Frontiers
2026, Vol. 6, No. 4, pp. 206–218
https://doi.org/10.11648/j.frontiers.20260604.17

Research Article

Development of Acid-Modified Clay for the Treatment of Simulated Textile Dye Effluents

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Abstract

The physiochemical properties of Natural Bentonite Clay (NBC) were modified in this work to increase its adsorption performance. The NBC was mined from Fika town in Yobe State and thereafter subjected to beneficiation to obtain various particle sizes. The modified NBC and Activated Bentonite Clay (ABC) were characterized using Fourier transform infrared (FTIR) spectroscopy for the determination of the effect of acid attack and the adsorbate Braunner-Emmet-Teller (BET) method for surface area determination was conducted on the clay sample before and after modification procedure. The surface areas of the adsorbents before and after modification were found to be 126.50 m^2/g and 160.40 m^2/g for NBC and ABC respectively. The raw and the modified samples had an adsorption capacity of 12.55 and 74.98 mg/g which were used to purify the simulated textile wastewater to investigate their adsorptive performance. The equilibrium data were fitted in Langmuir, Freundlich and Temkin adsorption isotherm models with the aid of origin 9 software using two statistical parameters- the correlation coefficient R and Sum of Square Errors SSE. Results showed the experimental data was best fitted in the Langmuir isotherm model where R values of ABC was consistently higher for dye 1-dye 4 than that of NBC. The SSE of ABC was also found to be consistently lower for all dye adsorption than that of NBC.

Keywords

Adsorption, Bentonite Clay, Adsorption Parameters, Dye Concentration, Particle Size

1. Introduction

Treatment of water contaminated with textile dyes has been the subject of several studies aimed at remediating the intensity of the colours and the quantity of organic matter [14]. Owing to wastewater from textile industries being hazardous contaminants, textile effluents is a major source of pollutants of water resources [9]. Dye effluents have the tendency of contaminating water resources and creating a water pollution on a massive scale [3] Even at low concentrations, dyes in water can have devastating effects on aesthetics as well as on the photosynthesis [11].

In view of these problems, it is important to control these

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Received: 25 July 2026; **Accepted:** 24 August 2026; **Published:** 11 November 2026

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dye effluents especially for the safety of both aquatic life and the ecosystem. The current campaign by the Federal Government of Nigeria for the diversification of the economy strongly suggests that revamping of the textile mill across the country is becoming inevitable, thus the attendant pollution from the dye in the effluent wastewater is a sure and foreseeable challenge now and in future. Generally, dyes can be classified based on their chromophoric properties, eg, either as azo dyes (-N=N-), whose properties show they are strong, good all-round properties, cost-effective; or the anthraquinone dyes ($C_4H_8O_2$) whose properties include being weak and expensive [5]. Dyes can also be classified based on their application e.g. dispersed dyes which have low solubility. However, [8], suggested that dyes can be classified as anionic: direct, acid and reactive dyes; cationic basic dyes; non-ionic dye: dispersed dyes. Among these classes, Azo dyes are the most common due to their simple synthesis and different routes and modifications can made to obtain the desired color properties, yield and particle size of the dye for improved dispersibility and are thus found in all kinds of textile wastewater. Over 60% of dyes used in textile industries are azo dyes and are synthetic, they are non-biodegradable thus, the reason why it has to be taken care of [7, 12],. Several methods for dye removal from wastewater abound, which includes: flocculation, chemical coagulation, oxidation, precipitation, adsorption and filtration [17]. Among these methods, adsorption is the most effective technique for the treatment of wastewater [7, 13].

The aim of this research study is to develop an adsorbent from Natural Bentonite Clay (NBC) for the purpose of removing azo acid dye pollutants from simulated textile dye effluents. First, the chemically and thermally modified natural bentonite clay was developed and characterized. The effects of adsorption parameters (i.e. contact time, dye concentration and particle size) on the adsorption capacity of the modified clay for the removal of mono azo dye from the textile effluents was evaluated. The adsorption parameters were optimized and the adsorption isotherm model parameters were estimated for the process.

2. Materials and Methods

2.1. Materials and Reagents

The adsorbent used in this research include montmorillonite (bentonitic clay) mined from Fika deposit, Yobe State, Nigeria while the hydrogen peroxide and Sulphuric acid used for beneficiating and activating the raw bentonite were obtained from Chemical Engineering Department, Ahmadu Bello University, Zaria, Nigeria.

2.2. Beneficiation of Clay Samples

This process was carried out using the procedure of [19] with some modification. The clay sample was pre-treated by suspension in water for 24 hours and subsequently decanted in order to remove sand and heavy non-clay materials. The sample was further treated to remove organic matter by adding 30% hydrogen peroxide solution and stirring the mixture until effervescence ceased. The mixture was decanted gently and washed five times with de-ionized water to remove all traces of hydrogen peroxide and then oven dried at 105 ^{o}C to constant weight. After cooling, the dry sample was pulverized and sieved through a 212 μm mesh size sieve and then stored in an air-tight container.

2.3. Acid Activation of the Clay Sample

The procedure for modifying the beneficiated was done adopting the method of [22]. The different adsorbent samples are summarized in Table 1. The clay material was prepared for activation as followed. At each run, 10 g of the prepared sample was weighed into the flask (250 ml capacity) and 100 ml of Sulphuric acid solution each with different concentrations was added. The reaction temperature was fixed at 90 ^{o}C and the mixture was agitated for 3 hours. The reaction was terminated after 3 hours with the addition of a large amount of distilled water until the sample was exhaustively washed and free of SO_4^{2-} and pH of 7 was maintained. The acid activated bentonite sample was filtered with Whatman filter paper number 41 and dried in an oven for 6 hours. The sample was then subjected to thermal activation at 300 ^{0}C for 90 min. The content was cooled, stored in an air-tight plastic bottle for further processing.

Table 1. *Code for Representing Different Adsorbent Samples.*

Adsorbent Sample	Concentration (M)
Control	0.025
ABC	0.050
ABC1	0.075
ABC2	0.100
ABC3	0.250
ABC4	0.500

2.4. Characterization of Bentonite Clay

Samples collected before and after the acid activation of the clay were both characterized based on the following analyses: FTIR, XRF, and BET.

