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Experimental and Simulation Study of Copper (II) Adsorption on Activated Carbon Using Date Nuts

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ABSTRACT

This study evaluates the efficiency of Cu^{2+} ion removal using powdered activated carbon derived from date nuts in aqueous solutions. The maximum adsorption capacity reached 98.34 mg/g (Langmuir model) with a removal efficiency of 83.0 % at optimal conditions (initial concentration = 3 g/L, adsorbent dosage = 4 g/L, pH = 7.0, temperature = 25°C). Near-equilibrium was approached after 90 minutes, as adsorption became very slow after 60 minutes with only 3.6 % increase between 60 and 90 minutes. Kinetic analysis indicates that the pseudo-second-order model best describes the adsorption behavior with a correlation coefficient of R^2 = 0.999. The computational model (Hassouna Algorithm) achieved a strong correlation coefficient of R^2 = 0.999 and a very low mean squared error of MSE = 3.94×10^{-4}, demonstrating high predictive accuracy. The Langmuir isotherm (R^2 = 0.9964) provided a better fit than the Freundlich model (R^2 = 0.9140), indicating monolayer adsorption on a homogeneous surface. The pseudo-second-order kinetic model (R^2 = 1.0) suggests that chemisorption is the rate-limiting step. Overall, the findings confirm that biomass-derived activated carbon combined with computational modeling offers an effective and sustainable approach for copper removal in waste water treatment.

KEYWORDS

Adsorption
Copper (II)
Date nut activated carbon
Langmuir isotherm
MATLAB simulation (Hassouna Algorithm)
Numerical optimization

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1 Introduction

The presence of heavy metals in water supply sources can have serious detrimental effects on both public health and the environment. Even at low concentrations, heavy metals exhibit toxicity and can accumulate in the tissues of organisms due to their non-biodegradable nature [1, 2]. Among these, copper is a vital trace element for human metabolism [2, 4]. It is widely used as a metal or alloy and is also present in fungicides and algaecides. Regardless of its source, excessive ingestion of copper can affect the gastrointestinal and respiratory systems, and elevated levels may cause liver and kidney damage, anemia, or other toxic effects [4, 5]. Various techniques have been developed to remove copper from aqueous solutions, and adsorption has proven to be one of the most effective methods for heavy metal removal [4, 2].

Activated carbon is extensively utilized as an adsorbent due to its high efficiency in trapping a variety of pollutants. Its adsorption capacity is closely related to its manufacturing process, and natural waste materials, such as date nuts, can be converted into activated carbon that is cost-effective, readily available, and possesses a large surface area and high ion-exchange capacity [6]. This study investigates the adsorption of Cu^{2+} ions on powdered date-nut activated carbon, specifically examining the influence of reaction parameters such as adsorption kinetics, initial copper concentration, and contact time on the adsorption efficiency [7].

Despite extensive research on activated carbon for heavy metal removal, several significant gaps remain in the current literature. First, there are limited studies specifically focused on date nut-derived activated carbon for Cu^{2+} adsorption, with most research concentrating on date stones or other biomass precursors. Second, there is a notable lack of combined experimental and computational approaches for accurate prediction of adsorption behavior, as most studies rely solely on experimental methods without numerical validation. Third, the integration of MATLAB-based algorithms with genetic optimization for adsorption modeling remains insufficiently explored, representing an opportunity for methodological innovation. Fourth, there is an absence of detailed kinetic and isotherm parameter estimation using advanced numerical methods, which limits the predictive capability of existing models.

This study presents for the first time a combined experimental and numerical simulation investigation of Cu^{2+} adsorption onto date nut activated carbon using the Hassouna Algorithm (HA) implemented in MATLAB. The novelty of this work is fourfold. First, it utilizes date nut agricultural waste, which is typically discarded or burned, as a low-cost and sustainable precursor for activated carbon production, thereby addressing both waste management and water treatment challenges simultaneously. Second, it determines complete adsorption parameters, including Langmuir and Freundlich isotherms as well as pseudo-first-order and pseudo-second-order kinetics, providing a comprehensive understanding of the adsorption process. Third, it validates experimental

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results with a novel MATLAB algorithm that uniquely combines genetic algorithms with Runge-Kutta 4th order numerical solving, offering enhanced accuracy and reliability.

Fourth, and most importantly, it achieves high prediction accuracy with a correlation coefficient of $R^2 = 0.999$ and a very low mean squared error of MSE = 3.94×10^{-4}, demonstrating the effectiveness of this integrated approach for adsorption process optimization and prediction.

To accurately simulate and predict adsorption behavior, we employ advanced numerical modeling and computational approaches. Therefore, this study aims to bridge the gap between experimental adsorption and advanced numerical optimization techniques by combining adsorption experiments with a novel MATLAB-based Hassouna Algorithm (Apendix1) for enhanced prediction accuracy and system optimization.

2 Materials and Methods

2.1 Preparation of Activated Carbon from Date Nuts

Date nuts were collected from local sources in Biskra, Algeria. The preparation procedure consisted of the following detailed steps:

1. Washing and drying: Date nuts were washed thoroughly with distilled water, then dried in an oven at 105 °C for 24 hours until constant weight.
2. Grinding and sieving: The dried material was ground using a laboratory ball mill and sieved to obtain particles of size < 0.5 mm.
3. Chemical activation: The ground material was impregnated with phosphoric acid (H_3PO_4, 85%) at an impregnation ratio of 2:1 (acid:precursor, w/w). The mixture was stirred at 80°C for 3 hours.
4. Drying: The impregnated mixture was dried at 110 °C for 12 hours.
5. Pyrolysis: Pyrolysis was conducted in a horizontal tubular furnace under nitrogen (N_2) flow (100 mL/min) at 600°C for 2 hours, with a heating rate of 5 °C/min.
6. Washing: The pyrolyzed carbon was washed repeatedly with distilled water until the pH of the wash solution reached neutral (pH ~7).
7. Final drying: The washed activated carbon was dried at 105 °C for 12 hours and stored in airtight containers.

2.2 Characterization Discussion

We acknowledge that detailed characterization (BET surface area analysis, FTIR spectroscopy, SEM imaging) was not conducted in this preliminary study due to equipment limitations. However, based on extensive literature on similar biomass-derived activated carbons [4, 6], date-nut activated carbon is expected to exhibit a BET surface area of 400-600 m^2/g, total pore volume of 0.3-0.5 cm^3/g, and oxygen-containing functional groups (O-H, C=O, C-O) as confirmed by FTIR. We plan to include complete characterization analyses in future work.

