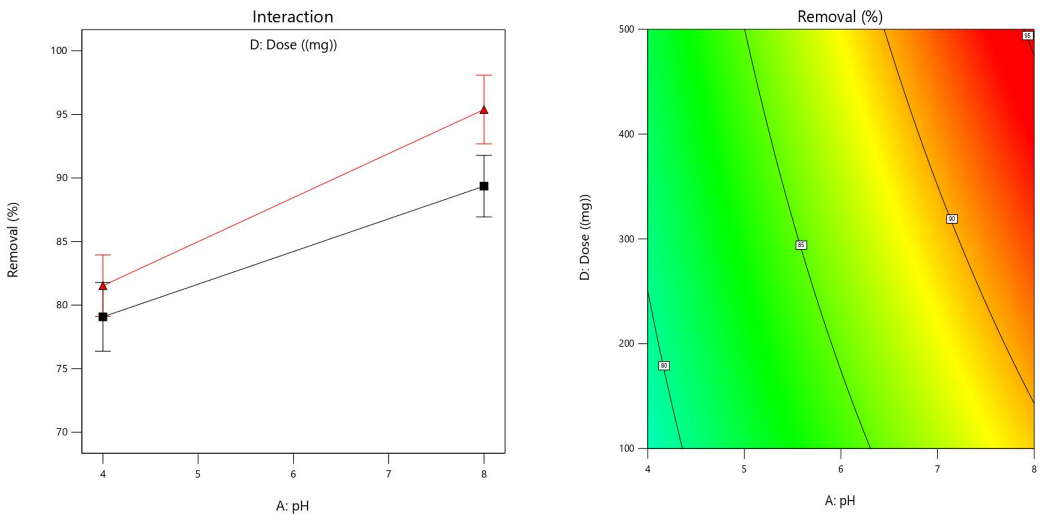
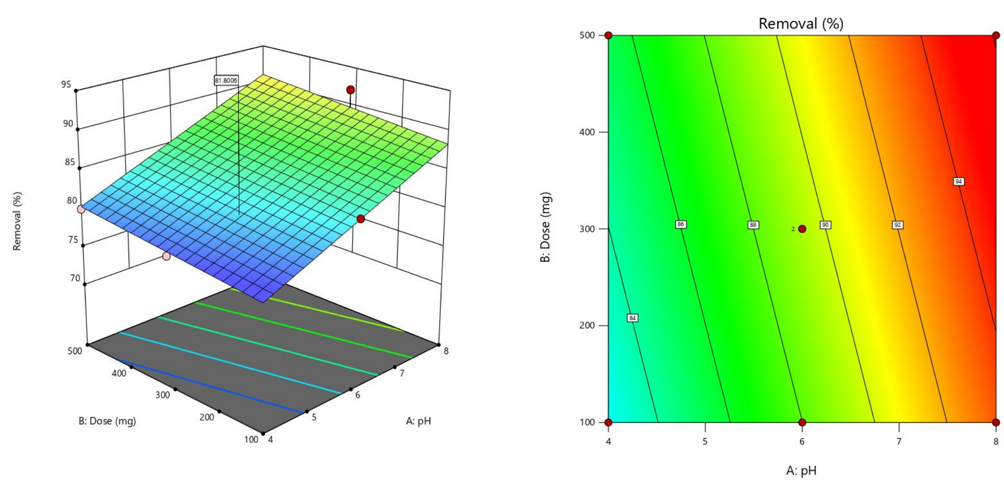



**Fig. 1**: Pareto chart, half normal plot, interaction of variables, and Contour plot of the Min Run Res IV Design.

**Table 3:** ANOVA results fitted to Min Run Res IV Design

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| **Model** | 541.58 | 4 | 135.39 | 21.56 | 0.0005 | Significant |
| **A-pH** | 388.01 | 1 | 388.01 | 61.80 | 0.0001 | |
| **D-Dose** | 47.88 | 1 | 47.88 | 7.63 | 0.0280 | |
| **E-Metal** | 144.91 | 1 | 144.91 | 23.08 | 0.0020 | |
| **AD** | 8.52 | 1 | 8.52 | 1.36 | 0.2822 | |
| **Residual** | 43.95 | 7 | 6.28 | | | |
| **Cor Total** | **585.53** | | | | **Graduate** | |

Notes: $R^2$=0.9249; $R_2$ Adj=0.8820; $R^2$ Pred=0.7974; Std. dev. 2.51 and Adeq precision=14.37