2.4.1. Fourier Transform Infra-Red (FTIR)

IR-spectra measurements were performed using Shimadzu FTIR-8400s spectrophotometer instrument (64 scans, 4 cm^{-1}). Background spectrum of air at ambient condition was conducted before sample analysis. 20 mg wafer of the catalyst sample consisting of 1% of the sample and 99% KBr window

was used. The mixture was pressed under pressure to produce a thin film wafer. The wafer was further inserted in the sample holder of the FTIR equipment, then, FTIR spectra of the sample was recorded from 500 to 4000 cm^{-1}.

2.4.2. BET

The specific surface areas of acid activated bentonite was estimated using BET method. The pore width was determined using BJH method. The sample tubes were loaded with 0.3g of samples. The samples were then degassed under vacuum at 378 K for 12h in Vacuum Prep 061 sample degas system prior to surface area measurements. The surface area and pore width determinations were based on isotherms of adsorption and desorption of nitrogen at 77K using Micrometrics gas adsorption analyzer.

2.5. Preparation of Synthetic (Formulated) Textile Effluent

The model effluent was prepared using dye and water. In which a 50g of dye was dissolved in 250 mL distilled water in a 500 mL volumetric flask. From which the resulting mixtures, representing a typical textile wastewater effluent was used to test the adsorption capacity of the developed adsorbent to ascertain it performance in terms of effectiveness and efficiency in the adsorption of dye from any potential effluent containing dye solution. The dye considered in this study are summarized in Table 2.

Table 2. Selected Dye Samples Considered for the Adsorption.

S/No	Dye IUPAC Name	Dye Code	Colour
1	Sodium 7-amino-3-((4-(cyclopenta-1,3-dien-1-yl) diazenyl)-4-hydroxynaphthalene-2-sulfonate	Dye 1	Light Purple
2	Sodium 3-((4-(cyclopenta-1,3-dien-1-yl) thiazol-2-yl) diazenyl)-4-hydroxynaphthalene-1-sulfonate	Dye 2	Faint Purple
3	Sodium 7-amino-3-((5-(ethoxycarbonyl)-4-methylthiazol-2-yl) diazenyl)-4-hydroxynaphthalene-2-sulfonate	Dye 3	Purple
4	Sodium 3-((5-(ethoxycarbonyl)-4-methylthiazol-2-yl) diazenyl)-4-hydroxynaphthalene-1-sulfonate	Dye 4	Dark Purple

2.6. Characterization of Simulated Effluent

Samples collected before and after the treatment of the effluent was analyzed for absorbance using a double beam UV-visible spectrophotometer (Spectra scan UV 2600) at different considered dyes' wavelength and the residual dye concentration was determined from absorbance - concentration graph (calibration curve).

2.7. The Batch Adsorption Studies

Batch adsorption was carried out by investigating the effect of various parameters. Initial dye concentration: The optimization of initial dye concentrations over a range of 10-60 mg/l was carried out. The contact time was over a range of (15-150 min) were done. Optimization of particles size of the adsorbent for the adsorption process over a range (75 - 250 μm) was determined.

Table 3. Experimental detail for batch adsorption of dye on activated clay.

Effect of System	Contact Time (min)	Initial Concentration (mg/L)	Particle Size (μm)
Effect of particle size	-	-	75, 125, 180, 212, 250
Effect of initial concentration	-	10, 20, 30, 40, 50, 60	-
Effect of contact time	15, 30, 45, 60, 75, 90, 105, 120, 135, 150	-	-

The variables used on a batch adsorption process studies was summarized in Table 3, where the various levels of the factors considered in the study are presented (fixed Parameters; Adsorbent mass=1g, Room temperature=303K, pH=3.5).

2.8. Method of Effluent Simulation

Analytical grade of dye 1-4 were used as an adsorbate. The chemical formula of dye 1-4 are

C17H13N4S2O4Na; CH18H12N3S2O4Na; CH17H15N4S2O6Na; CH18H14N3S2O6Na and their respective molecular weights are as follows; 448g/mol; 433 g/mol; 458 g/mol; 443 g/mol.

Stock solution of 1g/l of deionized water (1000ppm) was prepared by diluting 1L of deionized water with 1g of measured dye powder of which the resulting mixtures represent a typical textile wastewater effluent. The various concentration considered for this work were chosen to be 10 mg/L to 60 mg/L.

And they are prepared from the stock-solution using serial dilution method as follows: For instance, in order to prepare 10mg/L, equation (1):

$$C_1V_1 = C_2V_2 \quad (1)$$

C_1 =concentration of the stock solution, V_1 = volume fetched from the stock solution, C_2 = chosen concentration, V_2 = chosen volume meant to be diluted with V_1

$V1 = \frac{C2V2}{C1} = \frac{10\times100}{1000}$

$V1 = 1cm^3$

Hence 99cm^3 of deionized water was added to 1cm^3 of dye solution to make 100cm^3 of dye solution.

And their various λ_{max} were recorded by UV- Visible Spectrophotometer (UVD-3200) and were found to be 504 nm for dye1. 521 nm for dye 2, 504 nm for dye3 and 506 nm for dye 4.

2.9. Batch Adsorption Studies

Batch adsorption equilibrium experiment were conducted for the adsorption of dye 1- dye 4 on the adsorbent samples (ABC) as function of particle size, initial dye concentration, adsorbent dosage and contact time.

Batch adsorption equilibrium experiment was done by adding 1g of adsorbent to 100ml solution of adsorbate concentration 1g/L having a known pH in a conical flask and mixed on a magnetic stirrer at room temperature for 105 minutes. Based on the effect of the particle size 1.0g of adsorbent with different adsorbent particles passing through 75µm sieve mesh size and retained in 250 µm was added to different conical flask. The flasks contain 100ml of adsorbate solution of concentration 1g/L which was mixed for 105 mins.

Based on the effect of initial dye concentration 1.0g of adsorbent was added to each conical flask containing 100ml of adsorbate solution of different concentration of 10, 20, 30, 40, 50, and 60mg/L which was stirred for 105 minutes at room temperature 303k and at 3mg/L using 75µm particles size.

Based on the effect of contact time 1.0g of adsorbent was added to 100mL of adsorbate solution of concentration 1g/L and was stirred at different time intervals of 15, 30, 45, 60, 75, 90, 105, 120, 135, and 150 minutes. Moreover, the solution was withdrawn from the reaction mixture at the fixed time interval and was filtered using Whatman filter paper number 41.0. Fixed parameter are adsorbent dosage 1g, temperature 303k, and pH of 3.4.