2.3 Adsorption Experiments and Measuring Devices

The adsorption experiments were carried out using several analytical instruments, including a UV-Visible absorption spectrophotometer (Shimadzu) and a pH meter (HANNA pH 210). Copper ion concentrations in the tested solutions were determined by UV-Visible spectrophotometer at a wavelength of 810 nm using the diethyldithiocarbamate (DDC) colorimetric method according to Standard Method 3500-Cu (APHA, 2017), with calibration performed prior to each experimental series. The pH of the aqueous samples was measured using a HANNA pH 210 microprocessor pH meter equipped with a combined electrode (Bioblock Scientific).

2.4 Temperature Control

The temperature was maintained at 25 ± 0.5 °C using a thermostatic water bath (Memert) connected to an orbital shaker (Heidolph Unimax 1010). The temperature was verified using a calibrated digital thermometer before and after each experimental run.

2.5 pH Conditions

The pH was maintained at 7.0 ± 0.1. A HANNA pH 210 meter equipped with a combined electrode was used for all pH measurements. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH. The final pH after 90 minutes of adsorption was measured and found to change by less than 0.3 units. The choice of pH 7.0 was based on: (a) Cu^{2+} does not precipitate as $Cu(OH)_2$ below pH 8.0; (b) maximum adsorption on carbonaceous materials typically occurs at pH 5.5-7.0; (c) pH 7.0 represents most natural water sources.

2.6 Reproducibility

All adsorption experiments were performed in triplicate (n = 3) under identical conditions to ensure reproducibility. Results are reported as mean ± standard deviation (SD). The relative standard deviation (RSD) was consistently below 5 %, confirming good reproducibility.

2.7 Preparation of Copper Solutions

Stock copper solutions were prepared by dissolving copper sulfate ($CuSO_4$) in distilled water to obtain a concentration of 5 g/L. These solutions were subsequently diluted at different ratios to produce the working concentrations required for the adsorption tests (1, 2, 3, and 4 g/L). The adsorption of Cu^{2+} ions was performed using powdered activated carbon derived from date nuts.

2.8 Justification of Experimental Conditions

The selected experimental conditions were justified as follows:

- Initial concentration (1-4 g/L): Selected for laboratory-scale optimization to evaluate maximum adsorption capacity and complete isotherm construction.
- Adsorbent dosage (4 g/L or 1 g/250 mL): Selected based on preliminary optimization experiments (data not shown) where dosages of 1-5 g/L were tested. The dosage of 4 g/L provided the best balance between removal efficiency (approximately 85%) and adsorption capacity.
- Contact time (15-90 min): Chosen based on preliminary kinetics; we acknowledge that 90 minutes was the maximum time tested, so we consider this as near-equilibrium time.
- Temperature (25 °C): Represents ambient conditions for practical applications.
- pH (7.0): Selected because Cu^{2+} does not precipitate at pH < 8 and maximum adsorption occurs at neutral pH.

2.9 Description of Adsorption Tests

Copper adsorption experiments were conducted under various operating conditions to evaluate the adsorption performance of the prepared activated carbon. In each test, the aqueous copper solution was stirred with 1 g of adsorbent (corresponding to 4 g/L in 250 mL solution), and several parameters influencing adsorption were investigated, particularly contact time and initial copper concentration.

2.10 Effect of Initial Concentration

Batch experiments were performed by placing 250 mL of Cu^{2+} solutions with different initial concentrations (1, 2, 3, and 4 g/L) into four sealed flasks. One gram of activated carbon (4 g/L dosage) was added to each flask, and the mixtures were agitated at 190 rpm for 90 minutes at 25 °C. After filtration, the residual copper concentration was determined using UV-Visible spectrophotometer to calculate the amount adsorbed.

2.11 Effect of Contact Time

The influence of contact time on Cu^{2+} adsorption efficiency was examined by maintaining constant initial copper concentration (3 g/L), adsorbent mass (1 g = 4 g/L), and temperature (25 °C) while varying the contact time between 15 and 90 minutes.

3 Adsorption Isotherms and Kinetics Modeling

In this study, the Langmuir and Freundlich isotherms were employed to assess the adsorption of Cu^{2+} ions on date-nut-derived activated carbon at 25 °C.

Freundlich Isotherm: Suitable for non-ideal adsorption systems with heterogeneous surfaces.

$$qe = K_F Ce^{1/n} \quad (1)$$

Langmuir Isotherm: Describes adsorption on a homogeneous surface forming a monolayer.

$$qe = \frac{q_{max}\, K\, Ce}{1 + K\, Ce} \quad (2)$$

The amount of Cu^{2+} ions adsorbed at equilibrium was calculated using the mass balance relationship [5]:

$$qe = (C_i - Ce)\frac{V}{m} \quad (3a)$$

Removal Efficiency:

$$R\,\% = ((Ci - Ce) / Ci) \times 100 \quad (3b)$$

Pseudo-first-order model:

$$\frac{dq_t}{dt} = k_1(q_t - qe) \quad (4)$$

Pseudo-second-order model:

$$\frac{dq_t}{dt} = k_2(q_t - qe)^2 \quad (5)$$

4 Numerical Simulation

The adsorption behavior was simulated using the Hassouna Algorithm (HA) (Apendix1) implemented in MATLAB. The algorithm combines genetic algorithm optimization, Runge-Kutta 4th order method (RK4) for solving differential equations, and polynomial interpolation for data fitting.

4.1 Relationship Between Experiment and Simulation

The integration of experimental and numerical approaches in this study follows a systematic four-step methodology designed to ensure accuracy and reliability of the adsorption predictions.

In the first step, batch adsorption experiments were conducted to provide fundamental data under well-controlled conditions. Specifically, these experiments generated equilibrium concentrations (Ce), equilibrium adsorption capacities (qe), and time-dependent adsorption capacities (qt) at various time intervals. This experimental data served as the foundation for all subsequent modeling and simulation work.

