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EQUILIBRIUM AND KINETIC MODELING OF THE ADSORPTION OF NAPHTHALENE AND BENZENE ONTO CALCINED MODIFIED CLAY

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ABSTRACT: *This research examines the adsorption behavior of naphthalene and benzene onto thermally modified clay using equilibrium and kinetic modeling techniques. Kinetic approaches encompassing Pseudo-First Order, Pseudo-Second Order, Elovich, Intra-Particle Diffusion, and Power Function models were applied to both unmodified and modified clay. Among these, the Elovich model exhibited the highest correlation coefficient (R^2), indicating its superior ability to describe the adsorption process. For benzene adsorption, the Elovich model yielded an R^2 value of 0.9844 for unmodified clay and 0.9666 for modified clay, while for naphthalene adsorption, the Elovich model provided an R^2 of 0.9770 for unmodified clay and 0.9547 for modified clay. The equilibrium adsorption characteristics of both pollutants were evaluated, revealing that benzene achieved equilibrium in 26 hours, with concentration reductions from 5.2 mg/L on untreated clay to 2 mg/L on modified clay. Naphthalene reached equilibrium within 22 hours, experiencing significant concentration drops. The findings underscore the enhanced adsorption efficiency of calcined modified clay compared to its unmodified counterpart, positioning it as a viable material for wastewater treatment, pollution mitigation, and separation of organic contaminants.*

KEYWORDS: Adsorption Kinetics, Modified Clay, Unmodified Clay, Naphthalene Adsorption, Benzene Adsorption, Elovich Kinetic.

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INTRODUCTION

Environmental contamination caused by industrial activities poses serious risk to human health and the ecosystem (Naidu et al., 2021; Onuiri et al., 2024; Saravanakumar et al., 2022). Industrial sectors, including petrochemical plants, oil refineries, and chemical production units, significantly contribute to this challenge (Rovira et al., 2021; Tavella et al., 2025). They release hazardous chemicals as industrial waste, leading to severe contamination of water bodies and the atmosphere (S. Das et al., 2023; Wang et al., 2024). These pollutants, known for their carcinogenic and toxic properties, necessitate urgent intervention for effective remediation (L. C. Das & Mahmud, 2023; Lin et al., 2022; Shetty et al., 2023). Therefore, urgent attention to the effective treatment of our water bodies, soil, and food is needed (Chijioke et al., 2024; Lu et al., 2015; Mahmud & Islam, 2024).

Human-induced organic chemicals present in soil and groundwater are becoming a growing environmental issue (Onuiri et al., 2024), posing harm to both humans and animals (Münzel et al., 2023; Salim et al., 2024). The various types of soil are mainly as factor of their ability to hold water within a period of time (Alves et al., 2024; Eze et al., 2025; Kuok et al., 2023). Clay minerals are gaining recognition as effective materials for environmental remediation due to their widespread availability, affordability, and strong adsorption capabilities. However, unmodified clay typically has a lower efficiency in capturing organic pollutants (Yang et al., 2024). This constraint has prompted extensive research aimed at improving clay's adsorption efficiency through chemical treatments and thermal alterations (Ciğeroğlu et al., 2024; Hamidi et al., 2024). Calcined modified clay has shown potential for improved adsorption performance, but still lacked comprehensive studies focusing on its efficacy for specific organic pollutants like benzene and naphthalene (Gil et al., 2021; Uddin, 2017).

The adsorption technique is extensively utilized for eliminating organic compounds from water and wastewater due to its high effectiveness. While activated carbon remains the most commonly employed adsorbent, its usage is constrained by factors such as flammability and challenges in regenerating adsorbed high-boiling-point organic substances, and several more (Asheghmoalla & Mehrvar, 2024; Fouda-Mbanga et al., 2024). The adsorption capacity of clays is largely influenced by their pore structure and chemical composition. Since natural clay exhibits limited efficiency in capturing organic pollutants, its adsorption performance can be significantly enhanced through modifications to its inherent properties. (Ewis et al., 2022; Khan et al., 2023; N. Owabor et al., 2012). Applying kinetic models will provide valuable insights into the adsorption behavior of naphthalene and benzene when utilizing modified clay as an adsorbent (Abbas & Trari, 2015; Osman et al., 2023).

This study explores the potential of cost-effective, readily available natural materials, specifically clay minerals, for improved adsorption. Their effectiveness as adsorbents stems from their extensive surface area, strong structural and durability resilience, and diverse structural characteristics (Khan et al., 2023; Xie et al., 2024). Furthermore, it seeks to bridge this gap by examining the adsorption kinetics and equilibrium characteristics of benzene and naphthalene on thermally treated modified clay. Utilizing kinetic models like Pseudo-First Order, Pseudo-Second Order, Elovich, Intra-Particle Diffusion, and Power Function, the study offers an all-inclusive analysis of the adsorption techniques involved.

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METHODOLOGY

Materials

i. **Unprocessed Materials:** Natural clay (locally sources), Citric acid, Distilled water, Ethanol, naphthalene and benzene.

ii. **Apparatus:** Beaker, Stirrer, weighing balance, measuring cylinder, UV Spectrophotometer, stopwatch, oven, furnace.

Methods

This study utilized a systematic approach to investigate the adsorption of naphthalene and benzene onto calcined modified clay using the model in Figure 1:

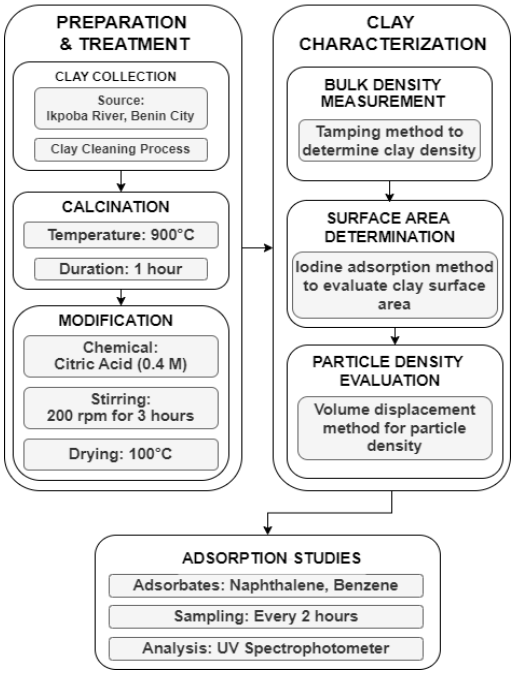

Figure 1: Adsorption of Naphthalene and Benzene Architecture

Preparation And Calcination of Clay Sample

Natural clay was sourced from the Ikpoba River, Benin City, Nigeria. The cleaning process followed by removing debris and large particles through sieving with a 220µm mesh. The clay was calcined at 900°C for one hour and left to cool naturally to room temperature, leading to calcined clay ready for modification.