The amount of unabsorbed dye in the supernatant solution was measured with the UV-VIS spectrophotometer at different wavelength of 504nm for dye 1 521 nm for dye 2, 504nm for dye 3 and 506 for dye 4. Therefore, the amount of adsorption of equilibrium (q_e) and the percentage adsorption were calculated as follows:

$$q_e = (C_0 - C_e)V / M \quad (2)$$

$$\% \text{ dye adsorbed} = [(C_0 - C_e) / C_0] \times 100 \quad (3)$$

Where C_o and C_e are initial and final dye concentration respectively in mg/L, V is the volume of the solution (L) and M is the mass of the adsorbent used (g)

2.10. Adsorption Isotherm and Model Evaluation

Data for the calibration curve were obtained by preparing solutions of known concentration (mg/L) and recording the corresponding absorbance by UV-spectrophotometer. A plot of absorbance against concentration was used to determine the equilibrium (residual) concentration, C_e, of the adsorbate remaining in solution after treatment under the optimized conditions from each parameter study. The Langmuir, Freundlich and Temkin isotherm constants were calculated from Equations (4), (5) and (6) respectively.

Langmuir Isotherm Model

$$C_e/q_e = (1/(Q_ob)) + (C_e/Q_o) \quad (4)$$

Freundlich Isotherm Model

$$\log q_e = \log K_f + (1/n) \log C_e \quad (5)$$

Temkin Isotherm Model

$$q_e = (RT/b_T) \ln A_T + (RT/b_T) \ln C_e \quad (6)$$

The isotherm model for the adsorption process was evaluated using curve fitting techniques with the aid of Origin 9 command where a linearized form of Langmuir, Freundlich and Temkin models were evaluated for fitness.

3. Results and Discussion

3.1. Characterization of the Adsorbent

3.1.1. FTIR Spectra for NBC and ABC

Fourier Transform Infrared Spectroscopy study was carried out to identity the functional groups present in the NBC and ABC samples ranging from 500cm^{-1} to 4000cm^{-1}. The FTIR spectrum of NBC and ABC is shown in Figure 1. The complex nature of clay is displayed in Figure 1 with new peaks detected on comparison of FTIR analysis of NBC with ABC sample. The changes noticed in the spectra of both clay samples confirmed that the activation process modified the clay sample [1]. The peaks at 3600-3200 cm^{-1} can be assigned to the stretching mode of hydroxyl groups with hydrogen bonding. A new band 3546 cm^{-1} for stretching mode of hydroxyl group appears on ABC which is absent in NBC which means the purifying effect of the sulphuric acid and thermal treatment used during activation enables the functional group to be observed. The band at 1427 cm^{-1} became more pronounced on activation; this peak represents stretching mode of the Si-O bond.

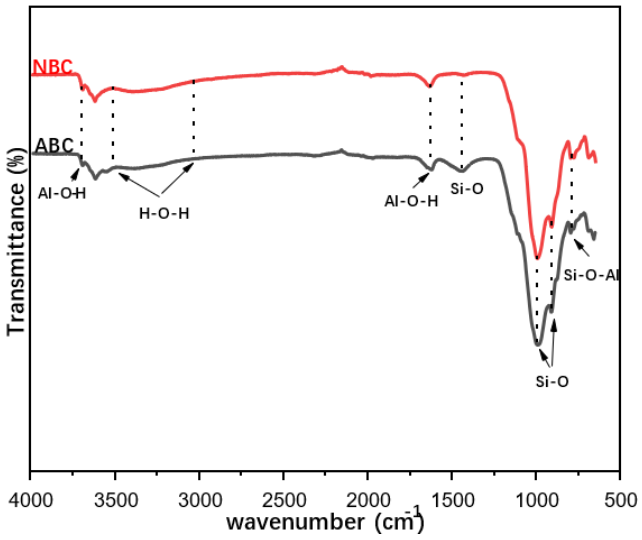


Figure 1. *FT-IR spectra for NBC and ABC.*

3.1.2. XRF Analysis

Table 4. *XRF Analysis of Bentonitic clay.*

COMPOSITION	NBC (%)	ACTIVATED (%)
SiO_2	51.63	56.74
Al_2O_3	20.23	18.85
MgO	3.23	2.74
CaO	3.82	2.33
TiO_2	0.24	0.62
MnO	0.66	0.05
Fe_2O_3	0.82	1.04
LOI	16.0	14.85

The XRF analysis is shown in Table 4 which investigated the chemical composition or elemental assay of the clay before and after acid activation. The clay contains alumina and silica in major quantities whereas oxides of Magnesium, Calcium, Potassium, Titanium and Zinc are present in trace amounts. Al_2O_3 content decreased from 20.23 wt% to 18.85 wt% for the modified sample this could be apparently due to acid dealumination of the bentonite. The moisture content of the both raw and modified clay which are 16.0% and 14.85% respectively both lie within the 8-18% recommended for clay.

Acid modification caused an increase in silicon oxide (which agrees with the increase in the Si-O stretching mode peak discussed in FTIR result), titanium oxide increased while manganese oxide calcium oxide and magnesium oxide decreased. This is because MnO, CaO and MgO are more reactive to sulphuric acid being basic oxides which translates to more percentage content of the other oxides which are less reactive. The net decrease in these oxides improves the purity of ABC and hence its adsorption capacity.

3.1.3. BET Analysis

The morphological structure of NBC and ABC using BET analysis is shown in Table 5. The specific surface area of ABC (160.40 m^2/g) is higher than that of NBC (126.50 m^2/g), the pore volume and pore size of ABC is also higher than NBC which implies ABC should have a higher adsorption capacity than NBC.

The relative increase in surface area of the activated clay is attributed to the acid treatment of the clay with H_2SO_4 due to selective leaching of the alumina and other metal oxides as discussed in XRF analysis section which is also responsible for the increase in pore size from 0.76nm to 0.88nm. This enlargement of pores creates more access for the dye particles to reach adsorbent sites inside the pore hence ABC is expected to have higher percentage of dye adsorption than NBC [10].

Table 5. *BET analysis for NBC and ABC.*

Samples	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Size (nm)
NBC	126.50	0.0420	0.76
ABC	160.40	0.0615	0.88

3.2. Effects of Acid Concentration on Dye 4 Removal

The effects of acid concentration on the adsorption of the dye 4 are presented in Figure 2 for the adsorption of dye 4 molecules from dye aliquot on ABC. Figure 2 shows the variation of the percentage adsorbed dye molecules as a function of acid concentration used in the activation process, and from the graph at 0.250 M, maximum adsorption of the dye recorded a 71.9% success. Beyond this concentration, adsorption capacity dropped as a result of the partial collapse of the clay structure by the excess acid [21].