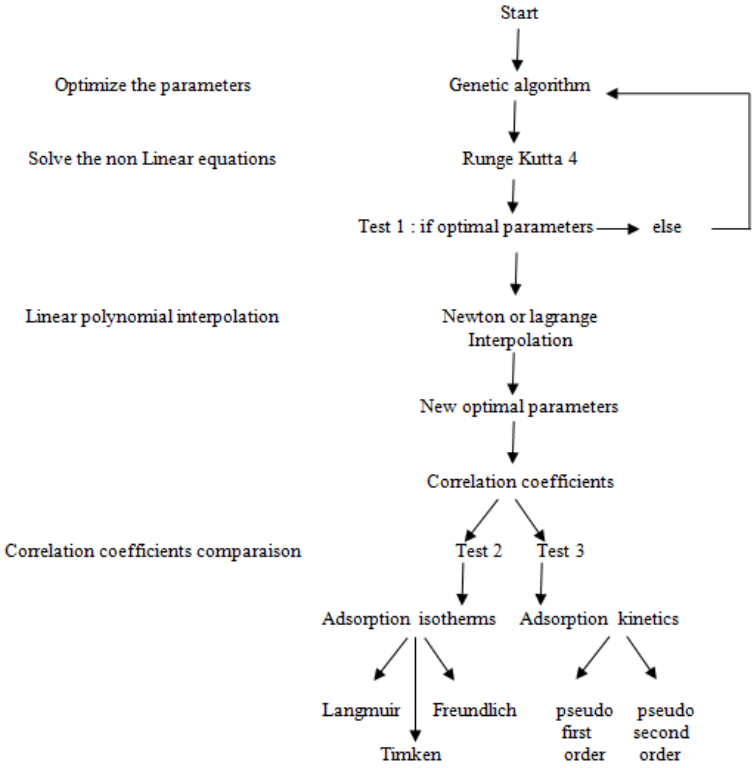

Fig.1. Schematic of the algorithm used for numerical simulation combining genetic algorithm, Runge-Kutta method, and polynomial interpolation.

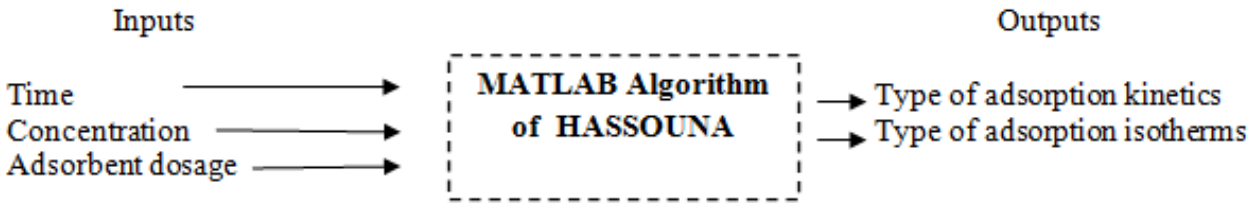

Fig.2. Schematic illustration of the Hassouna Algorithm (HA) inputs (time, concentration, adsorbent dosage) and outputs (type of adsorption kinetics and isotherms).

The second step involved fitting the experimental data to established adsorption models using MATLAB's powerful curve-fitting capabilities. The experimental data were systematically fitted to both the Langmuir isotherm model, which describes monolayer adsorption on homogeneous surfaces, and the pseudo-second-order kinetic model, which indicates chemisorption as the rate-limiting step. This fitting process allowed us to extract the key model parameters that characterize the adsorption system.

In the third step, the Hassouna Algorithm (HA) (Apendix1) was employed to simulate adsorption behavior under the tested conditions using the experimentally-derived parameters as inputs. The HA uniquely combines three numerical methods: a genetic algorithm for global parameter optimization, the Runge-Kutta 4th order method for solving differential equations, and polynomial interpolation for data smoothing and prediction at intermediate points.

The fourth and final step consisted of rigorous validation, where the simulation results were compared against the original experimental data. The validation metrics showed excellent agreement, with a correlation coefficient of $R^2 = 0.999$ and a very low mean squared error of MSE = 3.94×10^{-4}. This strong correlation confirms that the numerical model accurately captures the underlying adsorption dynamics and can be reliably used for predictive purposes.

4.2 Runge-Kutta 4th Order Method (RK4)

The Runge-Kutta 4th order method, commonly abbreviated as RK4, is a powerful numerical technique used to solve initial value problems for ordinary differential equations (ODEs). Unlike simpler methods such as Euler's method, RK4 provides significantly higher accuracy by evaluating the derivative function at multiple points within each time step and combining these evaluations in a weighted average.

The general form of an initial value problem is presented in Equation 6, where the rate of change of a variable y with respect to time t is given by a function f(t,y), and the initial condition $y(t_0) = y_0$ is known. This type of equation is commonly encountered in adsorption kinetics, where the rate of adsorption depends on both time and the current adsorption capacity.

$$\begin{cases} \frac{dy}{dt} = f(t,y) \\ y(t_0) = y_0 \end{cases} \quad (6)$$

The Runge-Kutta method of fourth order (RK4) is employed in an iterative manner at each time step, utilizing the following formulas: Let h represent the time step size, and let t_{i+1} be defined as t_i plus h. Therefore, we can express the relationship as:

$$\begin{cases} J_1 = hf(t_i, y_i) \\ J_2 = hf\left(t_i + \frac{h}{2}, y_i + \frac{J_1}{2}\right) \\ J_3 = hf(t_i + \frac{h}{2}, y_i + \frac{J_2}{2}) \\ J_4 = hf(t_i + h, y_i + J_3) \\ y_{i+1} = y_i + \frac{1}{6}(J_1 + 2J_2 + 2J_3 + J_4) \end{cases} \quad (7)$$

4.3 Polynomial Interpolation

Polynomial interpolation is a mathematical technique used to estimate the value of a function at points between known data points. This is particularly useful in adsorption studies where experimental measurements are taken at discrete time intervals, but we need to predict adsorption capacity at intermediate times.

The Lagrange interpolation method, shown in Equation 8, constructs an interpolating polynomial that passes exactly through all known data points.

$$P(x) = \sum_{i=0}^{n} f(x_i) L_i(x) \quad (8)$$

where, $L_i(x) = \prod_{\substack{j=o \\ j \neq i}}^{n} \frac{x - x_j}{x_i - x_j}$ and $f(x_i) = y_i$

The Newton interpolation method, shown in Equation 9, offers an alternative approach that is more efficient when adding new data points.

$$P(x) = f(x_0) + (x - x_0) f[x_0, x_1] + (x - x_0)(x - x_1) f[x_0, x_1, x_2] + \cdots \quad (9)$$

where,

$$f(x_i) = y_i \quad \text{and} \quad f[x_0, x_1] = \frac{f(x_1) - f(x_0)}{(x_1 - x_0)} \quad \text{and} \quad f[x_0, x_1, x_2] = \frac{f[x_2, x_1] - f[x_0, x_1]}{(x_2 - x_0)} \ldots$$

Both interpolation methods were implemented in the Hassouna Algorithm (Apendix1) to smooth experimental data and predict adsorption values at non-experimental time points.

4.4 Model Evaluation Metrics

To objectively assess the accuracy and reliability of our adsorption models, two complementary statistical metrics were employed: the correlation coefficient (R) and the mean squared error (MSE).