Clay Modification Using Citric Acid

The calcined clay was modified using a 0.4 M citric acid solution. This was mixed using a magnetic bar spoon for 1800 minutes at 200 rpm. The sample was centrifuged at 1500 rpm for 15 minutes. The sample was cleaned with distilled water and tested with a pH meter until it was neutral. Furthermore, the sample was dried at 100°C. Aqueous solution was made for each of naphthalene and benzene by dissolving 200mg each of naphthalene and benzene in 100mls

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of ethanol before an addition of 100mls of distilled water. Lastly, the solution was carefully stirred for homogeneity of the final solution.

Density Determination

Bulk density was measured using the tamping method. A 100-gram sample of clay was added to a 100 mL graduated cylinder, followed by careful vibration of the cylinder until all particle spaces were eliminated, while the clay level remained constant. At this point, the final volume was noted.

The surface area was measured using the iodine adsorption method. This involved estimating the determination of the aqueous solution's concentration by titrating a blank sample with a standard thiosulfate solution, then comparing those titration values to those of the iodine-containing sample (Wuana et al., 2016).

A 20g sample of oven-dried clay was placed in a measuring cylinder. After lightly tapping, the soil's volume was noted as V_1. Then, 50ml of water was carefully poured into the cylinder containing the clay, and the new volume was recorded as V_2.

The particle density was determined using this relationship (Tan et al., 2010, Sharma et al., 2005):

$$Particle\ Density = \frac{weight\ of\ soil\ (20g)}{Volume\ of\ soil\ taken\ (V_2 - V_1)}$$

$$= \frac{w}{V_2 - V_1} \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Adsorption Studies

i. **Preparation of Adsorbate Solutions:** Solutions of naphthalene and benzene were formulated by dissolving 200 mg of each substance in ethanol, then adding distilled water to achieve uniformity. These solutions served as the adsorbates for the study.

ii. **Adsorption Procedure:** Modified and unmodified clay samples were mixed separately with the naphthalene and benzene solutions. The mixtures were stirred slowly to maintain consistent interaction between the adsorbent and adsorbate. Samples were taken at 2-hour intervals, and the concentration of the adsorbates was measured using a UV spectrophotometer until equilibrium was attained.

Analytical Measurements

i. **Bulk Density**: Measured using the tamping method, where 100-gram of clay was added to a graduated cylinder, and vibrations were applied until no further volume changes were observed.

ii. **Surface Area**: Determined using the iodine adsorption method, comparing titrated values of iodine-containing samples against a blank.

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iii. **Particle Density**: Calculated using the volume displacement method with oven-dried clay samples.

This methodology ensures reproducibility and provides reliable data for assessing the adsorption properties of calcined modified clay.

RESULTS AND FINDINGS

Results Overview

Finding from the experiment demonstrate that calcined modified clay significantly enhances the adsorption capacity for benzene and naphthalene compared to unmodified clay that will be analyzed in this section.

Equilibrium Time Determination

The experimental results indicate that calcined modified clay exhibits significantly higher adsorption efficiency for both benzene and naphthalene compared to unmodified clay. The equilibrium time for benzene adsorption was 26 hours, with final concentrations reducing to 2 mg/L for modified clay and 5.2 mg/L for unmodified clay. For naphthalene, equilibrium was reached at 22 hours, with concentrations decreasing to 1.7 mg/L and 4.8 mg/L for modified and unmodified clay, respectively. Details are seen in Table 1.

Table 1. Equilibrium Time Determination Data for Unmodified Clay and Modified Clay Adsorption of Benzene and Naphthalene

Time (hr)	Unmodified Clay (mg/l) (Benzene)	Modified Clay (mg/l) (Benzene)	Unmodified Clay (mg/l) (Naphthalene)	Modified Clay (mg/l) (Naphthalene)
0	72.2	72.2	68.5	68.5
2	72.2	61.1	68.5	57
4	55.6	43.3	57.2	36.1
6	39.1	24.5	43.1	22.5
8	30.8	21	30.6	15.5
10	24.4	17.7	21.7	10.2
12	20.7	14.3	16.5	6.5
14	16.3	11.7	10.2	3.9
16	10.2	6.6	6.8	2.6
18	6.6	6	5.3	2
20	5.5	3.6	4.9	1.9
22	5.1	2.4	4.8	1.7
24	5.5	2.1	4.8	1.7
26	5.2	2	4.8	1.7
28	5.2	2	4.8	1.7
30	5.2	2	4.8	1.7
32	5.2	2	4.8	1.7
34	5.2	2	4.8	1.7

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36	5.2	2	4.8	1.7
38	5.2	2	4.8	1.7
40	5.2	2	4.8	1.7
42	5.2	2	4.8	1.7
44	5.2	2	4.8	1.7

Amount of n-hexane adsorbed (mg/l) on Unmodified Clay at equilibrium q_t was determined as:

$$q_t = [\, C_0 - \, C_t] x \frac{V}{M} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where:
C_0 = initial concentration (80.2 mg/l)
C_t = concentration at time t (mg/l)
V = Volume of the solution (11 litres)
M = Mass of adsorbent (100 g)

Example:
At = 28 hrs (Time when equilibrium was reached)
C_t = 8.4 mg/l

Hence

$$q_t = \, (80.2 \, - \, 8.4) \times \frac{1}{100} \, = 0.718 mg/g$$

The same step was used to calculate the q_t at various times and for the different organic adsorbates used in this work.

q_e is the q_t value when equilibrium has been achieved. This is also used to carry out calculations for the various organic adsorbates.