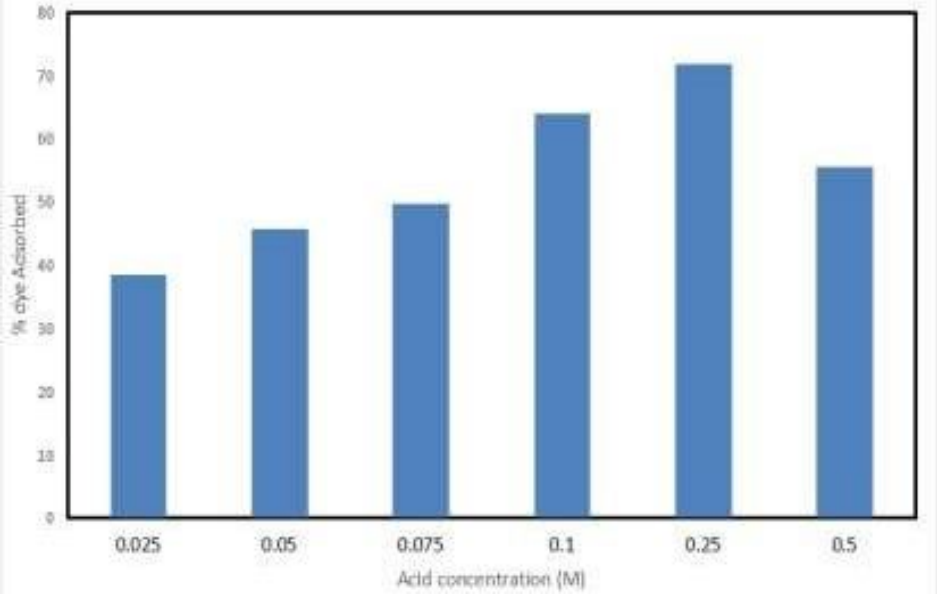


Figure 2. *Variation of Percentage dye adsorbed with acid loading on the clay at CT = 90 min, AM = 1 g, IC = 30 mg/L @ absorbance of 0.244, and RT = 303 K.*

3.3. Effects of Particle Size on Dye Removal

The influence of adsorbent particle size on the adsorption of the different dyes is presented in Figure 3, where removal of dye using activated bentonite clay of different particle sizes showed that removal rate decreases with increasing particle size. Particle sizes ranging from 75 to 250 μm gave percentages of dye adsorbed ranging from 81.60% to 49.70% for Dye 1, 75.60% to 49.80% for Dye 2, 84.30% to 52.60% for Dye 3, and 92% to 68% for Dye 4. The relatively higher adsorption with smaller adsorbent particle size is attributed to smaller particles yielding a larger surface area, providing a greater number of adsorption sites [18]. The similar trend of the adsorption curves for the dyes used is due to the same functional group present in the dyes.

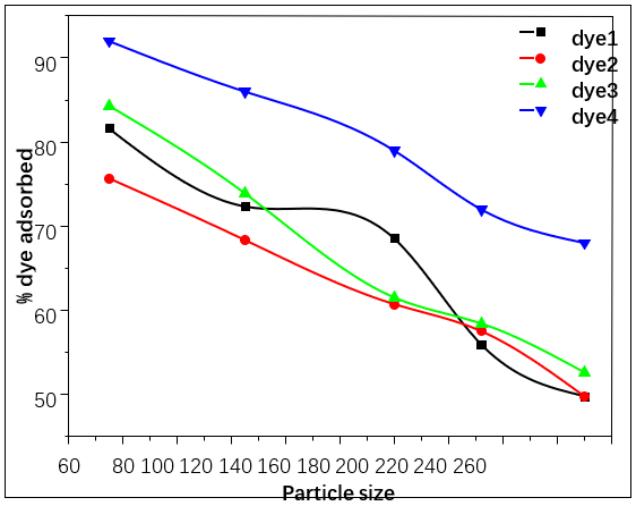


Figure 3. *Effect of particle size on ABC using dye 1-4 at MA = 1 g, RT = 303 K, CT = 105 min. IC = 30 mg/L at varying absorbances of 0.152 for dye 1, 0.170 for dye 2, 0.275 for dye 3, and 0.244 for dye 4.*

3.4. Effects of Contact Time on Dye 1-4 Removal by ABC

The contact time was found to play a significant role in the process of dye removal from wastewater by adsorption at a fixed temperature, adsorbent dosage, mesh size and initial dye concentration of the aliquot. The batch adsorption studies of dyes molecules, in acid-activated bentonite clay at different contact times (15, 30, 45, 60, 75, 90, 105, 120, 135 and 150 min) were as shown in Figure 4. The rapid uptake of the dye species and the establishment of equilibrium within the investigated time indicate the efficiency of the adsorbent. This information may be found valuable in designing a pilot-commercial scale treatment of this effluent in terms of the needed space-time for effective use of the adsorbent. It can be seen that the removal of the dye reaches its peak at 105 min for dye 1. 75 min for dye 2. 90 min for dye 3 and 105 min for 4 and gradually decreasing thereafter. [20].

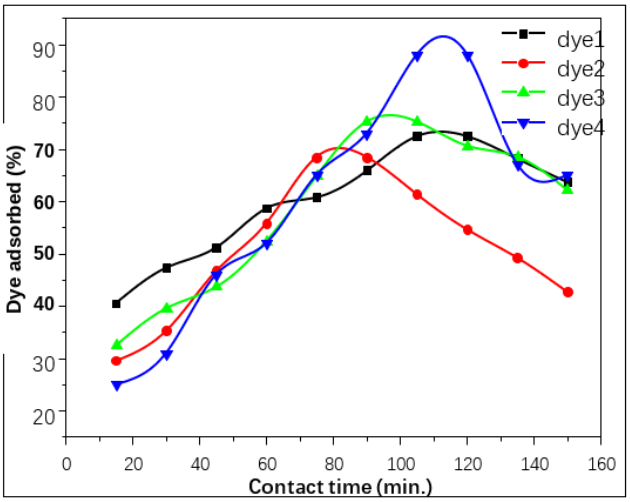


Figure 4. Effect of contact time on dye 1-4 removal by acid ABC at MA = 1 g. IC = 30 mg/L at absorbances of 0.152 for dye 1, 0.170 for dye 2, 0.275 for dye 3, and 0.244 for dye 4 RT = 303 K, and PS = 75µm.