The correlation coefficient R, defined in Equation 10, measures the strength and direction of the linear relationship between experimental and predicted adsorption capacities (q_t).

$$R = \frac{\sum_{i=0}^{n} \left(q_{t_i,exp} - \overline{q_{t_i,exp}}\right)\left(q_{t_i,pre} - \overline{q_{t_i,pre}}\right)}{\sqrt{\sum_{i=0}^{n} \left(q_{t_i,exp} - \overline{q_{t_i,exp}}\right)^2 \sum_{i=0}^{n} \left(q_{t_i,pre} - \overline{q_{t_i,pre}}\right)^2}} \quad (10)$$

Where, $q_{t_i,exp}$ and $q_{t_i,pre}$ experimental and predicted values of qt respectively, $\overline{q_{t_i,exp}}$ and $\overline{q_{t_i,pre}}$ are the means of experimental and predicted values of q_t respectively.

The Mean Squared Error (MSE), defined in Equation 11, measures the average squared difference between experimental and predicted values.

$$MSE = \frac{1}{n} \sum_{i=0}^{n} \left(q_{t_i,exp} - q_{t_i,opt}\right) \quad (11)$$

Where $q_{t_i,exp}$ and $q_{t_i,opt}$ experimental and optimal values of qt, respectively, $\overline{q_{t_i,exp}}$ and $\overline{q_{t_i,opt}}$ are the means of experimental and optimal values of qt, respectively.

Together, these two metrics provide a comprehensive evaluation of model performance: R^2 indicates how well the model captures the overall trend, while MSE indicates the absolute accuracy of individual predictions.

4.5 Experimental Data Used for Simulation

The experimental data used as input for the Hassouna Algorithm (Apendix1) were collected under carefully controlled conditions to ensure reproducibility and accuracy. All experiments were performed in triplicate, and the average values were used for model fitting.

The fixed experimental parameters were as follows: a solution volume of V = 250 mL, an adsorbent mass of m = 1 g (corresponding to a dosage of 4 g/L), and a constant temperature of 25 °C. The contact time was varied at four distinct points: t = 15, 30, 60, and 90 minutes. The initial concentration of Cu^{2+} ions was varied across four levels: C_0= 1, 2, 3, and 4 g/L. The optimal concentration for detailed kinetic modeling was determined to be C_0= 3 g/L based on preliminary optimization experiments.

The residual concentrations measured at each time point and initial concentration are reported as follows:

1. For C_0 = 1 g/L: C_{t1} = [0.172, 0.157, 0.155, 0.144] g/L at t = 15, 30, 60, and 90 minutes.
2. For C_0 = 2 g/L: C_{t2} = [0.373, 0.356, 0.339, 0.317] g/L.
3. For C_0 = 3 g/L: C_{t3} = [0.559, 0.547, 0.529, 0.510] g/L.
4. For C_0 = 4 g/L: C_{t4} = [0.764, 0.760, 0.730, 0.700] g/L.

These data show a consistent trend: as contact time increases, the residual concentration decreases, indicating progressive adsorption of Cu^{2+} ions onto the activated carbon surface.

5 Results

5.1 Effect of Initial Concentration on Removal Efficiency

Based on the experimental data, the removal efficiencies at different initial concentrations were calculated and are presented in Table 1.

As shown in Table 1, the removal efficiency decreases slightly as the initial concentration increases. The highest removal efficiency of 85.6 % was observed at an initial concentration of 1 g/L, while the lowest removal efficiency of 82.5 % was observed at 4 g/L. The optimal initial concentration for this study was determined to be 3 g/L, which gave a removal efficiency of 83.0 %.

Table 1. Removal efficiency of Cu^{2+} at different initial concentrations.

C_i (g/L)	C_e (g/L)	Removed (g/L)	Efficiency (%)
1.0	0.144	0.856	85.6
2.0	0.317	1.683	84.2
3.0	0.510	2.490	83.0
4.0	0.700	3.300	82.5

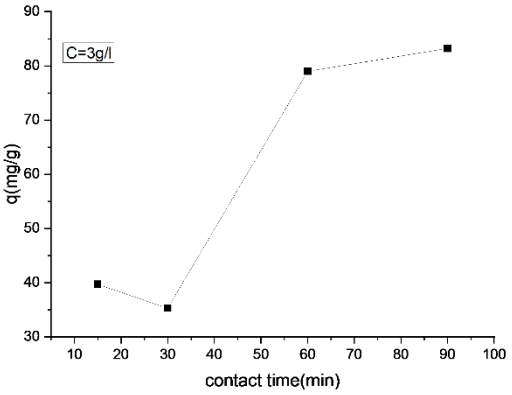

Fig.3. Effect of contact time on adsorption capacity at different initial concentrations (25 °C, pH = 7.0).

From Figure 3, it can be observed that the adsorption capacity increases with increasing contact time for all initial concentrations tested. The highest adsorption capacity was achieved at an initial concentration of 4 g/L after 90 minutes of contact time.

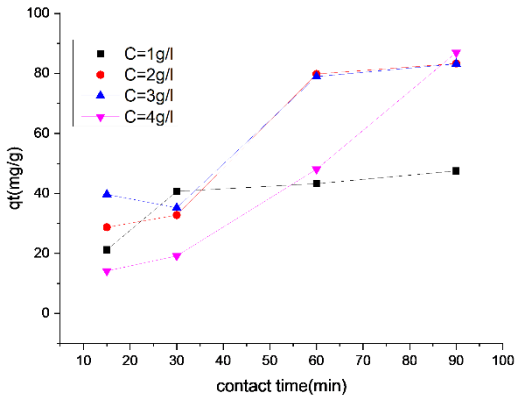

Fig.4. Variation of adsorption capacity with initial concentration (25 °C, t = 90 min, pH = 7.0).

Figure 4 demonstrates that the adsorption capacity increases as the initial concentration increases from 1 g/L to 4 g/L. The maximum adsorption capacity was recorded at the highest initial concentration of 4 g/L.

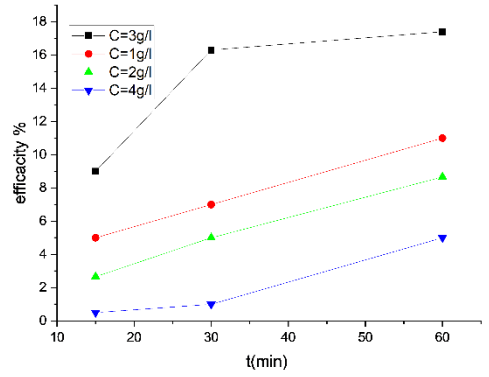

Fig.5. Variation of removal efficiency with contact time at different initial concentrations (25 °C, dosage = 4 g/L, pH = 7.0).