Based on the results from the experiment, detailed concentration time curve was obtained.

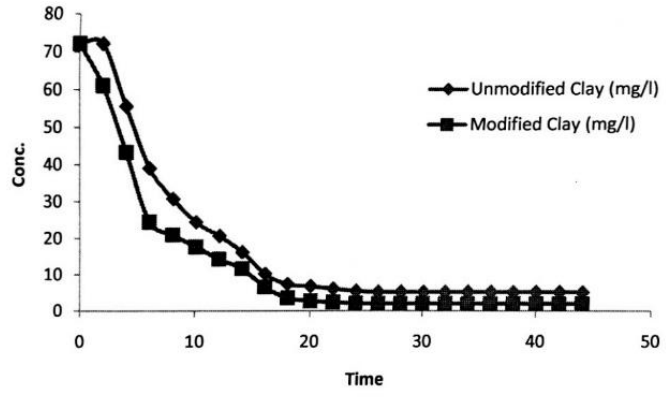

Figure 2 - Equilibrium Time for Adsorption of Benzene on unmodified and calcined Modified Clay.

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Figure 2 tracks the changes in Benzene concentration in the solution with time when it was mixed with Unmodified and modified clay. It was observed that after 26 hours, the concentration of Benzene in the solution generally reached equilibrium on both the modified and unmodified clay.

At equilibrium (where a consistent concentration was maintained over time), the benzene concentration decreased to 5.2 mg/l with unmodified clay, but dropped further to 2 mg/l with modified clay. This indicates that calcined modified clay demonstrates better adsorption efficiency for benzene. This is likely due to its extensive surface area, high porosity, and effective binding sites that enhance interactions with adsorbates, along with its hydraulic conductivity, which aids in the movement and retention of solutes.

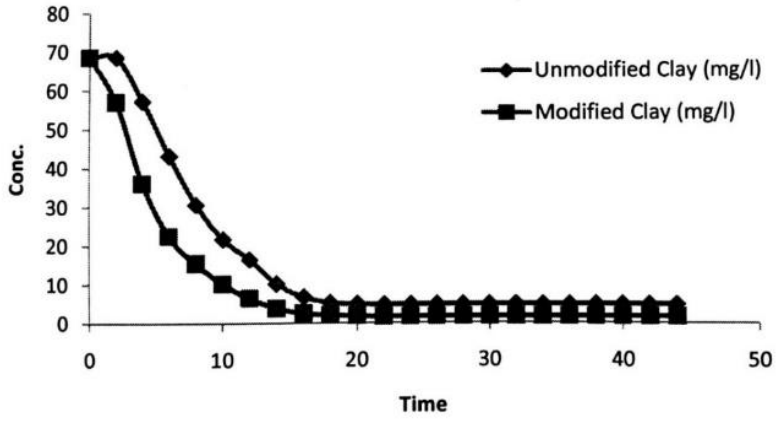

Figure 3. - Equilibrium Time for Adsorption of Naphthalene on unmodified and calcined modified clay

Figure 3 illustrates the variations in Naphthalene concentration over time when mixed with both unmodified and modified clay. It was observed that after 22 hours, the Naphthalene concentration in the solution reached equilibrium in both the modified and unmodified clay.

At equilibrium, the Naphthalene concentration decreased to 4.8 mg/l with unmodified clay, whereas it dropped to 1.7 mg/l with modified clay. This finding further confirms that calcined modified clay adsorbs more naphthalene than natural clay

Kinetic Models for Adsorption: Several kinetic models were utilized to evaluate the adsorption process

To gain a deeper understanding of the adsorption mechanism and rate-limiting factors, several kinetic models were used to assess the adsorption characteristics of benzene and naphthalene on both unmodified and modified clay.

i. Pseudo First Order Rate Model

$$\ln(q_e - q_t) = lnq_e - \left(\frac{k1t}{2.303}\right) \ldots\ldots (3)$$

q_e = Quantity of Adsorbate adsorbed at equilibrium (mg/g)
q_t = Quantity of Adsorbate adsorbed at time t (mg/g)
k1 = Rate constant of a pseudo-first order sorption (min^{-1})

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A plot of $\ln(q_e - q_t)$ vs t is made, and k1 is derived from the plot through the slope of the plot, which is k1/2.303.

ii. Pseudo-second Order Rate Model

$$\frac{t}{q_t} = \frac{1}{k2q_e^2} + \frac{1}{q_e t} \ldots\ldots\ldots (4)$$

$k2q_e^2$ = Initial sorption rate ($mgg^{-1}\,min^{-1}$)
k2 = Rate constant of pseudo-second order model ($gmg^{-1}\,min^{-1}$)

A plot of t/q_t vs t is made, and k2 is calculated from the intercept of the plot, which is $1/k2q_e^2$. The intercept with q_e is already obtained from the slope, which is $1/q_e t$.

iii. Elovich Kinetics Model

$$qt = \left(\frac{\ln(\alpha \cdot \beta)}{\beta}\right) + \left(\frac{\ln(t)}{\beta}\right) \ldots\ldots\ldots (5)$$

α = Initial adsorption constant
β = Desorption constant

A plot of q_t vs ln(t) is made, and β is obtained from the slope, which is 1/β. α is obtained from the intercept, which is ln(αβ)/β.

iv. Intra-particle Diffusion Model

$$Q_t = ki\, t^{0.5} \ldots\ldots\ldots (6)$$

ki = Rate of diffusion constant

A plot of q_t vs $t^{0.5}$ is made, with ki calculated from the slope, which is = ki.

v. Power Function Model

$$lnq_t = lnA + Blnt \ldots\ldots\ldots (7)$$

A plot of lnq_t vs lnt is made, and B is calculated from the slope, which is B, while A is calculated from the intercept, which is = lnA.