3.5. Effects of Initial Dye Concentration, Its Adsorption on Acid-Activated Bentonite

The initial concentration of adsorbate plays an important role in the adsorption process, as a given mass of adsorbent can adsorb only a certain amount of a solute. The concentrations investigated ranged from 10 - 60 mg/L as presented in Figure 5. The results showed that the more the concentration of dye in the solution, the lower the percentage of dye that a given mass of adsorbent can adsorb. Thus, the percentage of dye removal was dependent upon the initial concentration.

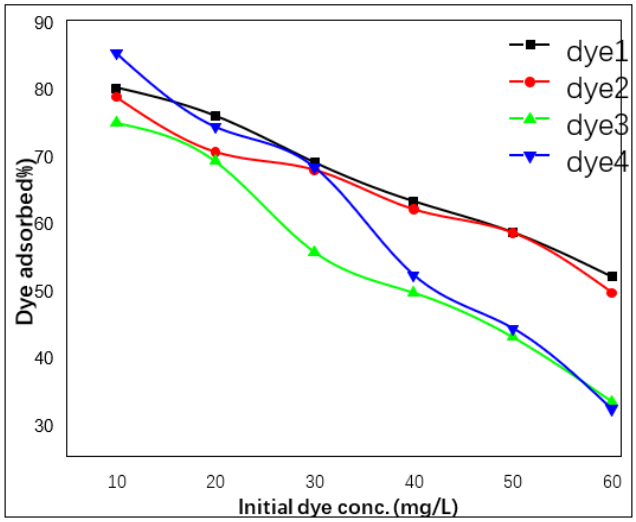


Figure 5. Effect of initial concentration on dye 1-4 and its adsorption on acid ABC at CT = 105 min, RT = 303 K, AM = 1 g, and IC at 30 mg/L of 0.152 absorbance, PS =.75 µm.

3.6. Comparison of Effect of Experimental Conditions on Adsorptive Potency of NBC and ABC

The effect of varying contact time, initial concentration and particle size at fixed adsorbent dosage and ambient temperature on percentage removal of dye molecules using NBC and ABC is shown in Figure 6. The trend is the same for both ABC and NBC when contact time is varied, as depicted in Figure 6a. The percentage of Dye 1 adsorbed increases with contact time until it reaches a maximum at 75 min (for both ABC and NBC), then begins to decline as time increases. The number of dye molecules adsorbed continues to increase as dye molecules attach to free active sites, explaining the increase in percentage of dye adsorbed from 0 to 75 minutes, while the subsequent decrease can be explained by classic Langmuir-model adsorption behaviour.

Adsorption on the adsorbent surface is monolayer; once the adsorption sites are exhausted, an interactive repulsive force exists between the azo dye molecules on the monolayer and those in the bulk phase, which could result in dislodgement (desorption) of monolayer azo dye molecules from the surface of ABC and NBC. The difference between ABC and NBC lies in the percentage of dye adsorbed — the amount of Dye 1 adsorbed per unit mass of ABC is higher than that of NBC at any given contact time. This is due to acid activation, which removes impurities and alters physical properties such as surface area and average pore volume, and also changes chemical properties such as cation exchange capacity and surface acidity of the clay [6].

The effect of particle size was also considered and found to be a useful parameter in the adsorption of azo dyes on activated bentonite clays. When particle size of both adsorbents (ABC and NBC) was varied, dye adsorbed decreased with increasing particle size from 75 to 250 µm, as shown in Figure

6b. The best (smallest) particle size used in this work, 75 µm, gave the highest percentage of dye adsorbed for both ABC and NBC. The percentage of Dye 2 adsorbed by ABC is higher than by NBC due to the improved physiochemical properties of the clay discussed above. Previous studies have shown that ease of mass transfer from the fluid to the surface, creation of greater interfacial surface area, and reduction of interparticle diffusion path length all favour smaller particles [2, 15, 18]. Active sites in closed voids, which would otherwise be inaccessible to adsorbate molecules, become available for adsorption when the adsorbent is broken into smaller particles.

In general, dye sorption is dependent on the initial concentration of the dye [12]. Figure 6c shows the effect of initial Dye 3 concentration on the percentage of Dye 3 adsorbed. It is apparent that the dye adsorbed by ABC is higher than that of NBC, for the same reasons given for variation in contact time and particle size. From Figure 6c, the percentage of dye adsorbed decreases as the adsorbate concentration increases from 10 to 60 mg/L. An increase in dye removal with increasing dye concentration is a common phenomenon in many studies [2]; however, in this study, and in other published work, the reverse was observed. This decline can be attributed to the 'adsorbed molecule-bulk adsorbate' steric effect, which occurs at high concentration [4, 15, 16, 23].

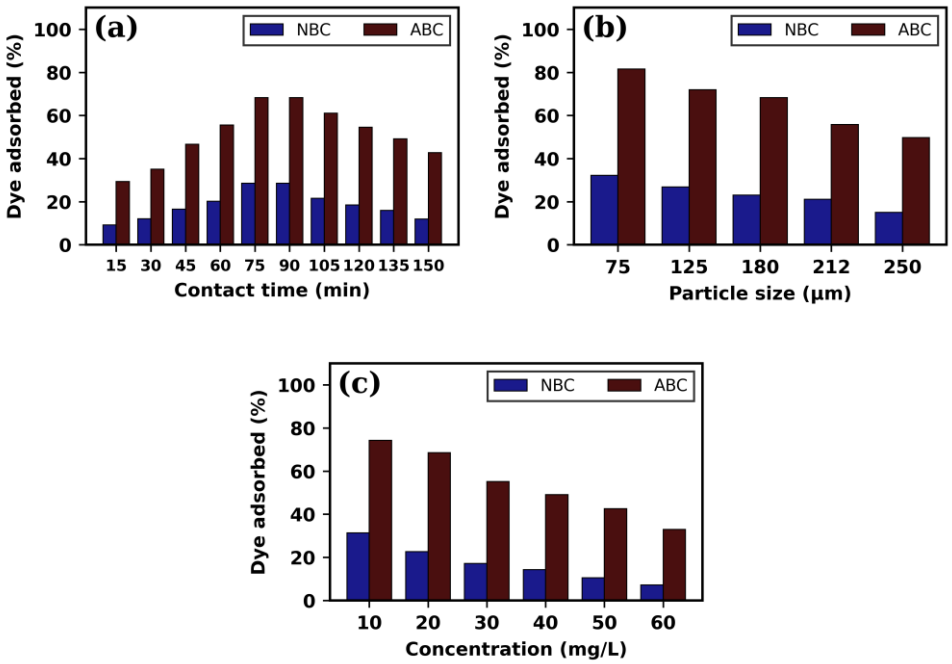


Figure 6. *Comparison of Adsorption of NBC and ABC at (a) different contact time (b) particle size and (c) Initial Concentration for azo acid dyes used.*