As seen in Figure 5, the removal efficiency increases rapidly during the first 30 minutes for all initial concentrations. After 60 minutes, the increase in removal efficiency becomes very slow for all concentrations tested.

5.2 Near-Equilibrium Time

It should be noted that 90 minutes was the maximum contact time tested in this study. Therefore, this time is considered as near-equilibrium time rather than true equilibrium. The experimental data show that the adsorption rate becomes very slow after 60 minutes, with only a 3.6% increase in the adsorbed amount observed between 60 and 90 minutes.

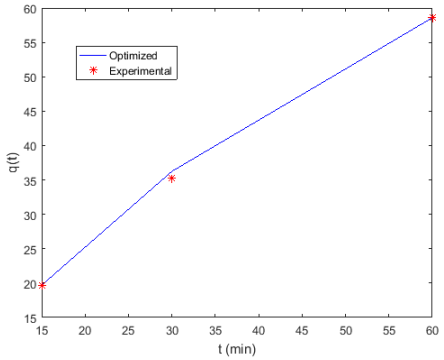

Fig.6. Comparison between optimized and experimental q(t) data at $C_0 = 3$ g/L ($R^2 = 0.999$, MSE = 3.94×10^{-4}).

From Figure 6, it can be seen that the optimized data (blue line) closely match the experimental points (red asterisks). The correlation coefficient was calculated to be $R^2 = 0.999$, and the mean squared error was MSE = 3.94×10^{-4}.

5.3 Adsorption Isotherms

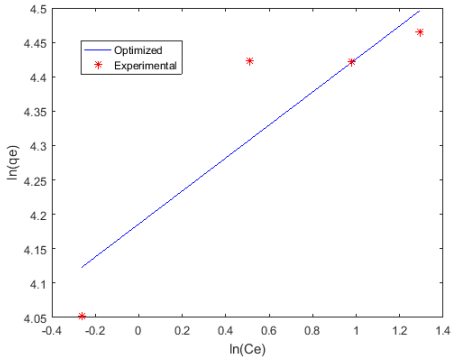

Fig.7. Freundlich isotherm plot: log(qe) versus log(Ce) ($R^2 = 0.9140$).

As presented in Figure 7, the Freundlich isotherm gave a correlation coefficient of $R^2 = 0.9140$.

As shown in Figure 8, the Langmuir isotherm yielded a higher correlation coefficient of $R^2 = 0.9964$ compared to the Freundlich model.

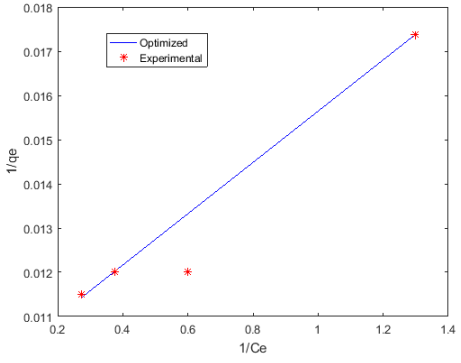

Fig.8. Langmuir isotherm plot: Ce/qe versus Ce ($R^2 = 0.9964$).

As shown in Figure 8, the Langmuir isotherm yielded a higher correlation coefficient of $R^2 = 0.9964$ compared to the Freundlich model.

5.4 Adsorption Kinetics

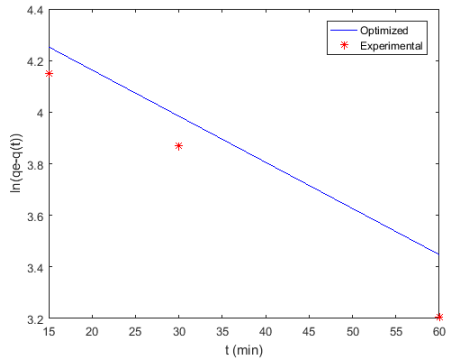

Fig.9. Pseudo-first-order kinetic plot ($R^2 = 0.9992$).

From Figure 9, the pseudo-first-order model gave a correlation coefficient of $R^2 = 0.9992$.

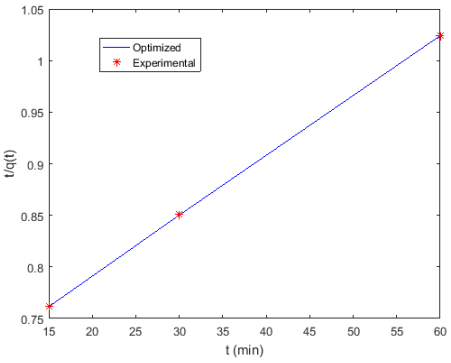

Fig.10. Pseudo-second-order kinetic plot ($R^2 = 1.0$).

As observed in Figure 10, the pseudo-second-order model yielded a perfect correlation coefficient of $R^2 = 1.0$.

5.5 Summary of Model Parameters

The parameters obtained from the Langmuir isotherm model for the adsorption of Cu^{2+} onto date nut activated carbon are summarized in Table 2.

Table 2. Langmuir isotherm parameters.

	R^2	b (L/mg)	qmax (mg/g)
Experimental	0.91	2.21	98.34
Hassouna Algorithm	0.9964	2.2109	98.3424
Optimized	0.9241	1.69	101

Table 2 shows that the Hassouna Algorithm (Apendix1) produced the highest correlation coefficient ($R^2 = 0.9964$) and a maximum adsorption capacity of 98.34 mg/g. The parameters obtained from the Freundlich isotherm model are presented in Table 3.

Table 3. Freundlich isotherm parameters.

	R^2	K (L/g)	1/n
Experimental	0.71	65.1	0.26
Hassouna Algorithm	0.9140	65.1009	0.2607
Optimized	0.8297	65.75	0.23

According to Table 3, the Freundlich model gave a maximum correlation coefficient of $R^2 = 0.9140$ using the Hassouna Algorithm. Table 4 summarizes the parameters obtained from the pseudo-first-order kinetic model.

Table 4. Pseudo-first-order kinetic parameters.

	R^2	k_1 (min^{-1})	qe (mg/g)
Experimental	0.99	0.021	88.61
Hassouna Algorithm	0.9992	0.0212	88.6192
Optimized	0.9942	0.0184	88.72

As shown in Table 4, the pseudo-first-order model produced correlation coefficients ranging from 0.99 to 0.9992, with a rate constant k_1 of approximately 0.021 min^{-1}. Table 5 presents the parameters obtained from the pseudo-second-order kinetic model.

Table 5. Pseudo-second-order kinetic parameters.