Data Correlation

$$r_{\{xy\}} = \frac{\sum_{i=1}^{n}(x_i - \bar{x}) \cdot (y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \cdot \sum_{i=1}^{n}(y_i - \bar{y})^2}} \ldots\ldots\ldots (8)$$

- Σ is summation symbol
- $(x_i - \bar{x})$ is the difference between each x-value and the mean of x
- $(y_i - \bar{y})$ is the difference between each y-value and the mean of y

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This formula is used to calculate the values of R^2 for each adsorbate and adsorbent above. With a benchmark of 1 (highly correlated) or 0 (no correlation) between the data.

Adsorption Kinetics of Benzene on unmodified clay and calcined modified clay.

A variety of adsorption kinetic models were evaluated, including the Pseudo-First Order, Pseudo-Second Order, Elovich, Power Function, and Intra-Particle Diffusion models, to identify the most accurate description of benzene adsorption kinetics on unmodified clay.

The kinetic modeling results for unmodified and calcined modified clay adsorption, obtained using the aforementioned models, are analyzed and presented below.

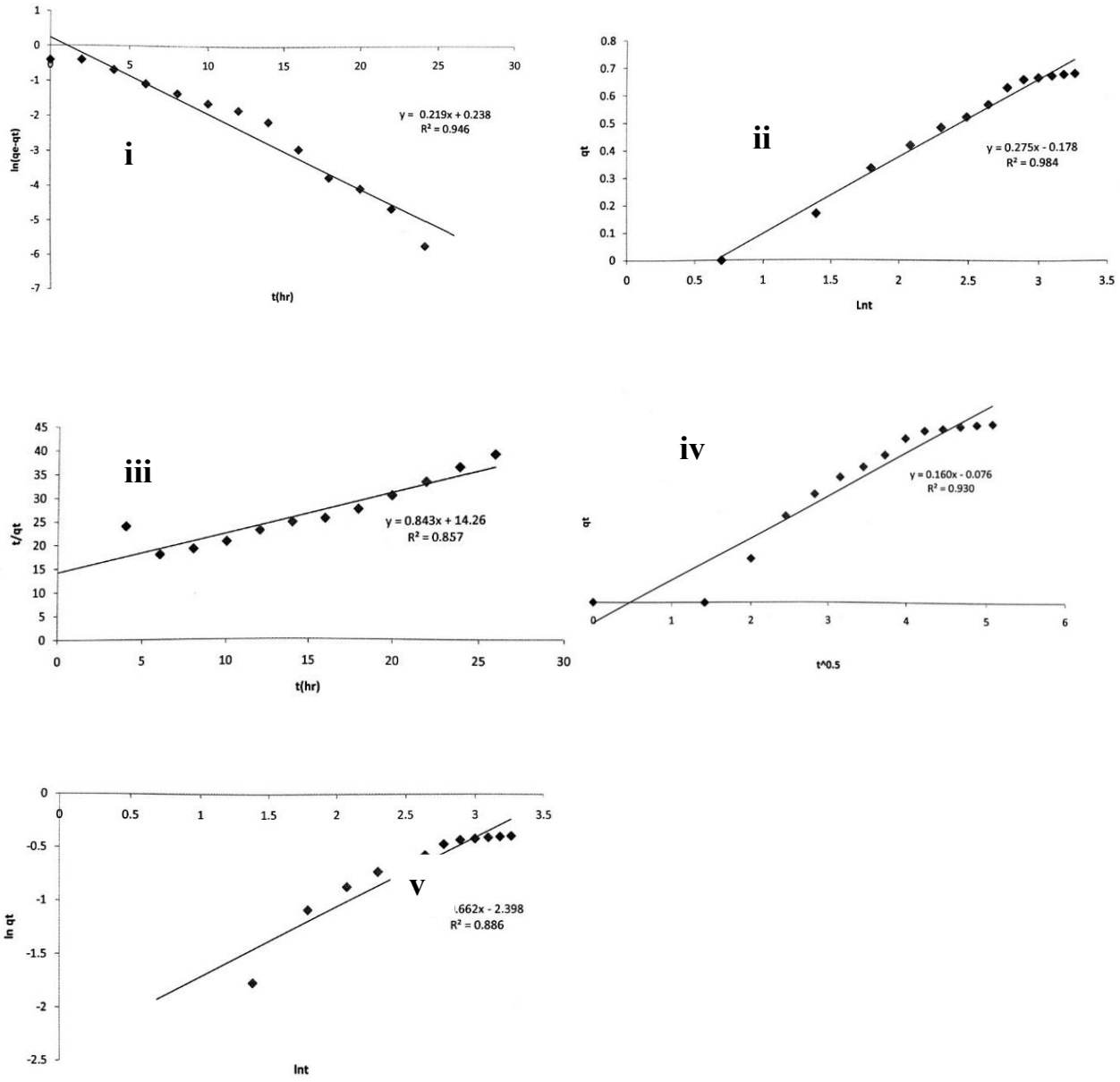

Figure 4: Models' outputs for Adsorption of Benzene on Unmodified Clay

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The regression values (R^2) of Pseudo-First-Order Kinetic model (i), Pseudo-Second-Order Kinetic model (ii), Elovich Kinetic model (iii), Intra-particle Diffusion model (iv) and Power Function model (v) for Adsorption of Benzene on Unmodified Clay in Figure 4 indicates how well the data points fit the statistical model. It is observed that all the kinetic models appear to be good fit for the modeling since the values of regression obtained from the graphs are very close to 1.0 (100%).

This is because as R^2 tends to 1, linear regression fit the data more efficiently. From the above models, it is observed that the Elovich model which gave an R^2 of 0.9844 appears to be the best fit for the modeling of the adsorption of benzene on unmodified clay.