3.7. Modeling of Isotherm for the Adsorption of Dye Molecules for Both NBC and ABC

This model describes quantitatively the formation of a monolayer adsorption on a finite number of identical sites on the outer surface of the adsorbent, at a one-off adsorption. Thereby, the Langmuir represents the equilibrium distribution of dye molecules between the solid and liquid phases.

The Langmuir model plot for dye 1 to dye 4 is shown in Figure 7, Freundlich model for dye 1 to dye 4 in Figure 8, Temkin model in Figure 9. The R^2 of ABC for dye 1 to dye 4 ranges from 0.803 to 0.971 is higher than that of respective R^2 values of Freundlich model for dye 1 to 4 which implies that the data for isotherms for the dyes are more fitted for Langmuir than Freundlich model. Since all four azo dyes used exhibit similar chemical properties hence the same isotherm model. For Freundlich dye 1 and dye 2 have their R^2 for the NBC (0.85357, 0.89815) higher than that of ABC (0.73449, 0.7594) which negates expectation because the ABC with less impurity and improved physiochemical properties should exhibit better fitness to the isotherm model than NBC.

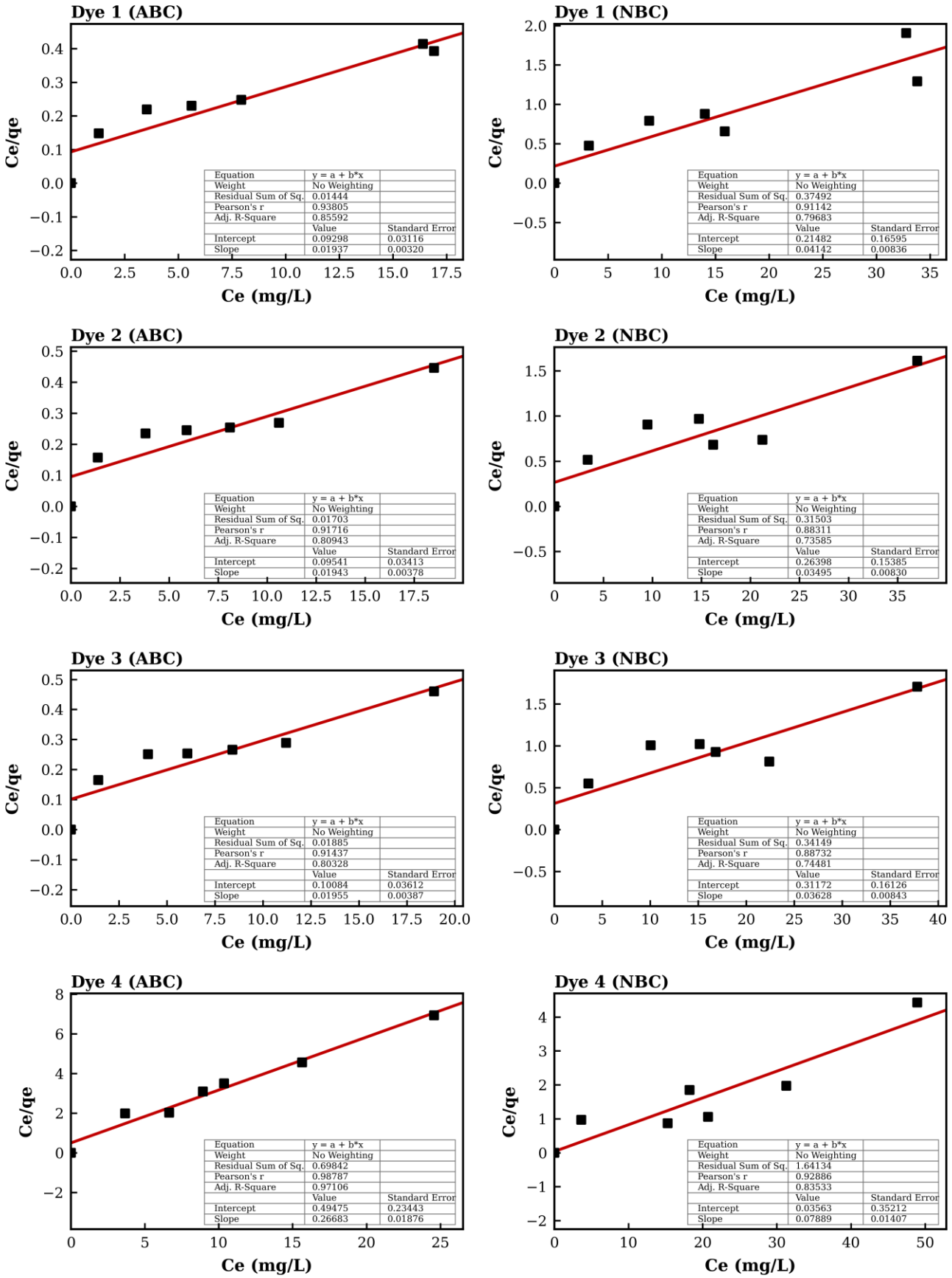


Figure 7. *Langmuir isotherm model graphs*

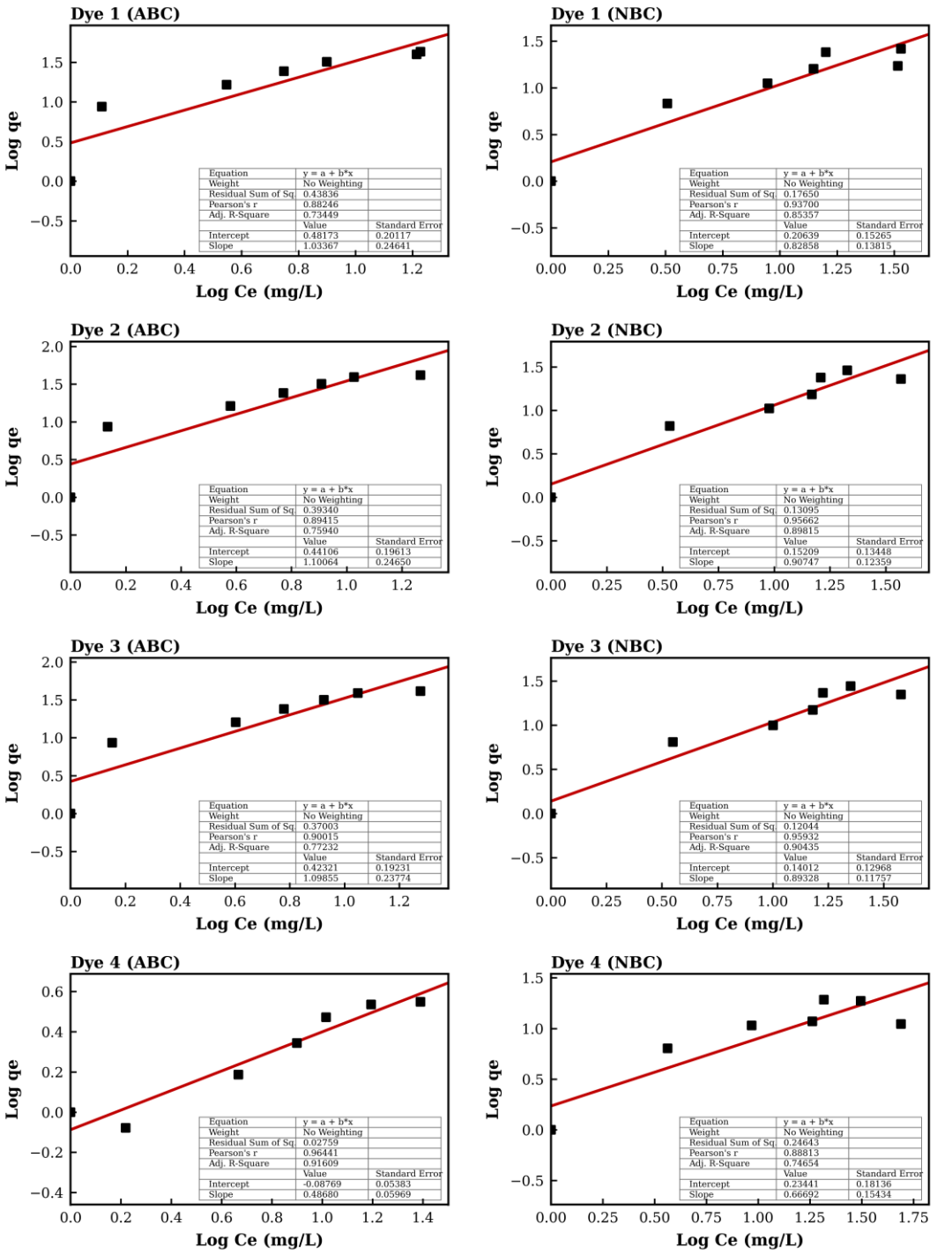


Figure 8. *Freundlich isotherm model graph for dye 1 to dye 4 treatment using ABC and NBC.*

The Temkin model on the other hand shows a negative R^2 for dye 4 since R^2 cannot be negative is interpreted as zero meaning Temkin model doesn't fit the data. Also, the R^2 of Temkin model for the adsorption of dye 2 using ABC (0.7763) is lower than NBC which further