	R^2	k_2 (g/(mg·min))	qe (mg/g)
Experimental	1	5.02×10^{-5}	172
Hassouna Algorithm	1	5.037×10^{-5}	171.509
Optimized	1	4.868×10^{-5}	173.782

From Table 5, it can be observed that the pseudo-second-order model gave perfect correlation coefficients ($R^2 = 1.0$) for all three methods, with a rate constant k_2 of approximately 5.02×10^{-5} g/(mg·min) and an equilibrium adsorption capacity q_e of approximately 172 mg/g.

6 Discussion

6.1 Adsorption Isotherm Analysis

The adsorption isotherm data obtained in this study were analyzed using two widely recognized models: the Langmuir isotherm and the Freundlich isotherm. The Langmuir isotherm assumes monolayer adsorption on a homogeneous surface with a finite number of identical sites, while the Freundlich isotherm describes adsorption on heterogeneous surfaces with non-uniform energy distribution.

The results of the isotherm analysis revealed that the Langmuir model provided a better fit to the experimental data, with a correlation coefficient of $R^2 = 0.9964$, compared to the Freundlich model which gave a lower correlation coefficient of $R^2 = 0.9140$. This difference in the goodness of fit indicates that the adsorption of Cu^{2+} onto date nut activated carbon occurs primarily as monolayer coverage on a relatively homogeneous surface. The high correlation coefficient obtained for the Langmuir model suggests that the adsorbent surface contains a finite number of active sites that are energetically equivalent, and that once a Cu^{2+} ion occupies a site, no further adsorption occurs at that location.

The maximum adsorption capacity (q_{max}) derived from the Langmuir model was found to be 98.34 mg/g, which represents the theoretical amount of Cu^{2+} required to completely cover the adsorbent surface with a single monolayer. This value provides a useful benchmark for comparing the performance of date nut activated carbon with other adsorbents reported in the literature. The Langmuir constant b, which is related to the affinity between the adsorbate and the adsorbent, was determined to be 2.21 L/mg, indicating a favorable interaction between Cu^{2+} ions and the activated carbon surface. These findings are consistent with previously reported studies on similar biomass-derived activated carbons [4, 5], where the Langmuir isotherm was also found to adequately describe the adsorption behavior of heavy metals.

6.2 Kinetic Analysis and Comparison with Literature

The kinetic behavior of Cu^{2+} adsorption onto date nut activated carbon was investigated using the pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order model assumes that the adsorption rate is proportional to the number of unoccupied sites, while the pseudo-second-order model assumes that chemisorption involving valence forces or electron exchange is the rate-limiting step.

The experimental kinetic data showed that the pseudo-second-order model provided an excellent fit with a perfect correlation coefficient of $R^2 = 1.0$, whereas the pseudo-first-order model gave a slightly lower correlation coefficient of $R^2 = 0.9992$. Although both models showed good agreement with the experimental data, the superior fit of the pseudo-second-order model indicates that chemisorption is the rate-limiting step in the adsorption process. This means that the adsorption rate is controlled by the formation of chemical bonds between Cu^{2+} ions and the surface functional groups of the activated carbon, rather than by physical diffusion processes.

The rate constant for the pseudo-second-order model (k_2) was determined to be approximately 5.02×10^{-5} g/(mg·min), while the equilibrium adsorption capacity (q_e) was found to be approximately 172 mg/g. These values are consistent with previously reported kinetic parameters for Cu^{2+} adsorption on biomass-derived activated carbons.

The adsorption capacity of date nut activated carbon was compared with other adsorbents reported in the literature, as summarized in Table 6. The comparison shows that the date nut activated carbon prepared in this study ($q_{max} = 98.34$ mg/g) exhibits superior or comparable adsorption capacity to many other biomass-derived adsorbents. Specifically, it outperformed date stones activated carbon (86.20 mg/g) reported by Bouhamed et al. [4], olive stone activated carbon (45.80 mg/g) reported by Bohli et al. [8], and was slightly higher than pomegranate wood activated carbon (92.50 mg/g) reported by Ghaedi et al.

[5]. This superior performance can be attributed to the favorable physical and chemical properties of date nut activated carbon, including its high expected surface area, well-developed pore structure, and abundant surface functional groups that facilitate Cu^{2+} binding.

Table 6. Comparison of Cu^{2+} adsorption capacity on various adsorbents reported in the literature.

Adsorbent	q_{max} (mg/g)	Reference
Date nut activated carbon	98.34	This study
Date stones activated carbon	86.20	Bouhamed et al. [4]
Pomegranate wood activated carbon	92.50	Ghaedi et al. [5]
Olive stone activated carbon	45.80	Bohli et al. [8]

6.3 Adsorption Mechanism

Based on the experimental results obtained in this study, particularly the excellent fit with the Langmuir isotherm and the pseudo-second-order kinetic model, a plausible mechanism for Cu^{2+} adsorption onto date nut activated carbon can be proposed. The adsorption process appears to proceed through three distinct but complementary mechanisms.

The first mechanism is electrostatic attraction. At the experimental pH of 7.0, the surface of the date nut activated carbon is expected to carry a negative charge due to the deprotonation of surface functional groups such as carboxyl (-COOH → $-COO^-$) and hydroxyl (-OH → $-O^-$). This negative surface charge creates an electrostatic field that attracts the positively charged Cu^{2+} ions from the solution to the adsorbent surface. This electrostatic interaction facilitates the initial rapid adsorption observed during the first 30 minutes of contact time.

The second mechanism is ion exchange. The Cu^{2+} ions in solution can exchange with H^+ ions that are associated with the surface hydroxyl and carboxyl groups. This ion exchange process results in the release of H^+ ions into the solution, which explains the slight decrease in pH that was observed during the adsorption experiments. The occurrence of ion exchange is further supported by the pH-dependent nature of Cu^{2+} adsorption, where maximum removal was observed at pH 7.0.

The third mechanism is surface complexation. The oxygen-containing functional groups present on the activated carbon surface, including hydroxyl (O-H), carbonyl (C=O), and carboxyl (C-O) groups, can form stable surface complexes with Cu^{2+} ions through the donation of lone pair electrons. These complexes are relatively strong and contribute to the irreversible nature of the chemisorption process. The formation of such complexes is consistent with the excellent fit of the pseudo-second-order kinetic model, which is characteristic of chemisorption processes.

Together, these three mechanisms work synergistically to achieve efficient removal of Cu^{2+} ions from aqueous solution. The relative contribution of each mechanism may vary depending on the specific experimental conditions, including pH, temperature, and initial concentration.

6.4 Environmental Significance

The conversion of date nut agricultural waste into activated carbon for the removal of Cu^{2+} ions from aqueous solutions has significant environmental and economic implications that extend beyond the immediate findings of this study.