**3D surface response** **Contour plot**

**Fig. 2:** 3D surface response and Contour plot of the glyphosate removal.

### 3.3 Adsorption models

Upon plotting the experimental data points of herbicide adsorption onto activated carbons as qe (equilibrium adsorption capacity) against Ce (equilibrium concentration), characteristic L-shaped curves were obtained, as depicted in Fig. 3. The shape of these curves classifies the isotherms corresponding to the herbicide as type-L, indicating a moderate affinity of the herbicides for the active sites of the adsorbents. From Fig. 3, the experimental adsorption capacities (qref) of the adsorbents were measured. The results indicate that the adsorption capacity of glyphosate is 16.8 and 13.6 mg/g for KAC and ZnAC, respectively.

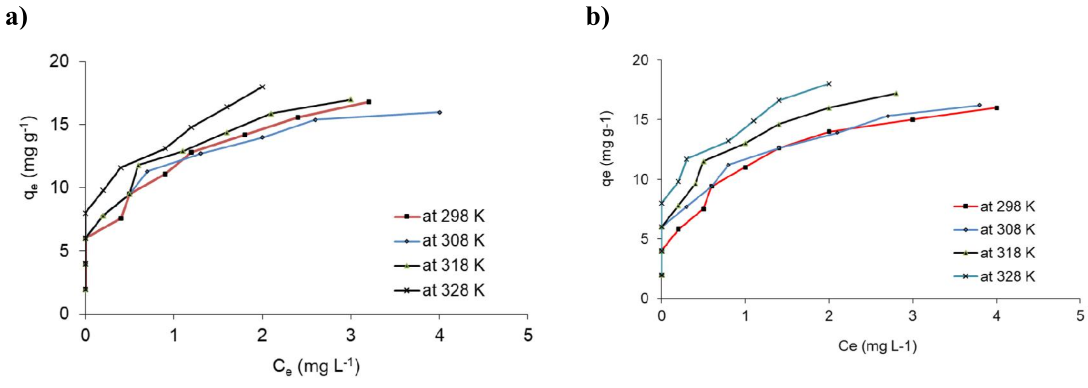



**Fig. 3:** Adsorption isotherm of glyphosate onto (a) KAC and (b) ZnAC at different temperatures.

### 3.3.1 Langmuir model

Linear plot of $C_e/q_e$ against $C_e$ of Eq. 7 (Figs. 4) for the adsorption of glyphosate herbicide onto activated carbons suggests the applicability of the Langmuir isotherm of the present system and demonstrates monolayer coverage of the adsorbate at the outer surface of the adsorbent. The values of $K_L$ and $a_L$ have been calculated using the least-squares method and are cited in Table 4. The values of the constant, $K_L/a_L$, correspond to the maximum adsorption capacity ($q_{max}$) of the herbicide. From this table and figures, it is found that the $q_{max}$ values onto different adsorbents, KAC and ZnAC are 16.8 and 16.6 mg.g$^{-1}$ for glyphosate, respectively. In addition, there is a small deviation between the calculated ($q_{max}$) and experimental ($q_{ref}$) results as it is cleared from Table 4, in which:

$$Deviation\ \% = \frac{q_{\max} - q_{ref}}{q_{\max}} \quad \text{and} \quad q_{\max} = \frac{K_L}{a_L}$$

These results of Langmuir isotherms (and the fact that the correlation coefficients, cited in Table 4, were very close to one indicating good linearity) confirm that the adsorption of glyphosate onto prepared activated carbon follow the theory of Langmuir adsorption isotherm. The essential characteristics of the Langmuir isotherm can be expressed in terms of a separation factor, $R_S$ (Rakhym *et al.,* 2020), which is defined by:

$$R_S = \frac{1}{1 + a_L.C_{ref}}$$

where $C_{ref}$ is equal to $C_o$. The values of $R_S$ have cited in Table 4. According to previous studies (El-Shamy *et al.,* 2019, Al-Ghouti and Da'ana 2020, Rakhym *et al.,* 2020) the values of $R_S$ parameter indicate the shape of the isotherm as follow:

| | |
|---|---|
| $R_S > 1$ | unfavourable isotherm |
| $R_S = 1$ | Linear isotherm |
| $0 < R_S < 1$ | Favourable isotherm |
| $R_S = 0$ | Irreversible isotherm |

The $R_S$ values were found to be 0.049 and 0.075 for the adsorption of glyphosate onto KAC and ZnAC, respectively. This means that the adsorption process of herbicide onto prepared activated carbons is very favourable isotherm ($0< R_S <1$) and the type of adsorption is physisorption (Attia *et al.,* 2008).