makes for the rejection of Temkin as a fitting model. The Langmuir R^2 values for all ABC dyes show high values (0.8033 to 0.9710) than that of NBC (0.7345-0.9161) which makes the adsorption data fit more to Langmuir than Freundlich and Temkin based on the statistical parameter R^2.

A second statistical parameter was used which is the sum of square errors (SSE). It measures the deviation of observed data from isotherm model. A small SSE indicates a tight fit of the model to the data Archdeacon, (1994). The SSE values of Temkin model for ABC are 31.94518, 55.63782, 1.92795, 0.81681, for dye 1, dye 2, dye 3 and dye 4 respectively and NBC are 89.49307, 83.63393 119.26279, 110.07215, for dye

1, dye 2, dye 3 and dye 4 respectively. These large figures indicate a great deviation of data from Temkin model. The Freundlich SSE values of model for ABC are 0.43836, 0.3934, 0.37003, 0.02759 for dye 1, dye 2, dye 3 and dye 4 respectively,0.13095 0.1765, 0.12044, 0.24643, for dye 1, dye 2, dye 3 and dye 4 respectively. The SSE vales of ABC for dye 1, dye 2 and dye 3 are less than that of the corresponding values of NBC this makes Freundlich model unfit for the set of adsorption data. The SSE values of Langmuir model for ABC are 0.01444, 0.01703, 0.01885, 0.69842, for dye 1, dye 2, dye 3 and dye 4 respectively, and NBC are 0.37492, 0.31503, 0.34149, 1.64134, for dye 1, dye 2, dye 3 and dye 4 respectively. they are the smallest numbers compared to that of Freundlich and Temkin which implies that the discrepancies of data from the Langmuir model is the least making it the model with the best fitting when SSE is considered.