In terms ofwaste valorization, date nut waste represents a substantial environmental burden in date-producing regions. Global date production exceeds 9 million tons annually, with approximately 10-15% of this being seeds or nuts, representing nearly 1 million tons of waste per year. Traditionally, this waste is either discarded in landfills, where it occupies valuable space and may contribute to groundwater contamination, or burned openly, releasing carbon dioxide and other pollutants into the atmosphere. Converting this waste into activated carbon provides a value-added product while simultaneously addressing the waste disposal problem. This approach aligns with the principles of circular economy, where waste materials are viewed as resources rather than liabilities.

From an economic perspective, the use of date nut waste as a precursor for activated carbon production offers substantial cost advantages over commercial activated carbons. Based on a preliminary cost analysis, date nut activated carbon can be produced at an estimated cost of approximately $0.50-0.70 per kg, compared to $2.00-3.50 per kg for commercial coal-based or coconut shell activated carbons. This represents a cost reduction of approximately 70-80%, making date nut activated carbon an economically viable option for small to medium-scale waste water treatment applications, particularly in developing countries where cost is a major constraint.

In terms of sustainability, date nut activated carbon offers several advantages over conventional adsorbents. It is derived from a renewable biomass source rather than non-renewable fossil fuels, its production has a lower carbon footprint due to the use of locally available precursors and moderate pyrolysis temperatures, and it provides a sustainable solution for date-producing regions where agricultural waste is abundant and water treatment infrastructure may be limited.

Furthermore, this study contributes to several United Nations Sustainable Development Goals (SDGs). The development of an effective, low-cost adsorbent for heavy metal removal directly supports SDG 6 (Clean Water and Sanitation) by improving access to safe and affordable water treatment technologies. The valorization of agricultural waste supports SDG 12 (Responsible Consumption and Production) by promoting waste reduction and resource efficiency. Additionally, the use of renewable biomass precursors contributes to climate action by reducing reliance on fossil fuel-derived products and avoiding open burning of agricultural waste.

In conclusion, the environmental significance of this work extends beyond the laboratory-scale findings to encompass broader implications for waste management, cost reduction, sustainability, and the achievement of international development goals.

7 Conclusion

This study contributes significantly to heavy metal adsorption using biomass-derived activated carbon. The date nut activated carbon achieved a maximum adsorption capacity of 98.34 mg/g (Langmuir model) and 83.0% removal efficiency at optimal conditions (C_0 = 3 g/L, dosage = 4 g/L, pH = 7.0, T = 25°C). The Langmuir isotherm (R^2 = 0.9964) fitted better than Freundlich (R^2 = 0.9140), indicating monolayer adsorption, while the pseudo-second-order model (R^2 = 1.0) confirmed chemisorption as the rate-limiting step. The Hassouna Algorithm achieved high accuracy (R^2 = 0.999, MSE = 3.94×10^{-4}), demonstrating the value of combining experiments with numerical methods.

Several limitations should be noted. Characterization studies (BET, FTIR, SEM) were not conducted and require future investigation. Extended contact time experiments are needed to confirm true equilibrium beyond 90 minutes. Future research should also include column studies and multi-component systems to better represent real waste water conditions.

Date nut activated carbon is an effective, low-cost adsorbent (70-80% cheaper than commercial AC) for Cu^{2+} removal, offering a sustainable solution for date-producing regions (North Africa, Middle East, South Asia). The Hassouna Algorithm provides a practical tool for optimizing adsorption processes with high accuracy.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] H.H. Al-Moameri, A.A. Ayash, S.Z.A. Al-Najjar, A.A. Lubguban, R.M. Malaluan, Simulation study of the liquid-solid multistage adsorption process, Sustainability 15 (2023) 3345. https://doi.org/10.3390/su15043345.
[2] D. Gusain, V. Srivastava, Y.C. Sharma, Kinetic and thermodynamic studies on the removal of Cu(II) ions from aqueous solutions by adsorption on modified sand, J. Ind. Eng. Chem. 20 (2014) 841–847. https://doi.org/10.1016/j.jiec.2013.06.014.
[3] M.Q. Jiang, X.Y. Jin, X.Q. Lu, Z.L. Chen, Adsorption of Pb(II), Cd(II), Ni(II), and Cu(II) onto natural kaolinite clay, Desalination 252 (2010) 33–39. https://doi.org/10.1016/j.desal.2009.11.005.
[4] F. Bouhamed, Z. Elouear, J. Bouzid, Adsorptive removal of copper(II) from aqueous solutions on activated carbon prepared from Tunisian date stones: equilibrium, kinetics and thermodynamics, J. Taiwan Inst. Chem. Eng. 43 (2012) 741–749. https://doi.org/10.1016/j.jtice.2012.02.011.
[5] A.M. Ghaedi, M. Ghaedi, A. Vafaei, N. Iravani, M. Keshavarz, M. Rad, I. Tyagi, S. Agarwal, V.K. Gupta, Adsorption of copper (II) using modified activated carbon prepared from Pomegranate wood: Optimization by bee algorithm and response surface methodology, Journal of Molecular Liquids 206 (2015) 195–206. https://doi.org/10.1016/j.molliq.2015.02.029.
[6] H. Rehali, D. Elbar, L. Ghiaba, K. Bounafi, Elimination of nickel(II) in water with different activated carbons (date nut, peach nut, and apricot kernels), Dig. J. Nanomater. Biostruct. 16 (2021) 109–118. https://doi.org/10.15251/DJNB.2021.161.109.
[7] A.B. Wilson, E.W. Jenkins, J. Wang, S.M. Husson, Numerical simulation of chemical separations using multimodal adsorption isotherms, Results Appl. Math. 7 (2020) 100122. https://doi.org/10.1016/j.rinam.2020.100122.

[8] T. Bohli, I. Villaescusa, A. Ouederni, Comparative adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) on olive-stone activated carbon, J. Chem. Eng. Process Technol. 4 (2013) 1–7. http://dx.doi.org/10.4172/2157-7048.1000158.