**Table 4:** Parameters in the Langmuir Adsorption Model

| Adsorbent | $K_L$ ($Lg^{-1}$) | $a_L$ ($Lmg^{-1}$) | $q_{max}$ ($mg.g^{-1}$) | $q_{ref}$ ($mg.g^{-1}$) | $C_{ref}$ $mg.L^{-1}$ | $R_S$ | Corr. Coef |
|---|---|---|---|---|---|---|---|
| **KAC** | 75.2 | 4.5 | 16.8 | 16.8 | 3.2 | 0.049 | 0.97 |
| **ZnAC** | 51.0 | 3.07 | 16.6 | 16 | 4 | 0.075 | 0.98 |

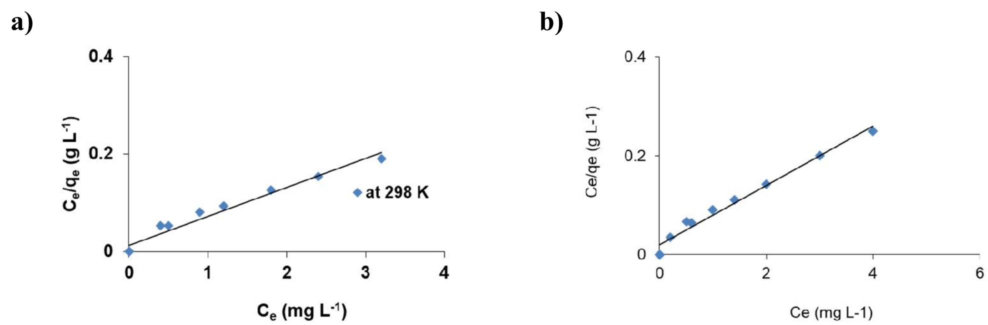



**Fig 4:** Adsorption isotherm according to Langmuir isotherm for glyphosate onto (a) KAC and (b) ZnAC.

### 3.3.2 Freundlich isotherm

The data obtained from the experimental equilibrium analysis of the adsorption of herbicides onto activated carbons (KAC and ZnAC) has been analyzed using the Freundlich isotherm considering Eq. 8. The results, exposed in Fig. 5, show that a straight-line plot of log qe against log Ce confirms the Freundlich isotherm for the adsorption. The Freundlich parameters, $K_F$ and n, have been calculated using the least-squares method and are cited in Table 5. The values of n being higher than one indicate that the adsorption of herbicides onto the activated carbons is favorable (Wang *et al.,* 2020). However, the correlation coefficients of the adsorption process of herbicides onto prepared carbons are lower than that of Langmuir, indicating that Langmuir isotherm is the best fitting model.

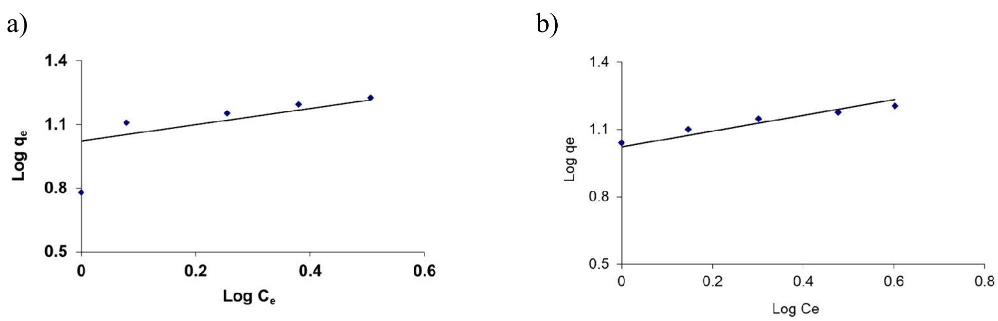



**Fig. 5**: Freundlich plot for the absorption of glyphosate onto (a) KAC and (b) ZnAC.

**Table 5:** Parameters in the Freundlich adsorption model

| Adsorbent | $K_F$ ($Lg^{-1}$) | N (-) | Corr. Coef. (-) |
|---|---|---|---|
| **KAC** | 10.51 | 2.61 | 0.59 |
| **ZnAC** | 10.5 | 2.84 | 0.97 |

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### 3.3.3 Simulation results and correlations