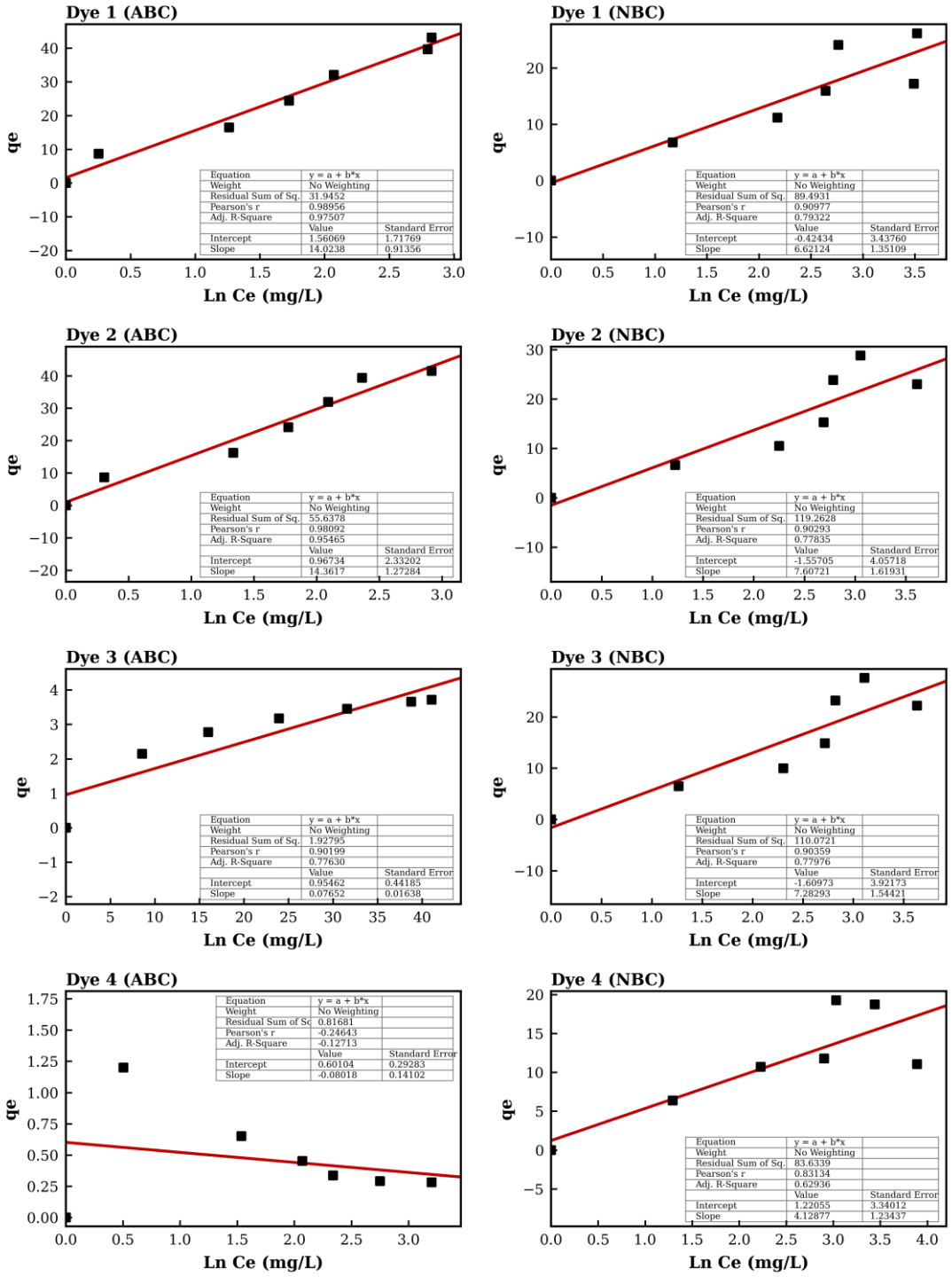


Figure 9. *Temkin Isotherm Model Plot for dye 1to dye 4 treatment using NBC and ABC at optimized conditions.*

A comparison of the values of the R^2 and SSE shown in Table 6, shows that the adsorption experimental data for all azo dyes used conformed better to the Langmuir adsorption isotherm and therefore, adsorption is monolayer which agrees with the earlier assumption for the results of variation of time and initial concentration in section 3.6.

R_L value is indicative of the adsorptive nature of the adsorbent for Langmuir model. The adsorption is termed unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$.

In this study, R_L value of the dye 1 to dye 4 adsorptions on ABC are within 0.050 to 0.128 and NBC 0.013 to 0.197 which all fall within $0 < R_L < 1$ as shown in Table 6.

Table 6. *Parametric Summary of Findings regarding Isotherm Model Applicability for NBC and ABC.*

Isotherm	Parameter	Dye-1-NBC	Dye-1-ABC	Dye-2-NBC	Dye-2-ABC	Dye-3-NBC	Dye-3-ABC	Dye4-NBC	Dye-4-ABC
Langmuir	R^2	0.797	0.856	0.736	0.809	0.744	0.803	0.835	0.971
	SSE	0.375	0.014	0.315	0.017	0.341	0.018	1.641	0.698
	R_1	0.129	0.121	0.177	0.123	0.197	0.128	0.013	0.050
Freundlich	R^2	0.854	0.734	0.898	0.759	0.904	0.772	0.747	0.916
	SSE	0.177	0.438	0.131	0.393	0.120	0.370	0.246	0.028
Temkin	R^2	0.793	0.975	0.778	0.955	0.780	0.776	0.629	0.127
	SSE	89.5	31.9	119.2	55.6	110.0	1.928	83.6	0.817

4. Conclusion

Raw bentonite clay was successfully beneficiated and thermo-chemically modified and its physiochemical properties improved as apparent in the characterization using FTIR, and BET. The results obtained from this research showed that the percentage of dyes adsorbed increased with contact time reaches a maximum then begins to decline with time. An inverse relationship was observed for percentage dye adsorbed with particle size of both NBC and ABC. The plot of percentage of dyes adsorbed with initial dye concentration also showed an indirect relationship. This seemingly unusual phenomenon was explained using the Langmuir adsorption model. The optimized particle size and initial concentration for all four dyes 75µm and 10mg/L using ABC and NBC while the contact time varies as 105 min, 75min, 90 min and 105 min for dye 1 to dye 4 respectively. Adsorptions on NBC and ABC using the four azo dyes are best fitted to the Langmuir model as compared to the Freundlich and Temkin model due it having highest estimated R^2 and lowest SSE Results also show that the adsorption of azo dyes on ABC fits more into Langmuir model than NBC due to improved physio-chemical properties. Generally, isothermal model studied revealed the sorption conformity in the order Langmuir > Freundlich >

Temkin. This work can reliably conclude that azo acid dyes could be successfully removed from aqueous solution using ABC as eco-friendly and economically viable adsorbent.

Abbreviations

ABC	Activated Bentonite Clay
BET	Brunauer-Emmett-Teller (Surface-Area Analysis Method)
BJH	Barrett-Joyner-Halenda (Pore-Width Analysis Method)
FTIR	Fourier Transform Infrared (Spectroscopy)
NBC	Natural (Raw) Bentonite Clay
R^2	Coefficient of Determination
R_1	Langmuir Separation (Equilibrium) Factor
SSE	Sum of Square Errors
UV-Vis	Ultraviolet-Visible (Spectrophotometry)
XRF	X-Ray Fluorescence

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Data Availability Statement

Data are available upon request.

Conflicts of Interest

The authors declare no conflict of interest.

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