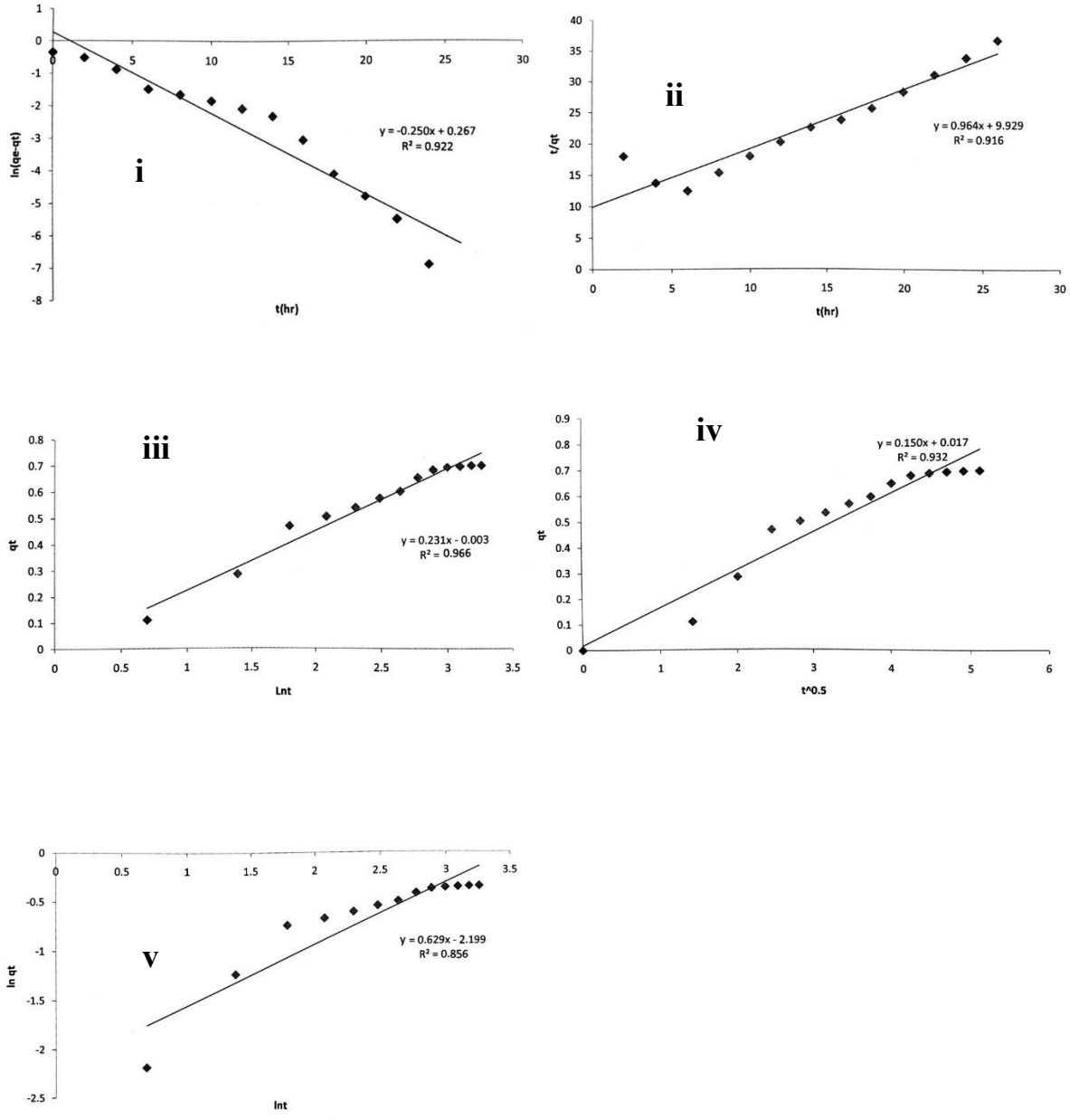

Figure 5: Models' Output for Adsorption of Benzene on modified Clay

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The regression values (R^2) of Pseudo-First-Order Kinetic model (i), Pseudo-Second-Order Kinetic model (ii), Elovich Kinetic model (iii), Intra-particle Diffusion model (iv) and Power Function model (v) for Adsorption of Benzene on modified Clay presented in Figure 5 shows that all the kinetic models appear to be a good fit for the modeling since the values of regression obtained from the graphs are very close to 1.0 (100%). From the above models, it is observed that the Elovich model, which gave an R^2 of 0.9666, also appears optimal (as the best fit) and suitable for the modeling of the adsorption of benzene on modified clay.

Adsorption Kinetics of Naphthalene on unmodified clay and calcined modified clay.

Multiple adsorption models were applied to analyze and identify the most suitable description of naphthalene adsorption on both unmodified and calcined modified clay samples. Analysis of the results of these kinetic modeling efforts are presented in Figure 6.