Using the appropriate constants from the Langmuir and Freundlich equations, theoretical isotherm curves were predicted based on known Ce values. Fig. 6 compares the experimental data points with both isotherm equations to determine the best fit. The results, along with high correlation coefficients, indicate that glyphosate herbicide absorbed onto the surface of prepared activated carbons according to both isotherms. The equilibrium adsorption data fit well with various isotherm models, including Langmuir and Freundlich. However, the data are best fitted with the Langmuir isotherm model, confirming monolayer adsorption of the herbicides onto the prepared KAC and ZnAC activated carbon (Wang *et al.,* 2021).

a) b)

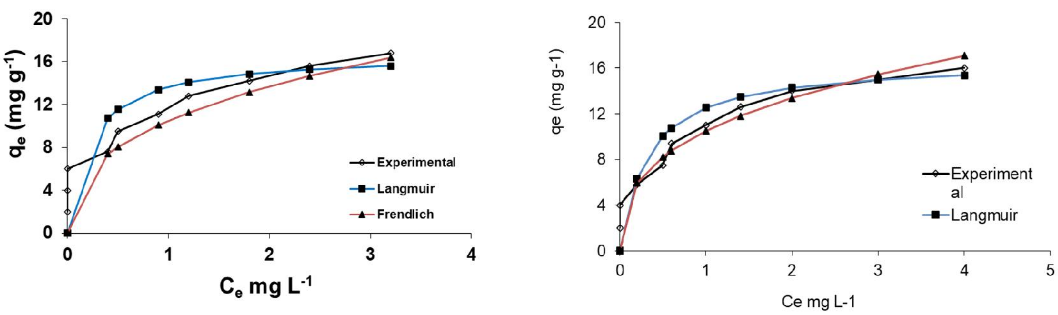


**Fig.6:** Comparison between the experimental and theoretical isotherms for onto (a) KAC and (b) ZnA

## 3.4 Kinetic Studies

Various kinetic models have been applied to study the adsorption of herbicides onto prepared activated carbons at different temperatures, 298, 308, 318 and 328 K. These models are the pseudo-first order equation and the pseudo–second order. These Kinetic models are only concerned with the effect of the observable parameters on the overall rate of sorption.

### 3.4.1 Pseudo first order

The rate constant (K1) and sorption capacity (qe) for the pseudo first-order kinetics were determined from the slope and intercept of the plots using Eq. 9. The plots of log(qe-qt) versus t at different temperatures are shown in Fig. 7, and the calculated values of qe and K1 are provided in Table 6. However, the results indicate low correlation coefficient values and significant deviations between the experimental and calculated qe values. This suggests that the adsorption of glyphosate herbicide onto KAC and ZnAC activated carbon does not follow first-order kinetics. The pseudo-first order rate constants ($K_1$) were determined from the slopes of the plots and are listed in Table 6.

**Table 6:** Kinetic parameters for pseudo $1^{st}$ order for glyphosate adsorption

| | **KAC** | | | | **ZnAC** | | | |
|---|---|---|---|---|---|---|---|---|
| **Temperature/K** | **298** | **308** | **318** | **323** | **298** | **308** | **318** | **323** |
| **$K_1$ ($mn^{-1}$)** | 0.0115 | 0.0223 | 0.0449 | 0.0386 | 0.0115 | 0.0297 | 0.0382 | 0.0453 |
| **$R^2$** | 0.80 | 0.86 | 0.83 | 0.87 | 0.85 | 0.80 | 0.89 | 0.91 |

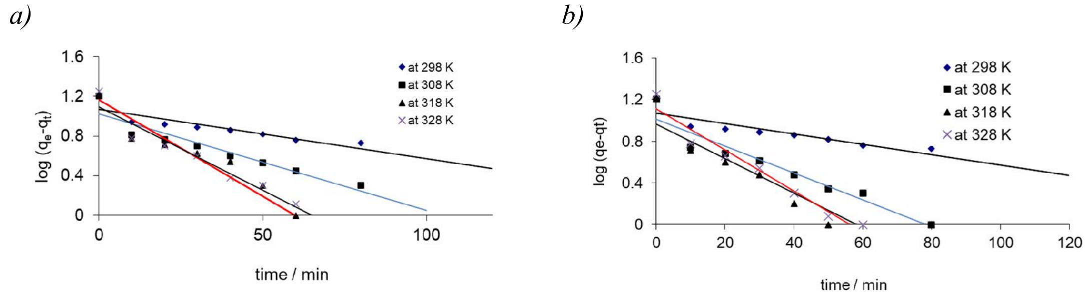


**Fig. 7:** Pseudo 1st order rate constants at different temperatures for glyphosate onto (a) KAC and (b) ZnAC.

**3.4.2 Pseudo second order**

In case of pseudo second order based on the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 . q_e^2} + \frac{t}{q_e}$$