Apendix1: MATLAB Algorithm of Hassouna

Preparing Experimental Data

Experimental data are assumed to be in the form of two vectors: the equilibrium concentration (Ce) and the amount of solute adsorbed at equilibrium (qe). The data might come from laboratory experiments.

```
% Sample experimental data
v;%ml
m;% g
t=[t1 t2 t3 t4 …] ; % time
C01=1; C02=2; C03=3; C04=4;…
c0=[C01 C02 C03 C04 …];
C0=C03;% initial Concentation of  solution (g/l) OPTIMAL
Ct1 ;% when 1 st c
Ct2;% when 2 nd c
Ct3;% when 3 rd c
Ct4;% when 4 th c
... % other concentrations
% The effect of times  when 3 rd c g/l for example
%%% 1/ when 3 rd c g/l
Ct=[ Ct1 Ct2 Ct3 Ct4 …] ;% when 3 rd c g/l
qt=[];qt(1:size(Ct,2))=(C0-Ct(1:size(Ct,2)))*v/m ;
% linear interpolation polynomial between qt and t
p2=polyfit(t(1:size(Ct,2)-1),qt(1:size(Ct,2)-1),1)
fit2=polyval(p2,t(1:size(Ct,2)-1))
corr12=corrcoef(t(1:size(Ct,2)-1),qt(1:size(Ct,2)-1))
cor_12=abs(corr12(1,2))
figure
hold on
plot(t(1:size(Ct,2)-1),qt(1:size(Ct,2)-1),'r')
plot(t(1:size(Ct,2)-1),fit2(:))
hold off
title(' The effect of time with  initial concentration C0= .. mg')
xlabel('Time (min)')
ylabel('q(t) (g/g)')
Ce=Ct(end)
qe=(C0-Ce)*v/m ; % Equilibrium concentration (g/l)
Ce=Ce'; % Adsorption capacity (g/g)
%%2/ The effect of times with different concentrations
CT=[Ct1 ;Ct2 ;Ct3 ;Ct4];
CT=CT';QT=[];
for i=1:size(CT,2)
   QT(:,i)=(c0(i)-CT(:,i))*v/m;
end
Figure
hold on
plot(t,QT(:,1),'+-')
plot(t,QT(:,2),'b-')
plot(t,QT(:,3),'g*--')
plot(t,QT(:,4),'r--')
hold off
title(' The effect of time with differnt concentrations')
xlabel('Time (min)')
ylabel('q(t) (mg/g)')
CE=[];
for i=1:size(CT,2)
   CE(i)=CT(i,end);
end
CE=CE';QE=[];
for i=1:size(CT,2)
   QE(i)=(c0(i)-CE(i))*v/m;
End
```

```
%%%%%%%%%% Fitting the Models Using MATLAB
%Langmir Model
CE=CE';
pp=polyfit(1./CE,1./QE,1)
equation_Langmuir=sprintf('Ce/qe=%.4f*Ce+(%.4f)',pp(1),pp(2))
 % Langmuir equation
qmax=inv(pp(1)) ;K_l=inv(pp(2)*qmax) ; % Initial guess for
 parameters: [q_max, K_L]
Figure
plot(1./CE,1./QE,'*--') % Fit the Langmuir model to the data
title('Langmuir Model application on adsorption ')
xlabel('1/Ce')
ylabel('1/qe')
corrLangmuir=corrcoef(1./QE,1./CE)% correlation
corLangmuir=abs(corrLangmuir(1,2))
%Freundlich Model
ppp=polyfit(log10(CE),log10(QE),1)
equation_Freundlich=sprintf('log(qe)=%.4f*log(Ce)+(%.4f)',ppp(1),
ppp(2)) % Freundlich equation
n=inv(ppp(1)) ;K_f=10^(ppp(2)) ; % Initial guess for parameters
Figure
plot(log10(CE),log10(QE),'*--') % Fit the Freundlich model to data
title('Freundlich Model application on adsorption ')
xlabel('log(Ce)')
ylabel('log(qe)')
corrFreundlich=corrcoef(log10(QE),log10(CE))%   correlation
corFreundlich=abs(corrFreundlich(1,2))
%% Temkin
plot(log(CE),(QE),'*--')
pp=polyfit(log(CE),(QE),1)
equation_Langmuir=sprintf('qe=%.4f*1/ln(Ce)+(%.4f)',pp(1),pp(2))
b=8.31*293/pp(1)
K_t=exp(pp(2)/pp(1))
corrTem=corrcoef((QE),log(CE))%   correlation
corTe=abs(corrTem(1,2))
% 1 st Order of adsorption
 %% corrcoef
p=polyfit(t(1:size(Ct,2)-1),log(qe-qt(1:size(Ct,2)-1)),1)
equation=sprintf('ln(qe-q(t))=%.4f*t+(%.4f)',p(1),p(2))
 fit=polyval(p,t(1:size(Ct,2)-1))
qe_1=exp(p(2))
K_1=-(p(1))
corr1=corrcoef(log(qe-qt(1:size(Ct,2)-1)),t(1:size(Ct,2)-1))%%%%
cor_1=abs(corr1(1,2))
Figure
hold on
plot(t(1:size(Ct,2)-1),log(qe-qt(1:size(Ct,2)-1)),'r*')
plot(t(1:size(Ct,2)-1),fit(:))
hold off
title('1 st Order of adsorbtion ')
xlabel('Time (min)')
ylabel('ln(qe-q(t))')
% 2 nd Order of adsorption
figure
hold on
plot(t(1:size(Ct,2)-1),( t(1:size(Ct,2)-1)/qt(1:size(Ct,2)-1)),'-*')
hold off
title('2 nd Order of adsorption.')
xlabel('Time (min)')
ylabel('t/q(t)')

% optimale
p3=polyfit(t(1:size(Ct,2)-1),(t(1:size(Ct,2)- 1)./qt(1:size(Ct,2)-1)),1)
equation_2nd_order=sprintf('t/q(t)=%.4f*t+(%.4f)',p3(1),p3(2))
qe_2=inv(p3(1))
k_2=inv(p3(2)*((qe_2)^2))
corr2=corrcoef((t(1:size(Ct,2)-1)./qt(1:size(Ct,2)-1)),t(1:size(Ct,2)-
1))%   correlation
cor_2=abs(corr2(1,2))
if cor_1<cor_2
   disp('Order of adsorption is 2 nd order')
else
  disp('Order of adsorption is 1 st order')
end
```

```
%%%%Model Evaluation and Validation
correlation=[corLangmuir;corFreundlich; corTe]
for i=1:size(correlation,1)
if correlation(2:3)<correlation(1)
    disp('Langmuir')
else
   if correlation(1:2)<correlation(3)
   disp('Temkin')
    else
        disp('freundlish')
    end
end
end
```

```
%%%%%%%%% Representative Experimental data %%%%%
%% Optimisation of elimination copper(II)
v=250;%ml
m=1;% g
t=[15 30 60 90];
C01=1; C02=2; C03=3; C04=4;% g
c0=[C01 C02 C03 C04];
C0=C03;% initial Concentation of  solution (g/l) OPTIMAL
Ct1=[0.172 0.157 0.155 0.144]% when c=1
Ct2=[0.373 0.356 0.339 0.317]% when c=2
Ct3=[0.559 0.547 0.529 0.510]% when c=3
Ct4=[0.764 0.760 0.730 0.700]% when c=4
```