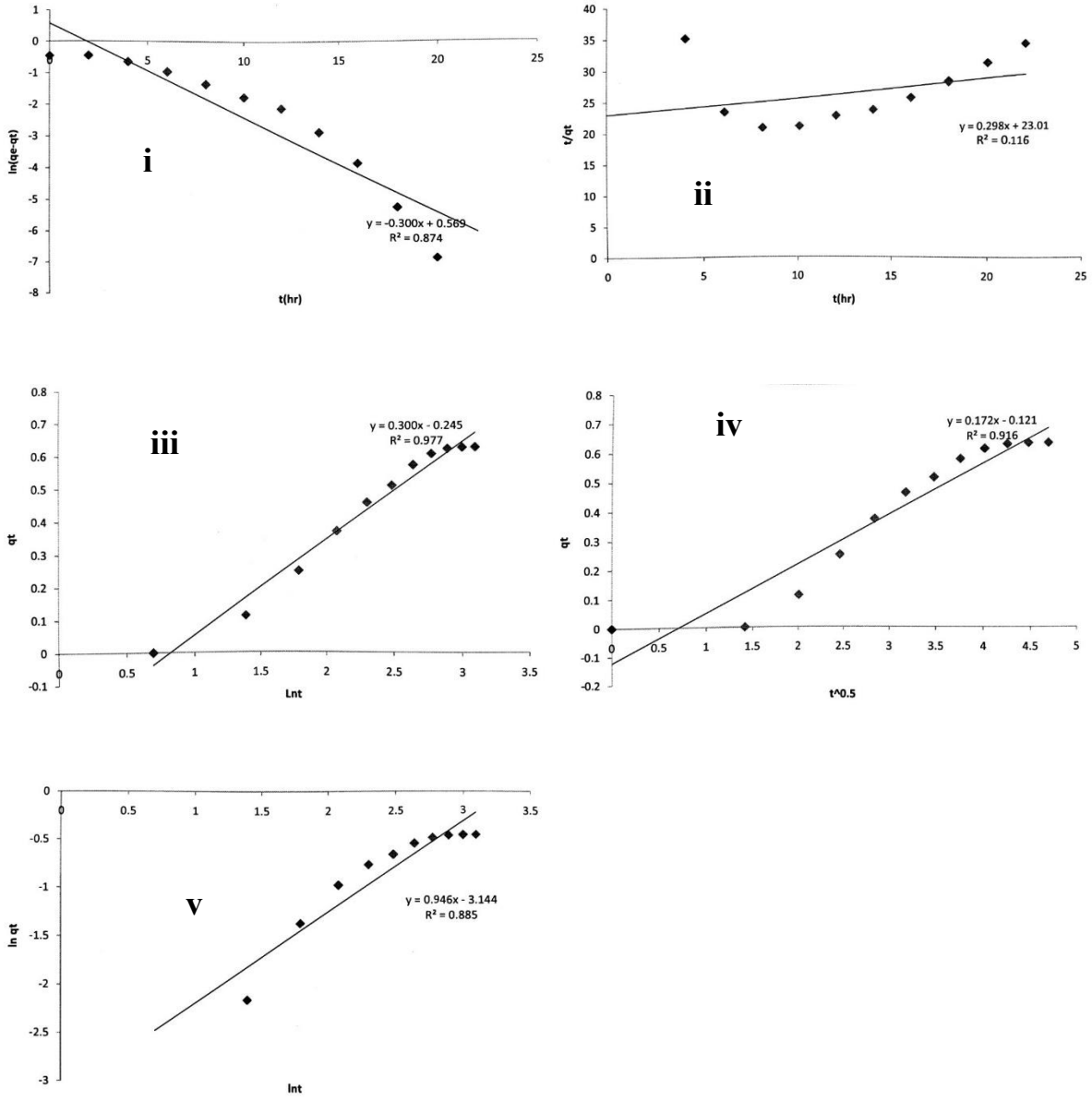

Figure 6: Models' Output for Adsorption of Naphthalene on Unmodified Clay

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Highlight from the 5 (five) kinetic models for Adsorption of Naphthalene on Unmodified Clay shows that the pseudo-first-order and pseudo-second-order models provided reasonable fits for the adsorption data, but the Elovich model consistently demonstrated the highest correlation coefficients ($R^2 = 0.9844$ for benzene and $R^2 = 0.9770$ for naphthalene). This indicates that the adsorption process was mainly controlled by chemisorption mechanisms, which involve electron sharing or transfer between the adsorbate and the adsorbent. Additionally, the kinetic models above show that the Pseudo-Second-Order Kinetic model is not suitable for this modeling, as it resulted in a very low regression value (R^2) of 0.1165.

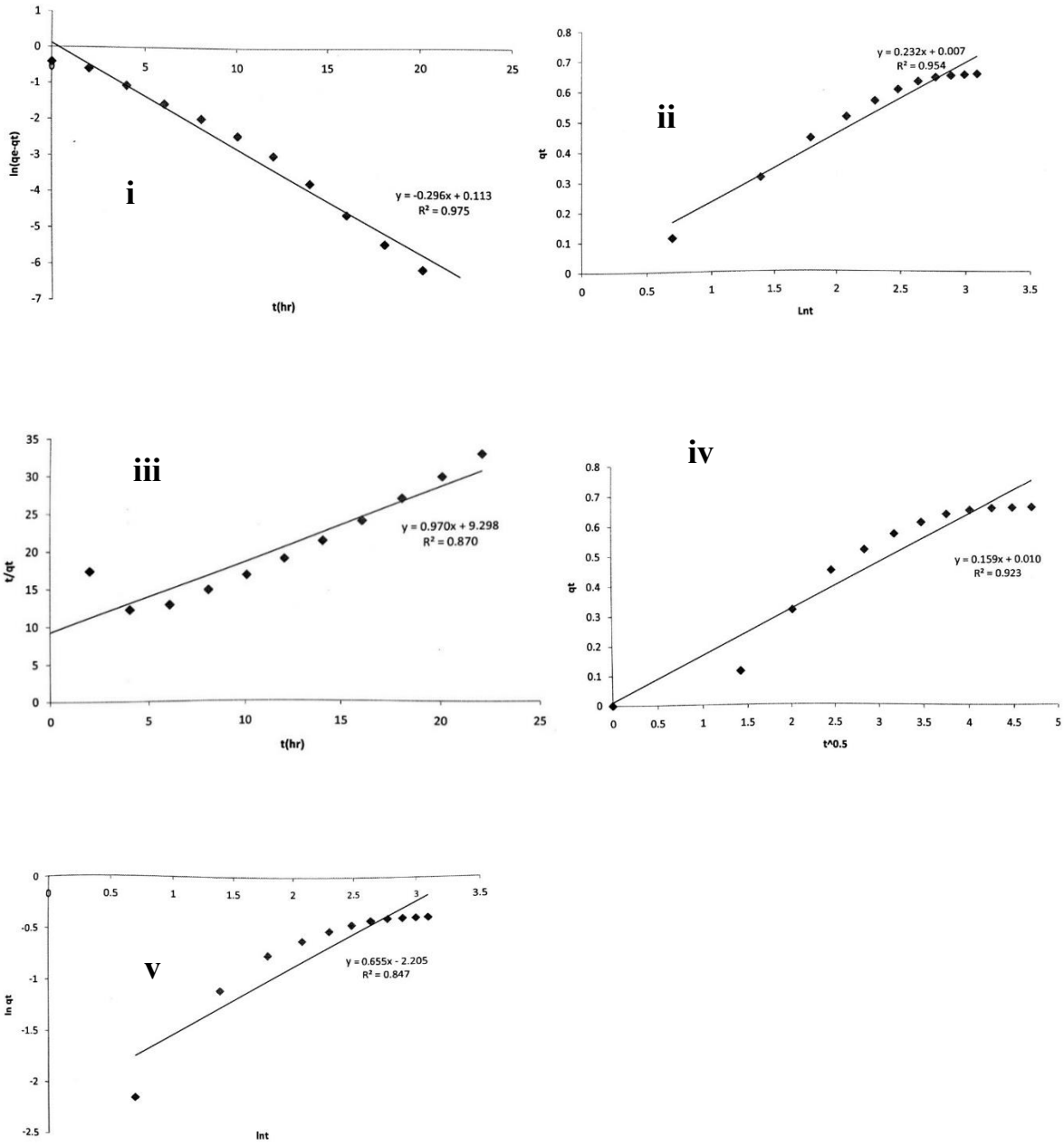

Figure 7: Models' Output for Adsorption of Naphthalene on modified Clay

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Regression Analysis for Adsorption Kinetics

To assess the reliability of the kinetic models applied, regression analysis was performed to establish the correlation between experimental data and theoretical predictions. The regression values (R^2) were then utilized to assess the accuracy of each model in characterizing the adsorption kinetics of benzene and naphthalene on both unmodified and modified clay.