The adsorption process follows second-order kinetics, as evidenced by the linear relationship observed in the plot of t/qt versus t. Both the sorption capacity (qe) and rate constant ($K_2$) can be determined from the slope and intercept of this plot. This approach is more reliable in predicting the adsorption behavior across the entire range. Fig. 8 and Table 7 present the linear plots, calculated rate constants, and sorption capacities for the adsorption of glyphosate onto the synthetic activated carbons. These plots demonstrate excellent linearity with correlation coefficients ($r^2$) close to 1, surpassing the performance of first-order kinetics. Additionally, the calculated values of qe closely match the experimental values. These findings suggest that the adsorption of herbicide onto activated carbons follows the pseudo second-order model, indicating that chemisorption, where chemical bonds are formed between the herbicide contaminants and the adsorbent surface, may be the rate-limiting step and these results suggest that in addition to adsorption onto surface sites, the adsorption process involves mass transfer and intraparticle diffusion (Konicki *et al.,* 2017).

**Table 7:** Kinetic parameters for pseudo 2nd order for glyphosate adsorption

| Adsorbent | Temperature K | $K_2$ g.mg$^{-1}$min$^{-1}$ | $R^2$ | $q_e$ mg g$^{-1}$ | U (mg g$^{-1}$min$^{-1}$) | $t_{1/2}$ (min) |
|---|---|---|---|---|---|---|
| **KAC** | 298 | $9.88\times10^{-3}$ | 0.995 | 12.62 | 1.57 | 8.10 |
| | 308 | $8.0\times10\text{-}^{3}$ | 0.996 | 15.4 | 1.89 | 8.12 |
| | 318 | $6.1\times10\text{-}^{3}$ | 0.9904 | 18.5 | 2.09 | 8.86 |
| | 328 | $6.9\times10^{-3}$ | 0.996 | 19.4 | 2.60 | 7.47 |
| **ZnAC** | 298 | $8.04\times10^{-3}$ | 0.996 | 15.4 | 1.90 | 8.1 |
| | 308 | $5.0\times10^{-3}$ | 0.99 | 17.9 | 1.60 | 11.2 |
| | 318 | $6.7\times10^{-3}$ | 0.996 | 19.4 | 2.52 | 7.7 |
| | 328 | $7.5\times10^{-3}$ | 0.997 | 19.8 | 2.94 | 6.7 |

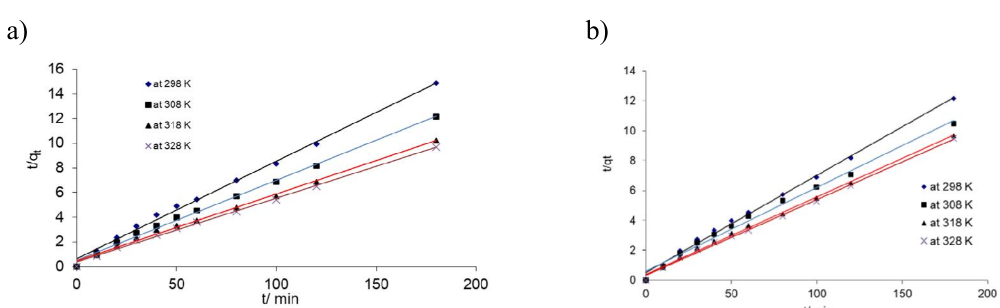


**Fig. 8:** Pseudo 2nd order rate constants at different temperatures for glyphosate onto (a) KAC and (b) ZnAC.

## 4. Conclusion

Rice husk is used as a source of activated carbon and activated by wo meals KCl and ZnCl2. The Min Run Res IV design investigated five variables including pH, temperature, time, dose of adsorbents, and type of metals. Furthermore, the three significant factors were further examined using 3D surface plots, and the optimal conditions were determined to be pH 5.8, dose 265 mg, and the KAC more effective than ZnAC. The equilibrium adsorption data fits well with various isotherm models, including Langmuir and Freundlich and the best fit is observed with the Langmuir isotherm model, indicating monolayer adsorption of the herbicides on the prepared KAC and ZnAC activated carbon. In addition, the obtained results of kinetic studies suggested that the adsorption of herbicide onto activated carbons conforms to the pseudo second-order model.

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