Table 2: Regression Values R^2 for Benzene Adsorption

	Model	Unmodified Clay	Modified Clay
i.	Pseudo-First Order	0.9123	0.9345
ii.	Pseudo-Second Order	0.8745	0.8921
iii.	Elovich	**0.9844**	**0.9666**
iv.	Intra-Particle Diffusion	0.9211	0.9312
v.	Power Function	0.9543	0.9445

Table 3. Regression Values R^2 for Naphthalene Adsorption

	Model	Unmodified Clay	Modified Clay
i.	Pseudo-First Order	0.9251	**0.9752**
ii.	Pseudo-Second Order	0.1165	0.8341
iii.	Elovich	**0.9770**	0.9547
iv.	Intra-Particle Diffusion	0.9143	0.9275
v.	Power Function	0.9415	0.9328

To support these kinetic model analyses, Tables 4 to 4.8 present detailed kinetic data for the adsorption of benzene and naphthalene on both unmodified and modified clay.

Table 4: Kinetic Data for Adsorption of Benzene on Unmodified Clay

Time (hr)	Clay (mg/l)	q_t	q_e-q_t	Ln(q_e-q_t)	t/ q_t	lnt	t^0.5	lnq_t
0	72.2	0	0.67	-0.40048	0	0	0	-1.79577
2	72.2	0	0.67	-0.40048	0	0.693147	1.414214	-1.79577
4	55.6	0.166	0.504	-0.68518	24.09639	1.386294	2	-1.10564
6	39.1	0.331	0.339	-1.08176	18.12689	1.791759	2.44949	-1.10564
8	30.8	0.414	0.256	-1.36258	19.32367	2.079442	2.828427	-0.88189
10	24.4	0.478	0.192	-1.65026	20.9205	2.302585	3.162278	-0.73814
12	20.7	0.515	0.155	-1.86433	23.30097	2.484907	3.464102	-0.66359
14	16.3	0.559	0.111	-2.19823	24.04472	2.639057	3.741657	-0.58161
16	10.2	0.62	0.05	-2.99573	25.80645	2.772589	4	-0.47804
18	7.4	0.648	0.022	-3.81671	27.77778	2.890372	4.242641	-0.43386
20	6.8	0.654	0.016	-4.13517	30.58104	2.995732	4.472136	-0.42465
22	6.1	0.661	0.009	-4.71053	33.2829	3.091042	4.690416	-0.414
24	5.5	0.667	0.003	-5.80914	35.98201	3.178054	4.898979	-0.40497
26	5.2	0.67	0	-*0.40048	38.80597	3.258097	5.09902	-0.40448

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Table 5: Kinetic Data for Adsorption of Benzene on Modified Clay

Time (hr)	Clay (mg/l)	q_t	$q_e - q_t$	$\ln(q_e - q_t)$	t/q_t	ln t	t^0.5	ln q_t
0	72.2	0	0.702	-0.35382	0	0	0	-2.19823
2	61.1	0.111	0.591	-0.52594	18.01802	0.693147	1.414214	-2.19823
4	43.3	0.289	0.413	-0.88431	13.84083	1.386294	2	-1.24133
6	24.5	0.477	0.225	-1.49165	12.57862	1.791759	2.44949	-0.74024
8	21	0.512	0.19	-1.66073	15.625	2.079442	2.828427	-0.66943
10	17.7	0.545	0.157	-1.85151	18.34862	2.302585	3.162278	-0.60697
12	14.3	0.579	0.123	-2.09557	20.72539	2.484907	3.464102	-0.54645
14	11.7	0.605	0.097	-2.33304	23.1405	2.639057	3.741657	-0.50253
16	6.6	0.656	0.046	-3.07911	24.39024	2.772589	4	-0.42159
18	3.6	0.686	0.016	-4.13517	26.23907	2.890372	4.242641	-0.37688
20	2.8	0.694	0.008	-4.82831	28.81844	2.995732	4.472136	-0.36528
22	2.4	0.698	0.004	-5.52146	31.51862	3.091042	4.690416	-0.35954
24	2.1	0.701	0.001	-6.90776	34.23638	3.178054	4.898979	-0.35525
26	2	0.702	0	-0.35382	37.03704	3.258097	5.09902	-0.35382

Table 6: Kinetic Data for Adsorption of Naphthalene on Unmodified Clay

Time (hr)	Clay (mg/l)	q_t	$q_e - q_t$	$\ln(q_e - q_t)$	t/q_t	ln t	t^0.5	ln q_t
0	68.5	0	0.637	-0.45099	0	0	0	-2.18037
2	68.5	0	0.637	-0.45099	0	0.693147	1.414214	-2.18037
4	57.2	0.113	0.524	-0.64626	35.39823	1.386294	2	-1.37042
6	43.1	0.254	0.383	-0.95972	23.62205	1.791759	2.44949	-0.97022
8	30.6	0.379	0.258	-1.3548	21.10818	2.079442	2.828427	-0.75929
10	21.7	0.468	0.169	-1.77786	21.36752	2.302585	3.162278	-0.65393
12	16.5	0.52	0.117	-2.14558	23.07692	2.484907	3.464102	-0.53957
14	10.2	0.583	0.054	-2.91877	24.01372	2.639057	3.741657	-0.53957
16	6.8	0.617	0.02	-3.91202	25.93193	2.772589	4	-0.48289
18	5.3	0.632	0.005	-5.29832	28.48101	2.890372	4.242641	-0.45887
20	4.9	0.636	0.001	-6.90776	31.44654	2.995732	4.472136	-0.45256
22	4.8	0.637	0	-0.45099	34.53689	3.091042	4.690416	-0.45099

Table 7: Kinetic Data for Adsorption of Naphthalene on Modified Clay

Time (hr)	Clay (mg/l)	q_t	$q_e - q_t$	$\ln(q_e - q_t)$	t/q_t	ln t	t^0.5	ln q_t
0	68.5	0	0.668	-0.40347	0	0	0	-2.16282
2	57	0.11	0.553	-0.59254	17.3913	0.693147	1.414214	-1.12701
4	36.1	0.32	0.344	-1.06711	12.34568	1.386294	2	-0.77653
6	22.5	0.46	0.208	-1.57022	13.04348	1.791759	2.44949	-0.63488
8	15.5	0.53	0.138	-1.9805	15.09434	2.079442	2.828427	-0.63488
10	10.2	0.58	0.085	-2.4651	17.15266	2.302585	3.162278	-0.53957

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12	6.5	0.62	0.048	-3.03655	19.35484	2.484907	3.464102	-0.47804
14	3.9	0.64	0.022	-3.81671	21.67183	2.639057	3.741657	-0.43696
16	2.6	0.65	0.009	-4.71053	24.27921	2.772589	4	-0.41703
18	2.1	0.66	0.004	-5.52146	27.10843	2.890372	4.242641	-0.40947
20	1.9	0.66	0.002	-6.21461	30.03003	2.995732	4.472136	-0.40647
22	1.7	0.66	0	-0.40347	32.93413	3.091042	4.690416	-0.40347

DISCUSSION

The experimental results reveal that calcined modified clay exhibits significantly enhanced adsorption performance compared to unmodified clay for both benzene and naphthalene. This improvement is evident in the faster equilibrium times and greater reductions in pollutant concentration. The kinetic modeling further supports this observation, with the Elovich model consistently yielding the highest correlation coefficients, indicating that chemisorption is the dominant mechanism. The modification process likely increased the surface area and introduced active sites, improving pollutant interaction. These findings underscore the effectiveness of thermal and acid-treated clay as a low-cost, efficient adsorbent for organic pollutant removal.

The regression coefficient (R^2) reflects how well the experimental data align with the applied statistical models. Based on the R^2 values obtained from the five kinetic models evaluated for the adsorption of naphthalene onto modified clay, all models demonstrated a strong fit, with regression values approaching 1.0, indicating high predictive accuracy. This suggests a strong linear correlation between the observed and modeled data. Among the models, the Pseudo-First-Order model, with an R^2 of 0.9752, emerged as the most suitable for describing the adsorption behavior. The Elovich model, which recorded an R^2 of 0.9547, also proved to be a reliable fit, further validating the chemisorptive nature of the adsorption process.

Adsorption Trends and Mechanistic Insights

The enhanced adsorption efficiency of modified clay can be ascribed to several factors:

i. **Thermal Stability**: Calcination at 900°C may have removed impurities and volatile compounds, increasing the structural integrity and adsorption capacity of the clay.

ii. **Increased Surface Area**: The calcination and citric acid modification processes likely enhanced the surface area and porosity of the clay, providing more adsorption sites for benzene and naphthalene molecules.

iii. **Improved Functional Groups**: The incorporation of citric acid introduces additional functional groups capable of forming stronger interactions with the adsorbate molecules, including hydrogen bonds and van der Waals forces.

These modifications enhance the clay's ability to interact with nonpolar and weakly polar organic molecules, aligning with principles of surface chemistry and adsorbate-adsorbent interactions.

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Comparison with Literature

The results are consistent with findings from similar studies in the field. For example:

i. **Adsorption Capacities**: Studies by Uddin (2017) (Uddin, 2017) and Gil et al. (2021)(Gil et al., 2021) report that modified clays exhibit adsorption capacities 2-3 times higher than natural clays for organic pollutants, aligning with the observed differences in this study.

ii. **Kinetic Model Fits**: The dominance of the Elovich model ($R^2 > 0.96$) in this study suggests a chemisorption-controlled process. This aligns with prior studies on organic pollutant adsorption onto acid-modified clay, which also found Elovich to be the best fit (Guerrero-Fajardo et al., 2025)

iii. **Equilibrium Time**: Similar equilibrium times (Li et al., 2020) corresponds to this findings for aromatic hydrocarbons on acid-modified clays, suggesting consistency across different pollutants and clay sources.

IMPLICATIONS FOR PRACTICAL APPLICATIONS

The results demonstrate that calcined modified clay is a feasible and efficient adsorbent for eliminating benzene and naphthalene from contaminated water. The shorter equilibrium times and higher adsorption capacities suggest its potential for large-scale environmental remediation, especially in regions with significant industrial pollution.

These findings highlight the significant improvements in adsorption efficiency achieved through clay modification. The observed trends align well with existing literature, confirming the suitability of calcined modified clay as an effective material for organic pollutant removal. In summary, it can be deduced that the Elovich kinetic model is best fit for the modeling of the adsorption of Benzene and naphthalene onto natural clay and calcined modified clay.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

In the experiment, kinetic models like the Pseudo-First Order Model, Pseudo-Second Order Model, Elovich Kinetic Model, Intra-particle Diffusion Model, and Power Function Model were used to model the adsorption of naphthalene and benzene onto calcined modified clay. From the results obtained, the Elovich Kinetic Model seems to be the most appropriate model for this study.

Based on the results, the Elovich Kinetic Model seems to be the most appropriate for describing the adsorption of benzene and naphthalene onto calcined modified clay. The equilibrium concentration of benzene and naphthalene over time was also analyzed, which supports the conclusion that calcined modified clay offers greater adsorption capacity than unmodified clay.

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Recommendations for Further Research

i. Investigate the adsorption behavior of other significant organic pollutants.

ii. Compare the adsorption properties of calcined modified clay with other materials like activated carbon and zeolite.

iii. Study the desorption characteristics of naphthalene and benzene from both unmodified and modified clay.

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